İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF REACTIVE INTERMEDIATES AND MACROMOLECULES BY CONTROLLED POLYMERIZATION AND COUPLING PROCESSES

Ph.D. Thesis by
Demet GÖEN ÇOLAK

Department : Chemistry

Programme : Chemistry

JANUARY 2010

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF REACTIVE INTERMEDIATES AND MACROMOLECULES BY CONTROLLED POLYMERIZATION AND COUPLING PROCESSES

Ph.D. Thesis by
Demet Göen ÇOLAK
(509012056)

Date of submission : 28 September 2009
Date of defence examination: 08 January 2010

Supervisor (Chairman) : Prof. Dr. Yusuf YAĞCI (ITU)
Members of the Examining Committee : Prof. Dr. Ümit TUNCA (ITU)
Prof. Dr. Nihan NUGAY (BU)
Prof. Dr. Turan ÖZTÜRK (ITU)
Prof. Dr. Nergis ARSU (YTU)

JANUARY 2010

<u>**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**</u>

KONTROLLÜ POLİMERİZASYON VE KENETLENME PROSESLERİ İLE REAKTİF ARA BİLEŞİKLER VE MAKROMOLEKÜLLER SENTEZİ VE KARAKTERİZASYONU

DOKTORA TEZİ
Demet Göen ÇOLAK
(509012056)

Tezin Enstitüye Verildiği Tarih : **28 Eylül 2009**
Tezin Savunulduğu Tarih : **08 Ocak 2010**

Tez Danışmanı : **Prof. Dr. Yusuf YAĞCI (İTÜ)**
Diğer Jüri Üyeleri : **Prof. Dr. Ümit TUNCA (İTÜ)**
Prof. Dr. Nihan NUGAY (BÜ)
Prof. Dr. Turan ÖZTÜRK (İTÜ)
Prof. Dr. Nergis ARSU (YTÜ)

OCAK 2010

FOREWORD

First of all, I would like to thank my thesis supervisor, Prof. Yusuf Yağcı, for giving me the opportunity to work in his group. I am deeply indebted to him for his kind guidance, valuable criticism, support, understanding and help in all possible ways throughout this research.

I also owe a debt of gratitude to Dr. Ioan Cianga for his kind contribution and help during the experiments and also for his continuous encouragement and sincere friendship. Endless thanks to Dr. Luminita Cianga not only for making helpful comments, but also for always feeling me and being near to me.

I would also like to express my deep thanks to Dr. Daniel A.M. Egbe for his kind contribution as well as his nice friendship and encouragement.

I gratefully acknowledge the effort, the time and valuable suggestions of the members of my thesis committee: Prof. Ümit Tunca and Prof. Nihan Nugay.

I wish to thank all the past and present members of "Yagci Group" for their help, friendship and the nice environment they created not only inside, but also outside the lab.

I also thank all the academic members and the staff of ITU, Faculty of Science & Letters and Department of Chemistry for the nice atmosphere I experienced for many years.

I wish to express my warm thanks to my best friends Burçin Gacal, Gökçe Merey, Müfide Karahasanoğlu, Şennur Öksüz Özçelik, M. Atilla Taşdelen and Muhammed U. Kahveci for always being next to me.

I am deeply grateful to my mother Mediha Göen and my brother İlkay Uğur Göen for their endless love, care, faith, support and understanding throughout my life.

Saving the most important for last, I would like to express my loving thanks to my husband Cengiz Çolak for his unconditional love and care, confidence, patience, support and encouragement. No words can reflect my love and my regard for him.

Finally, I would like to dedicate this thesis to my husband, my mother, my brother and to the memory of my dear deceased father Yusuf Göen.

This work is supported by ITU Institute of Science and Technology.

September 2009 Demet Göen ÇOLAK

Chemistry

TABLE OF CONTENTS

Page

ABBREVIATIONS

ATRP : Atom Transfer Radical Polymerization
ROP : Ring-opening Polymerization
PSt : Polystyrene
MMA : Methyl Methacrylate
^{1}H-NMR : Hydrogen Nuclear Magnetic Resonance Spectroscopy
IR : Infrared Spectrophotometer
GPC : Gel Permeation Chromatography
PCL : Poly(ε-Caprolactone)
PMMA : Poly(methyl Methacrylate)
DSC : Differential Scanning Calorimetry
CL : ε-Caprolactone
NMP : Nitroxide Mediated Polymerization
RAFT : Reversible Addition-Fragmentation Chain Transfer Polymerization
Sn(Oct)$_2$: Stannous Octoate
dppe : 1,2-Bis(diphenylphosphino)ethane
CRP : Controlled Radical Polymerization
RP : Radical Polymerization
SFRP : Stable Free Radical Polymerization
4-VP : 4-Vinyl Pyridine
Bipy : Bipyridine
dTBipy : Substituted Pyridine
dHBipy : Substituted Pyridine
dNBipy : Substituted Pyridine
TMEDA : *N,N,N',N'*-Tetramethylethylenediamine
PMDETA : *N,N,N',N'',N''*-Pentamethyldiethylenetriamine
HMDETA : *N,N,N',N'',N''',N'''*-Hexamethyltriethylenetetraamine
Me$_6$-TREN : Tris[2-(dimethylamino)ethyl]amine
DMF : Dimethyl Formamide
PtBuA : Poly(*tert*-butylacrylate)
MA : Methyl Acrylate
TBMA : *tert*-Butyl Methacrylate
LRP : Living Radical Polymerization
TEA : Triethylamine
NBS : *N*-bromosuccinimide
PPV : Poly(*p*-phenylene vinylene)
PP : Poly(*p*-phenylene)
PPE : Poly(phenylene ethynylene)

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS

$\boldsymbol{\lambda}$: Wavelength
$\mathbf{R}^{\cdot}$: Radical
$\mathbf{I}$: Initiator
$\mathbf{M}$: Monomer
$\boldsymbol{M}_{\mathrm{n}}$: The number average moleculer weight
$\boldsymbol{M}_{\mathrm{w}}$: The weight average moleculer weight
$\boldsymbol{M}_{\mathrm{w}}/\boldsymbol{M}_{\mathrm{n}}$: The moleculer weight distribution
$\mathbf{P}_{\boldsymbol{n}}^{*}$: Propagating species
$\mathbf{M}_{\mathrm{t}}^{\mathrm{n}}$: Transition Metal
$\mathbf{P}_{\boldsymbol{n}}^{=}$: Polymer having a double bond at the chain end due to termination by disproportination
$\mathbf{P}_{\boldsymbol{n}+\mathrm{m}}$: Polymer terminated by chain combination
$\mathbf{X}$: Halide group
$\boldsymbol{\Delta\nu}_{\mathrm{af}}$: The Stokes shift
$\boldsymbol{\Phi}_{\mathrm{f}}$: The relative fluorescence quantum yield
$\boldsymbol{\tau}$: The fluorescence lifetime
$\boldsymbol{k}_{\mathrm{f}}$: The fluorescence radiative constant
$\boldsymbol{k}_{\mathrm{nr}}$: The fluorescence non-radiative constant
$\mathbf{r}$: The fluorescence polarization

SYNTHESIS AND CHARACTERIZATION OF REACTIVE INTERMEDIATES AND MACROMOLECULES BY CONTROLLED POLYMERIZATION AND COUPLING PROCESSES

SUMMARY

Telechelic polymers are defined as macromolecules that possess two reactive end groups and are important building blocks for construction of various polymer architectures. The use of telechelics and the macromonomer technique has proved to be a useful tool for preparing graft copolymers and advanced polymeric materials that are of great interest since they exhibit novel characteristics required for many high-tech applications due to their diverse macromolecular structures. Thus, engineering macromolecular designs is one of the crucial targets of polymer chemists. Controlled polymerization methods are the most powerful and versatile tools in achieving this target. Controlled/living polymerizations lead to polymers with predetermined functionalities, molecular weights and narrow molecular weight distrubitions. Recent developments in controlled/living radical polymerizations have provided the possibility of synthesizing well-defined macromonomers via radical routes, as well. Atom transfer radical polymerization (ATRP) appears to be a robust methodology providing new possibilities in structural and architectural design of macromolecules.

Current interest in conjugated polymers is related to their interesting optical and nonlinear optical properties and electronic conductivity which lead to a vareity of practical applications such as information storage and optical signal processing, substitutes for batteries and materials for energy conversion. Furthermore, electroluminescence from conjugated polymers is a rapidly expanding field since the first report of polymeric light-emitting diodes (PLEDs) based on poly(*p*-phenylene vinylene)s (PPVs).

PPV and its derivatives are a promising class of high performance polymers due to their good film-forming properties, relatively high photoluminescence (PL) and electroluminescence (EL) quantum efficiencies, as well as good color tunability through molecular structure designs. They also show good mechanical properties and high chemical and thermal stability which allows the fabrication of electronic devices such as flexible LEDs.

PPV itself has a rigid structure and is inherently insoluble, thus making it impossible to process these materials into thin films required for the most applications. As a result, considerable effort has been directed toward the preparation of well-defined conjugated polymers with improved solubility, processability and stability.

Incorporation of conformationally mobile, relatively long and flexible side chains onto the polymer backbone has been important for synthesizing fusible and soluble rigid-rod conjugated polymers. Taking into account the substantial interest not only in the synthesis of new types of polymers, but also in the modification of commodity polymers to improve their properties to meet the requirements for high-tech

applications, polystyrene (PSt) or poly(methyl methacrylate) (PMMA) has been used in which nanostructured photoactive conjugated oligo(phenylene vinylene) segments are attached as side chains to the backbone. On combining a stiff, insoluble, rod-like polymer, such as PPV, with a soft coil [e.g. polystyrene (PSt) or poly(ε-caprolactone) (PCL)], it is possible to form a new polymer with novel and interesting properties.

The present work describes the synthesis and characterization of mid- and end-chain functional telechelics and macromonomers and their use in preparing comb-like conjugated polymers, such as PPVs and poly(Schiff-bases).

For this purpose, the first step was the preparation of effective initiators bearing proper functionalities for both; controlled polymerization methods and Suzuki coupling reaction. The general representation of the initiators used in the synthetic strategy is depicted in Figure 1.

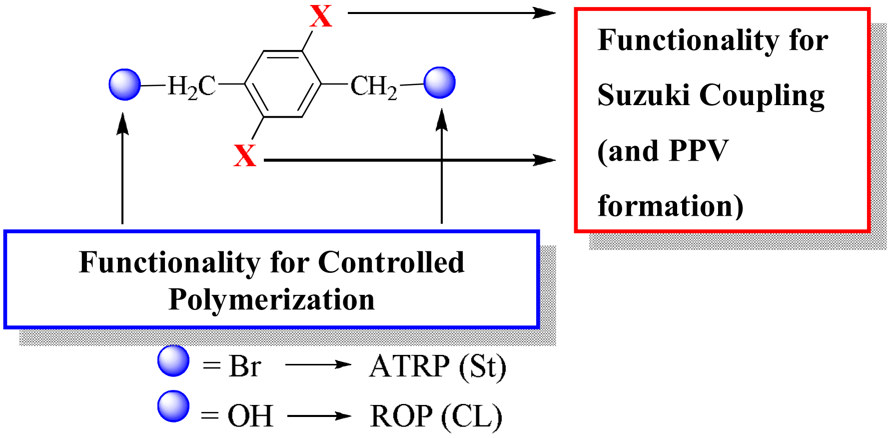


Figure 1: General representation of the initiators.

By the use of aforementioned initiators, well-defined PSt or PCL based polymers containing mid- or end-chain dibromobenzene moieties were prepared by controlled polymerization methods, such as ATRP or ring opening polymerization (ROP). 1,4-Dibromo-2-(bromomethyl) benzene, 1,3-dibromo-5-(bromomethyl) benzene, and 1,4-dibromo-2,5-di(bromomethyl)benzene were used as initiators in ATRP of styrene (St) in conjunction with CuBr /2,2'-bipyridine as catalyst. 2,5-Dibromo-1,4-(dihydroxymethyl)benzene initiated the ROP of ε-caprolactone (CL) in the presence of stannous octoate ($Sn(Oct)_2$) catalyst. Since these polymers were intended to be used in further reactions, efforts were directed towards obtaining a low molecular weight with a low polydispersity combined with convenient yields. Notably, precursor polymers still preserve the functionality needed for Suzuki coupling. So, the reaction of these polymers with amino- or aldehyde- functionalized monoboronic acids, in Suzuki type couplings, yielded the corresponding desired telechelics. Further functionalization was achieved by condensation reactions of these polymers with appropriate low molecular weight aldehydes or amines to form azomethine linkages. As a result, mid- or end-chain amino-, aldehyde-, pyrrolyl-, naphthyl- or hydroxy-functional telechelics were obtained as represented in Figure 2. These telechelics may serve as useful macromonomers in the preparation of various macromolecular structures displaying distinct characteristics.

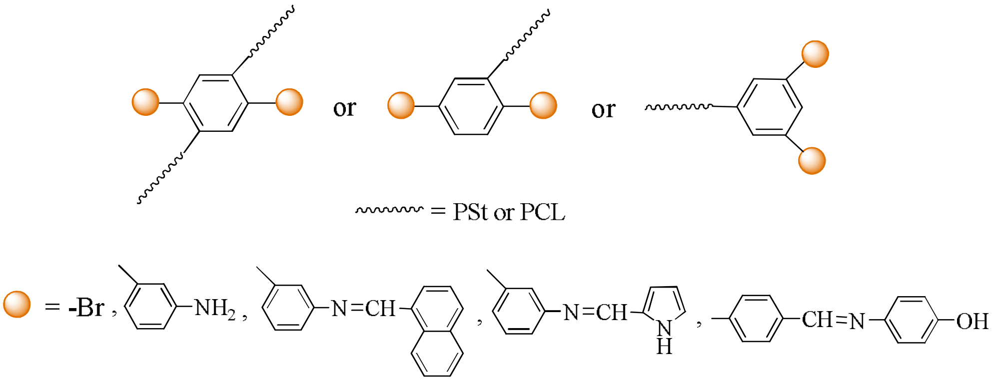


Figure 2: Representation of mid- or end-chain functional telechelics.

The next part of the thesis states the synthesis and characterization of PPV derivatives bearing well-defined PCL or PSt as lateral susbstituents. New macromonomers having dialdehyde functionalities at the middle or at the end of the chains were synthesized, in a similar way, in two reaction steps. ROP of CL or ATRP of St in the presence of above mentioned initiators, provided well defined low molecular weight polymers with dibromobenzene moieties. As the second step, Suzuki coupling of these dibromobenzene functions with 4-formylphenyl boronic acid yielded macromonomers having 4,4'-dicarbaldehyde terphenyl moieties. Poly(phenylene vinylene)s (PPVs), with lateral subtituents, PCL or PSt chains, were synthesized by following a Wittig polycondensation in combination with bis(triphenylphosphonium) salts in the presence of potassium *tert*- butoxide. The resulting colored PPVs, which are represented in Figure 3, were soluble in common organic solvents at room temperature just as the starting macromonomers. Hence, the structures of such complex macromolecules have been fully characterized by spectral methods (^{1}H- and ^{13}C-NMR, IR) and GPC measurements. Optical and detailed photophysical properties of the polymers were followed by UV and fluorescence spectroscopy in dilute solutions, thin films and bulk state. The final PPVs emit blue and exhibit very high relative and absolute photoluminescence quantum yield. Thus, excellent solubility combined with the optical properties favours the use of these materials in the design of highly efficient LEDs and in many applications in various areas.

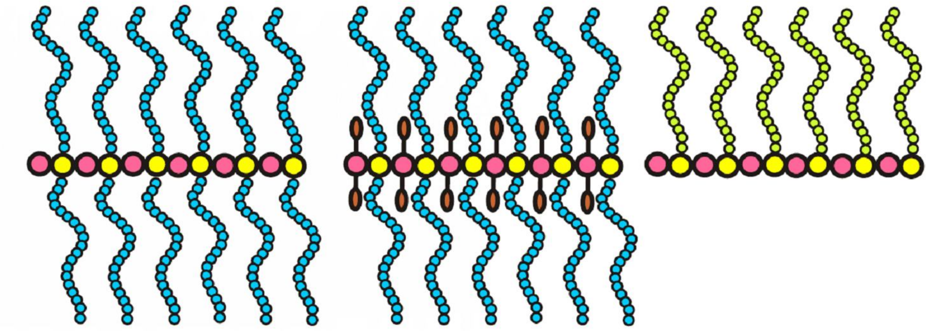


Figure 3: PPVs with well-defined PSt or PCL as lateral substituents.

KONTROLLÜ POLİMERİZASYON VE KENETLENME PROSESLERİ İLE REAKTİF ARA BİLEŞİKLER VE MAKROMOLEKÜLLER SENTEZİ VE KARAKTERİZASYONU

ÖZET

“Telechelic” polimerler iki reaktif uç gruba sahip makromoleküller olarak tanımlanırlar ve birçok polimerik mimarinin tasarımında önemli yapı taşlarıdırlar. Değişik ve çeşitli makromoleküler yapıları ile birçok ileri teknoloji uygulamalarının gerektirdiği özgün özellikleri göstermelerinden dolayı büyük ilgi gören aşı kopolimerleri ve ileri polimerik malzemelerin hazırlanmasında telechelic polimerlerin ve makromonomer tekniğinin kullanımı yararlı bir araç olarak görünmektedir. Nitekim makromoleküler tasarımlar polimer kimyacılarının en önemli hedeflerinden biridir. Kontrollü polimerizasyon yöntemleri bu hedefe ulaşmada en güçlü ve kullanışlı vasıtalardır. Kontrollü/yaşayan polimerizasyonlar fonksiyonel grupları ve molekül ağırlığı önceden belirlenebilen, dar molekül ağırlığı dağılımına sahip polimerlerin eldesine öncülük eder. Bu alandaki son gelişmeler, iyi-tanımlanmış makromonomerlerin radikal yollarla da sentezlenmesine imkan sağlamıştır. Atom transfer radikal polimerizasyonu (ATRP), makromoleküllerin yapısal ve mimari tasarımlarında yeni olanaklar sağlayan güçlü ve sağlam bir yöntem olarak görünmektedir.

Konjuge polimerlere olan mevcut ilgi, bilgi depolama ve optik sinyal üretimi, batarya yerine kullanım ve güneş enerjisi dönüşüm malzemeleri gibi birçok farklı uygulamalara liderlik eden ilginç optik ve elektriksel iletkenlik özelliklerine bağlıdır. Ayrıca, konjuge polimerlerden elektrolüminesans, poli(*p*-fenilen vinilen) (PPV) esaslı ilk polimerik ışık-yayan diodların (PLEDs) bildirilmesinden bu yana hızla gelişen bir alandır.

PPV ve türevleri iyi film oluşturma özellikleri ile yüksek fotolüminesans (PL) ve elektrolüminesans (EL) kuantum verimlerinin yanı sıra, moleküler yapı tasarımları ile ayarlanabilir renk özelliği göstermelerinden dolayı yüksek teknoloji polimerlerinin gelecek vaad eden önemli bir sınıfıdır. Ayrıca iyi mekanik özellik ve üstün kimyasal ve ısısal dayanıklılık göstermeleri de esnek LED’ler gibi elektronik cihazların üretimine olanak sağlar.

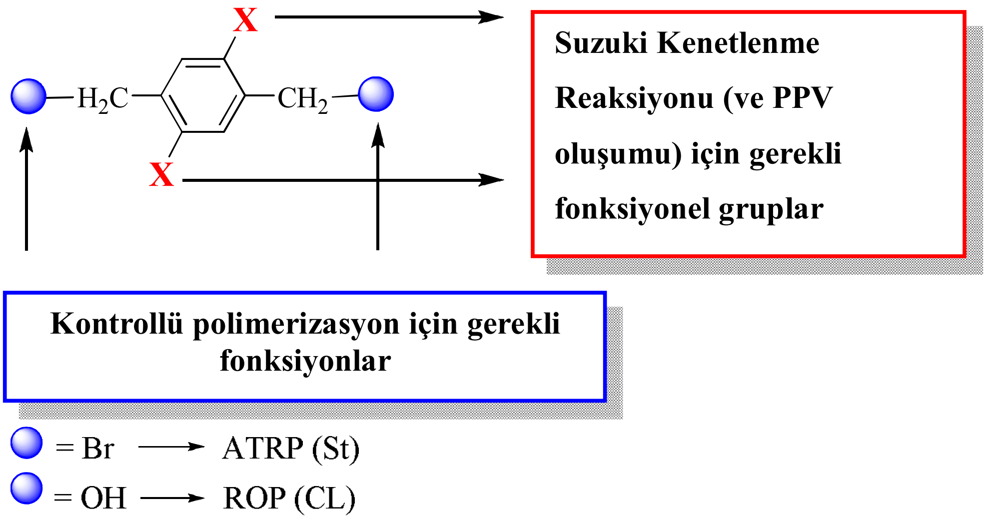
PPV’in kendisi sert bir yapıya sahiptir ve yapısı gereği çözünmezdir, bu da malzemelerin birçok uygulama alanı için gerekli olan ince filmlere işlenebilirliğini imkânsız kılar. Sonuç olarak, iyileştirilmiş çözünürlük, işlenebilirlik ve dayanıklılık özelliklerine sahip iyi tanımlanmış konjuge polimerlerin hazırlanmasına önemli bir çaba yönlendirilmiştir.

Polimer ana zincirine hareketli, uzun ve esnek yan zincirlerin eklenmesi eriyebilir ve çözünebilir sert yapılı konjuge polimerlerin sentezinde önem kazanmıştır. Sadece yeni polimerlerin sentezlenmesi değil, aynı zamanda var olan ve bilinen polimerlerin modifikasyonları da dikkate alınarak, polistiren (PSt) ve poli(metil metakrilat) (PMMA), ana zincirlerine oligo(fenilen vinilen) segmanlarının yan zincir olarak

eklenmesi ile kullanılmıştır. PPV gibi çözünmez, sert-çubuk şeklindeki bir polimer ile yumuşak bir zincirin (örn. PSt veya poli(ε-kaprolakton) (PCL)) birleştirilmesi yoluyla tamamen farklı ve ilginç özelliklere sahip yeni bir polimer oluşturulması mümkündür.

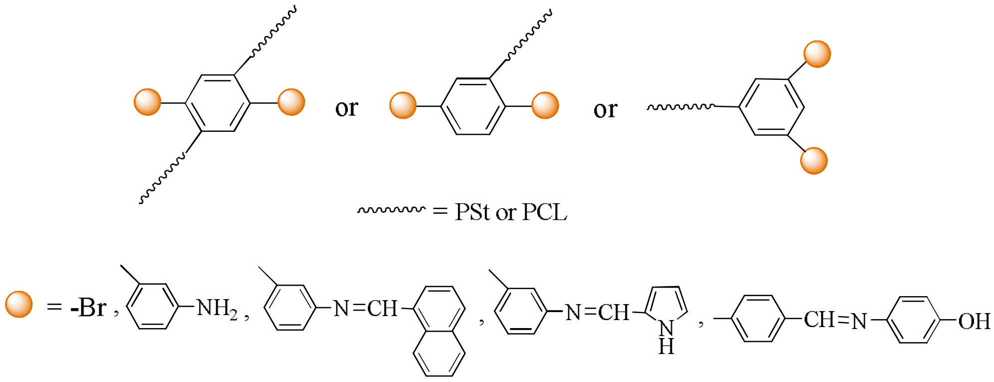
Bu çalışma, zincir-ortası ve zincir-sonu fonksiyonel telechelic polimerler ve makromonomerlerin sentezi ve karakterizasyonu ile bu polimerlerin PPV veya poli(Schiff-bazı) gibi tarak-tipi konjuge polimerlerin hazırlanmasındaki kullanımını ele almaktadır.

Bu amaçla birinci aşama, kontrollü polimerizasyon yöntemleri ve Suzuki kenetlenme reaksiyonu için uygun fonksiyonel gruplara sahip etkin başlatıcıların hazırlanmasıdır. Sentetik strateji kapsamında kullanılan başlatıcıların genel gösterimi Şekil 1'de verilmiştir.



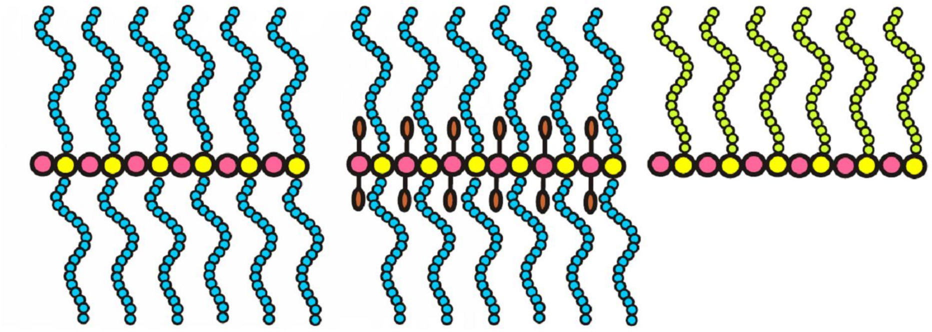
Şekil 1: Başlatıcıların şematik gösterimi.

Yukarıda bahsi geçen başlatıcılardan faydalanılarak, zincir-ortası veya zincir-sonu dibromobenzen grupları içeren iyi-tanımlı, PSt veya PCL esaslı polimerler ATRP veya halka açılma polimerizasyonu (ROP) gibi kontrollü polimerizasyon yöntemleri ile sentezlenmiştir. 1,4-Dibromo-2-(bromometil) benzen, 1,3-dibromo-5-(bromometil) benzen, ve 1,4-dibromo-2,5-di(bromometil)benzen CuBr /2,2'-bipridin katalizör sistemi ile stirenin (St) ATRP reaksiyonunda başlatıcı olarak kullanılmıştır. 2,5-Dibromo-1,4-(dihidroksimetil)benzen katalizör kalay oktoat ($Sn(Oct)_2$) varlığında ε-kaprolaktonun (CL) ROP reaksiyonunu başlatmıştır. Bu polimerler daha başka polimerizasyon reaksiyonlarında da kullanılacağından, yapılan tüm çalışmalar, uygun verimlerle düşük molekül ağırlıklı ve düşük polidispersiteli polimerlerin sentezine yöneliktir. Dikkat edilecek olursa, öncü polimerler Suzuki kenetlenme reaksiyonu için gerekli fonksiyonel grupları halen korumaktadır. Böylece, bu polimerlerin amino- veya aldehit-fonksiyonlu mono boronik asitler ile Suzuki tipi kenetlenme reaksiyonları hedeflenen telechelic polimerlerin eldesini sağlamıştır. Daha ileri fonksiyonlandırmalar, azometin bağları oluşturmak üzere bu polimerlerin küçük molekül ağırlıklı uygun aldehit veya aminler ile kondenzasyonları sonucu gerçekleştirilmiştir. Sonuç olarak, zincir-ortası veya zincir-sonu amin-, aldehit-, pirol-, naftil- ve hidroksi-fonksiyonel telechelic polimerler, Şekil 2'de gösterildiği gibi, elde edilmiştir. Bu fonksiyonel polimerler, farklı özellikler gösteren çeşitli moleküler yapıların hazırlanmasında makromonomerler olarak kullanılabilirler.



Şekil 2: Zincir-ortası veya zincir-sonu fonksiyonel polimerlerin gösterimi.

Tezin diğer bölümünde yan zincirler olarak iyi-tanımlı PCL veya PSt içeren PPV türevlerinin sentezi ve karakterizasyonu sunulmaktadır. Zincir ortasında veya sonunda dialdehit fonksiyonları içeren yeni makromonomerler, benzer şekilde, iki reaksiyon basamağı ile sentezlenmiştir. Yukarıda sözü edilen başlatıcılar varlığında CL'nun ROP reaksiyonu ve St'in ATRP reaksiyonu dibromobenzen yapıları içeren iyi-tanımlı, düşük molekül ağırlıklı polimerlerin eldesini sağlamıştır. İkinci basamak olan, dibromobenzen fonksiyonlarının 4-formilfenil boronik asit ile Suzuki kenetlenme reaksiyonu, 4,4'-dikarbaldehit terfenil yapıları içeren makromonomerlerin elde edilmesini sağlamıştır. PCL veya PSt yan zincirli PPV'ler potasyum *tert*-butoksit varlığında bis-(trifenil fosfonyum) tuzları ile Wittig polikondenzasyonu takip edilerek sentezlenmiştir. Elde edilen PPV'ler, Şekil 3'de gösterilmiştir, başlangıç makromonomerleri gibi genel organik çözücülerde oda sıcaklığında çözünebilmektedirler. Böylece, bu kompleks makromoleküllerin yapıları spektral yöntemler (^{1}H- ve ^{13}C-NMR, IR) ve GPC ölçümleri ile tam olarak karakterize edilmiştir. Optik ve fotofiziksel özellikleri seyreltik çözeltiler, ince filmler ve katı halde olmak üzere UV ve floresans spektroskopileri ile takip edilmiştir. Sonuç PPV'ler mavi ışık yaymaktadır ve oldukça yüksek fotolüminesans kuantum verimi göstermektedir. Sonuç olarak, mükemmel çözünürlükleri ve optik özellikleri, bu malzemelerin yüksek verimli LED'lerin tasarımında ve birçok alandaki çeşitli uygulamalarda kullanımlarını desteklemektedir.



Şekil 3: İyi-tanımlı PCL veya PSt yan zincirli PPV'ler.

1. INTRODUCTION

In the last few decades, the main interest in polymer science has been novel advanced materials that provide special mechanical and physical properties through different macromolecular designs for various purposes and high-tech applications. Getting the interdiciplinary connection between synthesis and material science is the driving force for polymer chemists in developing new synthetic strategies.

Telechelic polymers are described as macromolecules having two reactive end groups and are important building blocks in construction of various polymeric materials and architectures [1,2]. According to the functional groups, they can also participate in further polymerization reactions as “precursors” yielding block and graft copolymers or networks. Hence, they can aslo be called as “macromonomers”. Telechelic polymers having a variety of functional groups are prepared by a wide range of polymerization methods such as anionic, cationic, ring opening, group transfer, free radical, metathesis, step-growth polymerization and chain scission processes. Recent developments in “controlled/living” radical polymerization have provided possibility to synthesize well-defined telechelic polymers; with controlled functionalities, predetermined molecular weights and low polidispersities; via radical routes, as well [3-7]. Among the various controlled radical polymerization processes, atom transfer radical polymerization (ATRP), introduced by Matyjazewski and coworkers, is the most versatile on account of its simplicity and applicability to a wide range of vinyl monomers [8,9]. It appears to be a robust methodology for the synthetic polymer chemists providing new possibilities in structural and architectural designs and also in developing novel materials with currently available momomers.

The present concern of modern materials science is the generation of “smart” materials which are highly sensitive to environmental influences and are capable of responding to external stimuli such as electrical and magnetic field, light, temperature, etc. [10]. Conjugated polymers are valuable candidates for such materials due to their substantial π-electron delocalization along their backbones which gives rise to interesting optical properties and allows them to become good electronic conductors typically when oxidized or reduced [11]. These properties imply a variety of practical applications such as information storage, optical signal processing and materials for solar energy conversion. Moreover, after the pioneering report of polymeric light-emitting diodes (PLEDs) based on poly(p-phenylene vinylene) (PPV) by Burruoghes et. al. [12], electroluminescence from conjugated polymers is a rapidly growing field [13-16].

Among the vast kinds of conjugated polymers [17,18], PPVs and its deriavtives are still one of the most frequently studied class due to their good film forming properties, relatively high photoluminescence and electroluminescence quantum efficiencies, as well as good color tunability through molecular structure designs. They also exhibit good mechanical properties and high chemical and thermal stability which are needed for most of the applications and allows the fabrication of electronic devices such as flexible LEDs.

Unfortunately, PPV itself is insoluble in many organic solvents due to its rigid structure which limits the processability into thin films required for many applications. Therefore, significant efforts have been directed toward the synthesis of well-defined conjugated polymers with increased solubility, processability and stability. Attachment of relatively long and flexible side chains (such as alkyl or alkoxy groups) onto the polymer backbone is an important technique since it helps the preparation of fusible and soluble rigid-rod conjugated polymers. Regarding this aspect, it is possible to develop new polymers with novel and interesting properties through combining a stiff, insoluble, rod-like polymer, such as PPV, with a soft coil (e.g. polystyrene (PSt) or poly(ε-caprolactone) (PCL)). The macromonomer technique has proved to be useful in preparing graft copolymers [19] and may also serve as a practical tool in designing above mentioned new type of polymers.

This study describes the preparation of PCL- and PSt-based telechelics, macromonomers and their use in the synthesis of PPVs with macromolecular side-chains. Telechelics with desired functionalities were obtained by controlled polymerization methods, namely ATRP or ring opening polymerization (ROP), which were followed by Suzuki coupling reaction. Further functionalizations were achieved by condensation reactions via Schiff-base formation.

PPVs with well-defined macromolecular side chains (PSt or PCL) were synthesized by the use of dialdehyde functional macromonomers in Wittig polycondensation in combination with bis(triphenyl phosphonium) salts.

2. THEORETICAL PART

2.1 Controlled Polymerization

The first definition of “living polymerization” was made by Szwarc [20,21]. It was a chain growth process free of transfer and termination reactions. In living polymerization, the polymer chains keep their propagating ability for a long time and grow to a desired size with a negligible degree of chain-breaking reactions. Such a polymerization enables control over end-groups and synthesis of block copolymers by sequential addition of monomers, but falls behind in providing molecular weight control and low polydispersities necessarily. In order to use the term “controlled”, these two criteria should also be well addressed. In this view, the prerequisites to be fullfilled involves the consumption of initiator at early stages of the process (the rate of initiation should be at least comparable to that of propagation) and an exchange between species of different reactivities and lifetimes as fast as propagation [22-25].

For the synthesis of well-defined macromolecules, precise control of polymerization is of great significance. A recent term “macromolecular engineering” defines the ability to have control over polymerization processes for designing and preparing well-defined, complex macromolecular architectures. Varying the molecular architecture of well-known polymers leads to improved or new properties for new applications. Establishing the architecture and structure/property relationships can be achieved and advanced if and only uniform polymers with definite structures and predetermined properties are available.

Controlled polymerization can be described as the method which provides synthesis of polymers with predetermined molecular weights, low polydispersities and controlled functionalities. Transfer and termination reactions are reduced as possible by appropriate reaction conditions.

2.1.1 Controlled radical polymerization

Radical polymerization (RP) is the most widely used method in polymer synthesis on account of its simplicity, flexibility, relatively high tolerance to impurities and functional groups. It is applicable to various monomers under mild reaction conditions and high molecular weight polymers are obtained [6]. Moroever, many monomers can be copolymerized through a radical route leading a limitless number of copolymers with different properties according to the proportion of comonomers. However, RP yields polydisperse polymers without control of molecular weight and end-groups. Also synthesis of block copolymers and other advanced structures is practically not possible. Advanced structures can be synthesized by living polymerization techniques. Living ionic techniques (such as anionic polymerization [26]) allow the control of chain ends and the synthesis of materials with low polydispersities as well as block copolymers. But it is well-recognized that such processes suffer from strict reaction conditions, limited choice of monomers and sensitivity to functional groups in some cases. The polymerization systems must be devoid of impurities and requires great care in purification, drying solvents and monomers and in handling of initiator solutions. The optimum reaction temperature range is very low such as -20^{o}C to –78^{o}C.

The benefits of the RP and living polymerization should be combined in one method to overcome all the drawbacks. In this scope, to clear off the disadvantages of RP while keeping the benefits, a "living character" had to be brought to the free radical mechanism. Thus, a great deal of research has gone into the development and understanding of "controlled/living" radical polymerization (CRP)[27]. By the recent developments [6,27], it is possible to synthesize well-defined and functional polymers from a larger range of monomers under simpler reaction conditions, also via radical routes. New applications of CRP have opened a new pathway for the synthesis of polymeric materials having complex macromolecular architectures (comb, graft, star block), compositions or functionalities [28].

The main difference between free radical polymerization and CRP is the generation way of radicals. In free radical systems, radicals are formed at low concentration continously and irreversibly. The radical concentration is established by balancing continous initiation and irreversible termination. In CRP, radicals are formed reversibly at both steps, initiation and propagation. Radical concentration is essentially determined by the rates of activation and deactivation. At any time, only a small portion of the chains are active and the dormant species are dominant. The exchange between the active and dormant species provides a slow but simultaneous growth of all chains while retaining the concentration of radicals low enough to minimize termination.

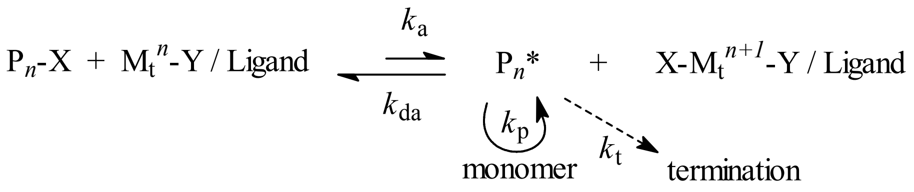
The three standard methods ensuring the living character are; atom transfer radical polymerization (ATRP) [29], nitroxide mediated polymerization (NMP) [30] or stable free radical polymerization (SFRP) and reversible addition-fragmentation chain transfer polymerzation (RAFT) [31].

Among the methods, the former will be discussed as the present thesis involves the use of ATRP in the experimental section.

2.1.1.1 Atom transfer radical polymerization (ATRP)

The principle key reaction for the uniform growth of the polymer chains is the “atom transfer” step, which gives the name of the method. It was disclosed by the design of a catalyst system, the use of an initiator with a suitable structure and the adjustment of the reaction conditions leading to a linear increase in molecular weight with conversion and polydispersities that are characteristic of a living system [8]. This enabled a novel control over the chain topology, the composition and the end functionality for a wide range of radically polymerizable monomers [32,33].

ATRP [8,34] involves reversible homolytic cleavage of a carbon-halogen bond by a redox reaction between an organic halide (R-X) and a transition metal complexed with a ligand. The general mechanism is illustrated in reaction 2.1.



(2.1)

Transition metal complex (activator, M_t^n –Y / ligand, where Y may be another ligand or a counterion) undergoes a one electron oxidation with a concurrent abstraction of a (pseudo)halogen atom, X, from a dormant species, P_n–X. Through this reversible redox process, radicals, namely the propagating species P_n*, are produced. Radicals react reversibly with the oxidized metal complexes, X–M_t^{n+1} / ligand (the deactivator), and the dormant species and the activator is formed again. Rate constants of these activation and deactivation processes are k_a, and k_{da}, respectively. Polymer chains form by the addition of free radicals to monomers. Propagation is in a similar manner to conventional radical polymerization, with a rate constant of k_p. Termination reactions (k_t) are also present in ATRP. They mainly occur through radical coupling and disproportionation. In a well-controlled ATRP, only a few percent of the polymer chains go through termination. Oxidized metal complexes act as persistent radicals and so the stationary concentration of the growing radicals is reduced and hence termination at later stages is minimized [35].

Initiation, propagation and termination steps are shown below [36] (2.2-2.6).

Initiation

$$\text{R-X} + \text{M}_t^{n}\text{-Y / Ligand} \underset{k_{da}^{o}}{\overset{k_a^{o}}{\rightleftharpoons}} \text{R} + \text{X-M}_t^{n+1}\text{-Y / Ligand} \tag{2.2}$$

$$\text{R} + \text{M} \xrightarrow{k_i} \text{P}_1 \tag{2.3}$$

Propagation

$$\text{P}_n\text{-X} + \text{M}_t^{n}\text{-Y / Ligand} \underset{k_{da}}{\overset{k_a}{\rightleftharpoons}} \text{P}_n + \text{X-M}_t^{n+1}\text{-Y / Ligand} \tag{2.4}$$

$$\text{P}_n + \text{M} \xrightarrow{k_p} \text{P}_{n+1} \tag{2.5}$$

Termination

$$\text{P}_n + \text{P}_m \xrightarrow{k_t} \text{P}_{n+m} \quad \text{or} \quad \text{P}_n^{=} + \text{P}_m^{\text{H}} \tag{2.6}$$

Both activating and deactivating components of the catalytic system must be concurrently present. Through a fast initiation and rapid reversible deactivation, with only a small contribution of termination, uniform growth of all the chains and thus a successful ATRP is achieved.

The basic constituents of ATRP are monomers, initiators, catalysts, ligands and the solvents.

Various *monomers*, such as styrenes, (meth)acrylates, (meth)-acrylamides, dienes, and acrylonitrile, have been used in ATRP. Some other monomers containing substituents which can stabilize the propagating radicals have also been polymerized using ATRP. Ring opening polymerization is possible, too [29]. Less reactive monomers yielding unstable reactive radicals such as α–olefins, vinyl chloride and vinyl acetate, are not susceptible to ATRP since the current catalysts are not adequate for their polymerization [6]. Other exceptions are unprotected acids, such as (meth)acrylic acid. Some monomers that exhibit side reactions due to the nature of reaction conditions are also not suitable for ATRP. 4-Vinyl pyridine can be given as an example for such monomers [37]. Due to its quarternization by the initiator alkyl halide, ATRP is unsuccessful. The most commonly used monomers are styrenes and methacrylates.

Initiators are generally (alkyl) halides. As mentioned before, initiation occurs through the reaction of an activated (alkyl) halide with the transition metal complex in its lower oxidation state. The halide group should move between the growing chain and the transition metal complex in a rapid and selective manner. Molecular weight control is excellent with bromines and chlorines. Copper-mediated ATRP of acrylates proceeds well with iodines. Iodines also conduct to controlled polymerization of styrene in ruthenium and ruthenium-based ATRP [38,39]. Various halogenated compounds have the possibility of initiating ATRP. Ethyl-2-bromoisobutyrate and 1-phenylethyl chloride have been used as initiators in ATRP of methacrylate and styrene, respectively [8,40]. Initiators like 2,2,2-trichloro-ethanol seem to be effective, yielding hydroxy functional polymers [41]. Sulfonyl chlorides have also been reported as initiators in ATRP [42]. Di-, tri- or multifunctional initiators afford polymer chains growing in two, three or more directions. Pseudo-halogens, particularly thiocyanates and thiocarbamates, have also been employed as successful initiators for the polymerization of acrylates [43].

An optional way for ATRP initiation is the use of conventional free radical initiators. These initiators are utilized in combination with a transition metal complex in its higher oxidation state, such as AIBN and a Cu(II) complex. On generation of the primary radicals and their monomer adducts, Cu(II) complex transfers a halogen to the newly formed chain, thus the copper complex is reduced and the chain is deactivated. This method of initiation is named as “reverse ATRP” [44].

Catalyst systems are of great importance in ATRP. The position of the atom transfer equilibrium and dynamics of exchange between the dormant and active species are determined by the catalyst. The prerequisites that should be fullfilled by an efficient transition metal catalyst can be noted as follows:

i. The metal center must have at least two readily available oxidation states distinguished by one electron.

ii. The metal center should have reasonable affinity towards to a halogen.

iii. The coordination sphere around the metal should be expandable upon oxidation to accommodate a (pseudo)halogen selectively.

iv. The ligand should complex the metal relatively strongly.

v. The position and dynamics of the ATRP equilibrium should be suitable for the specific system. For a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species [45].

A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The most widely used transition metal is copper. Fe [46], Ni [47], and Ru [48] have also been employed to some extent. Reported Ru-based complexes are the competitors of Cu-based systems. A particular Fe-based catalyst has also been used in polymerization of vinyl acetate through an ATRP mechanism [49].

Ligands have two major functions in ATRP. One is solubilizing the transition metal salt in organic media and the second is adjusting the redox potential and halogenophilicity of the metal center by forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex with the transition metal strongly. It should also enable expansion of the coordination sphere and selective atom transfer without elevating other reactions. The most commonly used ligands in ATRP systems are bipyridines, substituted bipyridines, alkyl pyridylmethanimines and multidentate aliphatic tertiary amines such as N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA), and tris-[2-(dimethylamino) ethyl]amine (Me_6-TREN). Some examples for copper-mediated ATRP are given in the Figure 2.1 [8,50].

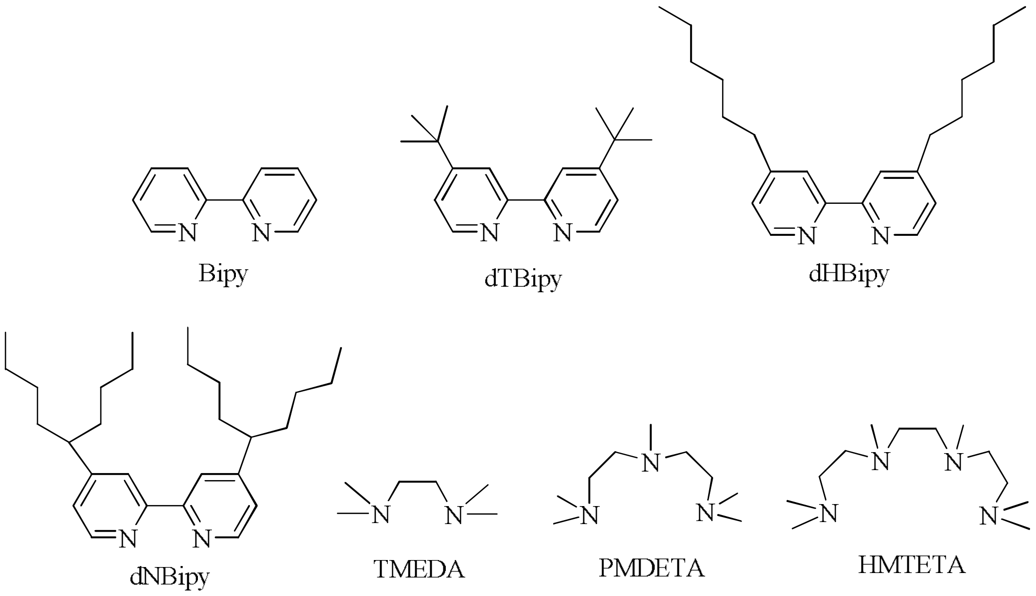


Figure 2.1: Some examples of ligands for copper-mediated ATRP.

ATRP can be performed in bulk, in solution, or in heterogeneous systems such as emulsion or suspension.Various *solvents*, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), alcohol, water, etc. have been utilized in the polymerization of different monomers. A solvent is required especially if the polymer is insoluble in its monomer (e.g., polyacrylonitrile). For the solvent choice several factors should be taken in account. Possible interactions of solvent and the catalytic system should be considered and chain transfer to solvent should be minimum. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP) [51] and solvent-supported side reactions, such as elimination of HX from polystyryl halides, which is more evident in a polar solvent, [52] should be minimized.

In short, ATRP is a powerful system providing the polymerization of a wide range of monomers without strict reaction conditions. With its versatility and simplicity, ATRP is approved to be a useful technique for synthesis and design of new and unusual materials with different architectures and compositions [32].

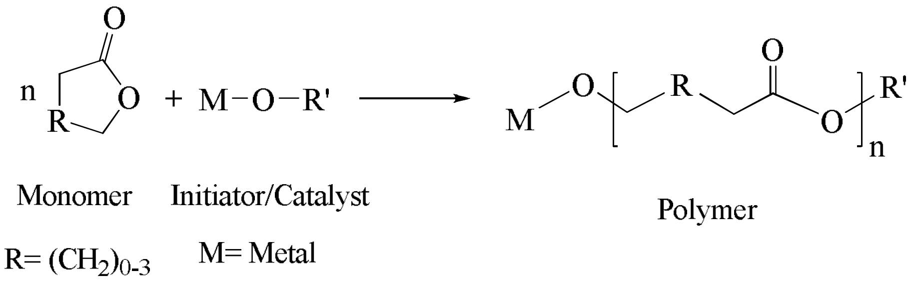
2.1.2 Controlled ring-opening polymerization

Preparation of novel polymer structures by ring-opening polymerization has been the point of research for a number of years. Aliphatic polyesters are an important class of polymers due to their use in biomedical and pharmaceutical applications. Moreover, the physical and chemical properties of such degradable polymers can vary over a wide range by copolymerization or macromolecular techniques.

Polylactones and polylactides can be synthesized through two different methods; by polycondensation of proper monomers or by ring-opening polymerization (ROP) of cyclic esters. Even the former method is less costly, obtaining high molecular weights with desired groups or preparations of well-defined copolymers are more difficult.

2.1.2.1 Ring-opening polymerization of cyclic esters

Polylactones and polylactides with high molecular weights are prepared by ROP of the corresponding cyclic monomers in the presence of a catalyst or initiator as presented in reaction 2.7.



(2.7)

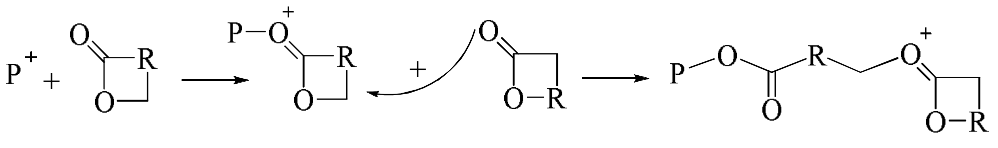
Each polymer possesses one functional group resulting from the termination reaction and another originating from the initiator. The nature of these functional groups can be varied according to the requirements by changing the catalyst or initiator and the termination reactions. The thermal stability and the hydrolytic stability of the final material are affected by the initiator and the end groups [53]. Through this strategy, other functional groups suitable for further polymerization reactions can also be established in the structure.

The ring-opening reaction can be carried out as bulk, or in solution, emulsion or dispersion, in the presence of a catalyst or initiator. In a short time, polyesters of high molecular weights and low polidispersities are obtained under mild conditions. Difficulties that accompany to condensation polymerization, such as precise stoichiometry, high temperatures and the removal of by-products are eliminated in ROP.

The polymerization follows three different major mechanisms [54] depending on the initiator; anionic, cationic or "coordination-insertion" mechanisms [55-57]. Radical, zwitterionic [58] or active hydrogen initiations are not widely used.

2.1.2.2 Cationic ring-opening polymerization

4-, 6-, and 7-membered cyclic esters can form polyesters upon reaction with cationic catalysts. In cationic ROP, the posistively charged species are attacked by a monomer which results in ring-opening through an SN_2-type process, as illustrated in reaction 2.8.



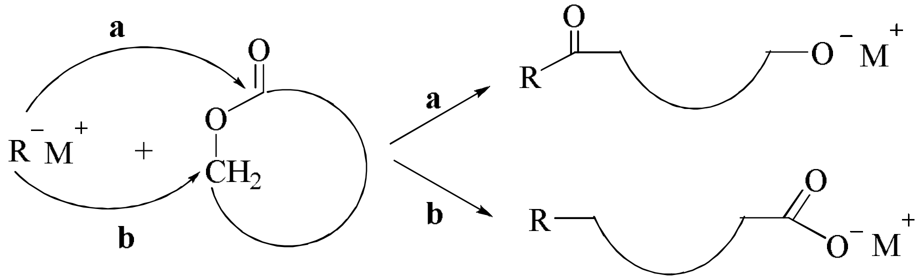
(2.8)

P = polymer

It is hard to control cationic polymerization and generally low molecular weight polymers are obtained. For more detailed information attentions should be directed to the published reviews [59,60].

2.1.2.3 Anionic ring-opening polymerization

In anionic ROP, a negatively charged initiator attacks the carbonyl carbon or the carbon atom adjacent to acyl oxygen and thus a linear polyester is formed. Reaction 2.9 summarizes the anionic ring-opening of a monomer via both ways, acyl-oxygen bond cleavage (a) or alkyl-oxygen bond cleavage (b) [54].



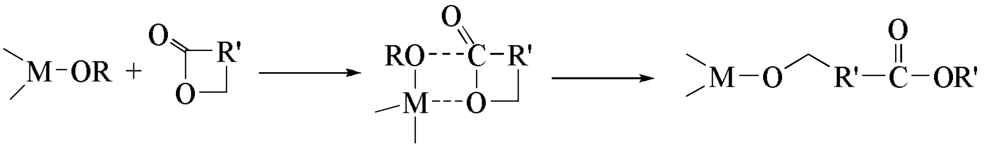
(2.9)

If the polymerization is performed in a polar solvent, high molecular weight polymers can be obtained. Well-defined high molecular weight polymers and copolymers of 4- and 5-membered lactones by living anionic ROP techniques has been reported [61]. The anionic ROP of 4-membered rings follows alkyl-oxygen or acyl-oxygen cleavage producing a carboxylate or alkoxide, while larger lactones (e.g.

ε-caprolactone, (ε-CL)) follow only acyl-oxygen cleavage forming an alkoxide as the active species. Back-biting is the problem faced in anionic ROP, and only low molecular weight polyesters are formed in some cases.

2.1.2.4 Coordination-insertion ring-opening polymerization

Coordination-insertion ROP is supposed to proceed via the coordination of the monomer to the active species. Then, by the arrangement of the electrons, insertion of the monomer into the metal-oxygen bond takes place [55-56]. Reaction 2.10 presents the considered reaction pathway.


(2.10)

During the propagation, the growing chain stays attached to the metal by an alkoxide bond. The reaction is terminated by hydrolysis resulting a hydroxy end group. Macromonomers bearing active end groups for further polymerization reactions can be prepared by functional alkoxy-substituted initiators.

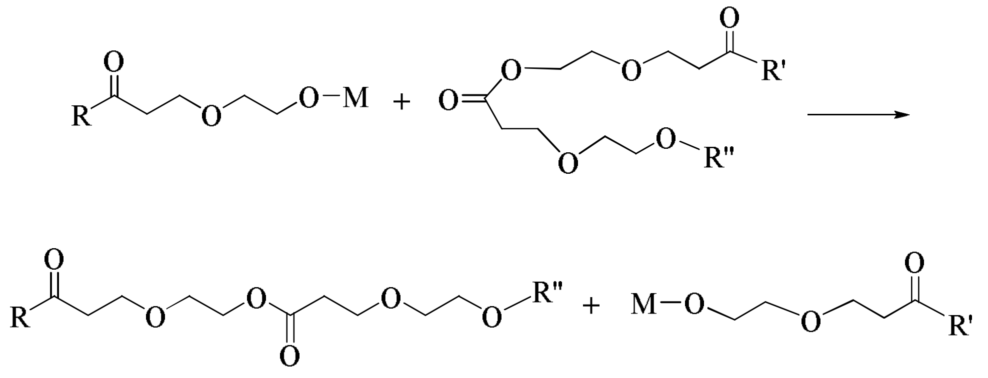
The coordination-insertion type of polymerization has been thoroughly investigated as it is possible to prepare well-defined polyesters through living polymerization [56]. In the case of two monomers with similar reactivities, by sequential addition to the living system, block copolymers can be obtained.

2.1.2.5 Initiators for ROP of lactones and lactides

A wide variety of organometallic compounds, such as metal alkoxides and metal carboxylates, has been used as initiators or catalysts for efficient polymer synthesis [62]. The reactions catalyzed by metal complexes are extensively specific and by the appropriate choice of metal and ligands, desired polymer structures can be formed. The covalent metal alkoxides with free *p* or *d* orbitals behave as coordination initiators. The most common and frequently used initiators and catalysts in ROP of lactones are stannous octoate and aluminum tri-isopropoxide.

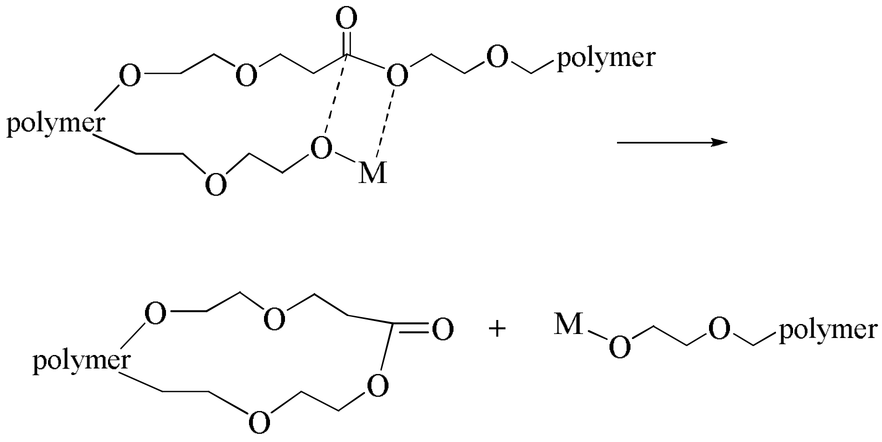
In ROP of lactones and lactides, at higher temperatures [63] or at long reaction times [64], side reactions such as inter- or intra-molecular transesterifications take place due to the catalyst or initiator, as shown in reactions 2.11 and 2.12.

Intermolecular Transesterification



(2.11)

Intramolecular Transesterification (back-biting)

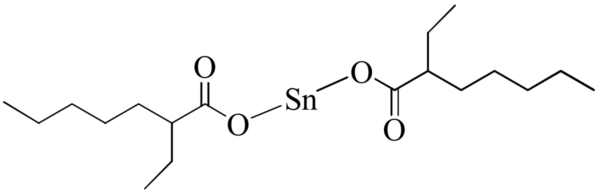


(2.12)

Intermolecular transesterification reactions change the sequences of copolylactones and hinder the formation of block copolymers while intramolecular transesterification reactions (back-biting) cause degradation of the polymer chain that result in cyclic oligomers. The polymer chain is broken randomly by each intramolecular transesterification and hence, after *n* tranesterifications, a copolymer of block-like structure would become a randomized copolymer. Both of the types lead a broadening in the molecular weight distribution.

The factors that affect the number of transesterification reactions are temperature, reaction time and the type and concentration of the catalyst or the initiator [65]. The side reactions are more or less favored by the initiator, depending on the metal used.

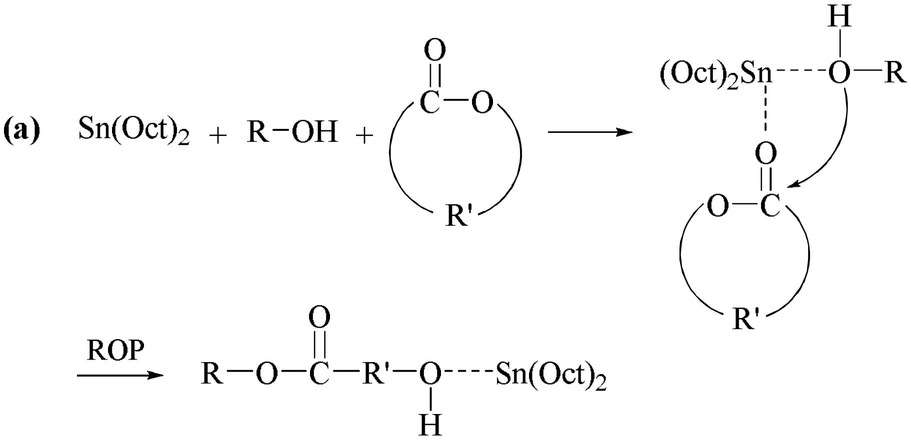
a) Tin(II) 2-Ethylhexanoate (Stannous Octoate)



(2.13)

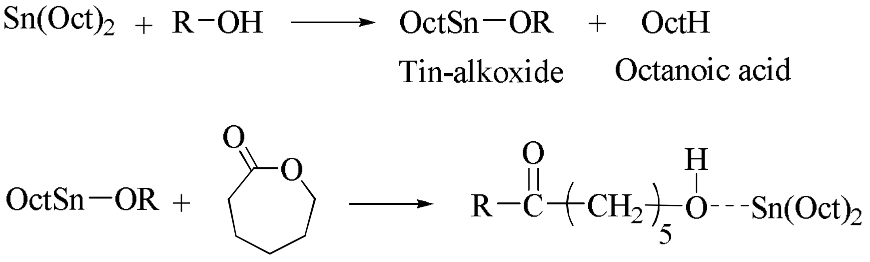
Tin (II) 2-ethylhexanoate, also known as stannous octoate [$Sn(Oct)_2$], is one of the most commonly used catalysts in the ROP of lactones and lactides [66]. The polymerization mechanism has been the subject of a debate [67-69]. As the molecular weight is not dependent on monomer-$Sn(Oct)_2$ molar ratio, it is not supposed to be the real initiator. "Coordination-insertion" mechanism is the most favorable one where a hydroxy functional group is supposed to coordinate to $Sn(Oct)_2$, yielding the initiating tin alkoxide complex.

Two slightly different reaction pathways have been suggested for the coordination-insertion mechanism. According to Kricheldorf and coworkers [69], the co-initiating alcohol functionality and the monomer are both coordinated to $Sn(Oct)_2$ complex throughout the propagation. Penczek and coworkers have proposed a mechanism [68] which involves the conversion of $Sn(Oct)_2$ complex into a tin alkoxide before complexing and ring-opening of the monomer. Tin alkoxide complex has been observed by using MALDI-TOF spectroscopy for the polymerization of both, lactide [68] and ε-CL. The two pathways are shown in reactions 2.14 and 2.15. In conclusion, the two main mechanisms suggested for ROP with $Sn(Oct)_2$ as catalyst are the complexation of monomer and the alcohol prior to ROP **(a)**, and formation of a tin alkoxide before ROP **(b)**.



(2.14)

(b)

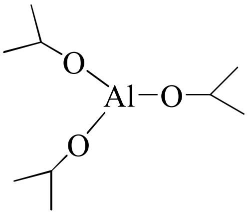


$$Sn(Oct)_2 + R{-}OH \longrightarrow \underset{\text{Tin-alkoxide}}{OctSn{-}OR} + \underset{\text{Octanoic acid}}{OctH}$$

(2.15)

The $Sn(Oct)_2$ catalyst favors the transesterification reactions strongly, resulting copolymers having a randomized microstructure [65]. The number of transesterification reactions grows by increasing temperatures or reaction times.

b) Aluminum Tri-Isopropoxide



(2.16)

Aluminum tri-isopropoxide has been widely studied by several groups as initiator for ROP since it affords well-defined polymers by living polymerization, which is a chain polymerization that proceeds without termination or chain transfer reactions [23].

“Coordination-insertion” mechanism is supposed for the polymerization where monomer complexation to active species and insertion by rearrangement of the covalent bonds take place. It follows the cleavage of the acyl-oxygen bond of the monomer and metal-oxygen bond of the propagating species. The propagation is almost free of side-reactions (such as transesterification). The reaction is generally carried out in solution at low temperature (0-25 °C).

c) Tin Alkoxides

The tin alkoxides are known as efficient tranesterification catalysts capable of initiating polymerizations at reasonable tempeartures [70]. Mono tin alkoxides, tin dialkoxides and cyclic tin alkoxides have been employed as initiators in ROP of cyclic esters. Cyclic tin alkoxides are resistant to hydrolysis and they offer a useful pathway for the preparation of macromonomers, triblock and multiblock copolymers.

The tributyl derivatives are comperatively soluble in lactones and they are moisture resistant.

With tin (II) alkoxides, the initiation and the polymerization is fast, no side reactions are observed, and it is possible to control the molecular weight [71]. The polymerization of lactones by tin alkoxides is supposed to proceed via “coordination-insertion” mechanism. The reaction follows the acyl-oxygen bond cleavage, keeping the configuration.

2.2 Telechelic Polymers

Telechelic polymers can be expressed as macromolecules bearing two reactive end-groups which show selective reactivity to form a bond with another molecule [1].

Telechelics are classified as mono-, di-, tri- and multifunctional telechelics which are also known as “polytelechelics”. The functionality is determined by the following formula:

$$f = \frac{\text{number of functional groups}}{\text{number of polymer chains}} \qquad \textbf{(2.17)}$$

Telechelic polymers are used as cross-linkers, chain extenders and precursors to block and graft copolymers. Star, hyper-branched and dendric polymers are also prepared by coupling reactions of monofunctional or multifunctional telechelics. By the reactions of telechelics several macromolecular architectures can be designed (Figure 2.2).

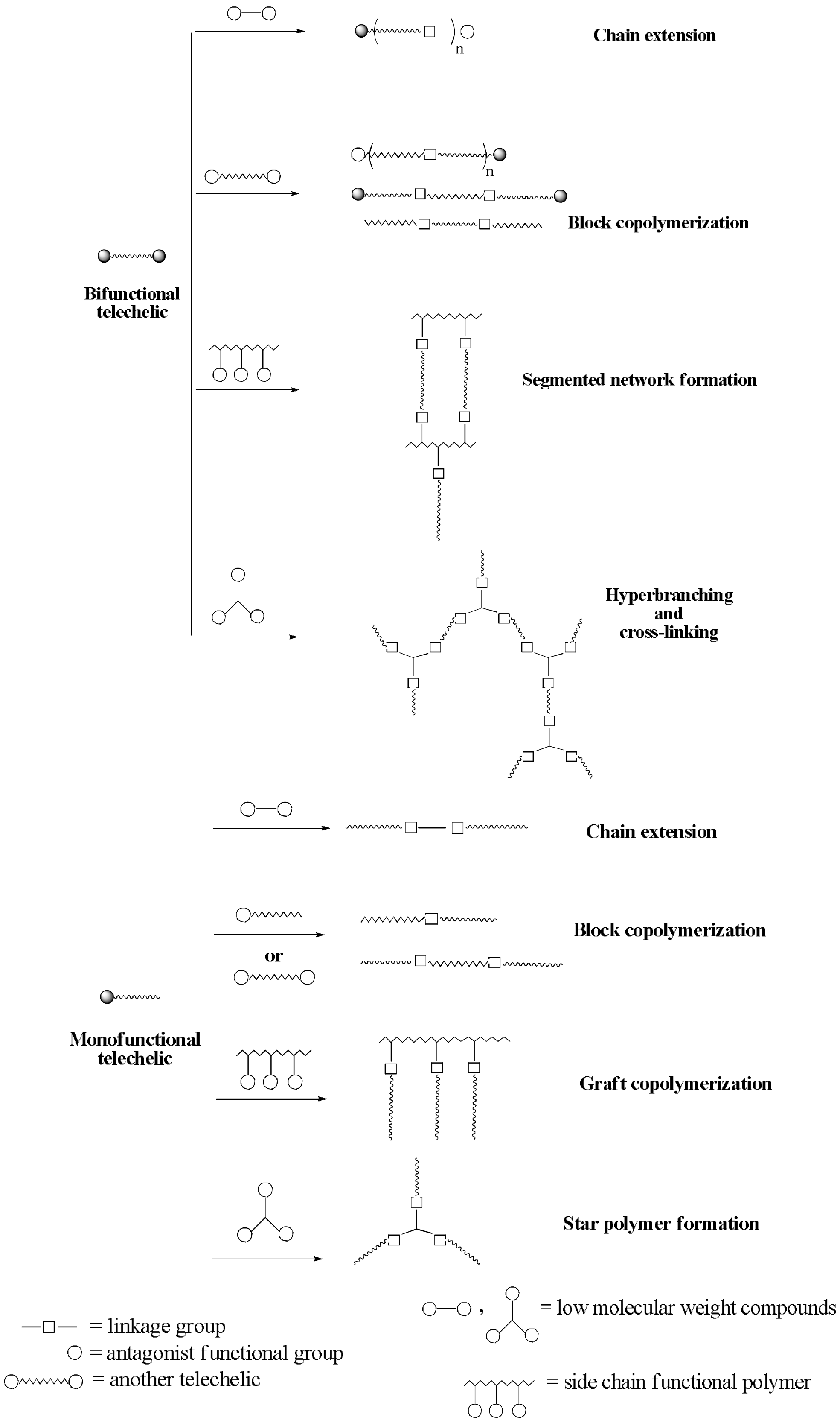


Figure 2.2: Several macromolecular structures designed by the reactions of telechelics.

The general techniques for the preparation of telechelic polymers are;

1) Radical polymerization
   a) By conventional radical polymerizations through;
      - Functional initiators (azo initiators, peroxides)
      - Free radical copolymerization of alkenes with unsaturated heterocyclic compounds.
      - Transfer techniques (transfer agents, addition-fragmentation agents, iniferters.)
   b) Controlled radical polymerizations
      - Atom transfer radical polymerization (ATRP)
      - Nitroxide mediated living-radical polymerization (NMP)
      - Reversible addition-fragmentation chain transfer polymerization (RAFT)
2) Anionic polymerizations
3) Carbocationic techniques
4) Ring-opening polymerizations
5) Metathesis polymerization
   a) Ring-opening metathesis (ROMP)
   b) Ring-closing metathesis (RCM)
   c) Acyclic diene metathesis (ADMET)
6) Chain scission (oxidation, reduction and other degradations)
7) Step-growth polymerization.

Here, in the scope of the thesis, an emphasis will be given on the preparation of telechelics by ring opening polymerization of lactones and ATRP as the controlled radical polymerization technique. More detailed information for the preparation of telechelics is present in literature [1,2].

If the end groups of telechelics are bifunctional or polymerizable they may contribute to polymerization reactions producing graft copolymers or networks. As further polymerizations are possible, these telechelics can be named as “macromolecular monomers” or “macromonomers” or “macromers”. Such groups may be heterocyclic, which is suitable for ring opening polymerization; dicarboxylic or dihyroxylic, which are suitable for step-growth polymerizations; or vinyl or acrylic. Moreover, by the appropriate modification of the end groups, they may participate in other polymerizations as one of the monomer component (e.g. synthesis of poly(*p*-phenylenes) (PPs) or poly(*p*-phenylene vinylenes) (PPVs)).

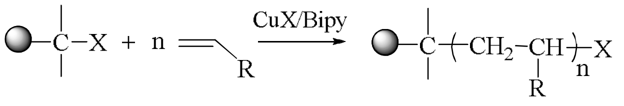
The macromonomers are often ideal starting materials and the technique has proven to be a useful tool [19] for the synthesis of well-defined graft copolymers as the length and the number of branches can be controlled by the molecular weight and the feeding ratio of macromonomers to comonomers.

Macromonomers with various functional groups can be prepared by a wide range of methods similar to telechelics as the chemistry involved is the same. A wider view can be found in the literature [1,72-75].

2.2.1 Preparation of telechelics by ATRP

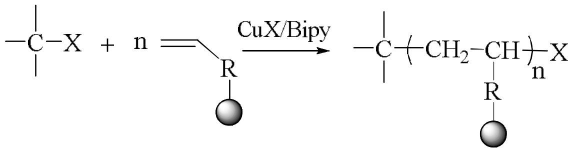
Polymer functionalization by ATRP can be accomplished by the use of functional initiators or monomers or by the chemical transformation of the halogen end groups as illustrated in reactions 2.18-2.20.

Through Initiator Functionality



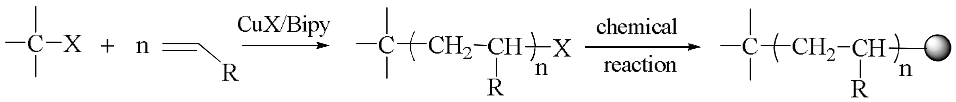
(2.18)

Through Monomer Functionality



(2.19)

Through Chemical Reaction of Halide End-Groups



(2.20)

A number of functional initiators were employed successfully in ATRP for the preparation of styrene and acrylate type polymers [76]. Initiator should carry both, the desired functional groups and the suitable functionality for a successful ATRP. It should be noted that aryl or carbonyl groups with directly bonded halogens are not appropriate initiators for ATRP as the radical generation is not facilitated. Additionally, the functional groups in the initiator should not interfere with the reaction conditions of ATRP, especially with the catalyst system. Due to catalyst poisoning, it is rather difficult to introduce carboxylic acid functionality by ATRP.

For this purpose protected initiators are used and the hydrolysis of the protecting groups results in the desired polymers [77]. Aromatic and aliphatic sulfonyl chlorides were also employed in ATRP as efficient initiators for the preparation of functional polystyrenes or polyacrylates [78]. Table 2.1 presents some examples of telechelic polymers and their functionalities introduced through the initators employed in ATRP.

Table 2.1: Monofunctional telechelics by ATRP through functional initiators.

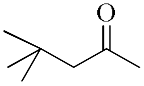
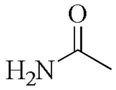
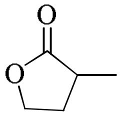
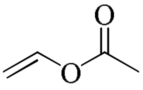
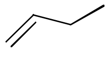
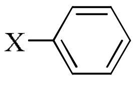
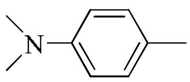
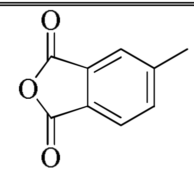
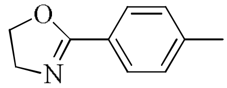
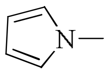
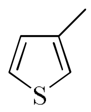
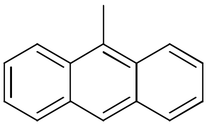
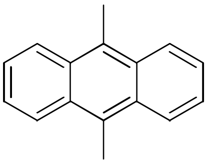
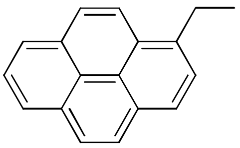
Functional group of the initiator	Polymer type[a]	Ref.
	PSt, PMA	[79]
	PSt	[79]
	PSt, PMA	[79]
OH	PSt, PMA, PBA, PMMA	[80, 81-88]
CN	PSt, PMA	[89-91]
COOH	PMMA	[92]
	PSt	[93]
	PMA	[94,95]
 X= H, CH_3, Br, CN, NH_2, CHO, NO_2, OCH_3	PSt, PMA	[96-98]
	PSt	[99]

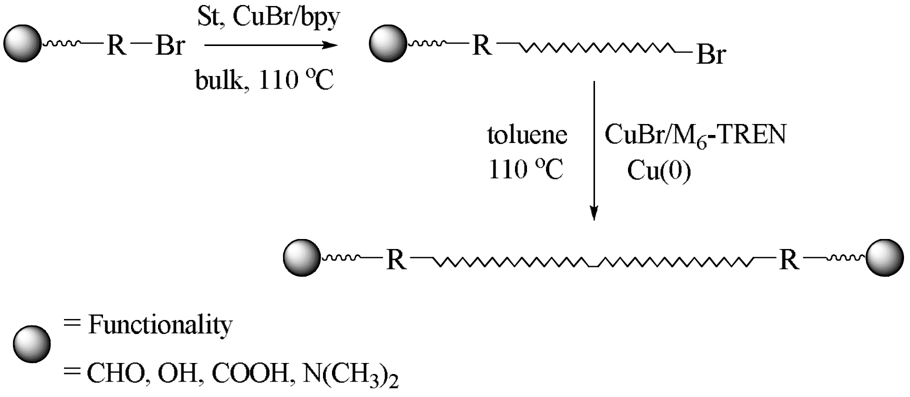
Table 2.1 (continued): Monofunctional telechelics by ATRP through functional initiators.

	PSt	[100]
	PSt	[100]
	PSt, PMMA	[101]
	PMMA	[102]
	PMA	[103]
	PSt	[104]
	PSt	[105,106]

[a]PMMA: poly(methyl methacrylate), PSt: polystyrene, PBA: poly(butyl acrylate), PMA: poly(methyl acrylate)

In ATRP, as one chain end always carries a halogen due to the fast deactivation process, generally monofunctional telechelics are obtained. As halogen is also a functionality, such polymers are named as “heterotelechelics”. For the preparation of α,ω-telechelics, halogen atom should be displaced by another group. Replacement of the halide end group can be achieved by means of nucleophilic substitution, free radical chemistry or electrophilic addition catalyzed by Lewis acids [107-112]. The halide displacement is important for the preparation of bifunctional hydroxy telechelics.

Bifunctional telechelics can be prepared via atom transfer coupling processes [113]. In this method, monofunctional polymers bearing different functional groups are prepared by ATRP of styrene and then by coupling of these polymers in atom transfer radical generation conditions (CuBr/M_6-TREN as catalyst system, Cu(0) as reducing agent, in toluene, without monomer) bifunctional telechelics with double molecular weights compared to the starting materials are obtained. The process is summarized in reaction 2.21.



(2.21)

More recently, combination of atom transfer radical polymerization (ATRP) and atom transfer radical cross coupling (ATRCC) processes has been reported as a route to prepare telechelic polymers [114]. Process is based on the activation of the dormant species at the chain ends of polystyrene (Br-PSt-Br or PSt-Br) prepared by ATRP and functional ATRP initiator (F-R-Br) in the absence of a monomer. Depending on the type of polystyrene used in the system, cross coupling of these active species resulted α,ω-polystyrene and ω-polystyrene telechelics.

For preparing polymers with reactive unsaturated end groups, a combined ATRP and catalytic chain transfer process is employed [115]. In the method, catalytic chain transfer agent is added to ATRP near to the end of polymerization. A one-pot synthesis of telechelics bearing unsaturated end groups has also been reported [116].

2.2.2 Preparation of telechelics by ring-opening polymerization

Preparation of telechelics by ring opening polymerization has been attractive due to the commercial potential of the resulting materials. The end groups can be incorporated by initiation, end-capping or transfer reactions.

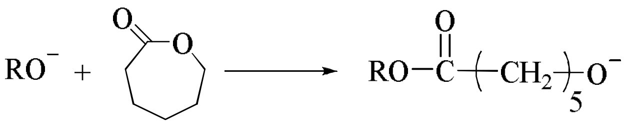
Telechelics has been successfully prepared via the appropriate routes from cyclic ethers (oxiranes, tetrahydrofuran), cyclic acetals, cyclic sulfides, cyclic amines, oxazolines and lactones [1].

Lactones can be polymerized in the presence of anionic and cationic initiators [62,117]. Four-, seven- and eight-membered rings polymerize whereas five- and six-membered rings do not.

Anionic initiators for β-lactones are organic bases such as tertiary amines. By the use of α,α-disubstituted-propiolactones (pivalactones, (PVL)), chain-transfer reactions can be avoided [118,119]. Telechelics from α,α-dimethyl-β-propiolactone have been prepared and used in the synthesis of block copolymers. An asymmetrical telechelic having α-cycloammonium and ω-carboxyl end groups has also been prepared from PVL in the presence of a cyclic amine initiator [120].

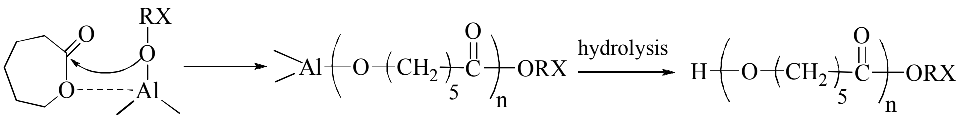
ε-Caprolactone (ε-CL)

Alcoholates can be used in the polymerization of ε-CL. However, an attack of an alcoholate end group to the ester groups of the chain can take place which results in broadening of molecular weight distrubition and formation of cyclic monomers [121].



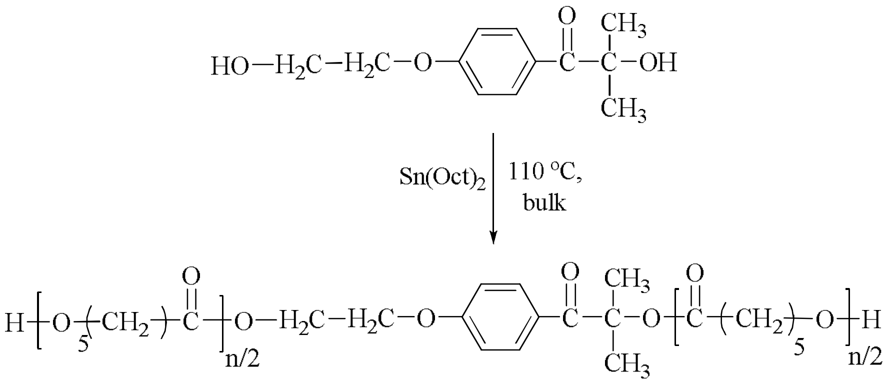
(2.22)

By the use of bimetallic oxoalkoxides and porphionato aluminum alcoholates, living polymers of ε-CL have been prepared [122]. Aluminum alkoxides having different functional alkoxy groups were used as initiators providing asymmetrical telechelics [123-125].



(2.23)

Zinc alkoxides are also effective initiators for ROP of ε-CL [126]. Telechelics, linear or star-shaped block copolymers or networks can be prepared via corresponding alkyl octoate formation when tin octoate, $Sn(Oct)_2$, is used in conjunction with hydroxy functional materials [127-131]. End-chain and mid-chain telechelics of PCL bearing photoactive groups have also been reported [132].



(2.24)

Hydroxy telechelics of PCL can be converted to thiol functionalized polymers by the use of 2,4-dinitrophenylthioaceticacid [133].

2.3 Metal-catalyzed C-C Bond Formations; Cross-Coupling Processes

Most of the carbon-carbon bond-forming reactions utilize stoichiometric quantities of the carbon nucleophile and the carbon electrophile [134]. Generally the nucleophilic species are formed in solution and the electrophile is added. These general processes work well with predictable results and most have been used successfully to design organic structures. Recently, there has been a great interest in discovery of new methods for C-C bond formations [135,136]. These methods employ transition metal-complexes as catalysts and have many advantages over classical ones:

i. Many new reactions are possible.
ii. Functional group requirements and/or limitations are overcomed.
iii. Reactivity of the catalyst can be modulated by ligands which leads
    - increased selectivity
    - high yields and efficiencies
    - single products rather than mixtures
iv. Stereoselection can be tuned via catalyst and ligands
v. Very small amounts of catalysts are used and thus workup and purification is simplified
vi. High atom economy is achieved; reaction mixture ends up in products, not by-products.

A large number of transition metals have been used to form C-C bonds in different reactions [137,138]. However, in particular, two metals have had the greatest attention. The use of palladium and ruthenium has led new strategies for the synthetic planning of different structures and architectures. The most common and general reactions catalyzed by these two metals are; Suzuki Coupling, Heck reaction and Stille coupling for palladium; olefin metathesis (by Grubbs catalyst) for ruthenium.

In the experimental part of the present thesis, Suzuki coupling reactions of 3-aminophenylboronic acid and 4-formylphenylboronic acid with aromatic dibromine functionalized macromolecules were utilized and thus amino- or aldehyde-functional precursor polymers were obtained. Therefore, the following discussion will rather focus on the mechanism of Pd-catalyzed C-C bond formations and Suzuki Coupling. However, a brief overview for Heck reaction and Stille coupling will also be presented since they are useful tools in preparation of poly(*p*-phenylene vinylene) (PPVs).

2.3.1 The mechanism of Pd(0)-catalyzed C-C bond formations

As mentioned above, the most important carbon-carbon bond forming catalytic reactions are based on the chemistry of Pd(0). Zero-valent palladium complexes, such as $Pd(PPh_3)_4$, are commercially accessible or can be prepared *in situ* by the reaction of Pd(II) salts, such as $Pd(OAc)_2$, $PdCl_2$, etc., with phosphines or other reductants.

Pd(0) complexes are most stable when the sum of *d* electrons from the metal and electrons from the ligands equals 18. In other words, they are coordinatively saturated and hence relatively unreactive and stable. Pd(0) has 10 *d* electrons and coordinates with four ligands, each donating a pair of electrons. Upon dissociation of one or two ligands, it becomes a 16- or 14-electron complex. In order to regain the 18-electron configuration it wills to be reactive.

A catalytic cycle for palladium(0)-catalyzed cross-coupling reactions involves three steps:

1. Oxidative addition
2. Transmetallation or insertion
3. Reductive elimination

A general catalytic cycle following oxidative addition-transmetallation-reductive elimination sequence is depicted in Figure 2.3.

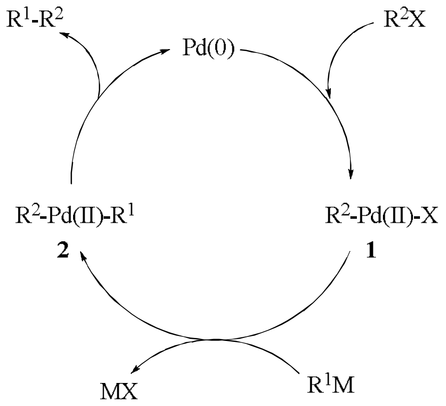


Figure 2.3: A general catalytic cycle for cross-coupling (oxidative addition transmetallation -reductive elimination).

Oxidative addition

The first step involved is the dissociation of two phosphine ligands yielding a 14-electron complex. This is followed by an oxidative addition which occurs through a covalent bond cleavage by the coordinatively unsaturated Pd(0) species, producing a new 16-electron complex, in which palladium is oxidized to Pd(II). (Reactions 2.25-2.26)

$$\mathrm{Pd(PPh_3)_4} \rightleftharpoons \underset{\text{Pd(0), 14 electron}}{\mathrm{Pd(PPh_3)_2}} + 2\,\mathrm{PPh_3} \qquad \textbf{(2.25)}$$

$$\mathrm{Pd(PPh_3)_2} + \mathrm{R{-}X} \longrightarrow \underset{\text{Pd(II), 16 electron}}{\mathrm{R{-}Pd{-}X(PPh_3)_2}} \qquad \textbf{(2.26)}$$

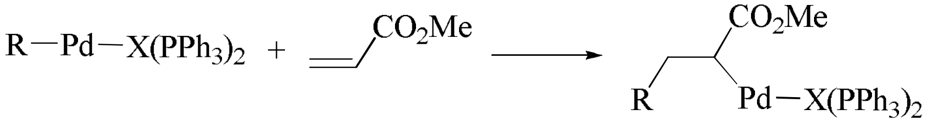
Functional tolerance of the palladium process is really remarkable. A variety of bonds undergo oxidative addition with Pd(0). The most common used ones are carbon to halogen and other good leaving groups like sulfonates, esters and phosphonates, which are recognized as C-X or R-X bonds. Since the carbon-palladium bond of oxidative insertion product is not influenced by most of the functional groups, substrate may have alcohols, amine, amides, esters, ketones, aldehydes and even carboxylic acids, without any interference with the addition reaction or any other following reactions. The most reactive bonds are vinyl and aryl C-X bonds. It should be pointed out that these are the least reactive ones for other metals.

Insertion

When the palladium-carbon bond adds across a π-bond, an insertion reaction takes place yielding a new organopalladium species (reaction 2.27). The reactive π-bonds are alkenes, dienes, alkynes and carbonyls. Alkenes and alkynes are the most commonly used ones.

$$\mathrm{R{-}Pd{-}X(PPh_3)_2} + \mathrm{A{=}B} \longrightarrow \mathrm{R{-}A{-}B{-}Pd{-}X(PPh_3)_2} \qquad \textbf{(2.27)}$$

Many factors affect the regiochemistry of the insertion. The carbon attached to palladium is electron rich and attacks the π-system at the most electron poor position and hence electron withdrawing groups lead faster reactions. Sterical effects are also important. R group attacks to the least hindered end of π-system. If there's no difference in the two ends of the π-system from the view of aforementioned points, then the regiochemistry depends on the reaction conditions and the ligands coordinating to palladium. Anyway, regiochemistry is predictable in most cases. The stereochemistry of insertion is syn by an arranged 1,2-addition across one face of the π-system (reaction 2.28).



(2.28)

Transmetallation

Transmetallation take place in the presence of compounds with bonds from carbon to several main-group elements, such as B, Al, Sn, Si and Hg. The palladium intermediate of oxidative addition goes through an exchange of palladium and the main-group element (M) yielding a second carbon ligand bonded to palladium. Tributyl tin compounds (R-$SnBu_3$) and boronic acids (R-$B(OH)_2$) are the most commonly used compounds for transmetallation. The most successful ones are the main-group elements bonded to aromatic rings or alkenes.

$$\mathrm{R{-}Pd{-}X(PPh_3)_2} + \mathrm{R'{-}M} \longrightarrow \mathrm{R{-}Pd{-}R'\,(PPh_3)_2} + \mathrm{MX} \qquad \textbf{(2.29)}$$

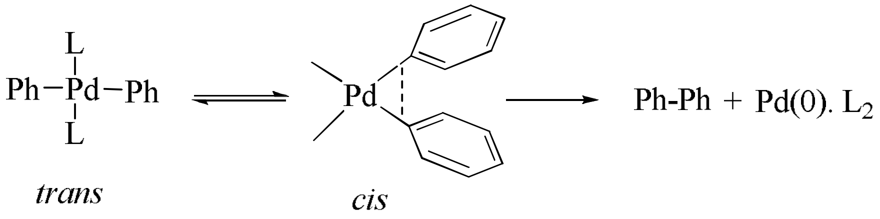
(M = main group element)

Reductive elimination

This is the last step of the process yielding the organic product and regenerating Pd(0) to restart the catalytic cycle. When two carbon ligands are attached to palladium, as in transmetallation, they couple with the ejection of Pd(0) and the carbon-carbon bond is formed (reaction 2.30).

$$R{-}Pd{-}R'\,(PPh_3)_2 \longrightarrow R{-}R' + \underset{Pd(0)}{Pd(PPh_3)_2} \qquad \textbf{(2.30)}$$

On the aryl-aryl coupling, the reaction occurs from *cis*-complex. In the case of *trans*-, the reaction takes place after its isomerization to the corresponding *cis*-complex (reaction 2.31).



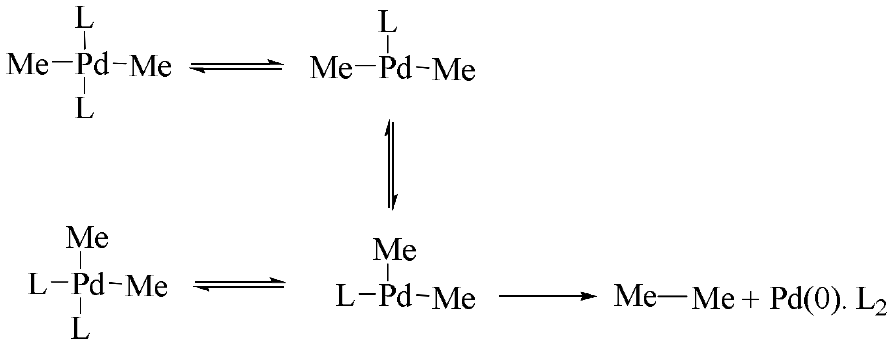
(2.31)

The reactivity order is:

diaryl- > (alkyl)aryl- > dipropyl- > diethyl- > dimethylpalladium(II).

As can be seen, during the bond formation, π-orbitals of the aryl groups have a participation.

On the alkyl-alkyl coupling the intermediate is a *cis*-(dialkyl)palladium(II)•L_2. Its thermolysis is inhibited by excess phosphine (ligand, L), thus the initiation is supposed to be by a rate-determining dissociative mechanism (reactions 2.32 - 2.33).



(2.32)

(2.33)

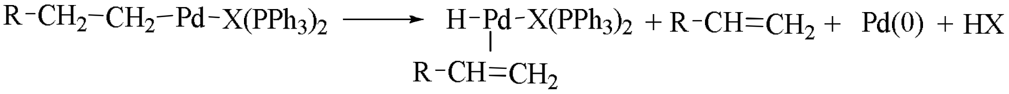
A phosphine ligand (L) dissociates yielding a three-coordinated *cis*-(dialkyl)palladium(II)•L complex, hence the effect of phosphine ligands is important and the order of their dissociation ease is:

$$\text{dppe} \ll PEt_3 < PEt_2Ph < PMePh_2 < PEtPh_2 < PPh_3$$

In the case of intermediates of *cis*-alkenyl- and *cis*-arylpalladium(II) complexes, organic products are directly eliminated from the four-coordinated complex by a non-dissociative mechanism (reaction 2.31).

β-Hydride elimination

Another common reductive elimination type is β-hydride elimination. This takes place if there's a hydrogen atom in β-position to the carbon-palladium bond (as in insertion). The palladium atom inserts into the β-carbon-hydrogen bond and yields a palladium hydride intermediate coordinated to the alkene. This is followed by the dissociation of alkene and elimination of HX, regenerating the Pd(0) catalyst. A base must be present in the reaction mixture as a strong acid is liberated.



$$\mathrm{R{-}CH_2{-}CH_2{-}Pd{-}X(PPh_3)_2} \longrightarrow \mathrm{H{-}}\underset{\mathrm{R{-}CH{=}CH_2}}{\underset{|}{\mathrm{Pd}}}\mathrm{{-}X(PPh_3)_2 + R{-}CH{=}CH_2 + Pd(0) + HX} \qquad \textbf{(2.34)}$$

In short, an electron-deficient compound (such as a vinyl halide) reacts with an electron rich compound (such as an alkene or an organoborane, etc.) in the presence of Pd(0) yielding a new carbon-carbon bond. The reagents come together and react at the catalytic center provided by metal complex. The talent of Pd(0) to catalyze these reactions is really unique as all take place just in the coordination sphere of Pd(0).

2.3.2 Suzuki coupling

The coupling of organoboron compounds with aryl and alkenyl halides or triflates is called the Suzuki reaction or Suzuki–Miyaura coupling and was discovered in the early 1980s [139-142]. It is an extremely versatile methodology for combining two carbon segments and is widely employed in the commercial manufacture of pharmaceuticals, in the synthesis of many organic compounds and in drug discovery. The versatility of the reaction originates from the mild reaction conditions and accessibility of the reagents. Moreover, it is not influenced by the presence of water, is highly tolerant to a wide variety of functional groups and proceeds regio- and stereoselectively. Non-toxicity and easy removal of the inorganic by product makes the reaction attractive for laboratories and industrial processes [143].

Suzuki coupling involves the oxidative addition, transmetallation and reductive elimination steps (Figure 2.3 or reactions 2.35-2.37).

$$\mathrm{R{-}X} + \mathrm{Pd(0)} \longrightarrow \mathrm{R{-}Pd{-}X} \qquad \text{oxidative addition} \qquad \mathbf{(2.35)}$$

$$\mathrm{R{-}Pd{-}X} + \mathrm{R'{-}B(OH)_2} \xrightarrow{\mathrm{NaOR''}} \mathrm{R{-}Pd{-}R'} \qquad \text{transmetallation} \qquad \mathbf{(2.36)}$$

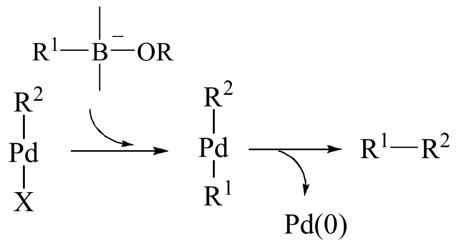
$$\mathrm{R{-}Pd{-}R'} \longrightarrow \mathrm{R{-}R'} + \mathrm{Pd(0)} \qquad \text{reductive elimination} \qquad \mathbf{(2.37)}$$

Alkenyl, alkynyl, allyl, benzyl and aryl bromides or iodides undergo oxidative addition yielding an organopalladium intermediate; trans-σ-palladium (II) complex. This step is often the rate-determining step. The order of relative reactivity is:

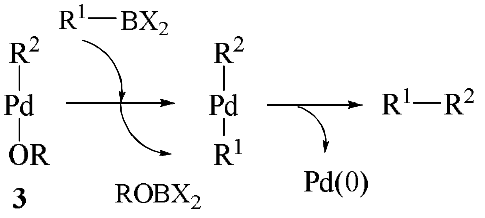
I> OTf > Br >> Cl

Aryl and alkenyl halides bearing electron withdrawing groups are more reactive than those with electron donating groups. Alkyl halides carrying β-hydrogen are not very useful since the oxidative addition is very slow and furthermore it is the possibility of competing with β-hyride elimination from the σ-organopalladium (II) species. Oxidative addition occurs with retention of configuration for alkenyl halides and with inversion for allylic and benzyl halides.

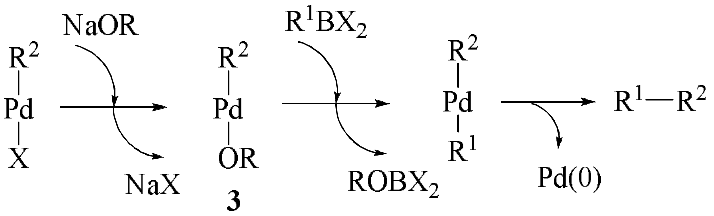
As the second step, the organopalladium intermediate undergoes transmetallation with the boronic acids or esters. This is the key step. Transmetallation may occur under neutral or basic conditions. The processes that are considered to be involved are illustrated by reactions 2.38-2.40.



(2.38)



(2.39)



(2.40)

In Suzuki coupling of organic halides and triflates with organoboron compounds, a base must be present for transmetallation to proceed, otherwise it doesn't occur readily due to the low nucleophilicity of the organic group on boron atom. The nucleophilicity can be improved by quarternization of the boron with negatively charged bases yielding the corresponding "ate" complexes. The most commonly utilized bases are alkoxides, carbonates and hydroxides. The bases can be employed as aqueous solution or as suspension in dioxane or N, N-dimethyl formamide (DMF). Transmetallation to palladium (II) halides is accelerated by quarternization of trialkyl boranes. Even no direct evidence is present for the effect of boronate ions, such as $RB(OH)^-_3$, on transmetallation, a similar effect of base for the transmetallation of organic boronic acids is reasonable to be considered. The reaction of aryl boronic acids with aryl halides at pH=7-8.5 is relatively retarded when compared to the reaction at pH=9.5-11. The pK_A of phenyl boronic acid is 8.8, thus suggesting the formation of the hydroxyboronate anion $[RB(OH)^-_3]$ at pH> pK_A and its transmetallation to palladium (II) halides.

In contrast, the cross-coupling reaction with certain electrophiles, such as allylic acetates, 1,3-butadiene monoxide and propargyl carbonates occurs under neutral conditions without any assistance of base.

An alternative transmetallation process is that organoboran compounds readily transfer their organic groups to (alkoxo)-palladium (II) complexes under neutral conditions (reaction 2.39). Allylic phenoxides and cinnamyl acetate react with 1-alkenyl borates under neutral conditions [144]. The (π-allylphenoxo)- and (π-allylacetoxo)palladium (II) intermediates generated from oxidative addition may undergo transmetallation without bases.

Eventually, it can be noted that in the palladium/base-induced cross-coupling reaction (reaction 2.40), the involvement of (alkoxo)palladium intermediate **3** is possible. The halogen ligand on organopalladium (II) is replaced by alkoxy, hydroxy or acetoxy anion yielding the reactive Pd-OR complexes **3** as reaction intermediates.

It is not so apparent in many reactions which process shown in reaction 2.38 or 2.40 is more dominant, but the formation of alkoxo-, hydroxo-, or acetatopalladium (II) intermediates should be considered as one of the crucial transmetallation processes in the base/palladium-induced cross-couplings.

The accepted mechanism of the Suzuki cross-coupling reaction under aqueous basic conditions is presented in Figure 2.4 [142].

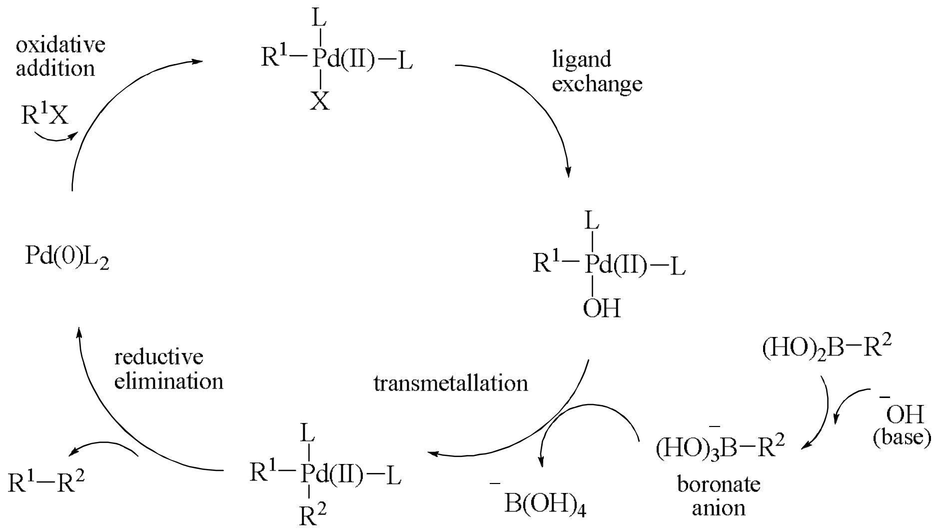


Figure 2.4: Suzuki cross-coupling reaction mechanism under aqueous conditions.

Aromatic, heteroaromatic, alkenyl and alkyl boronic acids or esters can be coupled effectively. The reaction is highly tolerant to functional groups.

The last step of Suzuki-coupling is the reductive elimination at which C-C bond formation takes place producing the product and regenerating the Pd(0) catalyst.

2.3.3 Stille coupling

It was developed in the early 1980s. It is used for coupling of aryl halides or triflates with organotin compounds via oxidative addition, transmetallation and reductive elimination in the presence of Pd (0) catalyst [134,136,137].

The transmetallation reaction step employs an organotin compound without any requirement for an oxygen base.

$$\mathrm{R{-}X + Pd(0) \longrightarrow R{-}Pd{-}X} \qquad \text{oxidative addition} \qquad \textbf{(2.41)}$$

$$R{-}Pd{-}X + R'{-}SnR''' \longrightarrow R{-}Pd{-}R' \qquad \text{transmetallation} \qquad \textbf{(2.42)}$$

$$R{-}Pd{-}R' \longrightarrow R{-}R' + Pd(0) \qquad \text{reductive elimination} \qquad \textbf{(2.43)}$$

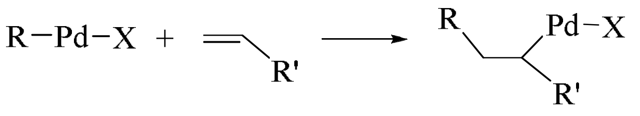
Usually there are four groups on tin compound which of only one involves in coupling and is transfered to palladium. These are alkynyl, aryl, allyl, alkenyl or benzyl groups. The other three are chosen as just simple alkyl groups, such as methyl or *t*-butyl, due to their lower transfer rate.

By the use of Stille coupling, biaryls, bis aromatic species of all types and ring closure of many sizes can be achieved easily.

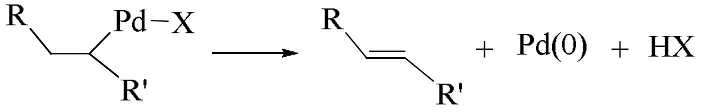
2.3.4 The Heck reaction

The Heck reaction was discovered in the early 1970s and is used for coupling of aryl or alkenyl halides with an alkene or terminal alkyne [145]. Reaction steps involve oxidative addition, insertion and β-hydride elimination. The product is an alkene.

$$R{-}X + Pd(0) \longrightarrow R{-}Pd{-}X \qquad \text{oxidative addition} \qquad \textbf{(2.44)}$$



insertion **(2.45)**



β-hyride elimination **(2.46)**

As the by-product a strong acid is liberated, a base must be present in the reaction mixture for scavenging. The success of the reaction is dependent on each step involved. Electron withdrawing groups attached to halides increase the rate of oxidative addition. With Pd (II) salts, it is believed that they are transformed to Pd (0) by redox processes. The insertion is stereospecific and syn. With alkenes bearing electron withdrawing groups, the rate of insertion increases. Sterical hindrance of alkene is also important at insertion step. β-hydride elimination is also syn, but in the case of acyclic alkenes, due to the free rotation, a stable *trans* alkene is obtained. Generally polar solvents (DMF, etc.) are used for the reaction.

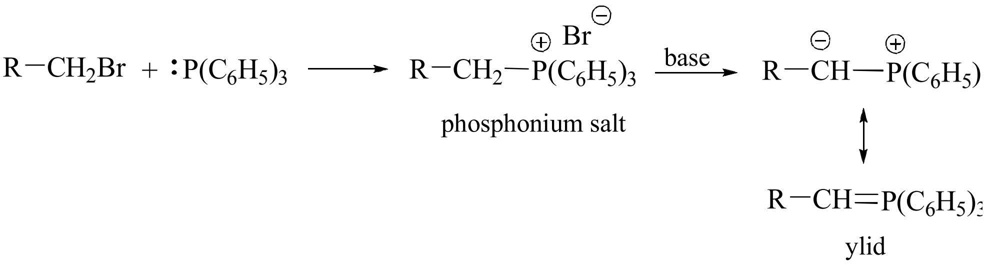
By intramolecular Heck reactions, ring systems are obtained with good efficiencies and free of limitations such as sterical hindrances, and also syn stereochemistry of both insertion and elimination steps are kept.

2.4 C=C Bond Formations

2.4.1 The Wittig reaction

The Wittig reaction is a very important olefin formation method. The reaction employs a phosphorus-stabilized carbanion (a ylid) as a nucleophile and a carbonyl compound as an electrophile.

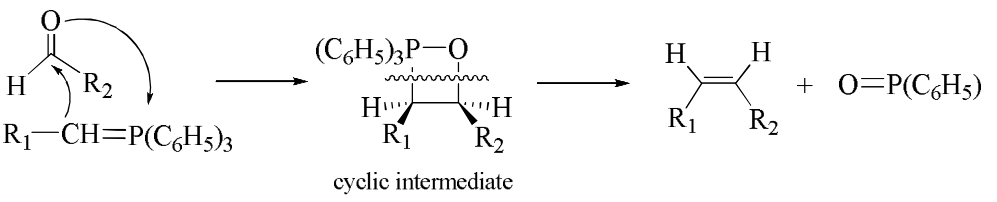
First a triphenyl phosphonium salt is formed and this is followed by the *in-situ* generation of the ylid in the presence of a strong base, such as lithiumdiisopropyl amide (LDA), alkyl lithum or potassium-*tert*-butoxide (reaction 2.47).



$$R-CH_2Br + :P(C_6H_5)_3 \longrightarrow R-CH_2-\overset{\oplus}{P}(C_6H_5)_3\ \overset{\ominus}{Br} \xrightarrow{base} R-\overset{\ominus}{C}H-\overset{\oplus}{P}(C_6H_5) \longleftrightarrow R-CH=P(C_6H_5)_3$$

(2.47)

Ylid is resonance stabilized by phosphorus and is a neutral compound. Due to the unfilled *d* orbitals in its valence shell, phosphorus atoms accept electrons from carbon and hence the resonance structure has a carbon-phosphorus double bond without formal charges. However, the carbon atom is electron rich and behaves as a good nucleophile and thus is capable of forming new C-C bonds via addition to carbonyl compounds.



(2.48)

Triphenylphosphine oxide is readily liberated from the cyclic intermediate at room temperature yielding an olefin. In short, an addition-elimination process occurs for C=C bond formation.

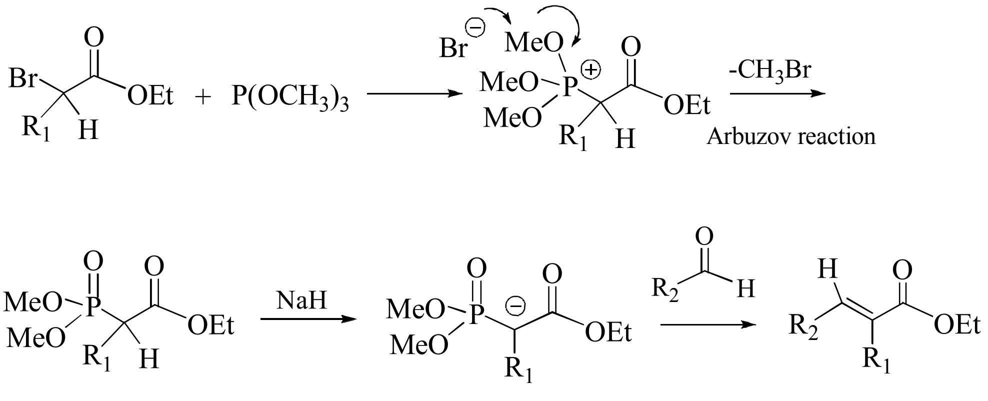
In the product the strong C=O of the starting compound is displaced with a weaker C=C bond, but the P-O bond is very strong thus its formation provides the proceeding of the reaction thermodinamically.

In Wittig reaction, the newly formed C=C bond is generally in less stable isomer, Z, indicating a kinetic control during the formation of the cyclic intermediate. In order to obtain the more stable anti-isomer, E, a strong base is added to the cold solution of the intermediate just before the elimination step. Even this enables the selective preparation of olefins up to an extent, generally Z and E isomers are obtained.

2.4.2 The Wittig-Horner reaction

The Wittig-Horner reaction is a variation of the Wittig reaction which employs carbonyl-activated ylids and trimethylphosphite as the phosphorus reagent. When a bromoester reacts with trimethylphosphite, a phosphite intermediate is formed. The intermediate is acidic and by addition of a base, such as sodium hydride (NaH), deprotonation takes place. The addition of an aldehyde or a ketone yields an α-β-unsaturated ester after the elimination of a phosphonate.

In Wittig-Horner reaction only the more stable E isomer is produced due to the equilibration of the intermediate just before the elimination.



(2.49)

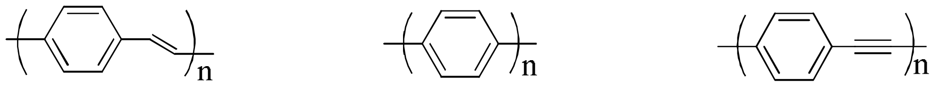
When bifunctional reagents such as bisphosphonium salts, bisphosphonates and dicarbonyl compounds are employed, both Wittig and Wittig-Horner reactions become useful methodologies for the synthesis of conjugated polymers such as PPVs (See section 2.5.3).

2.5 Poly(phenylene vinylene)s (PPVs)

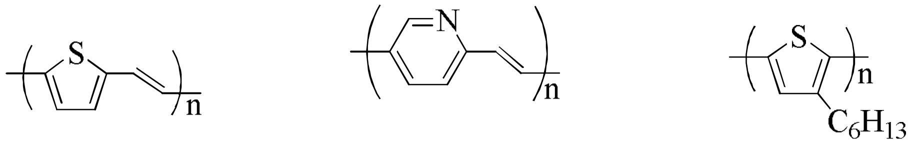
Conjugated polymers that emit light when an electric field is imposed on are known as “electroluminescent” polymers and have emerged a substantial academic and industrial interest as potential materials for electro-optical and opto-electronic applications [16].

Some examples for the types that belong to the family of π-conjugated polymers are poly(*p*-phenylene vinylene) (PPV), poly(*p*-phenylene) (PP), poly(*p*-phenylene ethynylene) (PPE), poly(*p*-theinyl vinylene), poly(*p*-pyridyl vinylene) (PPyV), poly(3-hexyl thiophene) and poly(9,9-dihexyl fluorene). The basic structures of these polymers are shown in Figure 2.5.

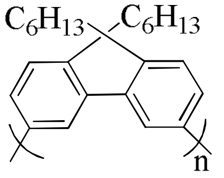
Since the first reports of electroluminescence from conjugated polymers by Holmes, Friend and coworkers [12,146], among the vast kinds of electroluminescent polymers, the most widely studied group is PPVs [147,148]. PPV and its derivatives are very attractive materials for optoelectronic devices such as polymer light-emitting diodes (PLEDs), photovoltaics and polymer field effect transistors (PFETs) due to their unique charge transport and luminescence properties.



Poly(*p*-phenylene vinylene) Poly(*p*-phenylene) Poly(*p*-phenylene ethynylene)



Poly(*p*-thienyl vinylene) Poly(*p*-pyridyl vinylene) Poly(3-hexylthiophene)



Poly(9,9-dihexylfluorene)

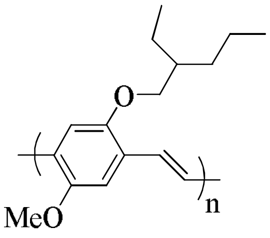
Figure 2.5 : Some types of π-conjugated polymers.

2.5.1 Properties of PPVs

2.5.1.1 Mechanical properties

The parent compound PPV (Figure 2.5) has a rigid structure and is inherently insoluble, interactable and infusible. This hinders its processability into thin films that is required for most of the applications. Consequently, tremendous efforts have been made for the design and synthesis of well defined conjugated polymers with improved solubility, processability and stability. These initial problems have been addressed by introducing conformationally mobile, relatively long and flexible side chains, such as alkyl or/and alkoxy groups to PPVs [149-151] and PPs [152,153] and PPEs [154-157].

Poly[2-methoxy-5-(2'-ethylhexyloxyl)-1,4-phenylene vinylene] (MEH-PPV) (2.50) represents the basic and the mostly investigated PPV derivative bearing alkoxy side groups and serves as a model providing solubility in common organic solvents [149] and processability for use in different applications [158].



(2.50)

MEH-PPV

A variety of other PPV types and derivatives bearing side-chains are summarized in Table 2.2.

Table 2.2: Different types of PPVs.

Polymer	Abbreviation	Ref.
Poly(2,5-bis-(N-methyl-N-hexylamino)phenylene vinylene)	BAMH-PPV	[159]
Dendritic PPV	BB-PPV	[160]
Poly(2,5-bis-(3,7'-dimethyl-octyloxy)-1,4-phenylene vinylene)	BDMO-PPV	[161]
Phenyl substituted PPVs	BDMP-PPV	[162]
	BDP-PPV	
Poly(2,5-bis-(2'-ethylhexyloxy)-1,4-phenylene vinylene)	BEH-PPV	[163]
Poly(2-butyl-5-(2'-ethyl-hexyl)-1,4-phenylene vinylene)	BuEH-PPV	[164]
Poly(2,5-bis-(octoxy)- 1,4-phenylene vinylene)	C_8-PPV	[165]
Cyano substituted PPV	CN-PPV	[166]
Poly(2,5-dimethoxy-1,4-phenylene vinylene)	DMeO-PPV	[167]
Poly(2-dimethyloctylsilyl-p-phenylene vinylene)	DMOS-PPV	[168]
Poly(2-phenyl-3-phenyl-4-(3,7'-dimethyloctyloxy)- 1,4-phenylene vinylene	DPO-PPV	[169]
Poly(2,3-diphenylphenylene vinylene)	DP-PPV	[170]
Poly(1,6-hexanedioxyl-4-phenylene-1,2-ethenylene-(2,5-dicyano-1,4-phenylene)-1,2-ethenylene-1,4-phenylene)	HCN-PPV	[171]
Poly(1-methoxy-4-cyclohexylethyloxy-2,5-phenylene vinylene)	MCHE-PPV	[172]
Poly(2-methoxy-5-(3',7'-dimethyloctyloxy)- 1,4-phenylene vinylene)	MDMO-PPV	[173]
Poly(2-methoxy-5-(n-hexadecyloxy)- 1,4-phenylene vinylene)	MH-PPV	[174]
Poly(2-methoxy-5-sulfopropoxy)-1,4-phenylene vinylene)	MPS-PPV	[175]
Poly(2,5-diphenylene-1,3,4-oxadiazolyle-4,4'-vinylene)	O-PPV	[176]
Poly(2-methoxy-5-triethoxymethoxy)- 1,4-phenylene vinylene)	PEO-PPV	[177]
Poly(2-phenoxy-1,4-phenylene vinylene)	PO-PPV	[178]
Poly((1',4'-bis-(thienyl-vinyl))-2-methoxy-5-(2'-ethylhexyloxy)- 1,4-phenylene vinylene	PTVMEH-PPV	[179]

2.5.1.2 Thermal properties

PPV exhibits a higher stability when compared to some other related π-conjugated polymers. Table 2.3 shows the thermal degradation temperatures for some of the polymers. The initial degradation temperature for PPV is at around 500^{o}C [180] and in the range of 500-600^{o}C, degradation products including toluene and xylene moieties are detected by *in situ* mass spectrometry. A slight increase, compared to neat PPV derivatives, is observed in the case of block copolymers of PPV and poly(methylmethacrylate) (PMMA) [181].

PPV can be converted into graphite at temperatures above 800◦C [182,183]. Pyrolysis at 3000 ^{o}C, strongly affects the electrical conductivity of PPV. When doped with sulfur trioxide, conductivities of 10^{5} Scm^{-1} can be obtained which is comparable to neutral graphite. A conductivity of $0,26.10^{3}$ Scm^{-1} is reported when PPV and other related polymers are pyrolyzed at 1700°C [184].

Table 2.3: Degradation temperatures of some π-conjugated polymers.

Polymer	Tg/ ^{o} C (as onset of degradation)	Ref.
Poly(acetylene)	200	180
Poly(*p*-xylene)	420	180
Poly(*p*-phenylene)	450	180
Poly(*p*-phenylene vinylene)	500	180

2.5.1.3 Electrical properties

For electronic applications, polymers should exhibit a fully π-conjugated structure. However, practically, conjugation of macromolecules is not “infinite” due to the saturated defects and an effective length of conjugation is the point at issue.

The two types of defects that are generally faced are structural defects and chemical defects [185]. Grain boundaries, crystallographic defects, chain end and oxidative defects are known as structural defects. Chemical defects can be in the polymer backbone itself or may be due to the impurities that are introduced during processing. If there are ethynylene moites instead of vinylene ones, these may behave as charge-carrier traps and trapping may take place at radiative or non-radiative states.

It is possible to determine the traps and identify their nature by techniques such as photoluminescence (PL) and electroluminescence (EL) spectroscopy, current voltage and capacitance voltage measurements, capacitance transient spectroscopy and admittance spectroscopy [185,186].

2.5.1.4 Optical properties

PPV is a bright yellow fluorescent polymer that shows emission maxima at 520 nm and 551 nm, in the yellow-green region of the visible spectrum [12]. In EL devices, besides being used as the light emitting component, PPVs are also used as the hole-transporting materials due to their good hole-transporting capability [187].

MEH-PPV shows a maximum at around 640 nm in PL spectra and it is red shifted with the increase in annealing temperature. In PPV, an increase in static pressure causes a red shift in PL spectra and meanwhile the intensity of the main peak decreases [188]. Due to interaction of the polymeric chains, the structure turns out to be more planar so the length of conjugation becomes longer.

2.5.1.5 Doping and dopants

Doping can be done by oxidation (p-doping) or reduction (n-doping) reactions in the backbone of the polymer. Structural and electronic modifications are created in the backbone and the electrical conductivity is improved by doping.

Two main doping methods are reactive doping and dye doping. Arsenic pentafluoride can be used as the dopant for PPV in reactive doping. A Friedel-crafts chain extension and cross-linking occurs and electrical conductivity is by hopping mechanism [189].

The modifications can be evidenced by infrared techniques, by the appearance of some new bonds due to the formation of new structures such as quinoid [190].

Dye doping is achieved by the addition of a fluorescent dye to polymer [191]. The solution method is not used to dope PPV as it is insoluble. Instead, vapor transportation method is used in which the dye molecules are introduced in the polymers in the gas phase, in vacuo [191].

2.5.2 Applications of PPVs

2.5.2.1 Light-emitting diodes (electroluminescent devices)

Since early 1960's, light emitting devices (LEDs) based on traditional inorganic electroluminescent materials have been commercially available. The development of devices employing low molecular weight electroluminescent organic materials was not so successful and competitive. Even the operating voltage was as low as 10 V, relatively low efficiencies and short lifetimes were still a problem ahead. The rearrangement of the molecules due to the heat generation leaded crystallization and so compromising of interfacial contacts and thus lifetimes of the devices were poor.

Apart from morphological stability and electronic features, the emission color of small organic molecules is affected by micro environment characteristics, such as polarity and their location in the device. The mobility of the chromophore is restricted when it is attached to a polymer chain and so the emission becomes dependent on the structural properties of the polymer, such as architecture, location and the distribution of the chomophores. Just with one polymer, only by varying its structure, color-tuning could be achieved. So, the most obvious way to improve the morphological stability and color tuning in organic LEDs was the use of light emitting polymers.

The discovery in 1990 by the Cambridge group, that it was possible to use PPV as the emitting component in a polymer-based LED, has led to new pathways and generated many research efforts [12].

The photoluminescence (PL) and electroluminescence (EL) spectra of PPV indicated that the emitting species are the same upon excitation by light or electric current. [16]. This novel improvement provided the possibility of combining the good mechanical and processing properties of the polymers with semiconductivity. Easy oxidation and reduction and forming polarons without affecting the σ bonds and thus the physical strength of the polymer is an important feature of electroluminescent polymers. The advantages concerning the use of electroluminescent polymers as a component in LEDs are the synthetic access and structure variations and thus color tunability, anisotropic light emission, light weight, large area displays, environmental factors (less toxicity compared to inorganic materials), and flexibility (a variety of unusual shapes of displays can be obtained) [192].

Electroluminescent polymers are generally aromatic π-conjugated polymers and that restricts their applications. Regarding this, the concepts, for which the efforts are targeted, include precursor polymers, solubilizing groups, polymers with conjugated and non-conjugated segments in the main chain or in the side chain. Electrical, optical and mechanical properties of such polymers may be affected by impurities, defects, structural disorders, effective length of conjugation and low-molecular weight. Smart synthetic approaches and well-defined structural designs and architectures are the scopes of the research area. The basic requirements for the choice of electroluminescent polymers to be used in a device are good film-forming properties, transparent films, good thermo-mechanical stability and excellent heat, light and environmental stability; and as the emitting component, color tunability and emission in the visible region. The basic architecture for a light emitting device is shown in Figure 2.6.

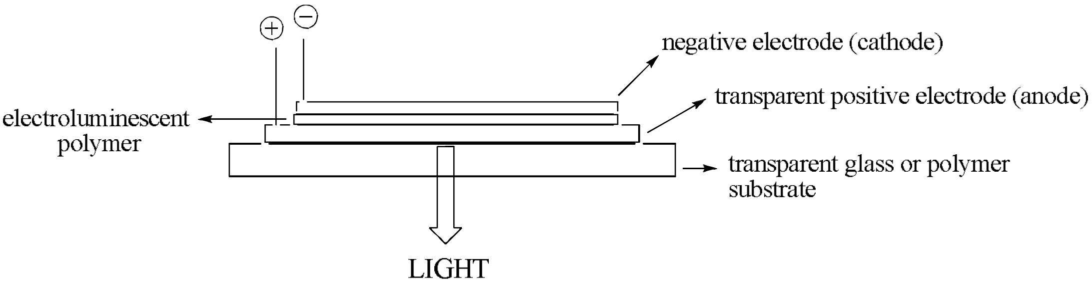


Figure 2.6: The basic architecture for a single layer LED device.

The main components of the device are a transparent glass substrate or a polymer carrier, an optically transparent anode, a light emitting polymer film and a metallic cathode. The anode is generally indium-tin oxide (ITO), coated on a transparent glass or polymeric substrate, as 15 nm in thickness, which allows to pass the light that is emitted from the polymer. The cathode is a low work function metal, such as Ca, Mg or Al. For the improvement of the operational stability, low work function metals (eg. Mg or Li) are sometimes alloyed with more stable metals with higher work functions (e.g. Al or Ag) to be used as the cathode material [193].

The light emitting polymer is deposited on ITO either by spin or dip-coating from solution as a very thin, smooth film, typically in the order of 100 mm in thickness, so that the electric field strengths occur $>10^5$ Vm^{-1}. The cathode material is evaporated on the polymer film in vacuo.

The basic working principle of such a device, which refers to a ligt emitting diode, can be explained as in Figure 2.7.

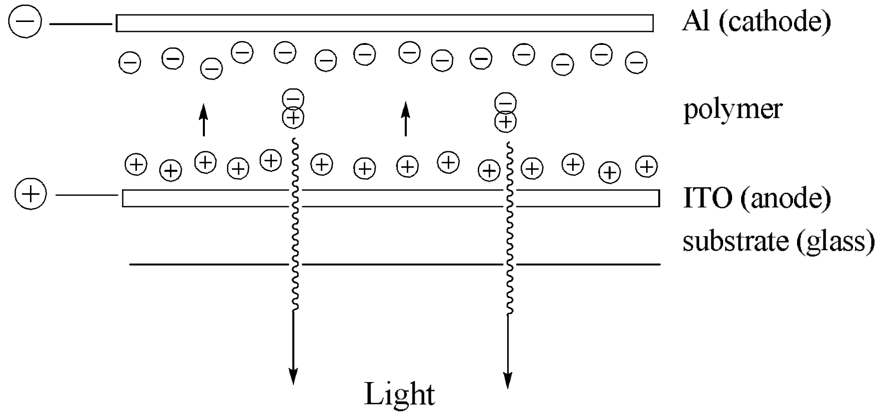


Figure 2.7 : The basic working mechanism of a LED.

When a voltage is applied to the electrodes of the device, the cathode injects "electrons" in the conduction band of the polymer (π*-state), which is the lowest unoccupied molecular orbital (LUMO), and the anode injects "holes" in the valence band (π-state), which is the highest occupied molecular orbital (HOMO). These injected charges are known as "polarons" and travel from one electrode to the other. Through the combination of electrons and holes, neutral species named as "excitons" are formed. Those excitons can be in singlet or triplet states. Only singlets can decay radiatively, and the light emissions follow the same mechanism path as in PL. The triplet state doesn't have sufficient energy to emit light in visible region. There is only one singlet for each triplet states and therefore material developments focus on enhancing the singlet states. A way to overcome this matter is the use of phosphorescent materials which can generate emission from both, singlet and triplet excitons [194-197].

The quantum efficiency is expressed as "photons emitted per electrons injected" and is about of 0,1-5 %. The quantum yield for luminescence is "the ratio of radiative processes to non-radiative processes" and is determined by the decays of excitons formed within the polymer. These excitons can travel along the chains and may be trapped at quenching sites where non-radiative processes may take place. They may also lose their energy in a thermal way by a photon emission or transfer their energy to impurities or convert into a triplet state by an intersystem-crossing and lose the energy without radiation. The energy gap between the LUMO-HOMO levels of the chromophore determines the energy of the released photon in radiative process. It is between 1.4-3.3 eV for organic polymeric chromophores and corresponds to 890-370 nm wavelengths which cover visible region. So the band gap energy controls the color of the emitted light. The energy differences between work functions of the electrodes, the electron affinity and the ionization potential of the polymer control the charge injection process, and hence the “turn-on voltage”.

The “turn-on voltage” is also a factor that affects the quantum yield of the device. A complete carrier recombination probability is only obtained when the two carrier concentrations are of equal level for a certain polymer. So, for a given electric field, the charge flow should be maximized, and by choosing the appropriate materials, energy barriers and hence the “turn-on voltage” should be minimized.

The balance of injected electrons and holes can be achieved by adjusting the ionization potential of the polymer to the work function of the anode (for ITO, -4,8 eV) and by adjusting the electron affinity of the polymer to work function of the cathode. Since the electron injection is more complicated than the hole injection in electroluminescent polymers, to improve the light-emitting efficiency in devices, polymers with high electron affinity are used as the organic layer and metals with low work functions are used as cathode.

The overall quantum efficiency is determined by the ratio of singlet exciton radiative decays to the sum of all competing non-radiative decays and exciton concentration.

In a basic device the polymer layer is a “single” layer. It is possible to fabricate thin film multilayer heterostructures with high control over the structural features and the thickness of the layers, and such “multilayer” organic devices are more common. A design for a multilayer device is shown in Figure 2.8 .

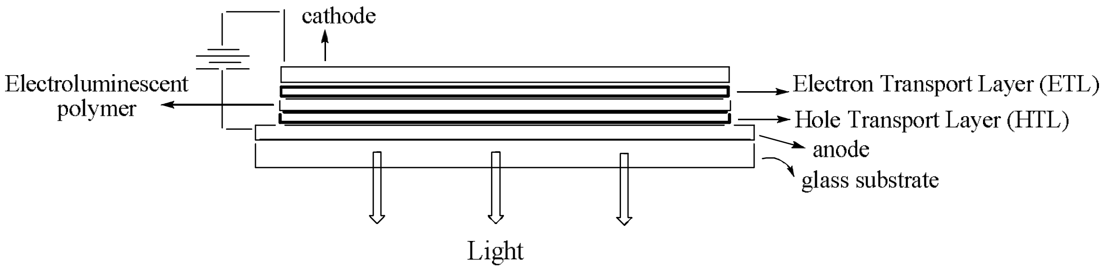


Figure 2.8 : Design of a LED with HTL and ETL.

As mentioned before, maximum charge carrier recombination is only possible if the two carrier concentrations are of equal levels. If excitons are formed at the interface of the polymer and the electrode, the carrier injection is lowered and the LED efficiency is reduced. Moreover, the defects are usually in these interface locations and can act as quenching sites [198,199]. So, additional layers of organic materials (low molecular weight or polymeric) are introduced between the chromophore film and the electrodes, which are called as “transport layers”, in order to decrease exciton quenching by separation and to facilitate charge transport and localize carriers by preventing their crossing the device without recombination or forming excitons. Hence, the photonic output and the device efficiency is improved.

Polymers used as charge carrier or charge barrier layers should not emit light in visible region (as they are not the emissive layers), but should reversibly form radical cations (hole transporting materials) and radical anions (electron transport materials) and should show good charge transport.

Materials used for electron transporting layers (ETL) are electron deficient compounds (e.g. oxadiazole compounds) in the free form or grafted to a polymer chain [200].

A variety of electron accepting polymers (e.g. PMMA with suitable pendant groups [201] have been used as hole transporting layers (HTLs).

In fabrication process, the polymer is generally applied by spin-coating or ink-jet printing and the electrodes are constructed by vacuum deposition or sputtering. Through fabrication, both wet and dry processes are required. Instead of depositing the sequential layer one by one, two separate parts, each formed on a substrate with different functional layers can be used to fabricate devices [202]. Thus, difficulties arising from the wet and dry processes and the costs of fabrication can be reduced and furthermore varying combination possibilities for the final device can be provided.

By using poly(9,9-dioctylfluorene) (POF) as the emissive layer, PPV as the hole transporting layer, tetra-n-butyl ammonium tetra fluoroborate as dopant and a Li-Al alloy as a cathode, bright blue electroluminescent devices have been fabricated [187].

Multilayer green light emitting devices have been fabricated from poly(N-vinyl carbazole) and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole. PPV layer thickness affects the EL, and the performance depends on the structure of the polymer. Bulky side groups decreases the intermolecular interactions and increases the performance [203,204]. However, the length of the side chains is also important

[205]. Long side chains may tilt or fold back and intermolecular distance may decrease again.

More examples of PPV related devices and their efficiencies are present in the literature [206-211].

2.5.2.2 Photovoltaic devices

The first development of photovoltaic cells was in 1950s as p-n junctions of inorganic materials. Since then, various cells as homojunctions, heterojunctions or other architectures using inorganic materials have been fabricated. Solar radiation is converted to direct-current electrical power by photovoltaic devices [212].

There are two types of photovoltaic devices [213]. One is the “regenerative” type. The electrons are transported to the anode. The external circuit and the holes are transported to the cathode and are oxidized by external circuit electrons. In this type, light is converted in to electrical power without any chemical change left behind. The other type is known as “photosynthetic type”. There two redox systems; one with the holes at surface of the electrode and the other with the electrons that enter the counter electrode.

Photovoltaic devices based on conjugated polymers have received considerable interest [173] and most commonly MEH-PPV based devices have been investigated. Organic devices are regenerative type. When compared, organic solar cells have several advantages over inorganic ones, such as light weight, flexibility and low cost of fabrication. Power conversion efficiency and long term stability are still the points that should be improved for practical applications.

In photovoltaic devices, when the light is absorbed, electric charges that are flowing to the electrodes are separated and a difference of electrical potential is built up. Photo induced charge generation and charge transport are two factors that affect the efficiency of the devices.

The region between photoactive layer and the electrode is the transition region and a resistance against a charge carrier may occur. A better charge crossing leads to an increase in the efficiency. To interrupt reactions between photoactive layer and the electrode, an electrically insulating transition layer can be introduced, but thickness of this should be kept as ≤ 5 nm not to hinder the charge carrier crossing [214].

Heterojunction means connection of layers that are from materials which have different electrical properties, e.g. band gaps. Bulk heterojunction means microscopically phase separated polymeric composites. Material or the composite should supply both electron donor and electron acceptor properties. PPV and poly(alkyl-thiophene)s are the most commonly used polymeric electron donors. Cyano substituted PPV and poly(*p*-pyridyl vinylene) are used as polymeric acceptors.

Phase separated devices show better photovoltaic performance. In spin-coating process, phase separation depends on evaporation time of the solvent because once solvent is evaporated, a further rearrangement becomes impossible and morphology is fixed. The use of different solvents causes big differences in the performance. Thermal annealing of the devices permits rearrangement of the polymers to a lower energy state and the desired alignment can be achieved.

The use of materials that have higher glass-transition temperatures improves the thermal stability of photovoltaic cells [215], which is attributed to a more stable bulk morphology.

Introduction of highly electron deficient units (e.g. oxadiazoles) as side groups into PPV/MEH-PPV enhances the solar cell performance due to the increase in exciton dissociation rate and promoted electron transport [216].

While PPV-based devices show high open circuit voltages, poly(thiophene)-based devices show a lower open-circuit voltage although the thiophene units exhibit good donor properties. Thus it is appropriate to combine both structures into one polymer. By such a combination, 1,2 % of power conversion efficiency can be achived [179,217].

Ordered lattices of materials that have different electron affinities can be achieved by ink-jet printing [218], such as MEH-PPV and cyano substituted PPV, and thus an efficient charge seperation is accomplished.

Photovoltaic devices are highly sensitive to oxygen and humidity in the atmosphere. This affects their service times. By the use of encapsulation, the service time of a solar cell can be improved from a few hours up to several months (4 months) [219].

2.5.2.3 Nanofibers

Nanofibers of PPV can be produced from an alcoholic solution of a PPV precursor polymer by electrospinning. The solution is streamed by an electrically charged needle so the droplets are stretched. Voltages of nearly 10 kV are applied and the PPV precursor polymer is converted into PPV fibers after annealing for 2h at 180◦C. The morphology of the fibers can be controlled by using poly(vinyl alcohol) (PVA)/ PPV precursor polymers and is characterized by scanning electron microscopy and fluorescence microscopy [220,221].

When compared to bulk material, nano fibers may show a blue shift, a stronger fluorescence intensity and a higher surface voltage [221,222]. Nanofibers of yellowish-green to blue fluorescence can be produced and may find applications in optical and electronic devices.

2.5.2.4 Nanotubes

Carbon nanotubes exhibit good electrical and thermal conductivity, good mechanical strength and low work function. They are of interest as electron guns and in flat panel displays. Nanotubes of PPV show noticably distinctive fluorescence decay times when compared to bulk [223]. Graphitic carbonized PPV nanotubes have been prepared. Moreover, nanotubes with gold nano particles were used in field of emitting devices [224].

2.5.2.5 Sensors

For medical, biological or some environmental applications, the detection of pH changes by sensors is of particular importance. A PPV-based pH sensitive photoconductor has been reported [225]. Changes in pH are determined by changes in photocurrent.

A bridged type PPV has been used as gas sensor [226]. The device showed selectivity to NO_2 among to other gases CO, NH_3 and SO_2. The electric current changed relatively according to NO_2 concentration.

Vapors of some organic compounds (e.g. acetone, ethyl acetate, diethyl ether, acetic acid, methanol, ethanol, hexane and toluene) can also be detected by devices of PPV-based block copolymers with phenylene oxide units [227].

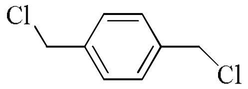
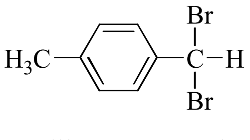
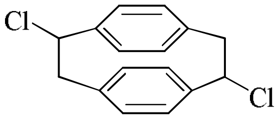
2.5.3 Synthesis of poly(phenylene vinylene)s

Synthetic polymer chemists should address many properties and meet the criteria that are required for most of the applications which are discussed previously.

As the polymer itself is insoluble and unprocessable due to its rigid-rod structure precursor polymer routes and a variety of other methods have been developed for synthesis of soluble and processable PPVs and its derivatives with different side groups and structures in order to be used for various applications. In the field of electronics, polymers should be perfectly π-conjugated with minimum defects which are responsible for their performance.

The routes used for the preparation of PPVs can be classified as the polymerizations via quinodimethane intermediates, polycondensations, transition-metal catalyzed polycouplings and metathesis polymerizations. Chemical vapor deposition and electropolymerization are the other methods that have also been used. Synthesis with representative structures will be discussed including advantages and disadvantages of each method. The basic structures of some of the monomers and the employed methods are summarized in Table 2.4.

Table 2.4: Some monomers and the employed methods for synthesis of PPVs**.**

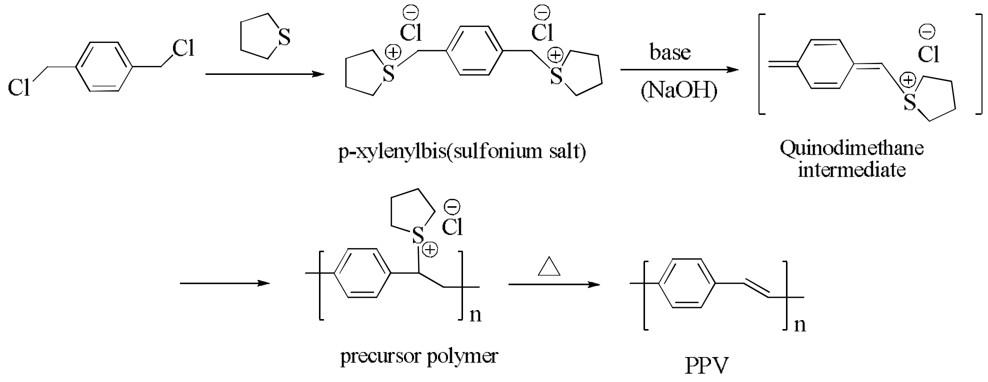
Monomer	Method
 1,4-Bis-(dichloromethyl)-benzene	Standard procedure (direct monomer for quinodimethane routes; indirect monomer for other methods)
 α, α-dibromo-*p*-xylene	Several methods
 1,9-Dichloro[2.2]-*p*-cyclophane	Chemical vapor deposition and some other methods

2.5.3.1 Polymerizations via quinodimethane intermediates

Wessling-Zimmerman route

Wessling-Zimmerman route is the first developed method for the preparation of PPVs and involves three steps [228].

The first one is the synthesis of *p*-xylenyl bis(sulfoniumsalt) by the reaction of 1,4-bis(dichloromethyl)benzene and tetrahydrothiophene. Some other related sulfur compounds can also be used. The second step is the treatment of *p*-xylenyl bis(sulfonium)salt with 1 equivalent of base, generating a quinodimethane intermediate, which polymerizes to give the sulfonium precursor polymer. The precursor polymer is water soluble, thus can be processed into thin films by spin coating, dip-coating or other techniques. Eventually by heating at about 180°C-300°C under vacuum, the final polymer, PPV, is obtained as thin films.



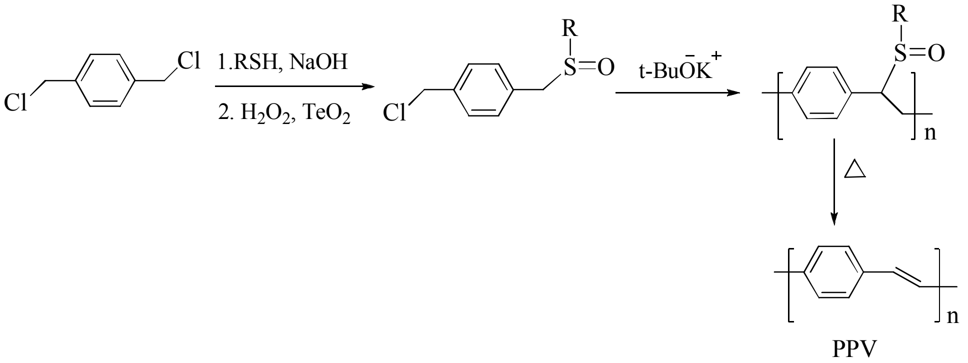
(2.51)

The polymerization pathway, either radicalic or anionic, has been the subject of a debate, but as the presence of oxygen lowers the molecular weight of PPV drastically, it is believed that radical mechanism is more dominant [229].

Including MEH-PPV, many other PPVs have been synthesized by the Wessling sulfonium precursor route [230] but due to unpleasant properties of the sulfur reagents such as toxicity and offensive odor, other routes are more preferred and variations on the route have been examined.

Vanderzande precursor route

The Wesling route has been modified by Vanderzande and co-workers by using different sulfur-based leaving groups, a sulfinyl or sulfonyl precursor polymer is formed [231-233]. Reaction 2.52 shows the synthetic pathway.



(2.52)

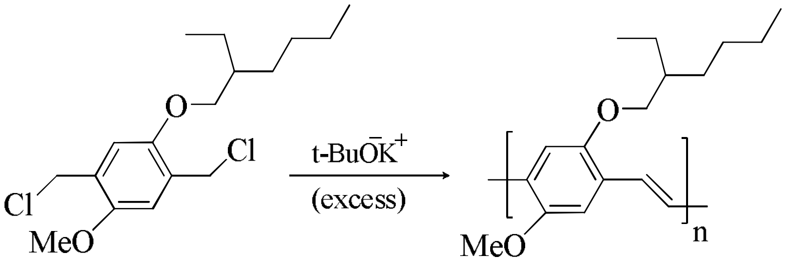
Polymers with high molecular weights are obtained and the mechanism is radicalic [234]. Although the monomer synthesis is more complicated, which is a disadvantage for the route, the final PPV shows less defects [235-237].

PPV precursor polymers bearing ester and carboxyl groups have also been synthesized via the sulfonium route. After conversion into PPVs, carboxyl functionalities can be changed to nitro, amino or aldehyde groups [238].

The Gilch route

The Gilch route has been one of the most frequently used method for the synthesis of PPVs [239]. The reaction involves the direct conversion of a dihalomethyl derivative in to PPV in the presence of an excess strong base such as potassium-*tert*-butyl alcoholate (reaction 2.53). If the base is not in excess, the halo-precursor monomer can be isolated and then converted to the final polymer via treatment by base or thermally in vacuum.

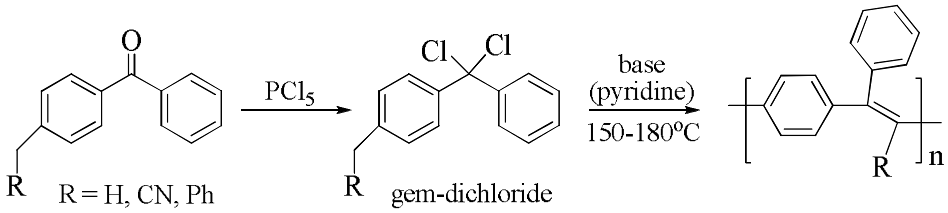
First, anionic mechanism was suggested for the reaction [240,241], but the recent studies [242,243] have shown that the reaction follows a radical pathway. The radical mechanism is also evidenced by the use 2,2,6,6-tetramethylpiperidine-N-oxyl as a scavenger [244].



(2.53)

Hörhold method

PPVs bearing subtituents, such as cyano and/or aryl, on vinylene bond can be synthesized by Hörhold-Method [245]. First a geminal-dichloride is prepared and then the final polymer is obtained by the self-condensation of this geminal-dichloride in the presence of base.



(2.54)

Polymerizations via quinodimethane intermediates possess two main limitations. The first one is that route is not accessable for every aromatic system [246-248]. The reactions depend on the properties and the polimerizability of the intermediate.

The second one is the formation of defects. According to the coupling of the intermediate ethyne or ethane moieties can be formed [249-251]. These defects can be reduced by choosing appropriate subtituents. Some possible non-regular couplings and the defects are shown in Figure 2.9.

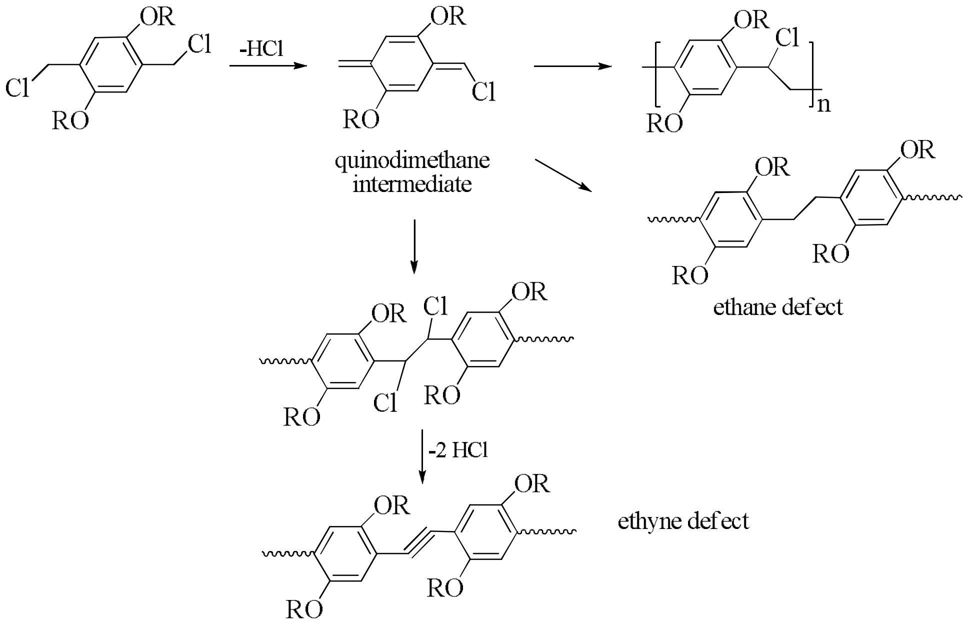
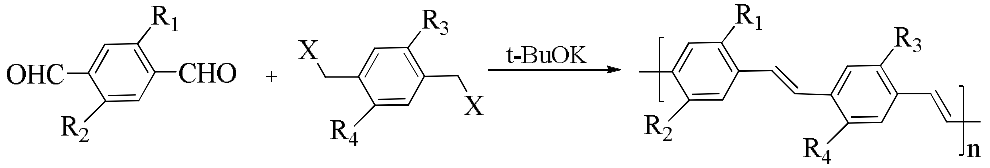


Figure 2.9: Defects formed in Gilch synthesis.

2.5.3.2 Polycondensation routes

The Wittig and Wittig-Horner polycondensations

In Wittig condensation [252], arylbisaldehydes are reacted with arylbisphosphonium salts, while in Horner method, they are reacted with bisphosphonates to produce PPVs. Reaction 2.55 summarizes the syhnthesis of PPVs by Wittig and Horner methods.



(2.55)

X= $\overset{\oplus}{P}Ph_3\overset{\ominus}{Cl}$ (Wittig Polycondensation)

X= $PO(OR)_2$ (Wittig-Horner Polycondensation)

These methods have two advantages over quinodimethane routes:

1) It is possible to prepare alternating copolymer structures.
2) Polymers do not possess defects (such as ethane or ethyne moieties as in Gilch route).

Although the molecular weights of the obtained polymers are lower when compared to Gilch route, they exhibit better optical properties due to lack of defects. On the other hand, "*cis*" and "*trans*" conformations of the vinylene bonds are possible.

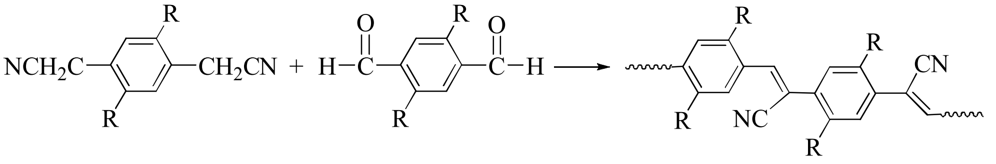
Horner condensation yields higher molecular weight polymers with all the vinylene bonds in *trans*- conformation. In Wittig condensation percentage of the double bonds in *cis*- conformation is higher and this affects the optical properties of the polymer [253-255].

MEH-PPV prepared by Horner condensation is much more soluble than the one obtained by Gilch route as its molecular weight is lower, but shows EL and PL properties of the higher molecular weight polymer [256].

Knoevenagel condensation

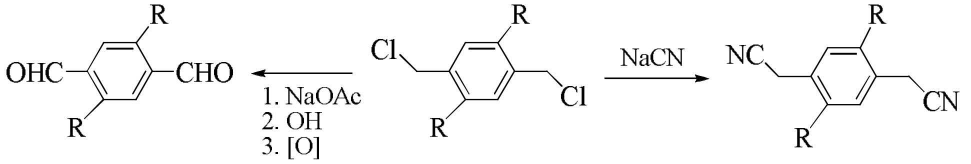
In Knoevenagel condensation, dialdehydes are condensed with bisnitriles and thus PPVs with alternating structures can be synthesized.

The method also allows the preparation of PPVs with substituted vinylene bonds in the backbone. PPVs bearing cyano groups on the double bonds with a high electroluminescence activity have been prepared [257,258]. The synthesis is described by reaction 2.56.



(2.56)

Both of the monomers can also be readily obtained from the bischloromethyl compound, which itself is a monomer for Gilch reaction, as shown in reaction 2.57.



(2.57)

2.5.3.3 Transition metal-catalyzed methods

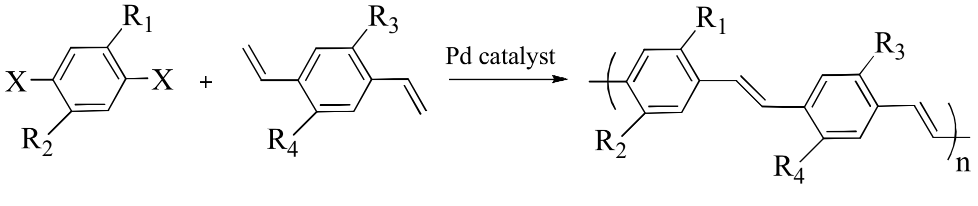
Transition metal-catalyzed cross-coupling processes offer a direct route for synthesis of PPVs as homopolymers or alternating copolymers. The monomers should be substituted in order to have soluble polymers; if not, immediately insoluble polymer is obtained.

With substituents, polymers that are soluble in common organic solvents such as chloroform, methanol or DMF are produced [259]. The catalyst transition metals should be removed completely otherwise the residues may reduce the service times of the polymers and hence the devices.

Heck coupling

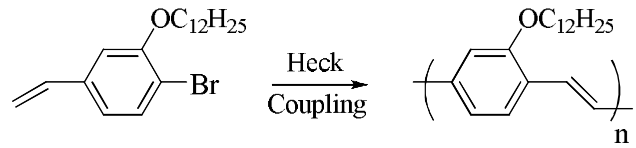
In Heck Coupling, dihaloarenes and divinylarenes are coupled in the presence of a palladium catalylst to produce PPVs.

Even the molecular weights of the polymers are lower when compared to Gilch route, they possess relatively less defects.



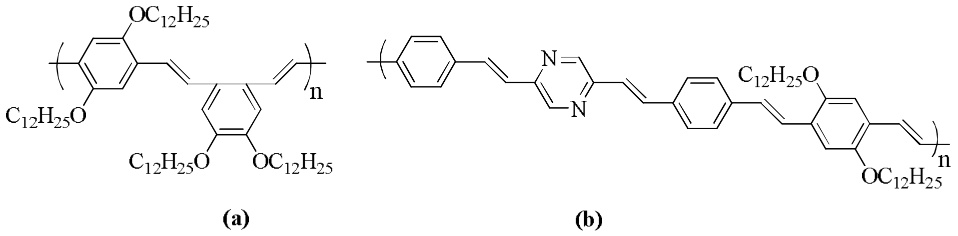
(2.58)

Self polymerization is also possible with monomers having both functionalities, such as substituted vinyl bromobenzenes [260].



(2.59)

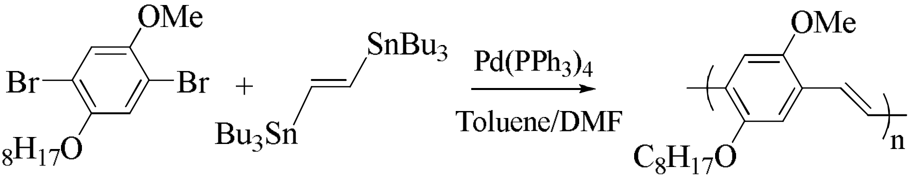
Some other examples of PPVs by Heck, which can not be obtained by the other methods discussed, are the copolymer with ortho-phenylene units (**a**) and the pyrazine containing copolymer (**b**), as shown in (2.60) [261,262].



(2.60)

Stille coupling

The Stille coupling of haloarenes with *trans*-1,2-bis(tributylstannyl)ethylene has also been used occasionally in the synthesis of substituted PPVs or copolymers, but the yields and molecular weights are generally low [263-265].

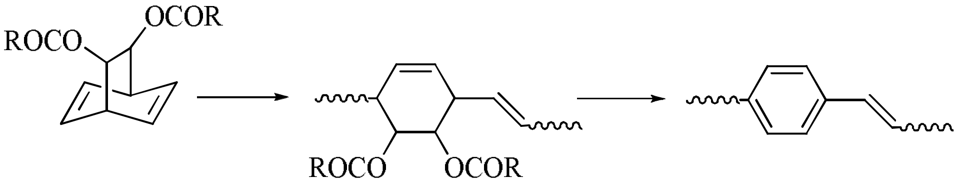


(2.61)

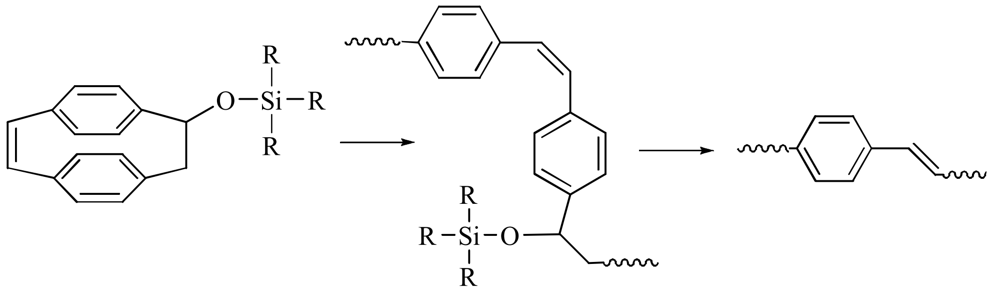
Metathesis Polymerization

Transition metal-catalyzed metathesis of divinylbenzenes has been used to prepare substituted PPVs but the obtained materials were just oligomers [266,267].

The second metathesis polymerization type is ring opening metathesis polymerization (ROMP) which has been introduced by Grubbs [268]. Precursor polymers of PPVs were obtained by conversion of substituted bicyclo [2.2.2] octa-2,5-dienes in the presence of molybdenum-based metathesis catalyst. The precursor polymer is aromatized by using trioctylamine at 200°C or at 280°C under inert conditions. Reaction 2.62 illustrates the synthesis. Siloxy substituted cyclophanes have also been used as the starting compound in ROMP [269] (reaction 2.63).

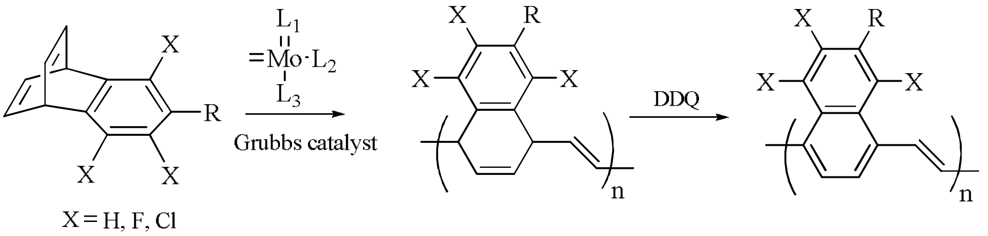


(2.62)



(2.63)

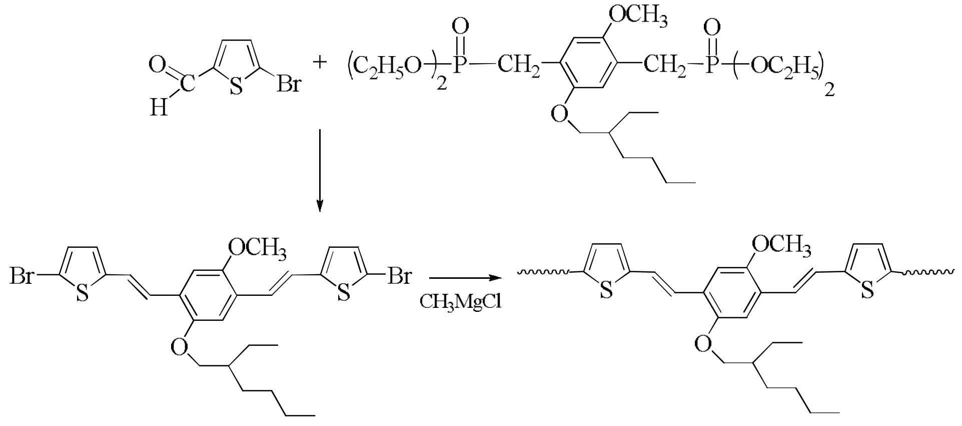
ROMP has also been used for the synthesis of poly(naphthalene vinylenes)s (reaction 2.64) [270].



(2.64)

ROMP is a living polymerization, thus allows control over molecular weight of the polymers. On the other hand, it is difficult to prepare the desired monomers and it is not a direct route for preparation of PPVs.

Substituted thiophenes can be polymerized via a living chain growth mechanism by Grignard metathesis polymerization, which is another variant of metathesis [179]. Reaction 2.65 shows the synthetic route.

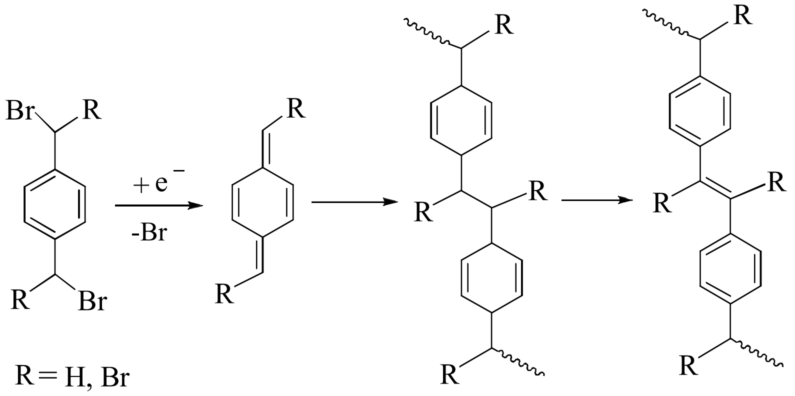


(2.65)

2.5.3.4 Other methods

Electropolymerization

Even a wide variety of substituents can be introduced by electrochemical method; monomers with easily reducible substituents are not suitable. The reaction takes place in an aprotic solvent, such as DMF, and proceeds via quinodimethane intermediates. Electropolymerization route is summarized in reaction 2.66 [271].

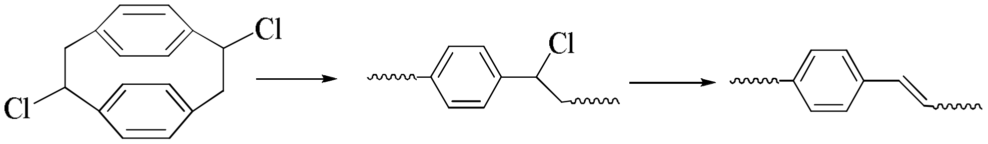


(2.66)

Random copolymers can be prepared from different 1,4-bis-(halomethyl)-arenes by co-electrolysis [272]. Water soluble polymer salts are obtained with carboxyl functional monomers.

Chemical vapor deposition

Different insoluble PPVs with required dimensions and shapes are prepared by chemical vapor deposition techniques [273]. 1,4-bis-(dichloromethyl)-benzene, α- α-dibromo-*p*-xylene or chlorinated cyclophanes are used to synthesize PPVs.



(2.67)

The starting material is deposited on a surface via an intermediate and then by the elimination of hydrojen chloride final PPV is obtained. Films of 10-100 μm in thickness can be produced. As cyclophanes are not easily available, 1,4-bis-(dichloromethyl)-benzene is used more often.

When two monomers are deposited, it is possible to prepare copolymers [274] and hence the tuning of electroluminescence. By varying the temperatures, copolymers of different units from a single monomer can be obtained. Copolymers of 1,4-phenylene vinylene and 1,4-phenylene-1,2-eth-anediyl units are prepared from *p*-(methoxymethyl)benzyl chloride in this manner by chemical vapor deposition [275].

2.5.4 Structure-property relationships in PPVs

As electroluminescent polymers are the active components in fabrication of various devices, some properties such as emission colors with high efficiency and intensity, good electrical and optical stability must be addressed while designing a synthesis. Meeting all these criteria is a big challenge for the synthetic chemists as the structure of the polymer has an important influence on the final properties of the materials and thus the device performance.

The conjugation length and effects of the substituents are two main structural factors which influence the emission color and efficiency of PPVs. Aggregation in solid state also affects the emission spectra by a red-shift and photoluminescence efficiency by enhancing the radiative decays.

2.5.4.1 Substituent effects on emission color of PPVs

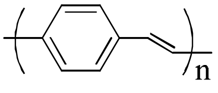
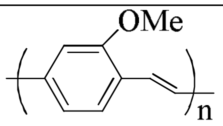
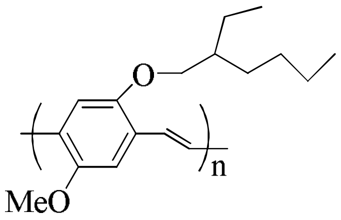
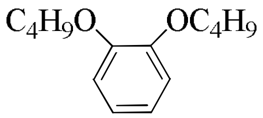
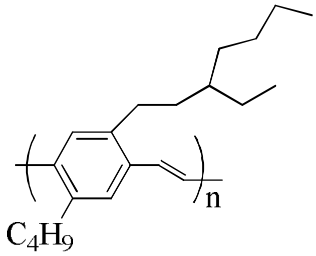
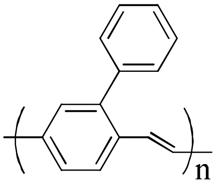
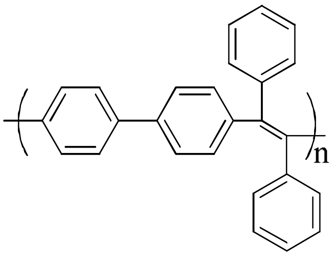
Besides improving the solubility and the subsequent processability, the side chains attached to the backbone of conjugated polymers lead to remarkable changes in their optical, electronic and transport properties [276-279].

By choosing the appropriate substituents, the emission color of PPVs can be tuned from blue-green to red and even into near infrared.

As mentioned before, unsubstituted PPV is a bright yellow polymer that shows emission maxima at 520 nm and 551 nm in the yellow-green region of the visible spectrum [12].

When alkoxy groups are attached to the phenylene ring, a red shift in the emission is observed. The position and the size of the subtituents are also important for the luminescence efficiency because of chain packing. Bulky side chains decrease the non-radiative decays due to interchain interactions, so PL and EL efficiency increases [150]. Interchain interactions may cause aggregate formation which leads to a redshift in solid-state emission [280,281]. Table 2.5 presents some examples of the substituent effects on the emission color of PPVs.

Table 2.5: Effect of substituents on the emission color of PPVs.

Polymer	Structure	Emission/effect on emission	Ref.
PPV		520 nm, 551 nm yellow-green	[12]
Alkoxy substituted PPVs		550 nm, yellow	[282]
		603,650 nm orange red	[149]
		530 nm green	[283,284]
Alkyl substituted		green	[285]
Aryl substituted		green	[286]
Substitution on vinylene		blue shift	[287,288]

Extremely large substituents reduces the conductivity and hence the EL efficiency. Steric effects cause a blue shift in the emission as the polymer backbone is twisted (out of plane) to decrease the steric interactions of substituents and hence effective conjugation is reduced. Alkyl, aryl or sillyl side groups do not cause a red-shift in the emission and all are green emitting polymers [285,286,289].

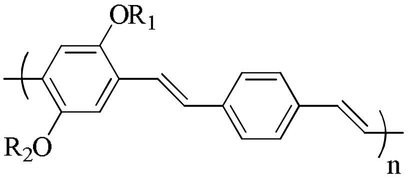
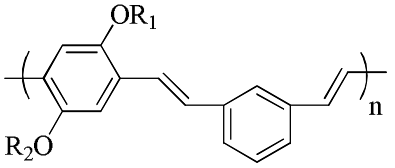
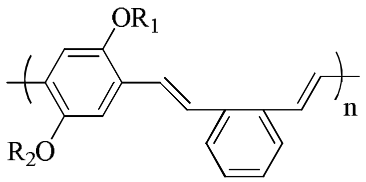
If the substituents on the vinylene moiety are bulky, they cause remarkable blue-shift on the emission maxima, if not, they seem to have no influence.

2.5.4.2 Effect of conjugation degree on emission color of PPVs

The conjugation length of chromophores within a conjugated polymer affects the emission color. The *ortho*, *metha* or *para*-positions of the phenylene units influence the conjugation.

All *para*-polymer shows an emission maximum of 550 nm, whereas for the polymer with *meta*-phenylene units λ_{max} is 490 nm as the conjugation is broken to some extent. In the case of *ortho*-phenylene units, a blue shift is observed (λ_{max} =500 nm) but this is more due to the twisting of the polymer backbone because of steric interactions, not to the disturbtion of the conjugation [290].

Table 2.6: Effect of *o*-, *m*- and *p*-positions of phenylene units on emission color of PPVs.

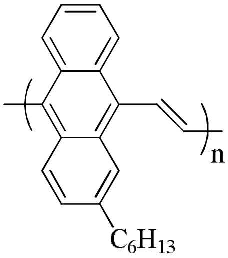
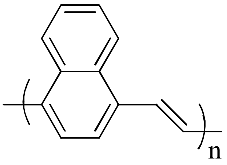
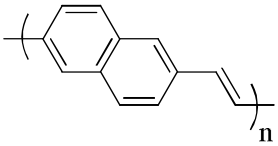
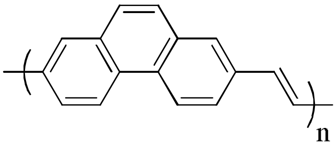
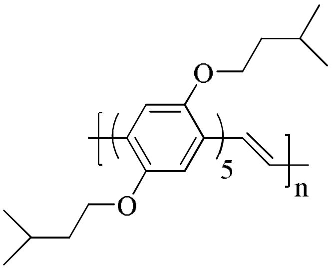
	all-*para* λ_{max}= 550 nm
	*metha*- λ_{max}= 490 nm
	*ortho*- λ_{max}= 500 nm
R_1, R_2 = alkyl	

Introduction of non-conjugated units into the polymer chain also affects the conjugation length and emission color. Low levels of non-conjugated units enhances the EL-efficiency due to exciton confinement, but high levels affects charge transport and decreases the efficiency [230,291,292].

2.5.4.3 Effect of phenyl group on the emission of PPVs

When a phenylene group is replaced by an "oligophenylene" unit (such as pentaphenylene) a blue-shift in the emission is observed [293]. Replacement by a heterocycle causes red-shifts [294]. It is more complicated in the case of fused aromatic polycyclics. When the phenylene unit is replaced by 1,4-naphthalane or 9,10-antharacene a remarkable red shift is observed, but in the case of 2,6-naphthalane and 3,6-phenanthrene slight blue-shifts are observed compared to PPV.

Table 2.7: Effect of "phenyl" groups on emission color of PPVs.

Polymer structure	Replaced unit	Effect on emission maxima	Ref.
	9,10-anthracene	red-shift	[295]
	1,4-naphthalene	red-shift	[296]
	2,6- naphthalene	slight blue shift	[297]
	3,6-phenanthrene	slight blue shift	[298]
	pentaphenylene	blue shift	[293]

In conclusion, the band gap of π-π* transition is related to the structure of the polymer and the light emitted (the color) depends on the band gap. Therefore any modification with any specific purpose in the polymer structure will affect the band gap and hence the emission color.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Styrene (St) (Aldrich)

It was first washed with 5% aq. NaOH solution in order to remove inhibitors, and then washed with water. It was dried with calcium chloride ($CaCl_2$) several hours and distilled over calcium hydride (CaH_2) at reduced pressure.

ε-Caprolactone (CL) (Aldrich)

It was vacuum distilled over CaH_2 just before use.

3.1.2 Solvents

Diethyl ether (J.T. Baker)

It was dried with $CaCl_2$ and distilled over sodium wire.

Dichloromethane and chloroform (J.T. Baker)

It was first washed with conc. H_2SO_4 until the acid layer remained colorless, and then with water, followed by another washing with 5% NaOH (aq.) and finally with water again. It was dried with $CaCl_2$ and distilled over CaH_2. It was stored over molecular sieves for use as a solvent in the experiments.

Tetrahydrofuran (THF) (J.T. Baker)

For use in chemical reactions, it was dried over potassium hydroxide, distilled over sodium wire, and finally distilled over sodium/benzophenone.

For chromatography as eluent it was used as received (HPLC Grade).

Methanol (Technical)

It was used for the precipitation of polymers without further purification.

Carbontetrachloride (J.T. Baker)

It was used as received.

Dimethylacetamid (Aldrich)

It was distilled and stored over molecular sieves for use as a solvent in the experiments.

3.1.3 Other chemicals

2,5-Dibromotoluene (Aldrich)

It was used as received.

3,5-Dibromotoluene (Aldrich)

It was used as received.

Sodium borohydride ($NaBH_4$) (Merck)

It was used without further purification.

Copper (I) bromide (CuBr) (Aldrich)

It was used as received.

2,2-Bipyridine (bpy) (Merck)

It was used as a ligand for ATRP without further purification.

Triethylamine (TEA) (J.T. Baker)

It was distilled over calcium hydride before use.

***p*-Xylene (Aldrich)**

It was used as received.

2,5-Dibromo-*p*-xylene (Aldrich)

It was used as received.

Acetic acid (Aldrich)

It was used without further purification.

Acetic anhydride (Aldrich)

It was used as received.

***N*-Bromosuccinimide, 99% (NBS) (Acros)**

It was used directly.

Triphenylphosphine (PPh_3) (Fluka, Acros)

It was used as received.

Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (Aldrich)

It was used as catalyst in Suzuki coupling reactions without further purification.

Tin octoate ($Sn(Oct)_2$) (Sigma)

It was used as initiator in ring opening polymerization of ε-caprolactone as received.

3-Aminophenylboronic acid hemisulfate (Acros)

It was used as received.

4-Formylphenylboronic acid (Aldrich)

It was used as received.

4-Aminophenol (Aldrich)

It was used as recceived.

2-Pyrrole carboxaldehyde (Fluka)

It was used as received.

1-Naphthyl carboxaldehyde (Fluka)

It was used as received.

Potassium-*tert*-butoxide (Aldrich)

It was used as received.

1,4-Bis(bromomethyl)benzene (Aldrich)

It was used as received.

***p*-Toluene sulfonic acid (Fluka)**

It was used as received.

Iron (III) chloride, anhydrous (Fluka)

It was used as received.

3.2 Analysis and Instrumentation

3.2.1 Elemental analysis

Elemental analyses were carried out by a CHNS-932 (LECO) instrument.

3.2.2 Spectral analysis

3.2.2.1 Nuclear magnetic resonance spectrometer (NMR)

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AC250 NMR Spectrometer (250 and 63 MHz, respectively) using $CDCl_3$ as solvent and tetramethylsilane as internal standart.

3.2.2.2 Infrared spectrometer (IR)

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer.

3.2.2.3 UV-visible and fluorescence spectrometer

The UV spectra were measured using an IBM 9420 Spectrometer or a Schimadzu UV 2600PC Spectrometer in THF or $CHCl_3$ solutions with the same concentration and as solid films cast on quartz plates.

Emission and excitation spectra were obtained using a Perkin-Elmer LS 50B spectrometer with xenon lamp light source. The maximum absorbance of polymer solutions was maintained at $A < 0.1$ in order to minimize errors due to internal filter effects.

More detailed photophysical properties of the synthesized PPV derivatives (in solution, thin film and bulk) were kindly investigated by Dr. Daniel A. M. Egbe and Dr. Eckhard Birckner in Eindhoven University of Technology (The Netherlands) and University of Jena (Germany).

Absorption spectra were recorded at room temperature on a LAMBDA 16 spectrophotometer (Perkin Elmer). Fluorescence emission and excitation spectra at room temperature and at 77 Kelvin were measured using a LS50B luminescence spectrometer (Perkin Elmer). Low temperature experiments recorded at 77 K used the low temperature accessory of the LS50B spectrometer and were performed with samples that had been placed in fused synthetic silica tubes of 2 mm inner diameter. The investigations in order to find phosphorescence were performed at 77 Kelvin using the phosphorescence modus of the instrument with delay time and gate time of 1 ms and 10 ms rsp.

Relative fluorescence quantum yields were calculated relative to quinine sulphate (purum; FLUKA) in 0.1 N H_2SO_4 (pro analysis; Laborchemie Apolda) used as a standard (Φ_f = 0.55). The absorbance at the excitation wavelength was kept below 0.05 for the samples and the reference.

The kinetics of fluorescence was investigated with a CD900 time correlating single photon counting spectrometer (Edinburgh Instruments). The excitation source was a hydrogen filled nanosecond flash lamp which yielded an instrument response pulse of 1.3 ns FWHM.

In order to calculate the fluorescence lifetime, the LEVEL 1 (up to 4 exponentials) package implemented in the Edinburgh Instruments software was used. Plots of weighted residuals and of the autocorrelation function and values of reduced residuals χ^2 were used to judge the quality of the fit. χ^2 values larger than 1.3 were not accepted.

For solid state studies, thin films of the macromolecules were prepared by either spin coating or inkjet printing and their absolute photoluminescence quantum together with those of the solutions and bulk materials were measured on a Hamamatsu C9920-02 system. An UV-VIS/Fluorescence plate reader (Flash scan 530) from Analytik Jena (Jena, Germany) was used to measure the respective fluorescence spectra of spin coated and printed films. Inkjet printed films were made using a piezo based, single nozzle inkjet printer from Microdrop Technologies. Concentration of the solutions for inkjet printing and spin coating was 4 mg/mL in a solvent mixture of toluene/o-dichlorobenzene (90/10) and films of approximately 100 nm thickness were obtained. For good film formation, following inkjet printing parameters were necessary: pulse width 40-70 V and pulse height 75 -150 V.

3.2.3 Thermal analysis

3.2.3.1 Differential scanning calorimeter (DSC)

DSC analyses were performed on a Perkin Elmer Diamond DSC with a heating rate of 10^oC/min under nitrogen flow.

3.2.3.2 Thermogravimetric analyzer (TGA)

Thermogravimetric data were obtained using a Perkin Elmer Diamond TGA, under nitrogen, with a heating rate of 10^{o}C/min.

3.2.4 Molecular weight measurements

3.2.4.1 Gel permeation chromatography (GPC)

Molecular weights were determined by gel permeation chromatography (GPC) equipped with Waters styragel columns (HR Series 2, 3, 5E) with THF as the eluent at a flow rate of 0.3 mL/min and a Waters 410 Differential Refractometer dedector.

3.3 Preparation Methods

3.3.1 Synthesis of ATRP initiators

3.3.1.1 Synthesis of 1,4-dibromo-2-(bromomethyl)benzene

1,4-dibromo-2-(bromomethyl)benzene was prepared by bromination of methyl groups of 2,5-dibromotoluene using N-bromosuccinimide (NBS) in CCl_4.

6.2g (0.0248mol) 2,5-dibromotoluene, 4.63g (0.26 mol) N-bromosuccinimide and 0.1g benzoyl peroxide were dissolved in 20mL CCl_4. The solution was maintained at reflux temperature for 4 h. After that time the solution was filtered. The succinimide was washed with a supplementary amount of CCl_4 and finally with a little quantity of CH_2Cl_2. The combined organic solutions were washed several times with water and than dried over $MgSO_4$. The solvent was removed by rotary evaporator. The product was purified by passing through a silicagel column using diethyl ether as eluent. Finally, the product was obtained as white crystals after recrystallizing twice from petroleum ether.

^{1}H-NMR ($CDCl_3$): δ(ppm) = 7.58 (s, 1H, Ar*H* -3-position), 7.43-7.40 (d, 1H, Ar*H* -5 position), 7.28-7.26 (d, 1H, Ar*H* -6 position), 4.51 (s, 2H, C*H*$_2$Br); m.p. (DSC): 94-95^{o}C.

Anal. ($C_7H_5Br_3$) Calc. C 25.57; H 1.53; Found C 25.63; H 1.73

3.3.1.2 Synthesis of 1,3-dibromo-5-(bromomethyl)benzene

1,3-dibromo-5-(bromomethyl)benzene was prepared in a similar way with 1,4-dibromo-2-(bromomethyl)benzene from 3,5-dibromotoluene.

^{1}H-NMR ($CDCl_3$): δ(ppm) = 7.58 (s, 1H, Ar*H* -5-position), 7.45 (s, 2H, Ar*H*- 4 and 6 positions), 4.34 (s, 2H, CH_2Br), white crystals, m.p (DSC): 97-98°C

Anal. ($C_7H_5Br_3$) Calc. C 25.57; H 1.53; Found C 25.32; H 1.66

3.3.1.3 Synthesis of 1,4-dibromo-2,5-bis(bromomethyl)benzene

1,4-Dibromo-2,5-bis(bromomethyl)benzene was prepared by bromination of methyl groups of 2,5-dibromo-*p*-xylene using NBS the same way.

^{1}H-NMR ($CDCl_3$): δ(ppm) = 7.65 (s, 2H, aromatic), 4.5 (s, 4H, CH_2), white crystals, m.p (DSC): 160-161°C.

3.3.2 Synthesis of initiator for ring opening polymerization (ROP)

3.3.2.1 Synthesis of 2,5-dibromoterephthaldehyde

2,5-dibromoterephthaldehyde was obtained by oxidation of 2,5-dibromo-*p*-xylene**,** in two steps:

A. 10g (0.0378 mol) of 1,4-dibromo-2,5-dimethylbenzene was suspended in a mixture of 50 mL of acetic acid and 100 mL of acetic anhydride. 35mL of sulfuric acid was added dropwise at the suspension, maintaining the temperature at 0°C. 21g (0.21 mol) of CrO_3 was added in portions as so the temperature of the reaction mixture didn't exceeded 10°C. Stirring was maintained for another 5 hours at 0°C. The greenish slurry was poured into ice water and filtered. The crude diacetate was washed with large amounts of water and finally with cold methanol and is pure enough for the next step. m.p. (DSC): 166-167°C.

^{1}H-NMR ($CDCl_3$) (δ, ppm): 7.82 (s, 2H, Ar), 7.72 (s, 2H, Ar-C*H*-), 2.14 (s, 12H, CH_3).

B. The diacetate was hydrolyzed by refluxing with a mixture of 50 mL ethanol, 50 mL of water and 5mL of sulfuric acid for 5 hours. After cooling, the pale yellow product was separated by filtration and washed with water. The purification was performed by chromatography through a silicagel column using dichloromethane as eluent and twice recrystallization from chloroform, resulting 4.964 g (Yield 45%) yellowish crystals. M.p. (DSC): 190-191°C

^{1}H-NMR (**10**) ($CDCl_3$) (δ, ppm): 10.32 (s, 2H, C*H*O), 8.13 (s, 2H, Ar)

IR (cm^{-1}): 1678 (CHO)

Anal. ($C_8H_4Br_2O_2$) Calc. C 32.92; H 1.38; Found C 32.85; H 1.56

3.3.2.2 Synthesis of 2,5-dibromo-1,4-(dihydroxymethyl)benzene

2,5-dibromo-1,4-(dihydroxymethyl)benzene was synthesized by reduction of 2,5-dibromoterephthaldehyde with sodium borohydride:

2,5-dibromoterephthaldehyde (1.38g, 4.72 mmol), and 5 mL of methanol were introduced into a 100 mL round bottom flask equipped with magnetic stirrer, condenser and a dropping funnel. 1.512 (40 mmol) $NaBH_4$ dissolved in 10 mL methanol were added slowly. The mixture was heated to reflux, for 2h, then stirred at room temperature over the night. Then the content of the flask was poured into cold water/HCl (10/1, v/v) and the solution was extracted several times with diethyl ether. The organic solutions were mixed, dried over $MgSO_4$, and the solvent was partially removed at rotaevaporator. Then the concentrated solution was passed through a silicagel column. Final recrystallization from benzene provided a white solid product, m.p. (DSC) = 217-218 °C (yield 92%).

^{1}H-NMR (**11**) (acetone-d_6) (δ, ppm): 7.74 (s, 2H, Ar), 4.65 (s, 4*H*, CH_2), 3.29 (s, 2*H*, OH)

IR (cm^{-1}): 3350 (OH), the peak from 1678 (CHO) from the spectrum of **10** disappeared.

Anal. ($C_8H_8Br_2O_2$) Calc. C 32.47; H 2.72; Found C 32.61; H 2.93

3.3.3 Synthesis of telechelics and macromonomers

3.3.3.1 General procedure for ATRP reactions

A round bottom-flask equipped with magnetic stirrer and a lateral neck with a tap was used. The system was vacuumed and back-filled with dry nitrogen several times. Catalyst (CuBr), ligand bipyridine (bpy), an initiators (1,4-dibromo-2-(bromomethyl)benzene or 1,3-dibromo-5-(bromomethyl)benzene or 1,4-Dibromo-

2,5-bis(bromomethyl)benzene and styrene were introduced under an inert atmosphere. The flask was placed in an oil bath warmed at 110°C and was stirred at that temperature for a given time, and after which the reaction was stopped and the mixture was diluted with THF and finally poured into ten-fold methanol. The solid was collected after filtration and dried in an oven at 40°C at reduced pressure overnight. The polymers were purified by passing through a silicagel column, using THF as eluent and reprecipitating in methanol.

3.3.3.2 General procedure for ROP of ε-caprolactone

Appropriate amounts of monomer (ε-caprolactone, CL), stannous octoate and bifunctional initiator 2,5-Dibromo-1,4-(dihydroxymethyl)benzene were added under nitrogen in previously flamed and nitrogen- purged Schlenk tubes equipped with magnetic stirrer. The CL polymerizations were carried out in bulk at 110°C. After 24h the mixtures were diluted with CH_2Cl_2 and poured into ten-fold excess of cold methanol. The polymers were collected after filtration and dried at room temperature in vacuum for three days.

3.3.3.3 General procedure for Suzuki coupling reactions

A 100-mL three-necked round-bottom flask equipped with a condenser, a rubber septum, a nitrogen inlet–outlet, and a magnetic stirrer was charged with 1 M $NaHCO_3$ (10 mL) aqueous solution and THF (15 mL). Solvents (THF and $NaHCO_3$ solution (aq)) were previously bubbled with nitrogen over a period of 30 min, and the mixture was refluxed under nitrogen for 4 h.

A 20-mL three-necked round-bottom flask equipped in the same way as the previous one was charged under inert atmosphere, with 0.208 mmol of polymer (obtained by ROP of CL or by ATRP of styrene), 1.04 mmol of 3-aminophenylboronic acid hemisulfate or 4-formylphenylboronic acid, and 0.01 g (0.008 mmol) of $Pd(PPh_3)_4$. The solvent mixture (4 mL) was introduced with a syringe through the septum. The mixture was refluxed under nitrogen for 4 days, maintaining vigorous stirring and with the exclusion of oxygen and light. The amino- or aldehyde-functionalized polymers were separated by precipitation in methanol, filtrated, washed several times with water for the removal of inorganic salts, and dried. Further, purification was performed by passing the polymers through a silica gel column, using THF as eluent and reprecipitating in methanol.

3.3.3.4 General procedure for condensation reactions for synthesis of pyrrolyl- naphthyl-, or hydroxyl functional telechelics

In a three-necked round-bottom flask equipped with a condenser, a nitrogen inlet–outlet, a Dean Stark trap, and a magnetic stirrer, 0.15 mmol of amino- or aldehyde-functional polymers (obtained by Suzuki coupling), and 0.9 mmol of respective aldehyde- or aminofunctional compounds, namely, pyrrole 2-carboxaldehyde, or 1-napthyl carboxaldehyde or 4-aminophenol, and catalytic amount of *p*-toluene sulfonic acid were introduced in 5 mL toluene. Nitrogen was purged in the flask and the reaction mixture was stirred and heated at reflux temperature for 24 h while water was removed by azeotropic distillation with toluene. Then, the reaction mixture was cooled and pyrrolyl-, naphthyl- or hydroxyl-functional polymers were separated by precipitation in methanol. Further purification of the products was achieved by dissolving the polymers in THF and reprecipitating them in methanol.

3.3.4 Synthesis of poly(Schiff-base)s by chemical oxidation

3.3.4.1 General procedure for chemical oxidation of pyrolyl or naphthyl telechelics

A typical procedure for oxidative polymerization is as follows: A 15-mL round-bottom flask equipped with magnetic stirrer and a lateral neck with a dropping funnel was used. The system was vacuumed and back-filled with dry nitrogen several times. $CHCl_3$ (5 mL) and 0.176 mmol $FeCl_3$ were introduced under inert atmosphere. Pyrrolyl or naphthyl (0.044 mmol) containing polymer in 3 mL $CHCl_3$ was added dropwise during 20 min at 0 ^{o}C. The reaction mixture was stirred at room temperature for 2 days. After that time the polymer was separated by precipitation in methanol, washed with water and methanol and dried under reduced pressure

3.3.5 Synthesis of poly(phenylene vinylene)s (PPV)s

3.3.5.1 General procedure for the synthesis of bis(triphenyl phosphonium) salts

In a 100 mL round-bottom flask equipped with a condenser and a magnetic stirrer was introduced 0.02 mol of 1,4-bis(bromomethylbenzene) or 1,4-dibromo-2,5-bis(bromomethyl)-benzene, 9.82 g (0.042 mol) of PPh_3 and 40 mL of DMF as solvent. First, by slightly heating, the mixture was solved and a white precipitate was observed. Then the heating was continued until reflux with stirring for 4 h. The white precipitate was filtered and washed several times with diethyl ether.

p-xylylenebis(triphenylphosphonium bromide) (**31**):

^{1}H-NMR ($CDCl_3$): δ (ppm): 7.76-7.4 (m, 30H, PPh_3), 6.83 (s, 4H, Ar), 5.37-5.2 (d, 4H, CH_2).

2,5-Dibromo-*p*-xylylenebis(triphenylphosphonium bromide) (**32**):

^{1}H-NMR ($CDCl_3$): δ (ppm): 7.92-7.38, (m, 30H, PPh_3), 7.36-7.32 (s, 2H, Ar), 5.66-5.58, (d, 4H, CH_2).

3.3.5.2 General procedure for the synthesis of PPVs with PCL or PSt side chains by Wittig reaction

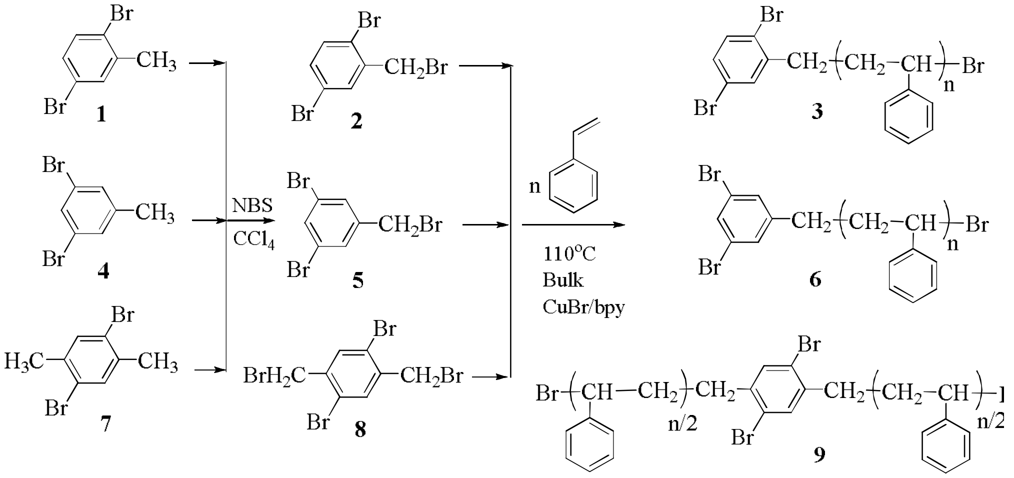
To a solution of 0.2 mmol of aldehyde functional macromonomers (obtained by Suzuki coupling) and 0.2 mmol of bis(triphenylphosphonium) salts in 3 mL of dry THF was added 0.135 g (1.2 mmol) of *t*-BuOK in 1 mL of THF dropwise under nitrogen, and the reaction mixture was stirred for 24 h at room temperature. Because during that time the viscosity of the reaction mixture increased, 1 mL of dry THF was introduced, under nitrogen; an appropriate stirring speed was then maintained. This operation was repeated two more times at 6 h intervals. Finally, after 48 h from the beginning of the reaction, the mixture was poured into cold methanol to precipitate PPVs. Further purification was achieved by passing the polymer through a silicagel column using THF as eluent and reprecipitating in methanol.

4. RESULTS and DISCUSSION

The first step of the strategy followed throughout the thesis was the preparation of polystyrene (PSt) or poly(ε-caprolactone) (PCL) based aromatic bromine functional precursor polymers by two controlled polymerization methods, namely, atom transfer radical polymerization (ATRP) or ring opening polymerization (ROP). Further Suzuki coupling and condensation reactions of these polymers yielded the desired mid- and end-chain telechelics, macromonomers and poly(*p*-phenylene vinylene)s (PPVs) with macromolecular side chains.

4.1 Synthesis of Aromatic Bromine-Functionalized Polymers by ATRP or ROP

The overall synthetic pathway for the preparation of ATRP initiators and corresponding aromatic dibromine functional PSt type polymers are shown in reaction 4.1.



(4.1)

The desired ATRP initiators; 1,4-dibromo-2-(bromomethyl)benzene (**2**), 1,3-dibromo-5-(bromomethyl)benzene (**5**) and 1,4-dibromo-2,5-bis(bromomethyl) benzene (**8**) were synthesized starting from commercially available dibromo aromatic derivatives, such as 2,5-dibromotoluene (**1**), 3,5-diromotoluene (**4**) and 2,5-dibromo-p-xylene (**7**), respectively. ^{1}H-NMR spectra of the initiators are shown in Figures 4.1, 4.2 and 4.3, respectively.

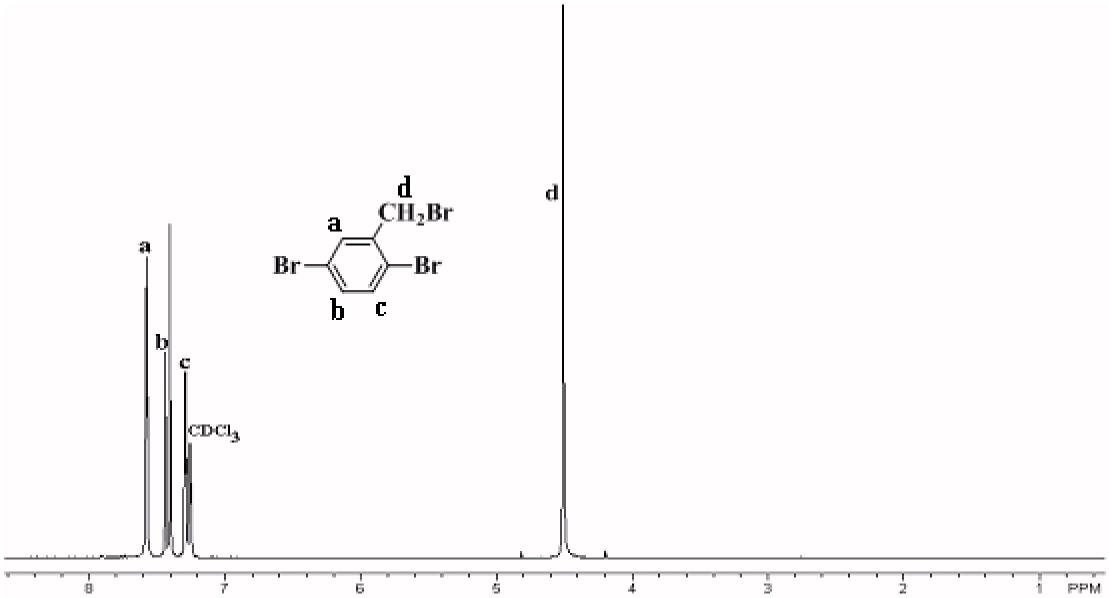


Figure 4.1 : ^{1}H-NMR spectrum of 1,4-dibromo-2-(bromomethyl)benzene (**2**) in $CDCl_3$.

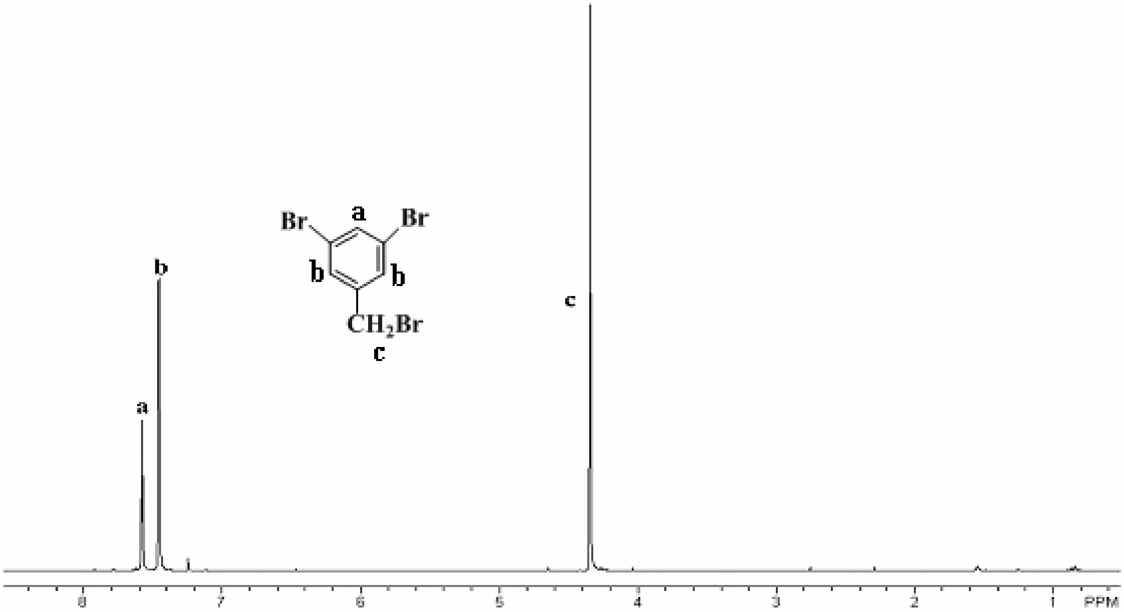


Figure 4.2 : ^{1}H-NMR spectrum of 3-dibromo-5-(bromomethyl)benzene(**5**) in $CDCl_3$.

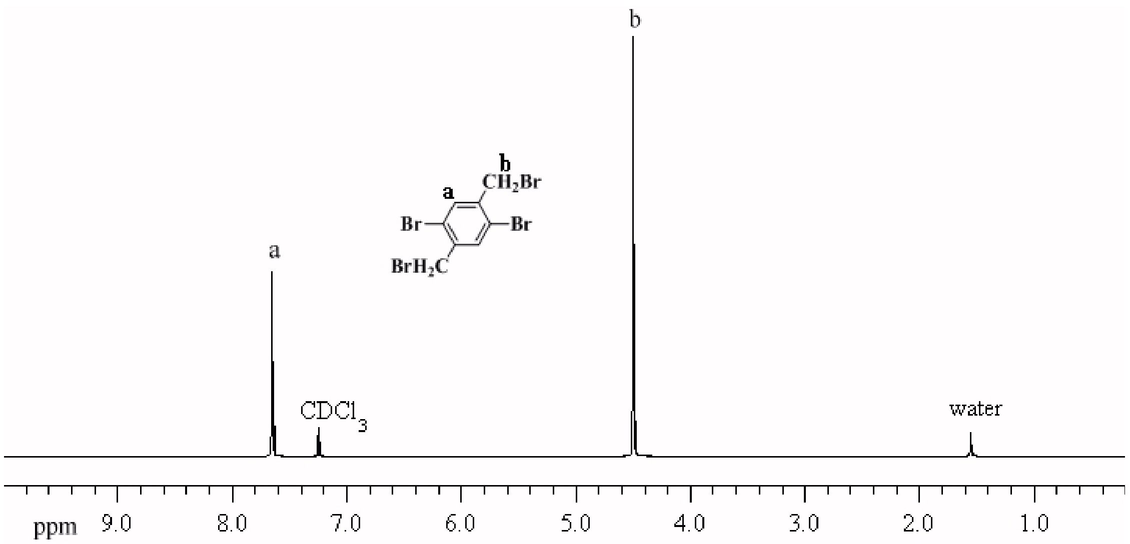
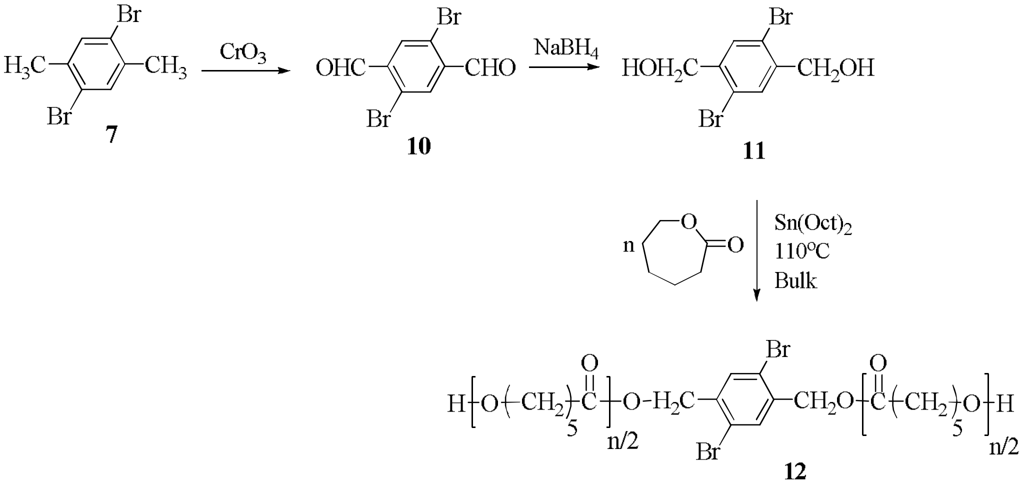


Figure 4.3 : ^{1}H-NMR spectrum of 1,4-dibromo-2,5-bis(bromomethyl) benzene (**8**) in $CDCl_3$.

Hydroxymethyl functional compounds can be used as initiators for the polymerization of ε-caprolactone (ε-CL) [299]. ROP initiator, 2,5-dibromo-1,4-(dihydroxymethyl) benzene (**11**), was synthesized following the reaction pathways presented in reaction 4.2. The structure was proved by ^{1}H-NMR spectrum, given in Figure 4.4.



(4.2)

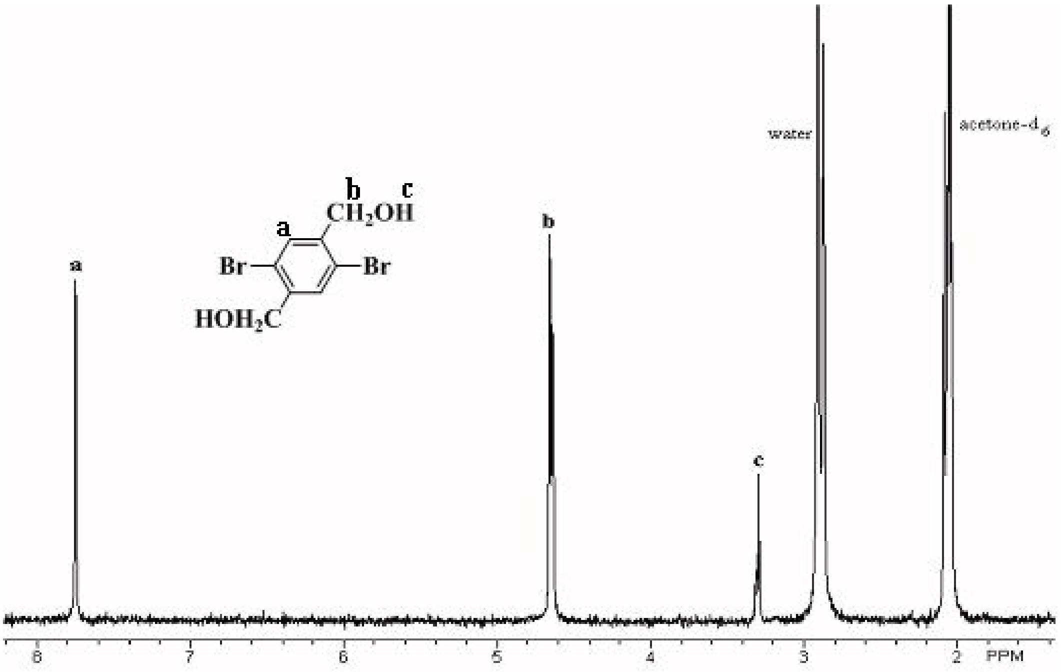


Figure 4.4 : ^{1}H-NMR spectrum of 1,4-dibromo-2,5-bis(bromomethyl) benzene (**11**) in acetone-d_6.

The initiators were subsequently used in ATRP of styrene (St) and ROP of ε-CL. Depending on the structure of the respective initiator end-chain (**3** and **6**) and mid-chain aromatic dibromo functional (**9** and **12**) polymers were formed.

4.2 Synthesis of Mid- and End-Chain Functional Telechelics

Synthesis of mid- and end-chain functional telechelics was achieved by coupling or condensation reactions of the aforementioned aromatic dibromo functional polymers [300]. So, as these polymers were intended to be used in further reactions, efforts were directed toward obtaining low molecular weights combined with convenient yields. The conditions of ATRP (high concentration of initiator 0.1–0.15 M and low reaction time, 45–60 min) were chosen to obtain a low molecular weight polymer, with a satisfactory conversion and polydispersity. The ratio CL/initiator was also justified to get the desired molecular weight. The reaction conditions for ATRP and ROP are summarized in Table 4.1.

Table 4.1: Conditions and results for aromatic dibromo-functional precursor polymers by ATRP or ROP.

Initiator	Method	Time	Polymer	$M_{n,\text{theo}}$	$M_{n,\text{HNMR}}$	$M_{n,\text{GPC}}$	PDI
2	ATRP[a]	55 min	**3**	2300	2250	2280	1.25
5	ATRP[a]	55 min	**6**	2510	2500	2550	1.25
8	ATRP[b]	1 h	**9**	4335	4300	4260	1.22
11	ROP[c]	24 h	**12**	4860	6000	5750	1.27

[a] Bulk, 120°C, [I]/CuBr/bpy=1/1/3

[b] Bulk, 120°C, [I]/CuBr/bpy=1/2/6

[c] Bulk, 120°C, [CL]/[I]=40/1, [OH]/[Sn(Oct)$_2$]=200/1

As can be seen from Table 4.1, **2**, **5**, and **8** are effective initiators for ATRP of St and the theoretical molecular weights calculated by using equation (4.3) fit very well with the measured ones,

$$M_{n,\text{theo}} = \frac{[M_0]}{[I_0]}(MW)(\text{conversion}) + M_\text{I} \tag{4.3}$$

where $[M_0]$ and $[I_0]$ are the initial molar concentrations of monomer and initiator, and (MW) and M_I are the molecular weights of the monomer and initiator, respectively. In the case of poly(ε-caprolactone) (PCL) polymer, a conversion of 100% was considered for the calculation of theoretical molecular weight.

The GPC traces are unimodal and narrow, indicating that no side reactions occurred (e.g., Fig. 4.8; polymer **12** for PCL).

Because of the low molecular weights of the polymers, the results could be verified by ^{1}H-NMR analysis. The peak corresponding to the final C*H*-Br protons appears very clearly at about 4.5 ppm in the case of PSt-type polymers (polymer **6**, Fig. 4.5 and polymer **9**, Fig. 4.7). So, molecular weights of the polymers were also calculated from ^{1}H-NMR spectra using the following formula:

$$M_{\text{n, H-NMR}} = M\text{w}\frac{2I_\text{Ar} - 2I_\text{CHBr}}{5I_\text{CHBr}} + M_\text{I} \tag{4.4}$$

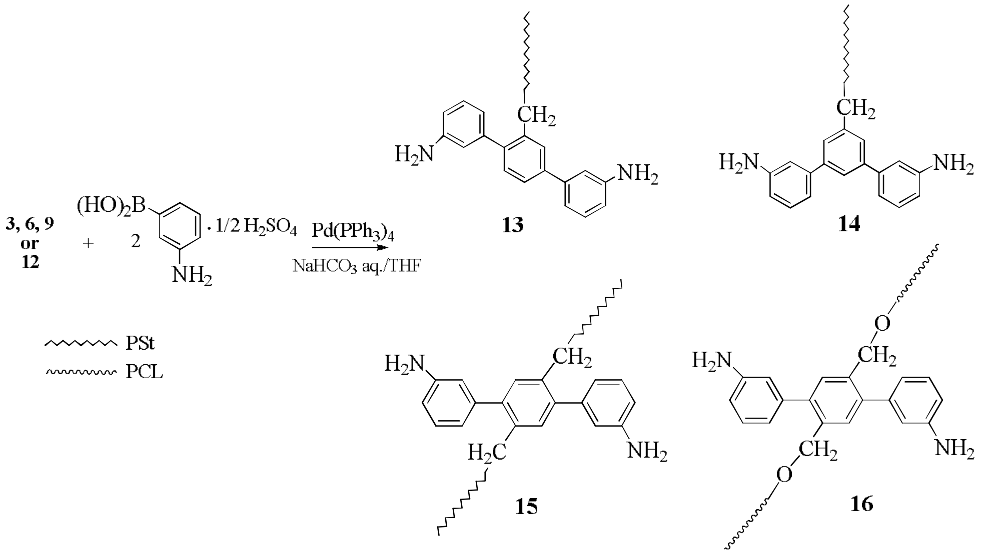
where I_Ar and I_CHBr are the intensities of the peaks from the aromatic region (6.3-7.3 ppm) and from 4.45 ppm, respectively. In the ^{1}H-NMR spectrum of polymer **6** (Fig. 4.5), the aromatic proton between the two bromine atoms (proton **a**) that belongs to the rest of initiator **5** gave a signal at higher ppm than the group of aromatic protons of PSt.

The protons belonging to the rest of initiator **11** were also clearly evidenced in the case of PCL-type polymer, **12** (**a** and **b** protons in Fig. 4.6). So, it was possible to calculate the molecular weight of the polymer by comparing the intensity of either aromatic **a** protons or Ar-CH_2 **b** protons to those of either O-CH_2 (**g** protons) or to CH_2-C=O (**c** protons) from the main chain. A value of n = 50 was found for the polymerization degree of PCL, corresponding to the $M_{n,\mathrm{H\text{-}NMR}}$ given in Table 4.1. In this case, the value of molecular weight calculated by ^{1}H-NMR spectrum was considered more reliable than that estimated by GPC measurement, calibrated with PSt standards, and was taken into account for further calculations.

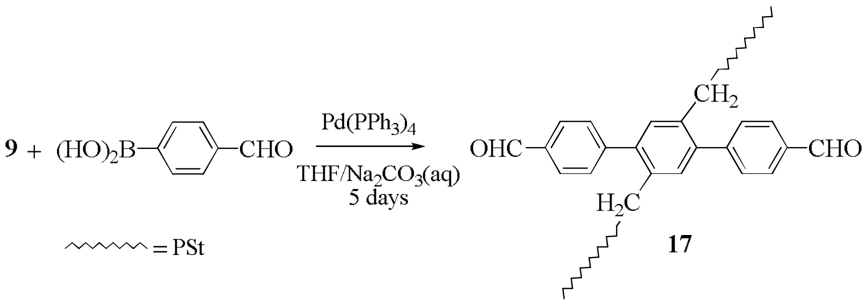
4.2.1 Synthesis of amine- or aldehyde- functional telechelics by Suzuki coupling

As mentioned in theoretical part (see section 2.3.2), the reaction between aryl halides and aryl boronic acids (Suzuki coupling) is one of the most convenient methods for C-C bond formation. The reaction is quite simple and insensitive to moisture. Moreover, it can be employed to monomers carrying functional groups. This method has also been employed by our group in the synthesis of poly(*p*-phenylene)s (PPPs) with complex architectures [301].

The next step in preparation of telechelics was the reaction of macromonomers possessing end-chain (**3** and **6**) or mid-chain (**9** and **12**) aromatic dibromines with monoboronic acids having different functionalities. The Suzuki coupling with 3-aminophenylboronic acid hemisulfate or 4-formylphenylboronic acid in the presence of a $Pd(PPh_3)_4$ catalyst yielded respective amino- or aldehyde telechelics [300]. The synthetic pathway is shown in reactions 4.5 and 4.6.



(4.5)



(4.6)

The reaction conditions (high excess of boronic acid and long reaction times) were chosen so as to assure complete functionalization. Notably, the newly formed telechelics also contain a conjugated sequence (triarylene). Therefore, they are expected to be good candidates for the synthesis of conducting polymers with macromolecular side chains (see section 2.4.1 and 4.3).

Figure 4.5 presents the ^{1}H-NMR spectra for polystyrene (PSt) based polymers (the precursor polymer **6** and end-chain amino functional telechelic **14**). In the ^{1}H-NMR spectra of the PSt polymers **13–15**, the rests from the boronic acid could not be identified, as the aromatic protons originating from the styrene units give peaks in the same region. However, amino protons appear at 3.8–3.4 ppm as was confirmed by their disappearance with D_2O exchange. Additionally, in the case of polymer **14**, having a 3,5-disubstituted moiety (Figure 4.5), the proton **a**, originating from the rest of ATRP initiator **5**, is still visible.

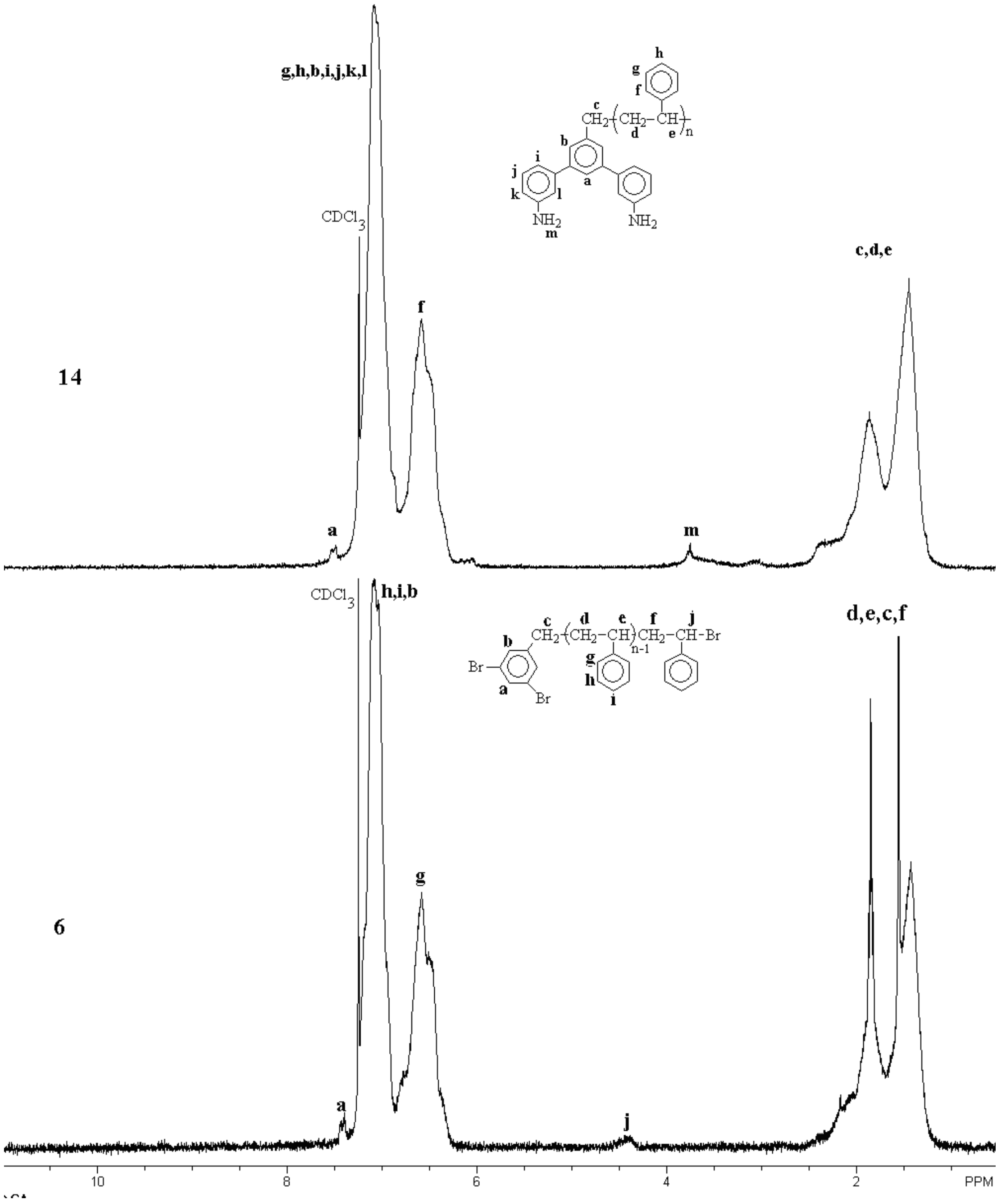


Figure 4.5 : ^{1}H-NMR spectra of precursor polymer 6 and end-chain amino functional telechelic **14** in $CDCl_3$.

Figure 4.6 shows the ^{1}H-NMR spectra for PCL-based polymers; the precursor polymer **12** and mid-chain amino functional telechelic **16.**

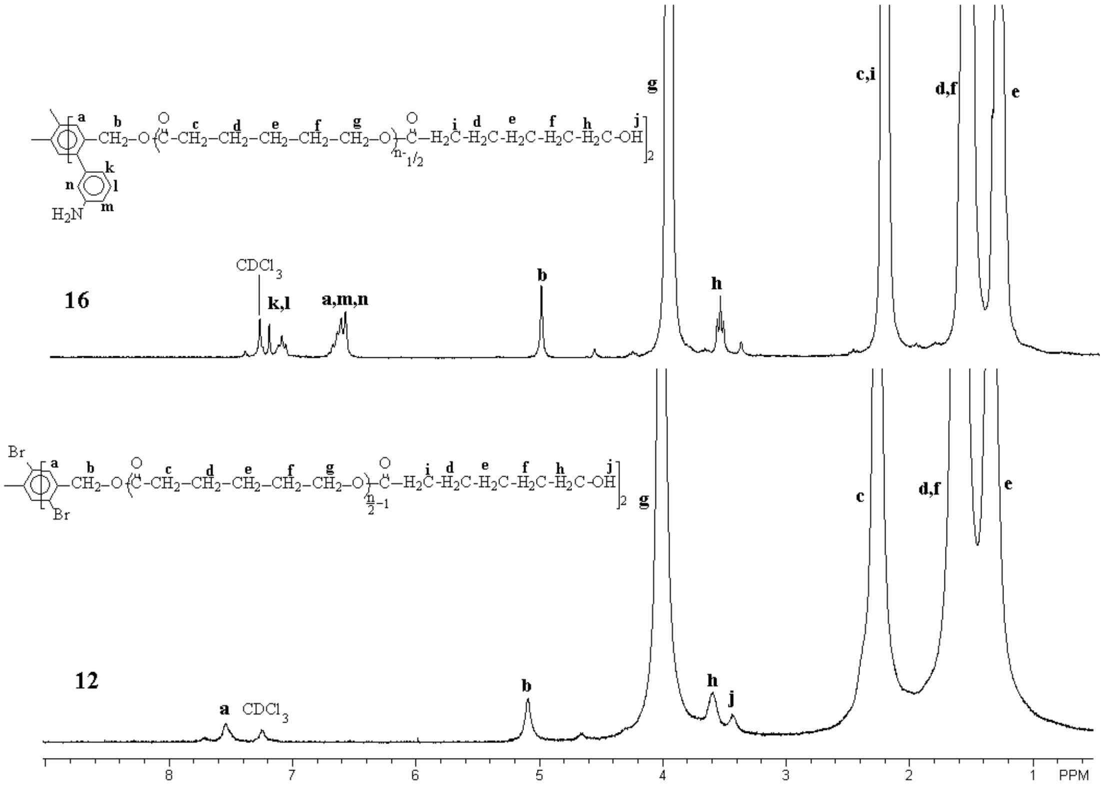


Figure 4.6 : ^{1}H-NMR spectra of precursor polymer **12** and mid-chain amino functional telechelic **16** in $CDCl_3$.

In the ^{1}H-NMR spectrum of **16**, the aromatic region is free of signals originating from the polymer, thus in addition to aromatic protons belonging to the starting initiator used for ROP of CL, the aromatic protons of the newly introduced groups can be seen very clearly (protons **k-n**, Figure 4.6). By comparing the intensity of Ar-CH_2 protons (**b**) with those of **c** or **d** belonging to the PCL main chain, the polymerization degree of the polymer was calculated and the same value as in the case of precursor polymer **12** was found.

^{1}H-NMR spectra of PSt-based mid-chain aldehyde functional telechelic **17** and the aromatic dibromo functional precursor polymer **9** is given in Figure 4.7. Spectrum of polymer **17** exhibits clear peaks resulting from the end-groups. Signals at 10.03 ppm (C*H*O- proton **j**) and 7.73 ppm (Ar-*H ortho* to C*H*O- proton **i**) prove the formation of the expected structure.

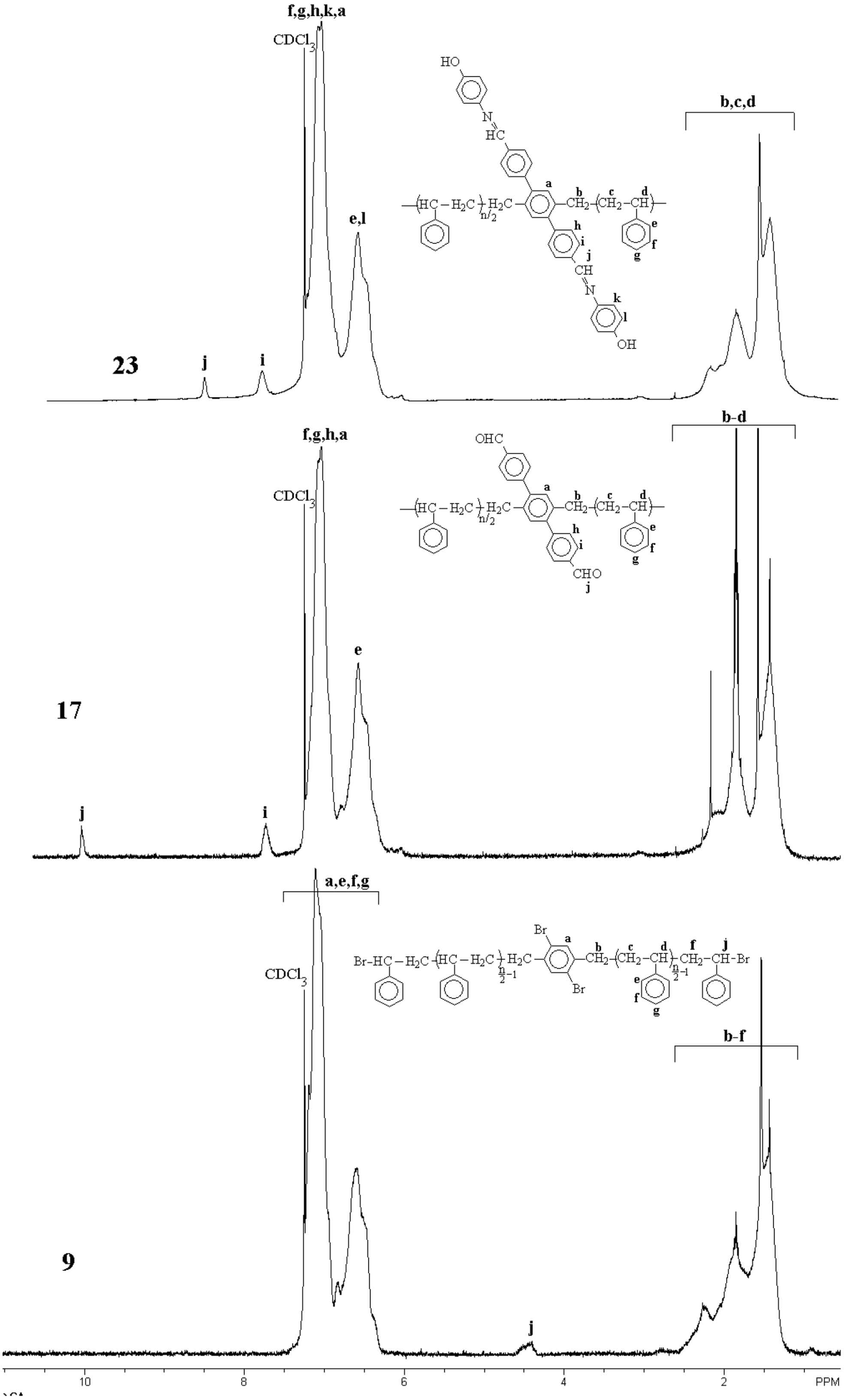


Figure 4.7 : ^{1}H-NMR spectra of **9**, **17** and **23** in $CDCl_3$.

The same calculation, as in the case of polymer **16**, could also be performed for polymer **17**, by comparing the intensity of aldehyde peak **j** with those of aromatic protons of St units and a polymerization degree of 38 was found which is close to that of precursor **9**.

This fact shows that functionalization of **16** and **17** was complete. Such an evaluation could not be performed for diamino-functionalized PSt-based polymers, owing to the fact that the amino group peaks can cause errors due to the humidity of the deuterated solvent. GPC trace of polymer **16** is also unimodal and symmetrical as shown in Figure 4.8.

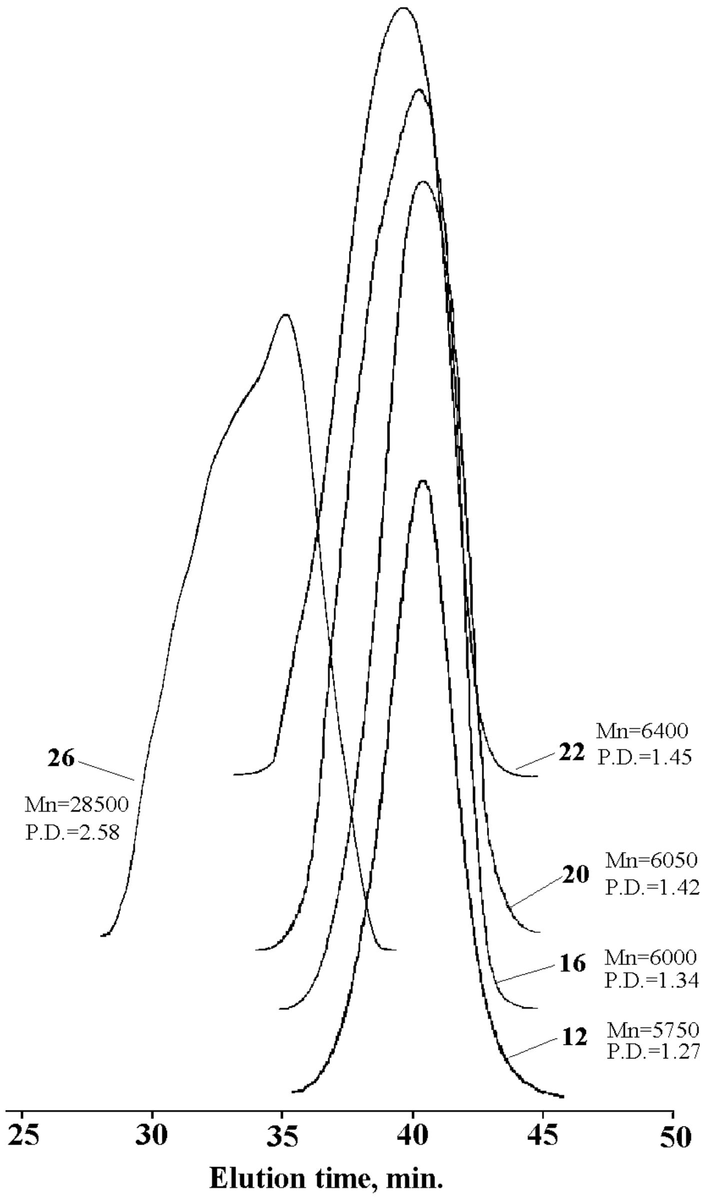


Figure 4.8 : GPC traces of polymers **12**, **16**, **20**, **22** and **26** in THF.

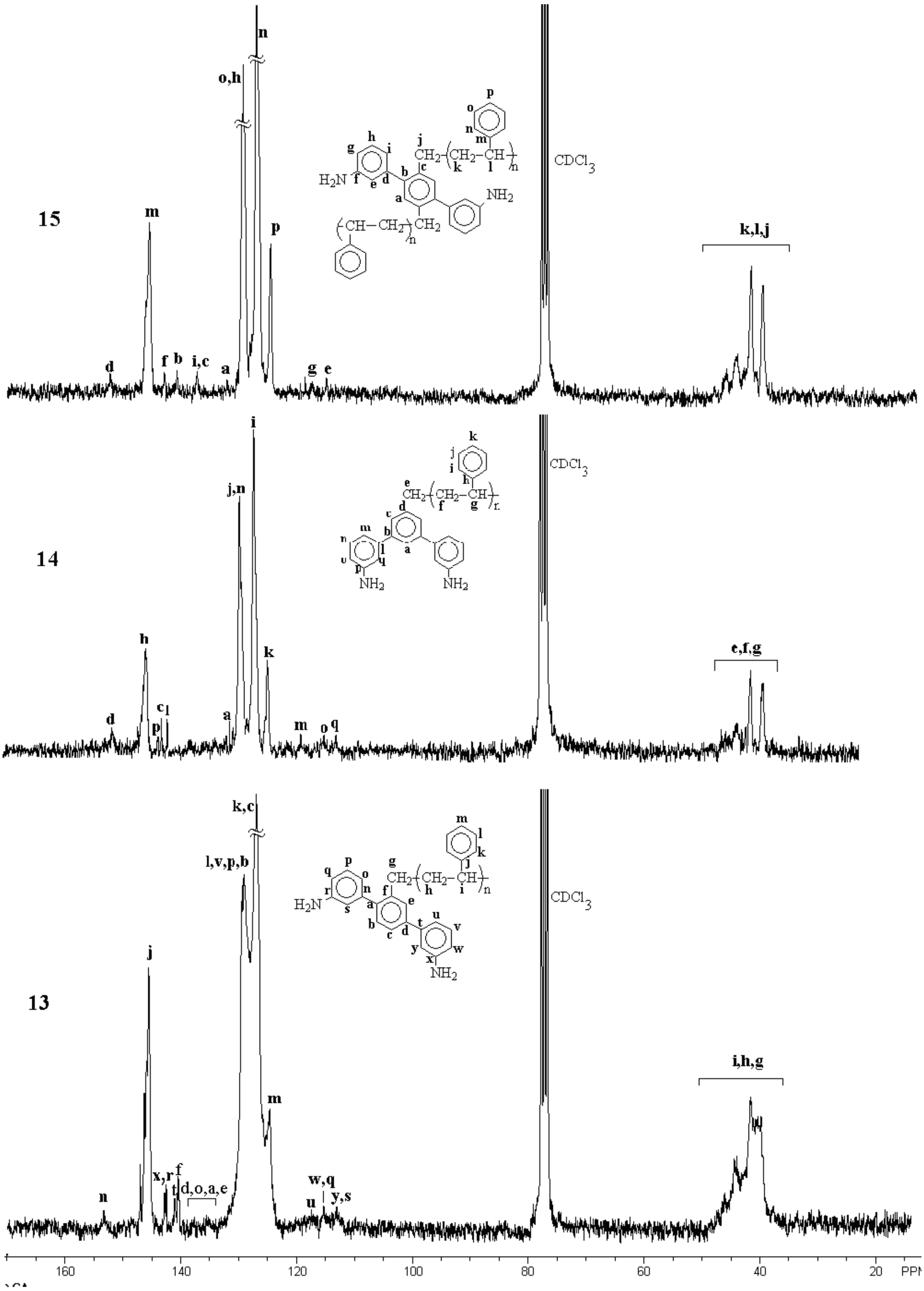


Figure 4.9 : ^{13}C-NMR spectra of PSt-based amino-functional telechelics (**13**, **14** and **15**) in $CDCl_3$.

Additional evidence for the presence of the new moieties in the polymer structures is obtained by ^{13}C-NMR spectra given in Figure 4.9. Carbons belonging to the rest of the ATRP initiator and boronic acid in the amino-functionalized PSt polymers can be identified. Thus, for polymer **13,** in the vicinity of the peaks specific to PSt, signals were detected at 153 ppm, (**n**), 142.2 ppm (**x**, **r**), 140.8 ppm (**t**), 140.3 ppm (**f**), 138.15–133.68 ppm (**d**, **o**, **a**, **e**), 117.18 ppm (**u**), 115.29 ppm (**w**, **q**), and 112.79 ppm (**y**, **s**). For polymer **14**, most of the carbons from the rest of ATRP initiator and boronic acid (ppm) can also be identified by the peaks existing at 152.2 (**d**),143.19 (**p**), 142.68 (**c**), 141.65 (**l**), 130.87 (**a**), 118.96 (**m**), 114.49 (**o**), and 112.78 (**q**).

In the case of polymer **15**, the peaks corresponding to the carbons belonging to the rest of the ATRP initiator and boronic acid appear at 152 ppm, (**d**), 142.8 ppm (**r**), 140.6 ppm (**b**), 137 ppm (**i**, **c**), 132 ppm (**a**), 117.25 ppm (**g**), and 114.8 (**e**).

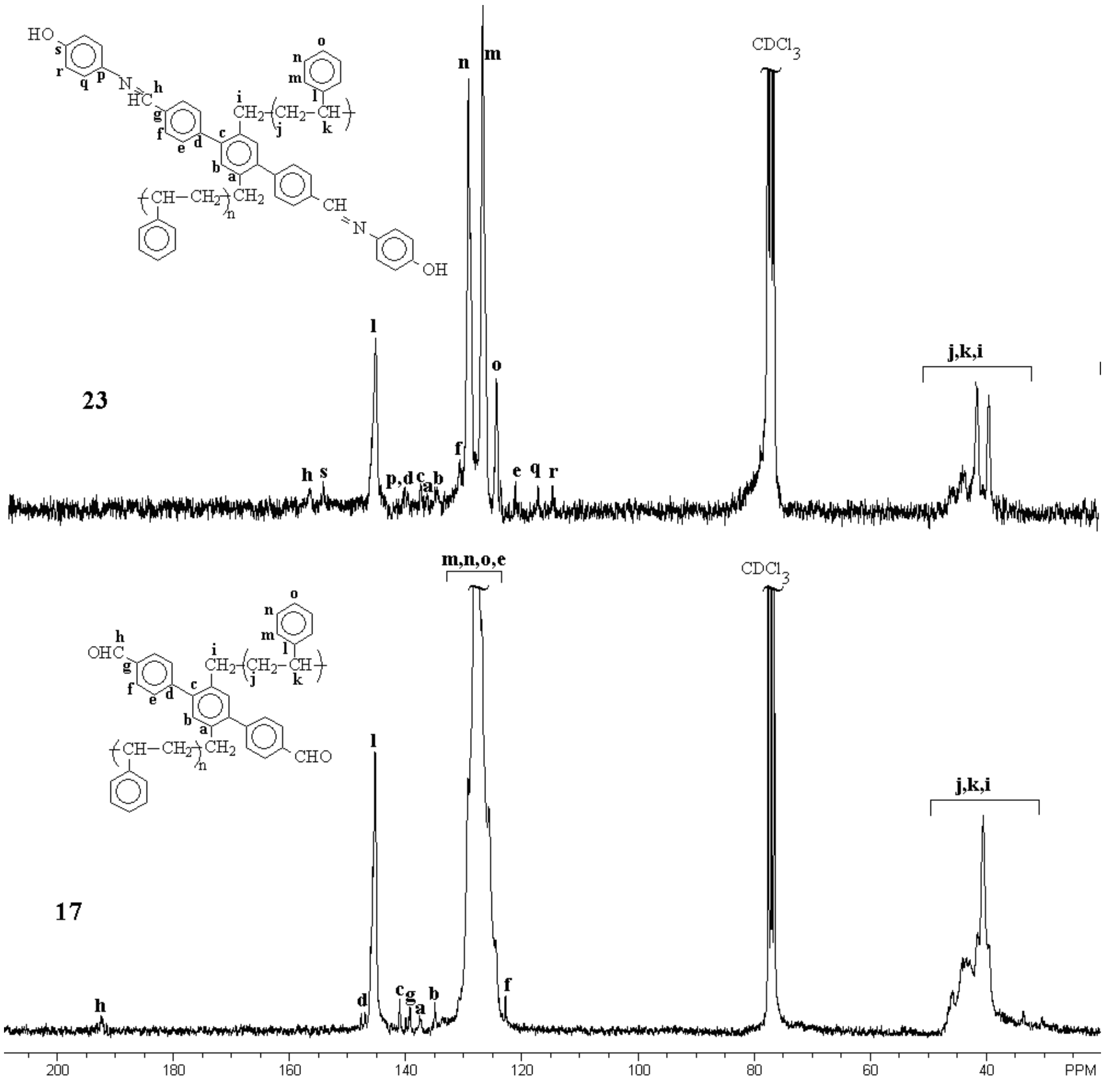


Figure 4.10 : ^{13}C-NMR spectra of **17** and **23** in $CDCl_3$.

Further proof for the presence of the new moiety in the aldehyde-functionalized polymer, **17**, is provided by the peaks appearing at (ppm) 192.2 (**h**), 147.04 (**d**), 141.07 (**c**), 139.36 (**g**), 137.1 (**a**), 134.5 (**b**), and 122.31 (**f**) in the ^{13}C-NMR spectrum given in Figure 4.10.

IR spectroscopy (given in Figure 4.11) might, as well, provide further insight into the polymer structures. The PSt polymers **13**, **14**, and **17** display usual PSt absorptions at 3058 and 3025 cm^{-1} (aromatic CH stretching); 2970, 2851, and 2848 cm^{-1} (aliphatic CH stretching); 1937, 1867, 1798, 1665, and 760 cm^{-1} (out-of-plane hydrogen deformation); 1598, 1489, and 1446 cm^{-1} (in-plane-bend-stretching vibrations of phenyl ring); and 758 and 697 cm^{-1} (out-of-plane hydrogen deformation). The peaks at 3456 and 3378 cm^{-1} in the case of polymers **13** and **14** are characteristic to the asymmetric and symmetric vibration modes of amino groups. The IR spectrum of **13** presents an absorption at 910 cm^{-1} in the region of 650–950 cm^{-1}, which is characteristic for the in-plane vibration of CH bond (βCH) of 1,2,4-trisubstituted aromatic ring. The peaks at 865 and 825 cm^{-1} indicate the out-of-plane deformations (γCH) of the CH bonds for the same substitution type. The benzene rings with 1,3-substitution give absorptions in this region, which are covered by the peaks of PSt; however, the shoulder appearing at about 798 cm^{-1} can be attributed to this type of aromatic rings. Regarding the IR spectrum of **14**, the peak at 859 cm^{-1}, not present in the spectrum of **13**, is attributed to the 1,3,5 trisubstitution of the benzene ring. Polymer **17**, with aldehyde moieties, has an intense absorption at 1702 cm^{-1} (υC=O), which clearly indicates the presence of this group in the structure.

IR spectrum of **16** displays very intense peaks specific to PCL (e.g., 1723 cm^{-1} —υC=O; 1293 cm^{-1} —υC—O *as*; and 1046 cm^{-1} —υC—O *sim*, etc), as well as absorptions due to the rests of initiator and boronic acid incorporated in the polymer structure. In the region between 700 and 900 cm^{-1}, where characteristic bands for γCH of aromatic rings exist, absorptions appear at 869 cm^{-1} (1,2,4,5-tetrasubstituted benzene ring from initiator rest) and 840, 800, 732, and 707 cm^{-1} (1,3-disubstituted benzene ring from the boronic acid rest). Regarding PSt polymers (**13** and **14**), the absorptions at 3530 and 3440 cm^{-1} are attributed to the vibration modes of the amino groups.

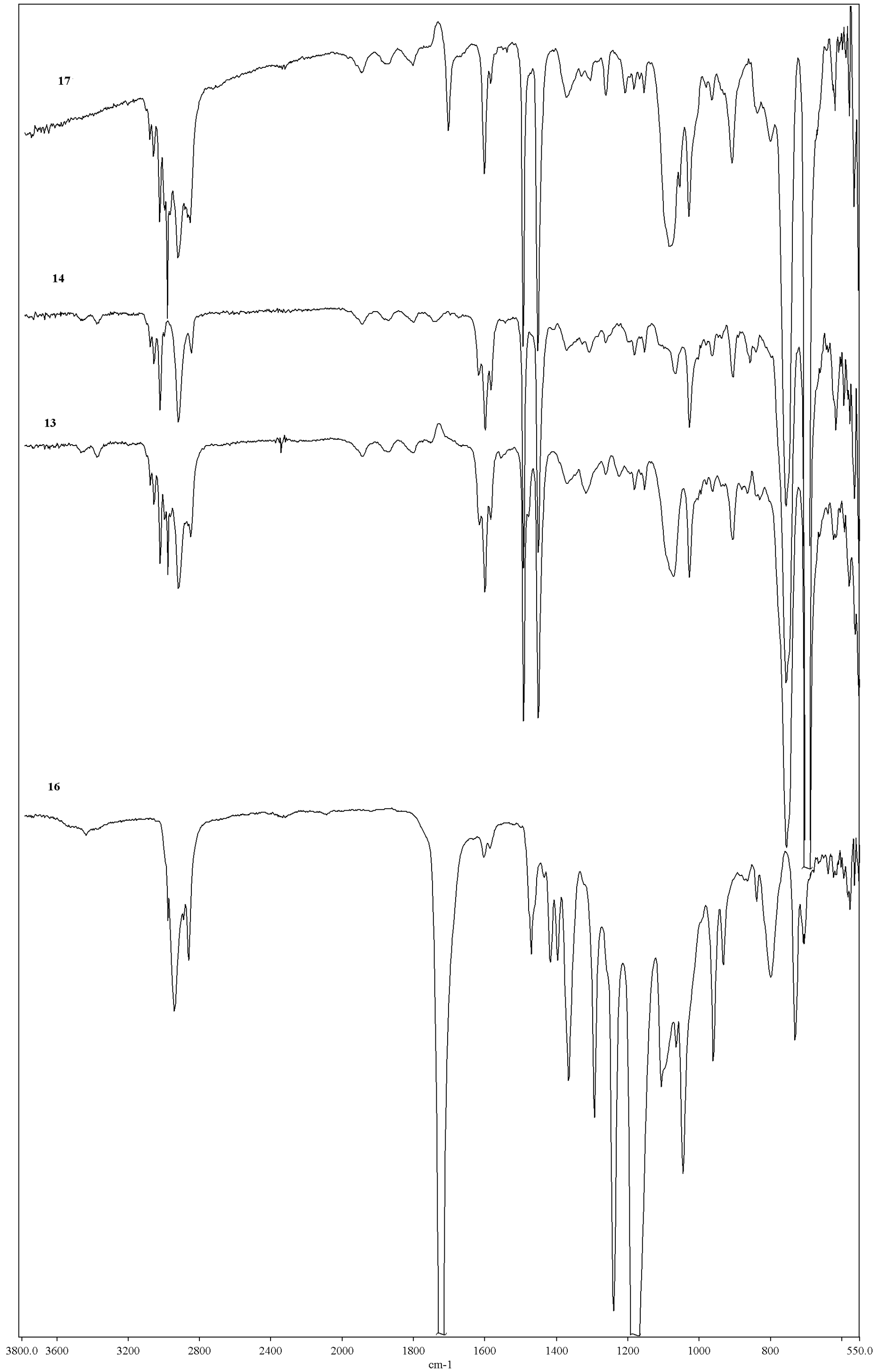


Figure 4.11 : IR spectra of polymers **13**, **14**, **16** and **17**.

4.2.2 Synthesis of pyrrolyl-, naphthyl-, or hydroxyl functional telechelics by condensation reactions (Schiff-base formation)

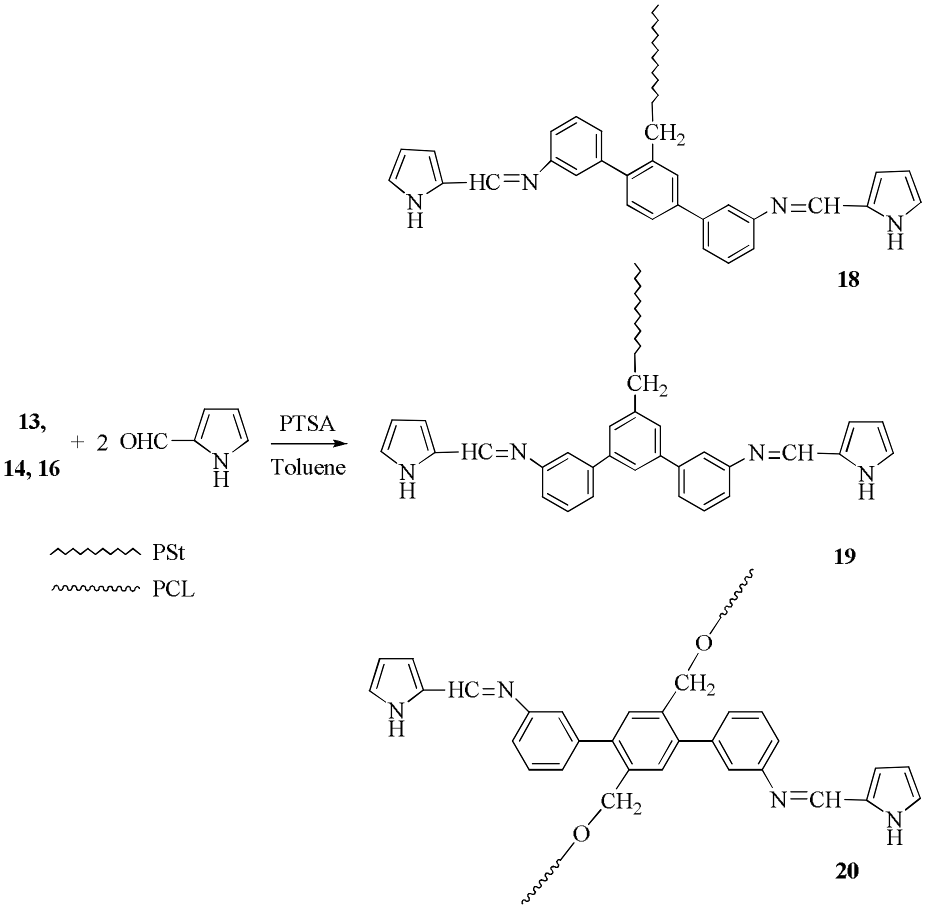
Further functionalization of the macromonomers **13–17** can be achieved by employing the amino or aldehyde groups in specific reactions [300]. At the same time, this step can also be considered as a further evidence for the successful diamino- and dialdehyde-functionalization of the polymers, at the second stage.

The condensation reaction between aldehyde and amino derivatives with the formation of azomethine linkage (Schiff bases) is also an unpretentious organic reaction like Suzuki Coupling, not sensitive to various other functional groups and nearly quantitative yields are often achieved if water is continuously removed from the reaction medium. On the other hand, fully aromatic polyazomethines have been known as an important class of thermally stable and highly conjugated materials. The classical synthetic methods reported for their synthesis are especially based on the conventional solution polycondensation of aromatic diamines with aromatic dialdehydes [302]. Polymers **13–17** can be used in such reactions, having as partner an aromatic dialdehyde or diamine derivative. Because of the difficulty in assuring the equimolecularity of the coreactants (the big difference between molecular weights of the macromonomer and low molecular weight compound and also possible difficulties in sufficiently precise determination of molecular weight of the macromonomers), very important in polycondensation reactions, attempts in obtaining successful results by this route have frequently failed.

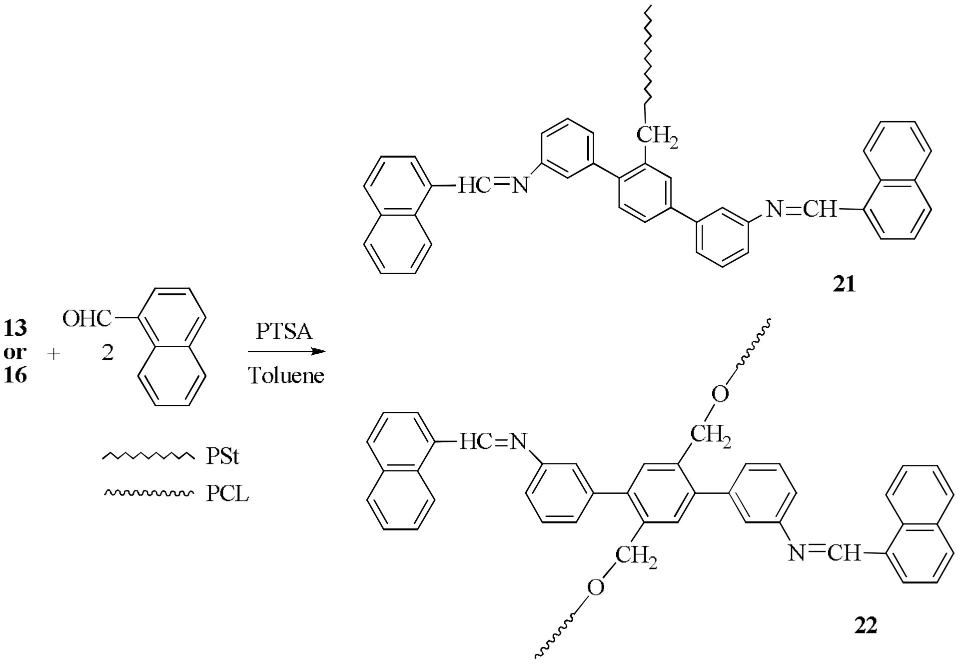
In recent years, a method was reported for the synthesis of poly(Schiff bases) by cation-rad-ical polymerization of conjugated monomers containing —CH=N— preformed groups and oxidizable groups at the extremities:

$$\mathrm{Ox{-}CH{=}N{-}R{-}N{=}CH{-}Ox} \qquad \textbf{(4.7)}$$

where R is an aromatic residue and Ox is an oxidizable group as 2-pyrrolyl, 2-thienyl, or 1-naphthyl [303,304]. By chemical or electrochemical polymerization, polymers containing 2,2’-bipyrrolediyl or 2,2’-thienyldiyl rings or 1,1’-binaphthyl in the main chain, spaced by conjugated sequences containing azomethine units, are obtained. A similar approach has been applied in our case upon the reaction of amino telechelics with 2-pyrrolyl aldehyde or 1-naphthyl aldehyde, macromonomers having a fully conjugated sequence with oxidizable groups at the extremities were synthesized as shown in reaction 4.8 and 4.9. The resulted polymers are colored specifically to Schiff bases (ranging from yellow to dark brown).

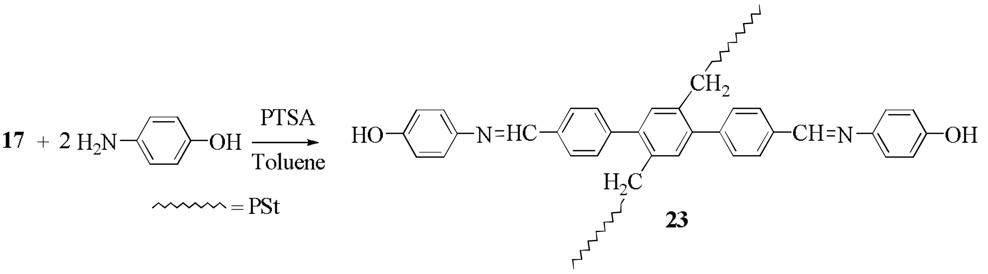


(4.8)



(4.9)

Furthermore, other functional groups can also be introduced by this method. For example, a hydroxy-functional telechelic polymer has been prepared by a condensation reaction between dialdehyde functional PSt macromonomer **17** and 4-aminophenol, as shown in reaction 4.10.



(4.10)

To assure complete functionalization, long reaction times were attained, with the use of high excess of low molecular weight compounds.

^{1}H-NMR spectra of pyrrolyl- and naphthyl functionalized polymers (**18**, **19**, **20** and **21**) are given in Figure 4.12. In the case of pyrrole-functional PSt-based polymers (**18** and **19**), peaks originating from pyrrole ring are covered by aromatic protons of the main polymer. On the other hand, the azomethine linkage proton gives a distinct signal at 8.32 ppm (Fig. 4.12, polymer **19**). The peak at 3.77 ppm was attributed to the —NH protons of pyrrole groups (**q**). A polymerization degree of about 20 for polymer **18** and 22 for polymer **19** was calculated by comparing the integrals of **m** protons with the aromatic ones. The found values are close to those of the starting materials (**3** and **6**, respectively). The azomethine linkage is a further proof for the presence of amino groups in polymers **13** and **14**.

A more clear ^{1}H-NMR spectrum was obtained in the case of pyrrole-functionalized PCL polymer **20**. As PCL does not give any signals in the aromatic region, not only the peaks belonging to the rest of initiator for ROP of CL and rest of boronic acid, but also the signals that are clearly attributed to the newly formed azomethine group and pyrrole moeity can be identified as follows: 8.31–8.24 ppm (**o**), 7.52– 7.3 ppm (**n**, **l**), 7.23–7.06 ppm (**k**, **m**), 7.06–9.92 ppm (**s**), 6.84–6.58 ppm (**a**, **m**), 6.36–6.20 ppm (**q**), 5.18–4.94 ppm (**b**), 4.27–3.77 ppm (**g**), 3.67– 3.55 ppm (**h**), 2.49–1.97 ppm (**c**, **i**), 1.82–1.45 ppm (**d**, **f**), and 1.45–0.92 ppm (**e**). By comparing the intensities of the peaks corresponding to the end groups (e.g., **o**, **q**, or **b**) with those of PCL (**g** and **h**, or **c** and **i**), a polymerization degree of n = 46 is found. Also, by adding the molecular weights of the end groups, a value of $M_{n,\mathrm{H\ NMR}} = 5725$ is calculated, which is almost the same with that calculated from ^{1}H-NMR spectrum of the original starting material (polymer **12**, Table 4.1). The GPC trace of **20** (Fig. 4.8) is still unimodal and symmetrical.

^{1}H-NMR spectrum of **21** (napthyl-functionalized PSt polymer) exhibits very clear peaks belonging to the new introduced napthyl moieties, over 7.4 ppm (Fig. 4.12). Moreover, the azomethine protons appear at 9.17 ppm (**q, q'**), proving the proposed structure of the polymer. By comparing the intensities of the integrals of the end group peaks (naphthalene and azomethine) with the aromatic ones between 6 and 7.3 ppm, the polymerization degree of the polymer could be estimated as 23, which is a similar value to that of polymer **3**, in Table 4.1.

In the case of hydroxy-functional polymer **23**, the ―OH group could not be identified, probably because of the humidity of the deuterated solvent. On the other hand, if we compare the spectra of the polymers **17** and **23,** given in Figure 4.7, we notice that the peak at 10.03 ppm (C*H*O― proton **j**) from polymer **17** is not present in the case of **23**, while a new peak appears at 8.5 ppm, specific to the proton of azomethine linkage. Moreover, ^{13}C NMR spectrum of **23** (Fig. 4.10) shows not only peaks of the main polymer chain or originating from the rests of initiator or boronic acid, but also due to the newly introduced moiety. The peaks are as follows: 156.9 ppm (**h**), 154.36 ppm (**s**), 145.35 ppm (**l**), 142–139.7 ppm (**p** and **d**), 137.4–136.4 ppm (**c** and **b**), 134.7 ppm (**a**), 130.72 ppm (**f**), 129.27 ppm (**n**), 126.85 ppm (**m**), 124.38 ppm (**o**), 121.13 ppm (**e**), 117.08 ppm (**q**), and 114.67 ppm (**r**).

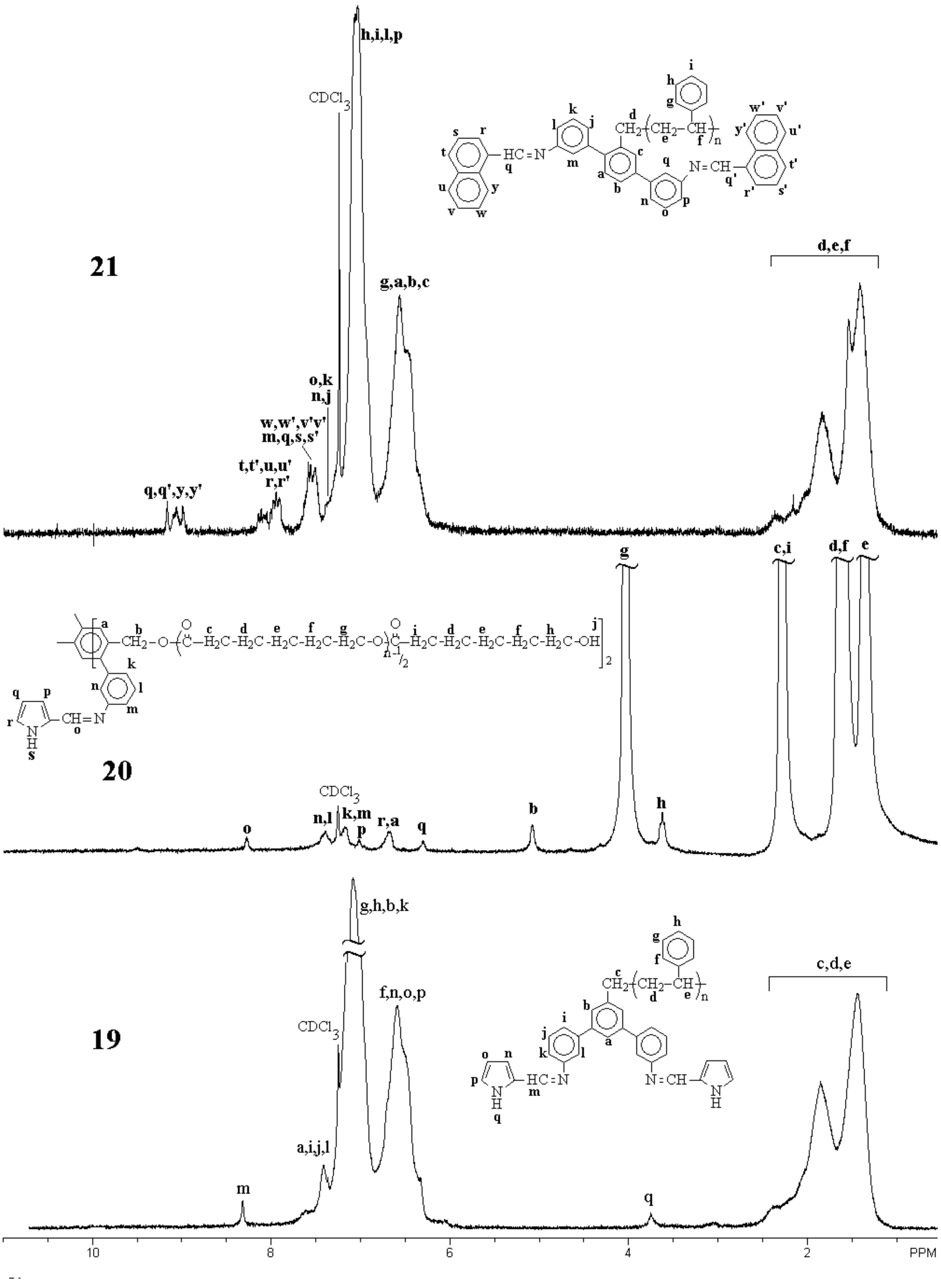


Figure 4.12 : ^{1}H-NMR spectra of naphthyl and pyrrolyl functional telechelics (**19**, **20**, **21**) in $CDCl_3$.

Figure 4.13 presents the IR spectra of naphthyl and pyrrolyl functional polymers (**18**, **19**, **23**). IR spectra of **18** and **19** exhibits new absorptions as compared with that of the starting **13** and **14**, respectively, (Fig. 4.11). The absorptions are at 3420 (υNH), 1665 (υC=N), 1417 (υ pyrrole ring), and 879 cm^{-1} (β pyrrole ring) that confirms the

NMR results. For **21**, the naphthyl-functionalized PSt, near the absorption at 1690 cm^{-1} attributed to the azomethine linkage, a new peak at 803 cm^{-1} could be assigned to the γCH vibration of naphthyl moieties (1,2-substitution at the benzene ring). IR spectra of **20** and **22** (PCL based polymers) do not show very clearly the absorption of azomethine linkage, because the very intense peaks centered at 1720 cm^{-1} (*υ*C=O of ester groups) cover the region at about 1650 cm^{-1}. As compared with **17** (Fig. 4.11), in the IR spectrum of **23** (Fig. 4.13), new absorptions at 3535 (*υ*OH) and 1623 cm^{-1} (*υ*C=N) can be noticed. In the region of 700–900 cm^{-1}, the peaks have the same position as those of **17** (but with some changes in the relative intensities), because by the introduction of the new moiety, the type of substitutions at the aromatic rings did not change (1,2,4,5-tetrasubstitution and 1,4-disubstitution). Also, the peak at 1702 cm^{-1} (*υ*C=O in aldehyde group) in the spectrum of **17** is missing in the case of **23**, which implies the disappearance of the aldehyde group through the condensation reaction.

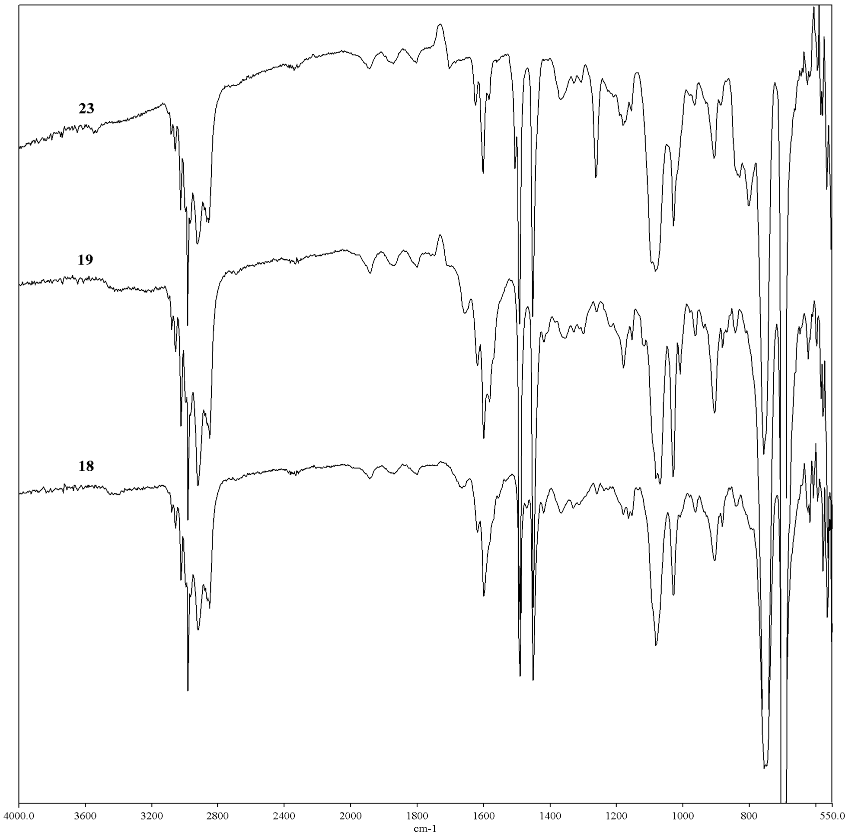
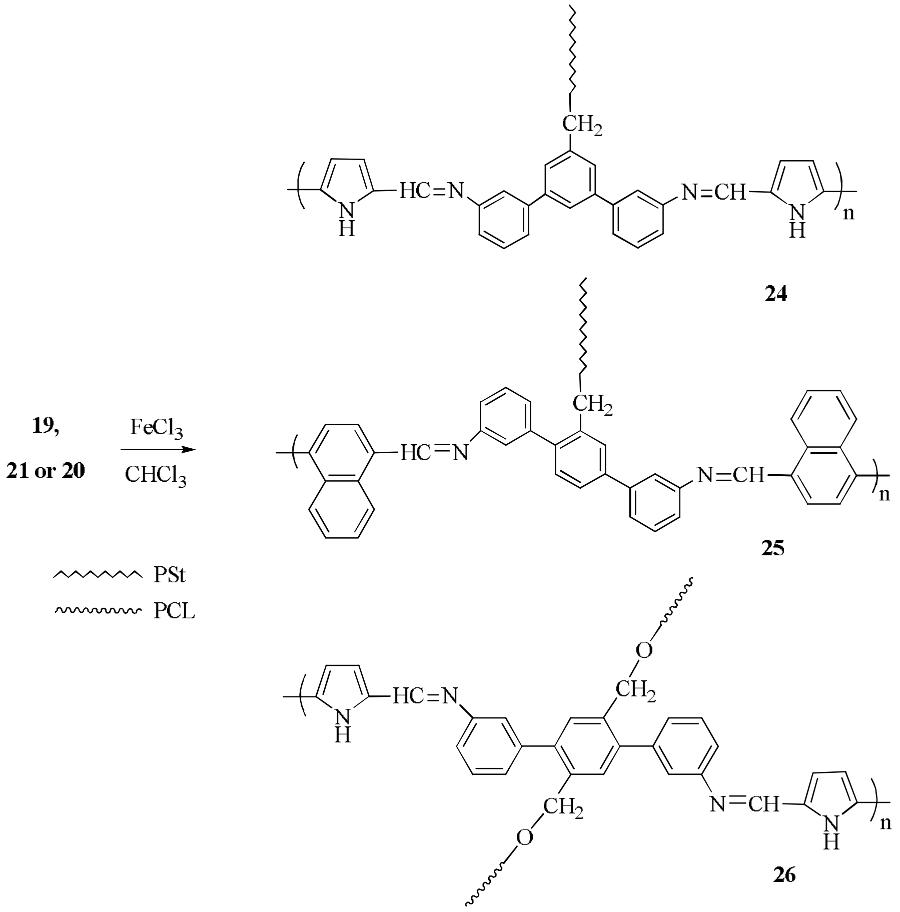


Figure 4.13 : IR spectra of **18**, **19** and **23**.

It is important to remark that polymers **18**–**22** have a relatively long fully conjugated sequence in the middle or at the end of the chain, and the sequence being terminated with oxidizable groups. So, these polymers can be used for the synthesis of poly(Schiff base)s with macromolecular side chains by oxidative polymerization (chemically or electrochemically), as mentioned previously.

Oxidative polymerization experiments of functionalized pyrrolyl or naphthyl polymers were performed at room temperature, using $FeCl_3$ (anhydrous) as oxidant agent and $CHCl_3$ as solvent, as shown in reaction 4.11.



(4.11)

Colored (ranging from light brown to black) polyheteroarylenes are obtained. The polymers have good solubility in usual organic solvents (benzene, chlorinated solvents, THF, DMAc, and DMF) similar to PSt or PCL macromonomers.

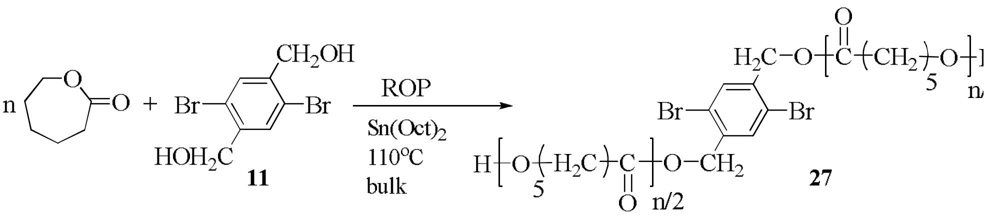
However, when reaction temperature is increased to about 50°C, insoluble fractions in THF were obtained as well. Because of the increasing of the molecular weight, together with the broadening of the polydispersity, NMR analyses fail to give valuable information for the characterization of these compounds. However, GPC analysis shows that new polymers were formed (e.g., polymer **26** from Fig.4.8), and the traces being shifted to higher molecular weights.

In the same time, the molecular weights measured by GPC based on PSt standards, should be taken as the minimum estimation because of the highly branched or comb-like structure of the obtained polyheteroarylenes.

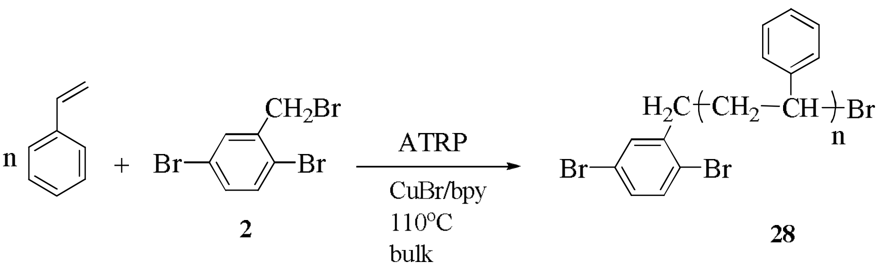
In conclusion, a variety of amino-, aldehyde-, 2-pyrrolyl-, 1-naphthyl- or hydroxyl functionalized telechelics have been synthesized [300]. These telechelics might be useful in the preparation of various macromolecular structures displaying distinct characteristics. For example, by using amino functional telechelics, A_2B and A_2B_2 type miktoarm star copolymers [305] and thermally curable benzoxazine functional PSt macromonomers [306] were synthesized. The pyrrolyl and naphthyl containing polymers can serve as macromonomers for the synthesis of comb-like conjugated polymers by oxidative or electrochemical polymerization routes. The electrochemical copolymerization of pyrrolyl functional polymer **19** with pyrrole resulted freestanding, stable and electrically conducting copolymer with a band gap value of 2.40 eV at 393 nm, with a yellow color in fully reduced form and a blue color in the fully oxidized form [307].

4.3 Synthesis of Poly(phenylene vinylene)s with Well-Defined Poly(ε-caprolactone) or Polystyrene Side-Chains

The same synthetic strategy as in telechelics was employed for the synthesis of poly(phenylene vinylene)s, PPVs, with well-defined macromolecular side chains [308]. The first step was to obtain aromatic dibromo functionalized polymers as described in section 4.1. Polymer **27** was synthesized by ROP of ε-caprolactone by using [2,5-dibromo-(4-hydroxymethyl)pheny)]methanol (**11)** as bifunctional initiator in the presence of stannous octoate (reaction 4.12). PSt based macromonomer **28** was synthesized by ATRP of styrene using 1,4-dibromo-2-(bromomethyl)benzene (**2)** as initiator in the presence of CuBr/bpy as catalytic system (reaction 4.13).



(4.12)



(4.13)

In both cases the GPC traces are unimodal and narrow, indicating that no important side reactions occurred (e.g., Figure 4.14, polymer **27** for PCL).

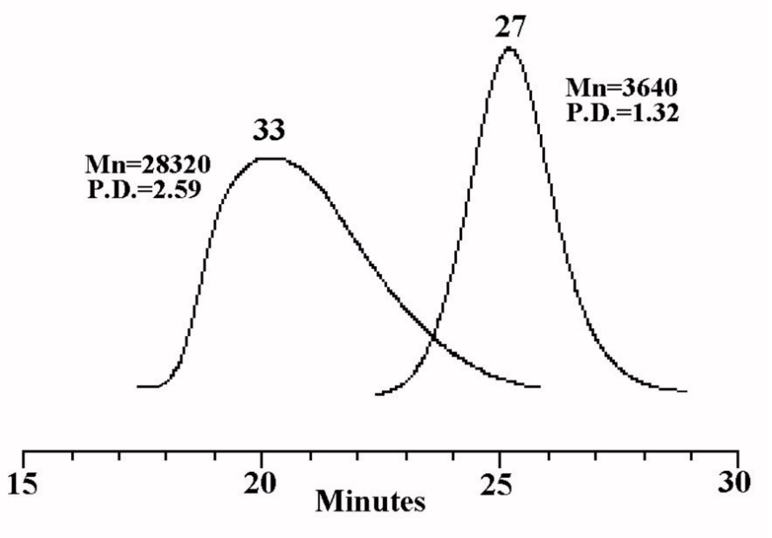


Figure 4.14 : GPC traces of starting PCL (**27**) and the final PPV (**33**) with PCL side chains in THF.

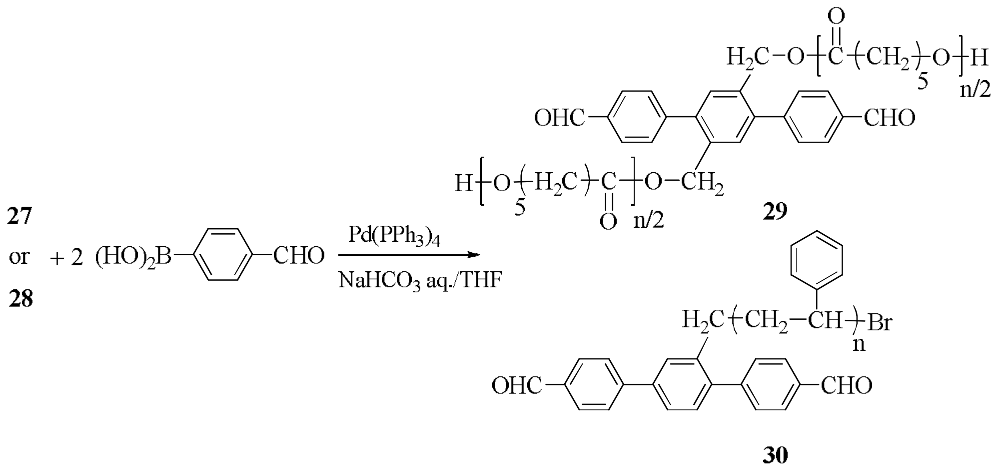
As these polymers were intended to be used in further reactions, efforts were directed towards obtaining low molecular weights, combined with convenient yields. Some characteristics are presented in Table 4.2.

Table 4.2: Molecular weights of the polymers calculated from ^{1}H-NMR spectra and obtained from GPC measurements.

Starting macro-monom.	M_n, ^{1}HNMR	M_n, GPC PDI	-CHO func. macro-monom	Colour	M_n, ^{1}HNMR	M_n, GPC, & PDI	PPV	Colour	M_n, GPC & PDI
27	3264	3640 1.32	**29**	White	3314	3720 1.36	**33**	Bright Yellow	28320 2.59
							34	Dark Yellow	32000 2.31
28	2270	2400 1.3	**30**	White	2420	2480 1.34	**35**	Bright Green	18600 3.05

In the case of the PCL macromonomer (**27**), the molecular weight calculated from ^{1}H-NMR spectrum was considered to be more reliable and used for further calculations.

As the second step PCL or PSt containing either a center or an end chain conjugated sequence (triphenylene) (**29** or **30** in reaction 4.14) were prepared by Suzuki coupling of **27** and **28**, respectively with 4-formylphenylboronic acid.

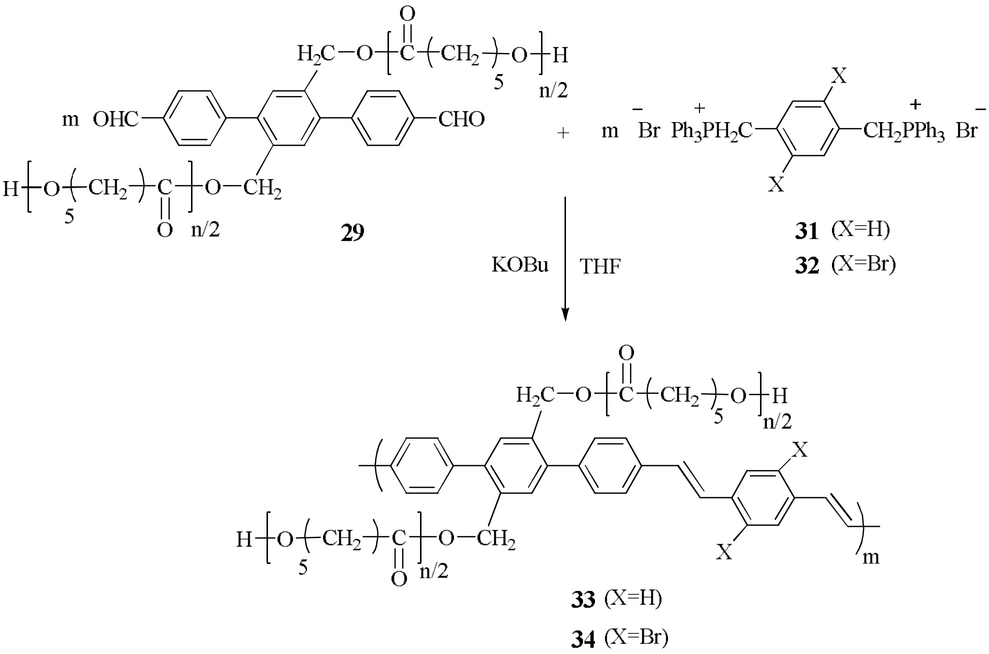


(4.14)

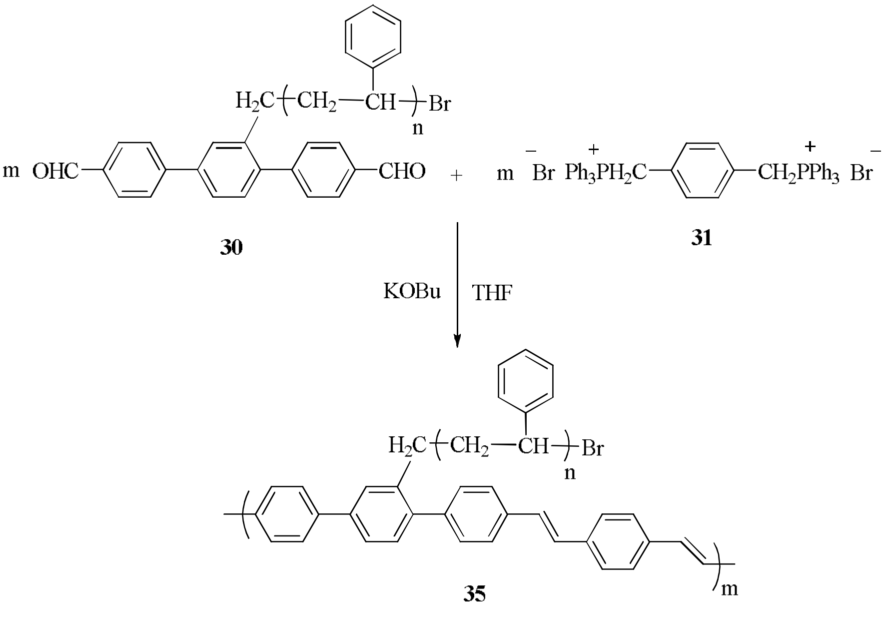
The reaction conditions (high excess of boronic acid and long reaction times) were chosen to assure a complete functionalization. A slight increase of molecular weights were noticed for **29** and **30** as compared to **27** and **28**, due to the introduction of new end-groups (Table 4.2).

As the conjugated sequences contain aldehyde groups at both ends, the functionalized polymers are candidates for synthesis of conjugated polymers with macromolecular side chains (PPVs or Schiff base type polymers). We applied the

Wittig method in combination with p-xylylenebis(triphenylphosphonium bromide) (**31**) or 2,5-dibromo- *p*-xylylenebis (triphenylphosphonium bromide) (**32**) and PPVs having as lateral substituents the respective PCL (**33**, **34** in reaction 4.15) or PSt (**35** in reaction 4.16) chains were synthesized.



(4.15)



(4.16)

The polymerization reaction was perfomed in THF in the presence of *t*-KOBu. Coloured polymers, listed in Table 4.2, with good solubility in common organic solvents and good film forming properties (similar to those of the starting macromonomers) were obtained. The solution of the polymers also show fluorescence under daylight and UV light (366 nm): blue for polymer **33** and **34** (less for the latter) and green for polymer **35** (Figure 4.15). This behaviour is interesting as the composition of these polymers contains 85-90% PCL or PSt. It can be noted that when polyphenylenes with macromolecular side chains were obtained starting from such macromonomers [309-313,28], they usually resulted as white polymers, similar to the starting materials.

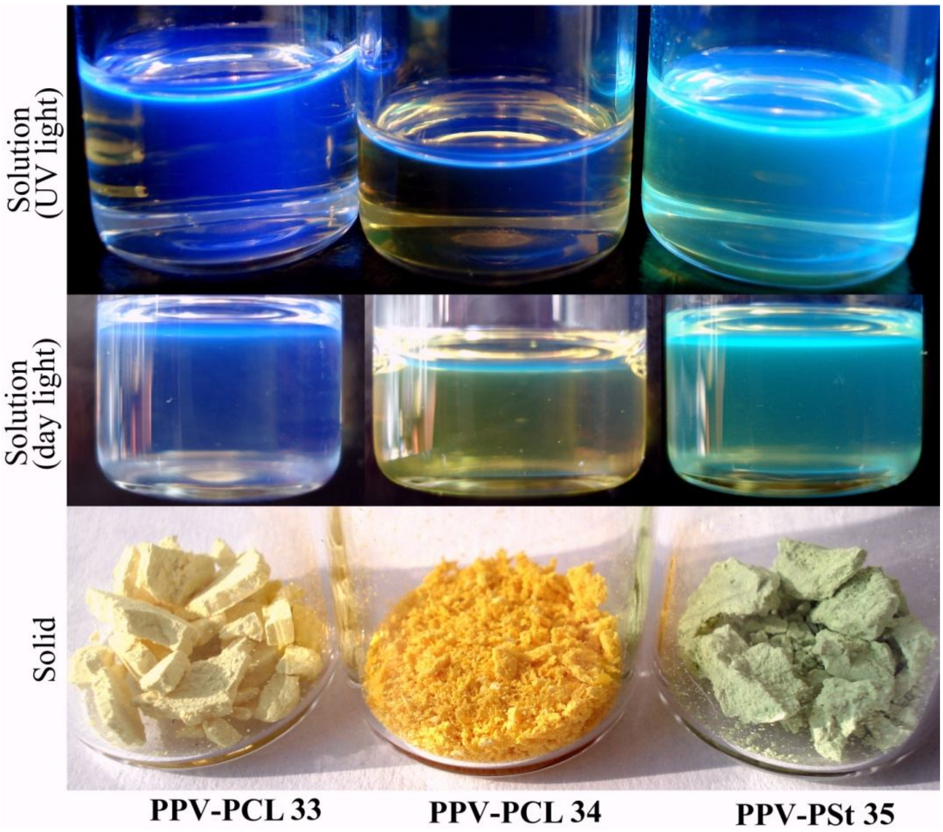


Figure 4.15 : Photos of the PCL and PSt substituted PPVs in solid and solution form (in $CHCl_3$, 0.1g/L).

Characteristics of the PPVs are shown in Table 4.2. The molecular weights measured by GPC based on PSt standards, should be taken as the minimum estimate because of the highly branched or comb-like structure of the obtained polymers.

Figure 4.16 shows the ^{1}H-NMR spectra of the PCL based polymers **27**, **29** and **33**. In the case of the dibrominated PCL based macromonomer **27**, the protons belonging to the rest of the initiator (**a** and **b** in Figure 4.16) are clearly in evidence and their integrals were compared with those of O-CH_2 protons in the PCL chain. Polymerization degree was calculated to be 26, corresponding to a molecular weight of $M_{n,\text{HNMR}}$=3264.

The ^{1}H-NMR spectrum of the aldehyde functionalized polymer (**29**) also confirms the proposed structure. The aldehyde proton **m** at 10.1 ppm, the new aromatic signals **l** and **k** at 7.99 and 7.56 ppm, together with **a** and **b** protons originating from the rest of the ROP initiator, permitted a recalculation of the polymerization degree of PCL is similar with the starting one. This result proves not only that during the Suzuki reaction no degradation process of the PCL chain occurred, but also that the functionalization of the polymer was complete.

The ^{1}H-NMR spectrum of PPV **33** (Figure 4.16) shows different signals in the aromatic region as comparing with **29**. The aldehyde peak from 10.1 ppm in the spectrum of **29** has disappeared, in this case due to the consumption of this group during the Wittig reaction. The peaks in around 7.0-7.8 ppm are broader and partial overlapping due to the increasing of polydispersity of the new polymer together with increase in conjugation length. Some authors observed the possibility of *cis – trans* conformations in the case of PPV; it has been reported that the *cis* proton appears usually around 6.5 ppm [314,315]. In our case, the small doublet at 6.65-6.61 ppm suggests that some *cis* conformations at the newly formed vinylic bonds also appeared ($\mathbf{n}_{cis}$ in Figure 4.16). Although protons in the *trans* conformation are not sharply defined in Figure 4.16 ($\mathbf{n}_{trans}$ appears together with other aromatic protons, while $\mathbf{m}_{trans}$ is too close to the **l** ones to permit a precise integration) an evaluation of the *cis* percentage could be done by comparing the integral of $\mathbf{n}_{cis}$ with the integral of **b** protons.

$$I_{\mathbf{b}}/4 = (I\mathbf{n}_{cis}+I\mathbf{n}_{trans})/2 \qquad \textbf{(4.17)}$$

Thus,

$$\%cis = 2I\mathbf{n}_{cis} \cdot 100/(I_{\mathbf{b}}-2I\mathbf{n}_{cis}) \qquad \textbf{(4.18)}$$

where $I_{\mathbf{b}}$ and $I\mathbf{n}_{cis}$ are the integrals of the protons from 5.0-5.1 ppm and 6.65-6.61 ppm, respectively.

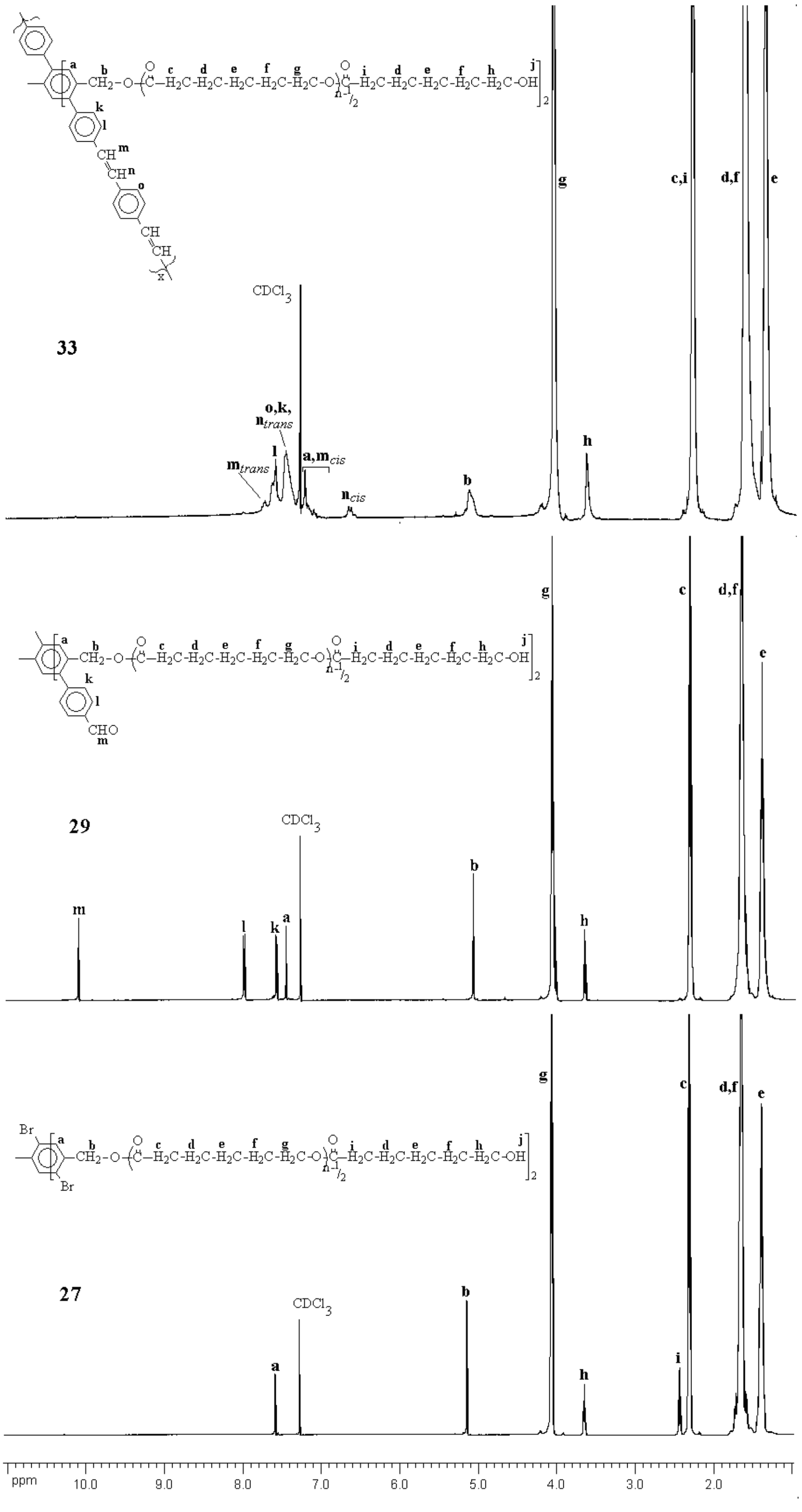


Figure 4.16 : ^{1}H-NMR spectra of the starting PCL (**27**), aldehyde functionalized polymer (**29**), and the final PPV with macromolecular side chains (**33**) (50% cis) in $CDCl_3$.

The same calculations can be made by comparing the integral of $\mathbf{n}_{cis}$ with that of all the other protons between 7-7.8 ppm, as every repeating unit has 18 aromatic protons. In the case of **33** it was found that about 50% of the double bonds are in a *cis* conformation. Taking in account the macromolecular nature of the PPV substituents, the result is probably due to sterical hindrance. As the protons **b** and **h** of the initial macromonomer are still clearly resolvable, their integrals were used also for verifying the polymerization degree of PCL and was found again to be 26. This fact shows that no degradation of the polymer chain took place during the formation of the PPV.

For a better understanding of the spatial arrangement of the PPV main chain in *cis* or *trans* conformations of the vinylene bonds, as well as the distribution of PCL side chains around the rigid core, model molecules for polymer fragments were obtained by molecular mechanics (MM+). The three dimensional ball-and stick models are shown in Figure 4.17 obtained after energy minimization. The shown copolymers, obtained by the copolymerization of a macromonomer with a low molecular weight partner, are graft copolymers, an interesting class of self-assembling materials with domain sizes in the nanometer regime [311]. In general, graft copolymers are considered special branched polymers that are expensive to produce commercially. However, the introduction of branches onto a polymer chain facilitates control over the processability and rheological properties and moreover such copolymers show different morphologies due to the microscopic phase separation in the solid state and selective solvation in solution. This intrinsic morphology can be used to design materials for nanoscale devices. In the models presented in Figure 4.17 in both cases (*cis* and *trans* configuration) the molecule structure is of “hairy-rod” type with a pronounced cylindrical symmetry in the case of the *trans* conformation. The literature has reported the backbone of cylindrical symmetry of the hairy-rod molecules can be modified by attaching long or short side chains [315]. The slight deviation from the cylindrical symmetry of the backbone observed in Figure 4.17 (*cis*) could be due to the type of conformation of the vinylene double bond. By comparing with conventional polymers, the importance of such cylindrical objects consists in that their diameter is on the order of a few nanometers rather than few angstroms. As a consequence, the rigidity is so high that the persistence length of an individual chain is not on the order of 10 nm, but may instead exceed 50 nm. Such cylindrical rods, due to their high bending moduli, could potentially be used for constructions on the nanometer scale [28].

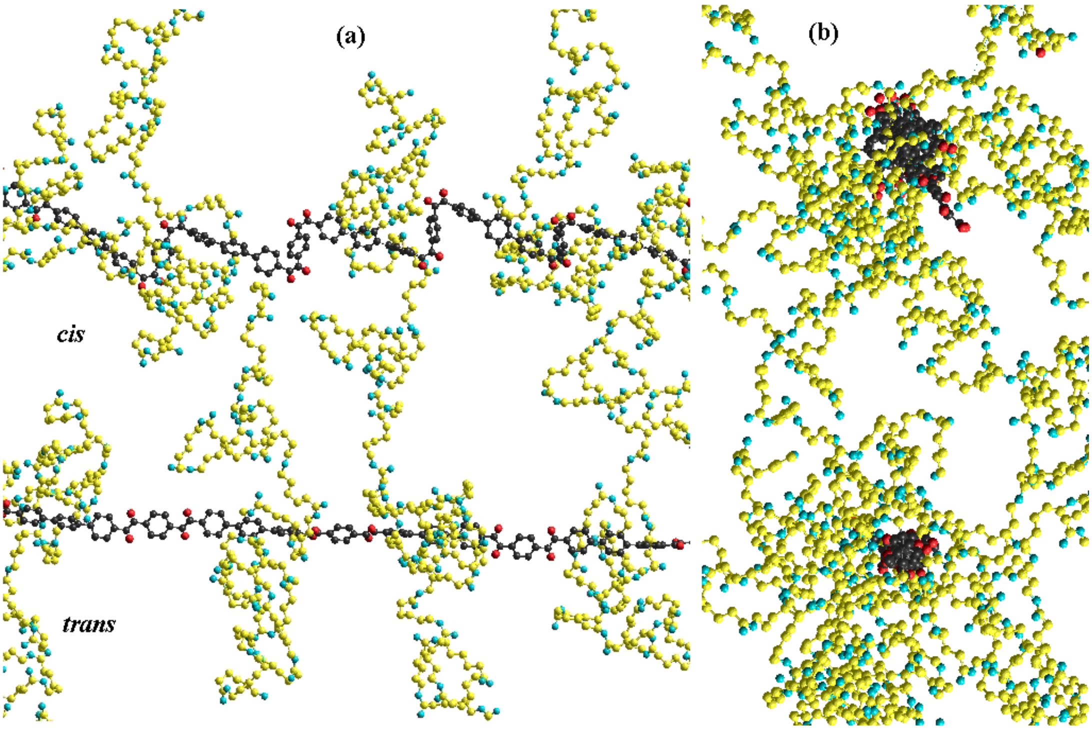


Figure 4.17 : Three dimensional ball-and stick models of **33** in cis and trans conformations, up (**a**) and frontal (**b**) images**.**

In the case of the other PCL substituted PPV, **34**, in which bromine atoms alternates with polymeric substituents, the ^{1}H-NMR spectrum also shows that some double bonds are in the *cis* conformation (Figure 4.18). The intensity of signals from 7.12-7.15 ppm ($\mathbf{n}_{cis}$) and 6.64-6.75 ppm ($\mathbf{m}_{cis}$) regions could be compared again with the intensity of the **b** proton peak. In this case, also the **o** protons belonging to the bromine substituted ring appear separately from the other aromatic protons, so the percentage of double bonds in the *cis* conformation (75%) could be calculated. The increase in the amount of *cis* vinylene linkages comparing with polymer **33** can be due to the presence of bulky bromine atoms as side groups near the PCL ones.

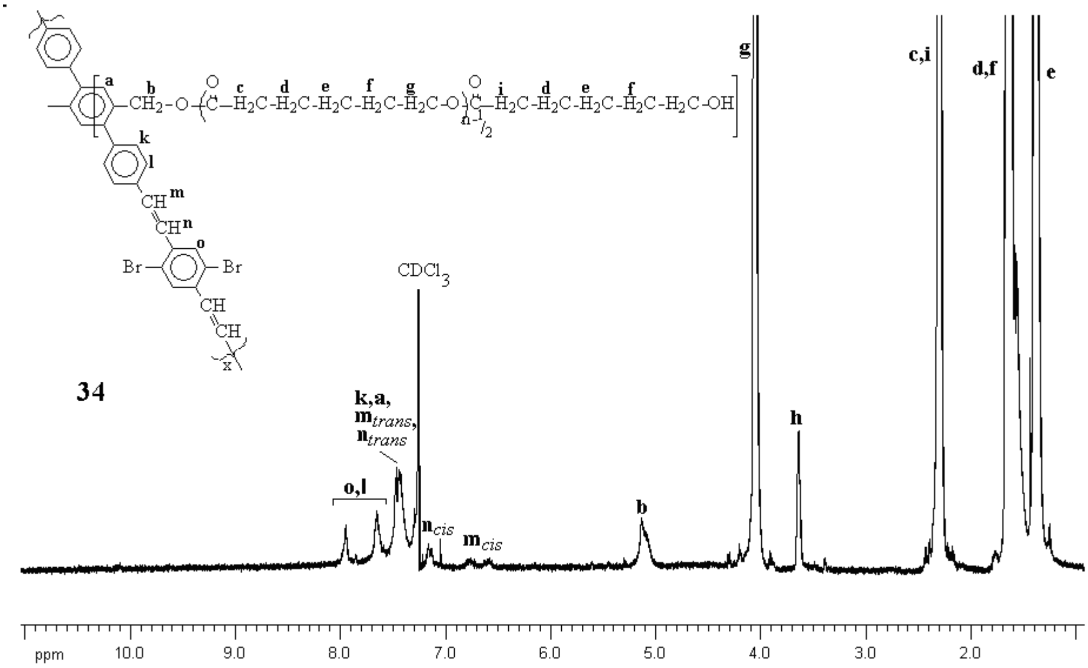


Figure 4.18 : ^{1}H-NMR spectrum of the PPV **34** with PCL side chains (75% cis) in $CDCl_3$.

Figure 4.19 presents the ^{1}H-NMR spectra of the PSt based polymers. In the ^{1}H-NMR spectrum of the polystyrene starting macromonomer **28**, obtained by ATRP, the peak from about 4.5 ppm corresponding to the final Ar-C*H* proton, directly linked to the final bromine atom, was used for calculating the molecular weight of the polymer. The result is close to that found from GPC. The spectrum of the aldehyde functionalized polymer **30** shows clear peaks of the newly introduced end groups. As the substitution at the benzene ring originating from the ATRP initiator is not symmetrical as in the case of PCL polymer **29**, the peaks from the aromatic region that are outside the PSt main signals (beyond 7.3 ppm) can be the result of contributions of several aromatic protons (**m**, **k**, **l**, **j**). Despite this the peaks of the aldehyde protons appear very clearly at 10.02-10.07 ppm and could be used for calculating the molecular weight of **30**. As in the case of **29**, the slight increase of molecular weight as comparing to the starting **28**, can be due to the introduction of new end groups in the polymer chain.

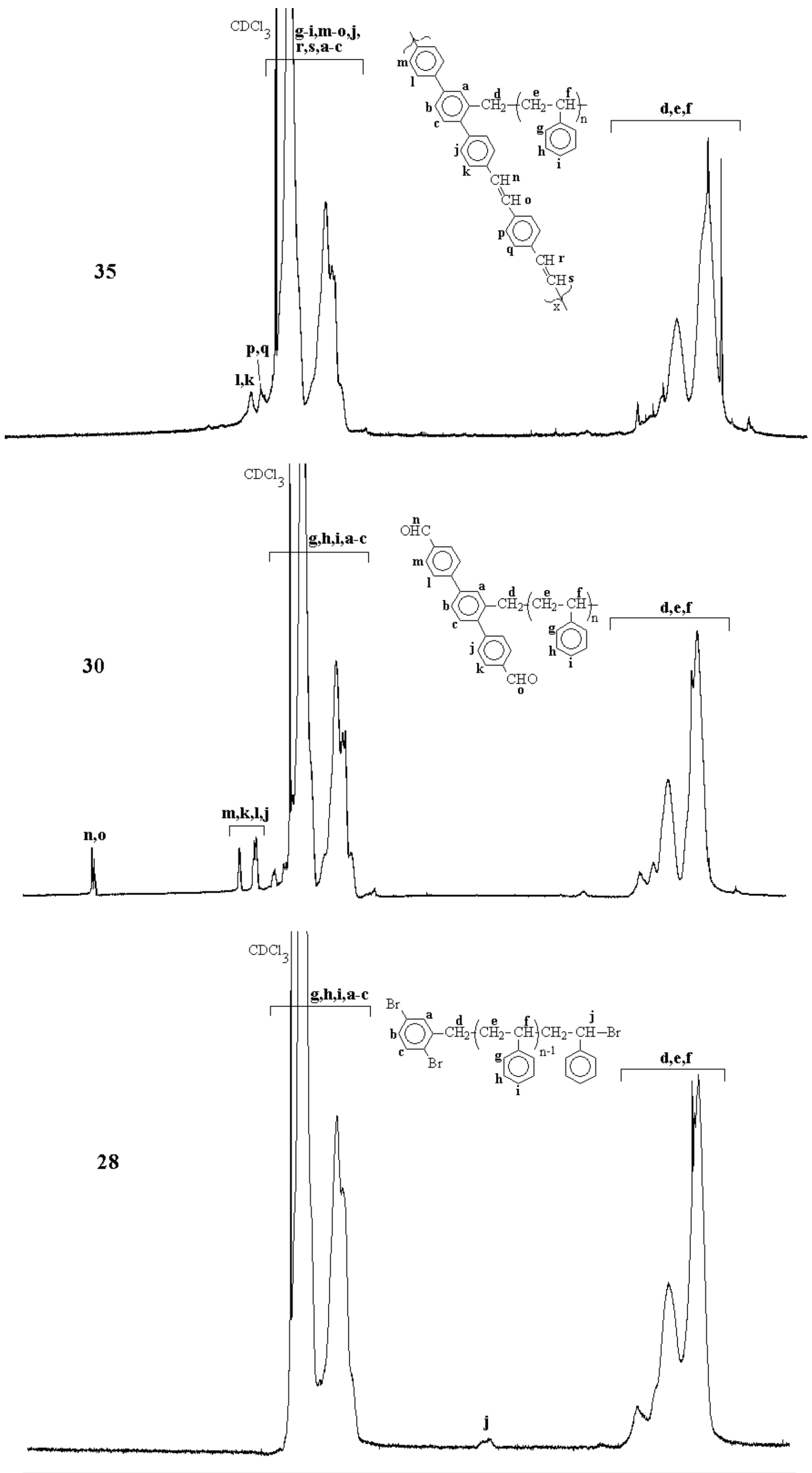


Figure 4.19 : ^{1}H-NMR spectra of the starting PSt (**28**), aldehyde functionalized polymer (**30**), and the final PPV with macromolecular side chains (**35**) in $CDCl_3$.

Because of the partially overlapping of the protons of the conjugated chain with the aromatic ones in the PSt repeating units, together with the increase of polydispersity, the spectrum of **35** offers less information regarding the final polymer structure. In this case it is not possible to determine if *cis* conformation are also present. Despite this, the different arrangement of the aromatic protons from the region beyond 7.3 ppm (the region uncovered by PSt), together with GPC data and the results of other analyses, indicates that the desired PPV was formed.

^{13}C-NMR analysis can also give information on the polymers structures. Figure 4.20 presents the spectra of PCL based PPVs (**33** and **34**) in comparison with the aldehyde functionalized macromonomer (**29**). The spectrum of macromonomer **29** presents not only the usual signals of PCL (173.47 ppm - **j**, 129.8 ppm – **f**, 62.47 ppm – **o**, 34.05 ppm – **k**, 26.23 ppm – **n**, 25.59 ppm – **l**, 24.47 ppm – **m**), but also peaks of the carbons originating from the end groups (191.55 – **h**, 145.63 ppm – **d**, 140.94 ppm – **b**, 135.66 ppm – **c**, 133.6 ppm – **a**, 131.14 ppm – **e**, 62.28 ppm – **q**, 32.17 ppm – **p**) proving the proposed structure. In the case of the ^{13}C-NMR spectra of PCL based PPVs **33** and **34**, the number of peaks in the aromatic region significantly increases in this region (150-125 ppm), while the signal from 173.47 ppm of the aldehyde carbons from **29**, disappears. Although the distribution of the peaks suggests in both cases the existence of *cis-trans* conformations, no certain conclusions regarding this aspect can be depicted from the spectra. ^{13}C-NMR spectra of the PSt based polymers are even more complicated. Due to the asymmetrical substitution of the PSt chain on the benzene ring, all the aromatic carbons of the end groups differ. Moreover, some of the aromatic carbons of the end-groups in the case of **30** or of the conjugated main chain in the case of **35** are covered by the aromatic carbons of PSt itself. Despite this in the case of **30,** the aldehyde carbons appear separately at 181.6 ppm and this peak disappears in the case of PPV **35**. Also, some of the carbons of the end-groups or conjugated PPV main chain could be identified in the domains not covered by the aromatic signals of PSt (144 ppm-132 ppm and 123 ppm-117 ppm) proving the proposed structures, but no information on the cis-trans conformations is obtained.

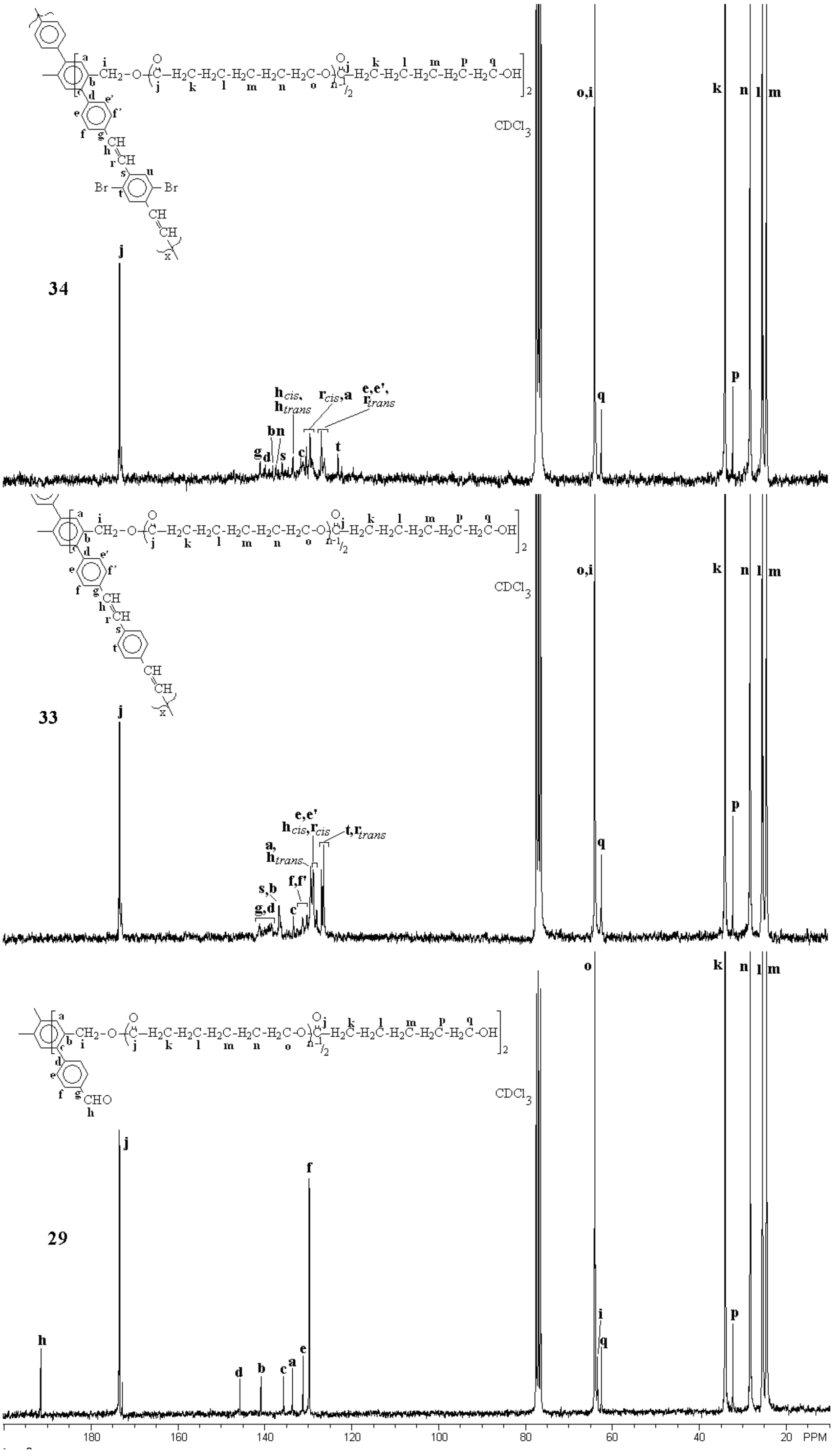


Figure 4.20 : ^{13}C-NMR spectra of PCL polymers **29**, **33** and **34** in $CDCl_3$.

IR spectra of PCL based polymers (**27**, **29**, **33**, **34** - Figure 4.21) display strong specific peaks for CL repeating units (e.g. 1723 cm^{-1}-νC=O; 1293 cm^{-1}-νC-O *as* and 1046 cm^{-1}-νC-O *sym*, etc).

In the case of the aldehyde functionalized polymer a new signal at 1607 cm^{-1} is attributed to υC=O from the CHO group. The shifting of this absorbance to lower frequency than usual is explained in this case by the association of this carbonyl group by intramolecular hydrogen bonding with the final OH groups in the PCL moieties. Also, we notice new peaks compared to the starting macromonomer. The absorption at 1572 cm^{-1} can be attributed for νC=C of the new aromatic rings from the rest of the boronic acid that are in conjugation with the initial benzene ring from the center of the polymer chain. On the other hand, the peak at 838 cm^{-1} from the spectrum of **27**, that could be attributed to the γ CH of 1,2,4,5-tetrasubstituted benzene ring, is more intense in the case of **29**, due to the γ CH of the new *p*-disubstituted benzene rings.

In the spectra of PPV type polymers **33** and **34** the absorbance attributed to the aldehyde group in **29**, has almost disappeared. Because of the presence of intense PCL peaks in the regions around 965-980 cm^{-1} (*trans* γCH for vinylene bonds) and 675-730 cm^{-1} (*cis* γCH for vinylene bonds), less information on their conformaation can be obtained from the IR spectra of these polymers. Despite this, a new peak at 860 cm^{-1} in the case of **34**, or 1460 cm^{-1} for both **33** and **34**, can be attributted to a *cis* conformation of the vinylene bonds. Also, the new peak from 1015 cm^{-1} can be due to the *trans* conformation in the PPV main chain.

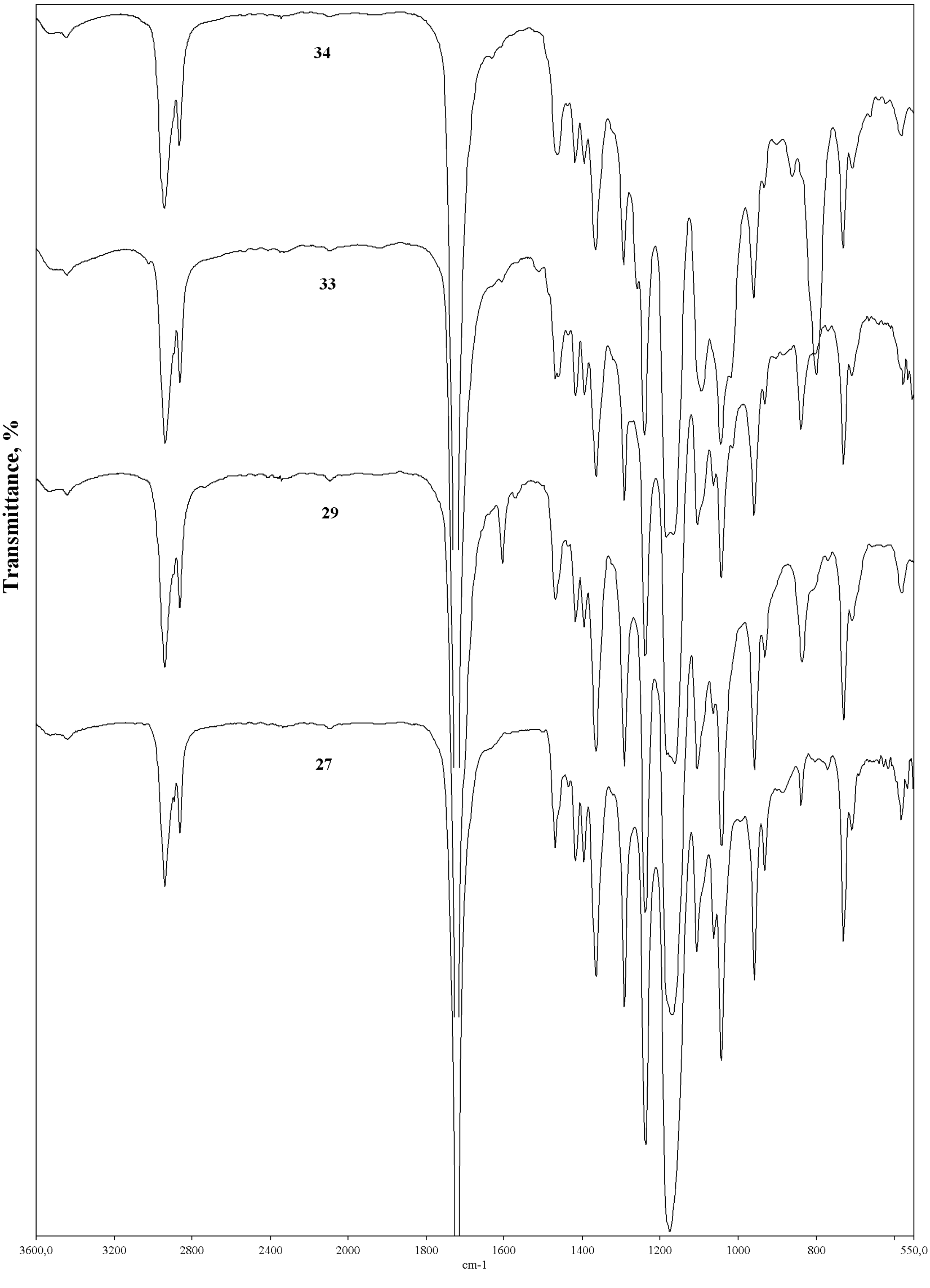


Figure 4.21 : IR spectra of PCL based polymers.

The IR spectra of **28**, **30** and **35** (Figure 4.22) display the usual absorptions of PSt at 3058 cm^{-1}, 3025 cm^{-1} (aromatic CH stretching), 2970 cm^{-1}, 2851 cm^{-1}, 2848 cm^{-1} (aliphatic CH stretching), 1937 cm^{-1}, 1867 cm^{-1}, 1798 cm^{-1}, 1665 cm^{-1} and 760 cm^{-1} (out-of -plane hydrogen deformation), 1598 cm^{-1}, 1489 cm^{-1}, 1446 cm^{-1} (in-plane-bend -stretching vibrations of phenyl ring), 758 cm^{-1} and 697 cm^{-1} (out-of-plane hydrogen deformation).

The absorptions from 808 cm^{-1} and 910 cm^{-1} in the spectrum of **28** are characteristic of out-of-plane deformations (γCH) of the CH bonds of a 1,2,4-trisubstituted aromatic ring. The latter signal is also present in the spectra of **30** and **35.** New peaks appear in the case of IR spectra of **30** and **35** (with small intensities in the latter) in the region 800-850 cm^{-1} due to the presence of *p*-disubstituted benzene rings (γCH).

The appearance of an intense absorption at 1702 cm^{-1} (νC=O) in the spectrum of **30** indicates the presence of aldehyde groups. This peak disappears in the spectrum of PPV **35**. Because of the overlapping of PSt absorptions with those of the double bonds from the main PPV chain, as well as the broadening of the peaks, no information about *cis*-*trans* conformations can be obtained from the IR spectrum of **35**.

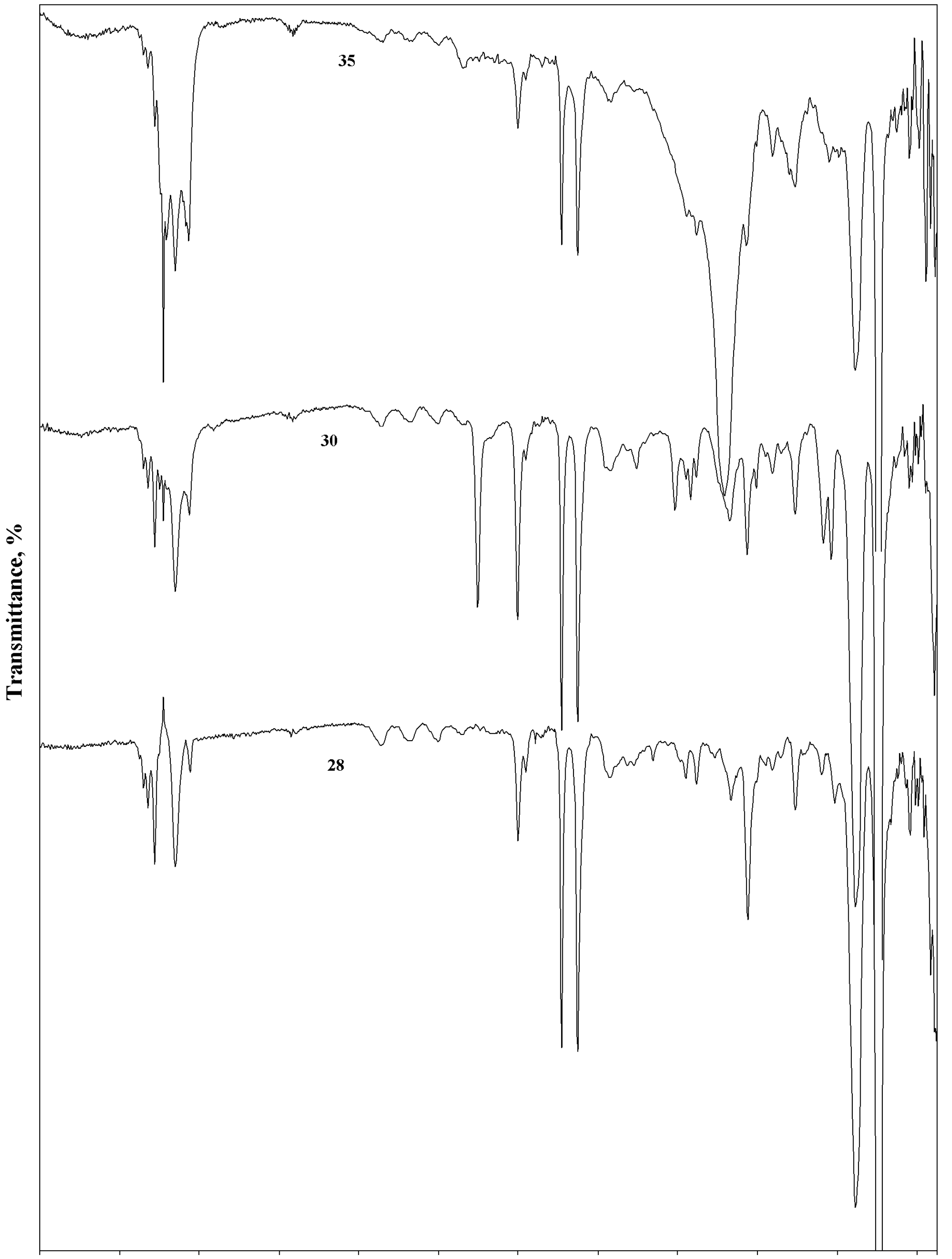


Figure 4.22 : IR spectra of PSt based polymers.

The thermal behaviour of the polymers was followed by differential scanning calorimetry (DSC) (30-300°C) and thermogravimetric analysis (TGA) (30-800°C), under nitrogen, with a heating rate of 10°C/min. Some characteristics are presented in Table 4.3

Table 4.3: Thermal properties of the synthesized polymers.

Polymer	M.p[a] (°C)	T_g[a], (°C)	IDT[b], (°C)	T_{w10}[c], (°C)	Yc $_{800}$[d], (%)
27	51	-	270	340	2
29	47	-	318	378	0
33	41	-	302	390	9
34	38.5	-	231	262	11
28	-	91	180	375	3
30	-	99	250	377	13.6
35	-	120	300	405	8

[a] From DSC analysis
[b] Initial degradation temperature (IDT)
[c] The temperature at which the weight loss is 10 % (T_{W10})
[d] The percent of char yield at 800⁰C (Y_C)

The endothermic peaks characteristic to the melting phenomenon of the PCL chains are evidenced at 51°C, 47 °C , 41 °C and 38.5 °C in the DSC traces of **27, 29, 33** and **34,** respectively. A decrease of the melting temperature of PCL with the increasing of the complexity of polymers can be seen. The introduction of the conjugated end group in the case of **29** can disturb the length of ordering of PCL chains, so the melting point decreases as compared with **27**. The phenomena is more evident in the case of PPVs. The PCL molecules are linked to a rigid conjugated chain, at certain distances so the lengths of ordering and consequently the melting points are decreased. The Br substituents (that alternate with PCL ones) linked at the PPV chain of **34**, also has an influence on this characteristic. In the case of the PSt based compounds the Tg of this polymer is slightly shifted to higher values as the complexity of the molecules increases. This behaviour can be a consequence of the decreasing of mobility of PSt segments in the new polymers.

The thermal stability of the synthesized polymers containing oligomeric side chains of PSt or PCL are presented in Table 4.3. In the case of the series containg PSt (**28**, **30** and **35**) an increase of the IDT and T_{w10} for compounds **30** and **35** can be observed. For the starting macromonomer **28** the initial degradation temperature and T_{w10} have been reported as 180°C and 375°C , respectively [309], whereas in the new synthesized macromonomer **30**, the IDT substantially increased at 250°C. This fact could be attributed to the triphenylene sequence contained in its structure. The highest values for IDT and T_{w10} were registered for the PPV **35** (300°C and 405°C, respectively). A similar trend can be observed for the series containing PCL. The lowest values (IDT=231°C, T_{w10}=262°C) were obtained for the polymer **34** that contains near to the PCL side chains also Br atoms directly connected to the phenylene ring, the loss of which is expected at a lower temperature. For the polymer **33** the IDT value is comparable with that one of the macromonomer **29**. It was reported in the case of polyphenylenes with PCL side chains [316], the thermal degradation of the polymeric structure starts with the substituents. It can be concluded from the data presented in Table 4.3 that the thermal stability of PPVs **33** and **35** is similar with that of poly(biphenylene vinylene) derivatives reported by Yamamoto et al (ca. 300°C) [317].

Thermal degradation characteristics, via direct pyrolysis mass spectrometry, of the starting materials (**27**,**28**), macromonomers (**29**, **30**) and the final PPVs (**33**-**35**) have also been studied and reported [318,319]. The results were comparable with the above mentioned thermal characteristics. Detection of an increase in thermal stability of the PCL and PSt side chains was attributed to higher thermal stability of the PPV backbone. At the same time it was concluded that the presence of thermally less stable side chains affects the thermal stability of the PPV backbone negatively.

For the investigation of the optical properties, the absorption and emission spectra of the polymers were followed in THF and $CHCl_3$ solutions and as films. Starting brominated polymers **27** and **28** show UV absorptions situated between 250-300 nm with tails until 280-320 nm (Figures 4.23 and 4.24).

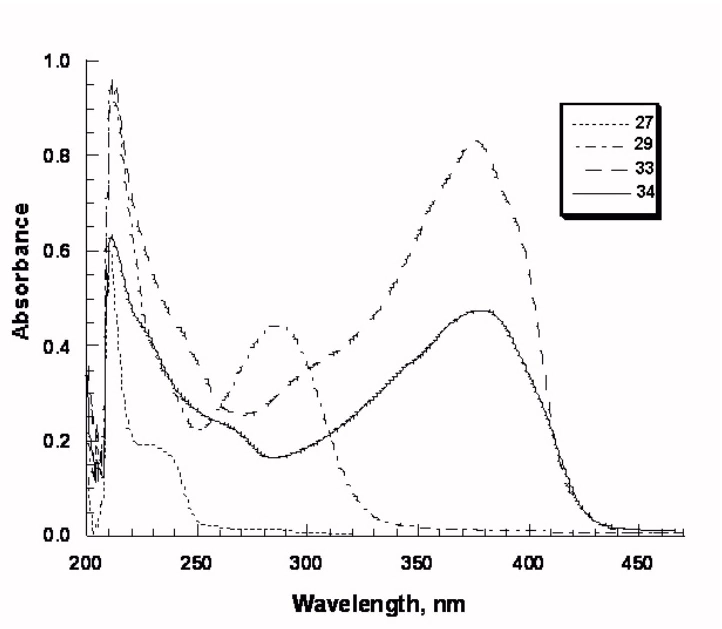


Figure 4.23 : UV spectra of PCL polymers in THF.

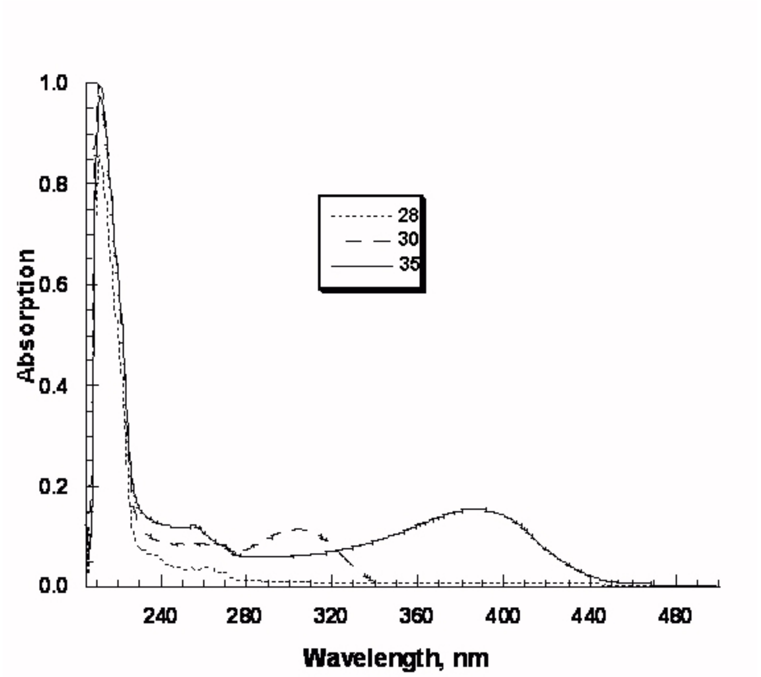


Figure 4.24 : UV spectra of PSt polymers in THF.

Aldehyde functionalized macromonomers **29** and **30** differ from the corresponding **27** and **28** by replacement of bromine atoms with 4-substituted phenylene rings and a conjugation in the triphenylene sequence is possible. As a result, new maxima appear in the UV spectra. Table 4.4 summarizes UV absorption and emission data for the macromonomers, monomers and polymers measured in THF solutions.

Table 4.4: Photophysical properties of polymers in THF solutions (0.04 g/L).

Starting Macromonomer		Aldehyde Functionalized macromonomer			PPV		
Code	λ_{max}^{Abs} (nm)	Code	λ_{max}^{Abs} (nm) ^{a}	λ_{max}^{PL} (nm)	Code	λ_{max}^{Abs} (nm) ^{a}	λ_{max}^{PL} (nm)
27	212, 225	**29**	212; 284^{a}	356	**33**	212; 378	450
					34	212; 378	460
28	257	**30**	257; 293^{b}	360	**35**	257; 388^{b}	456

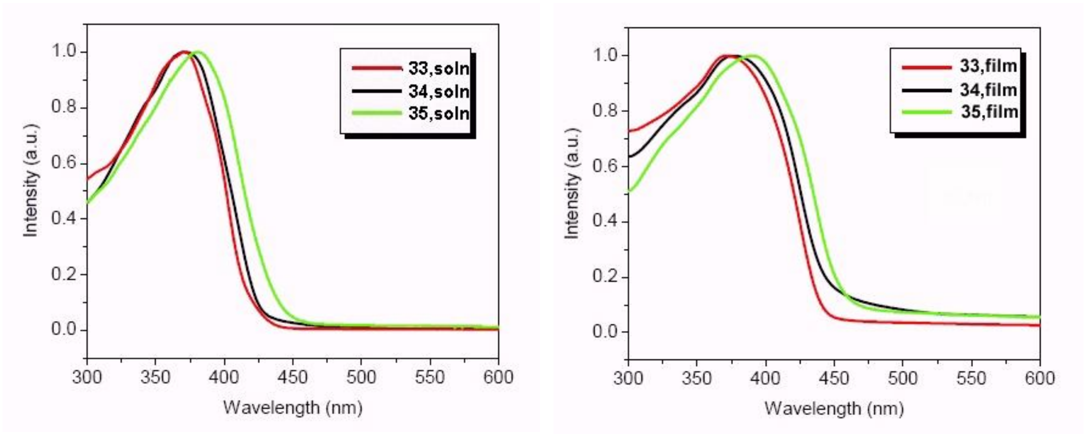
[a] Excitation wavelength for PL spectra of PCL polymers
[b] Excitation wavelength for PL spectra of PSt polymers

The Wittig polycondensation of **29** and **30** led to PPVs having absorption spectra with the same maxima as the corresponding monomers, however new maxima can be observed assigned to the conjugated chain and also, the absorption range is larger and red-shifted comparatively with their monomers (Figures 4.23 and 4.24). A clear bathocromic shift of the λ_{max} emission is observed for all polymers with respect to macromonomers due to extending of the conjugation length.

The UV spectra of PPVs **33-35** in $CHCl_3$ solutions and for films are presented in Figure 4.25 while the photoluminescence spectra under excitation wavelength of 370 nm are shown in Figure 4.26. The peak wavelengths are listed in Table 4.5.

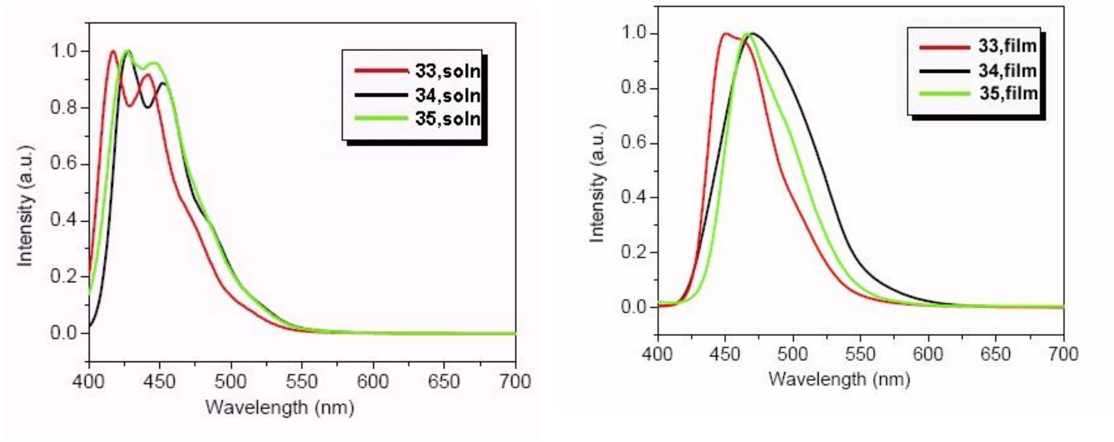
Table 4.5: Photophysical properties of **33-35** in $CHCl_3$ solutions and in film.

Polymer	λ_{max}^{Abs} (nm) ^{a}	λ_{max}^{Abs} (nm) ^{b}	λ_{max}^{PL} (nm) ^{a}	λ_{max}^{PL} (nm) ^{b}
33	373	380	418	451
34	373	376	428	470
35	382	390	428	467



(a) **(b)**

Figure 4.25 : UV-vis spectra for **33-35** in chloroform at room temperature (**a**) and as solid films cast on quartz plates (**b**); spectra are normalized for comparison.



(a) **(b)**

Figure 4.26 : Photoluminescence spectra for **33-35** in chloroform (**a**) and as solid films cast on quartz plates (**b**).

The PL spectra of all polymer films showed a red shift and some broadening of the emission bands in comparison to their solution spectra. The red shifts in PL are due to intermolecular interactions in the films.

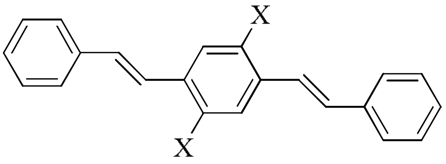
Detailed photophysical properties of the PPV derivatives laterally decorated with PSt or PCL have also been investigated [320]. Photophysical properties of the polymers were examined in dilute chloroform solution, in thin films (spin coated and inkjet printed) and in bulk. Table 4.6 summarizes the dilute chloroform photophysical data of the studied compounds, namely the absorption maximum, λ_a, the maximum of the fluorescence excitation spectrum, λ_{exc}, the fluorescence maximum, λ_f, the Stokes shift, $\Delta\nu_{af}$, the relative fluorescence quantum yield, Φ_f, the fluorescence lifetime, τ, the fluorescence radiative constant, k_f, the fluorescence non-radiative constant, k_{nr}, and the fluorescence polarization, r.

The absorption and emission of the macromolecules are essentially determined by the basic chromophore system distyrylbenzene (DSB) or dibromodistyrylbenzene (Br_2-DSB) and the steric influence due to the type and the number of laterally grafted macromolecules. For comparison reason the model compounds DSB and Br_2-DSB, as shown in (4.19), have been taken into consideration.

Table 4.6: Spectral and photophysical properties in dilute chloroform solution.

Polymer	λ_a nm	$\lambda_{exc.}$ nm	λ_f [a] nm	$\Delta\nu_{af}$ cm^{-1}	Φ_f	τ ns	k_f ns^{-1}	k_{nr} ns^{-1}	r
PPV-PSt (35)	381	389 335	430/450 ca. 390	3000	0.82	0.71	1.2	0.25	0.26
PPV-PCL (33)	373	378	417/440	2800	0.67	0.65	1.0	0.51	0.25
PPV-PCL-Br (34)	370	382	428/453	3660	0.26	0.34	0.76	2.2	0.25
DSB	354		413	4036	0.85				
Br_2DSB	355		401/ 425	3230	0.23				

[a] Underlined values are main emission bands.



(4.19)

X= H: DSB X=Br : Br_2-DSB

As mentioned above, the basic chromophore of PPV derivatives is located around distyrylbenzene. The twist (caused by the polymeric substituents) in the adjacent phenylene units –Ph-Ph-Ph- hinders an extension of conjugation and leads to a segmentation of the conjugated polymeric chain. The small differences in the position of the absorption and fluorescence bands are related to steric and electronic effects (Figure 4.27). For instance, less steric hindrance in the case of substitution with only one macro-side chain, as in **PPV-PSt** (**35**), leads to longer wavelength absorption and fluorescence as well as higher fluorescence quantum yield. The donor effect of bromine in **PPV-PCL-Br** (**34**) causes a bathochromic shift of the fluorescence as compared to the non bromine substituted compound **PPV-PCL** (**33**). The fluorescence spectra show comparable vibronic structures as in **DSB**. This suggests planarization of their S_1 states. PPV compounds without Br-substitution fluoresce intensively. A comparison of the rate constants of the deactivation processes shows high k_f values for all compounds, which is synonymous to strong allowed fluorescence transition.

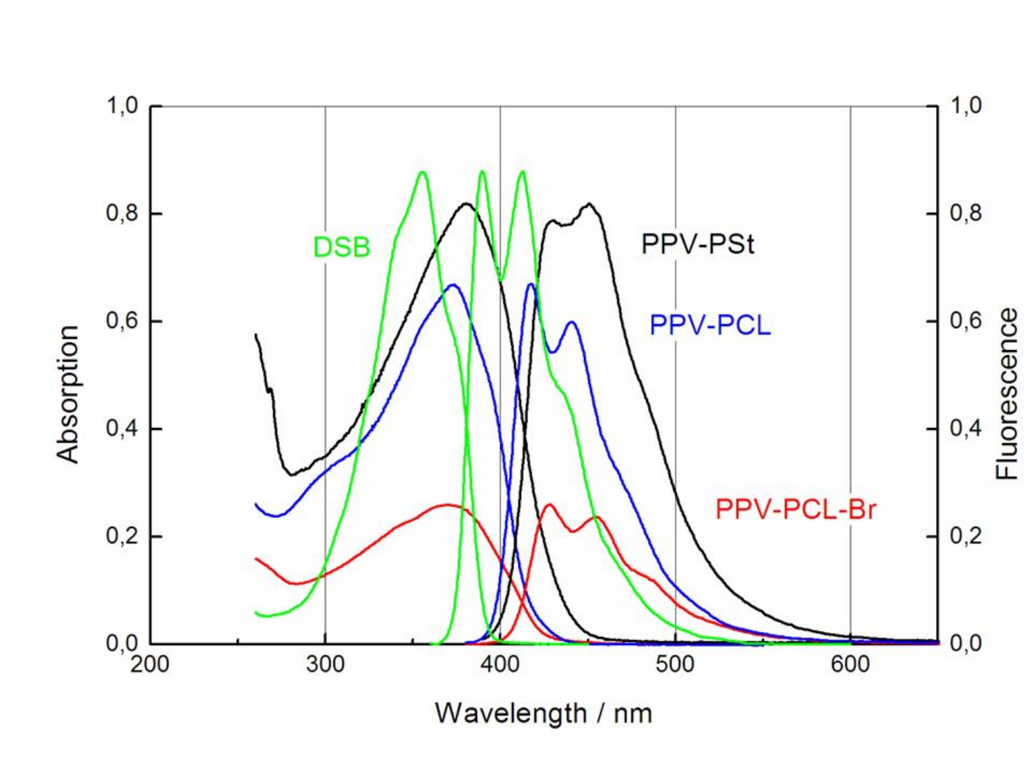
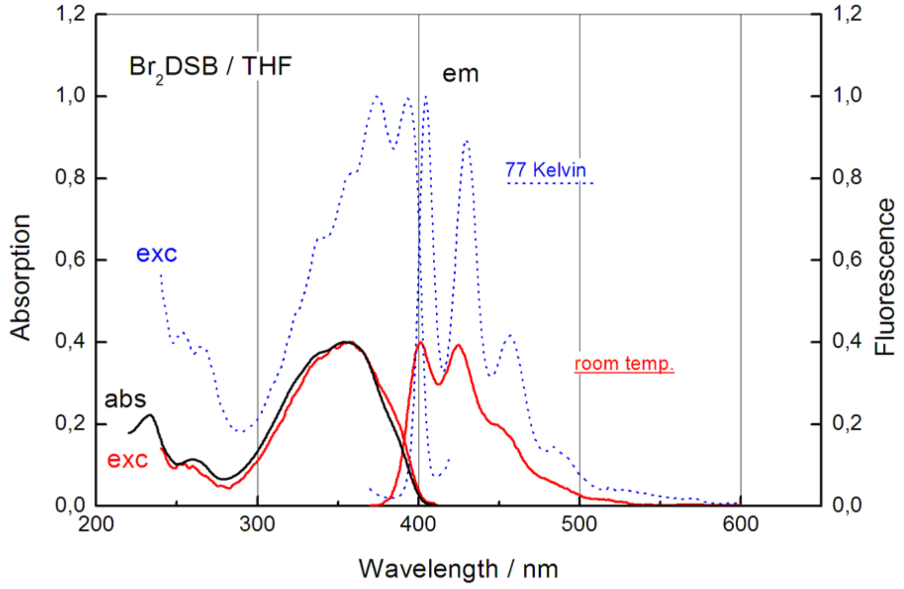


Figure 4.27 : Normalized absorption and emission spectra of the PPV derivatives and distyrylbenzene.

The low fluorescence quantum yield of the Br-substituted compound **PPV-PCL-Br** (**34)** can be clearly ascribed to high radiationless deactivation, whereby intersystem process from S_1 to T_1 can be assumed, which is related to so called “heavy atom effect” due to the presence of bromine atoms [321]. Similar decrease of Φ_f from 85 to 23 % is observed when comparing the model compounds **DSB** and **Br_2-DSB**.

In order to prove the strong population of the T_1 state, low temperature (77 Kelvin) measurements were carried out with **PPV-PCL-Br** (**34**) and **Br_2-DSB**. The highly structuring of the resulting fluorescence spectra leads to an enhancement of the fluorescence intensity as compared to room temperature (Figure 4.28). However no phosphorescence (radiative decay from T_1 to S_0) could be observed.

(a)



(b)

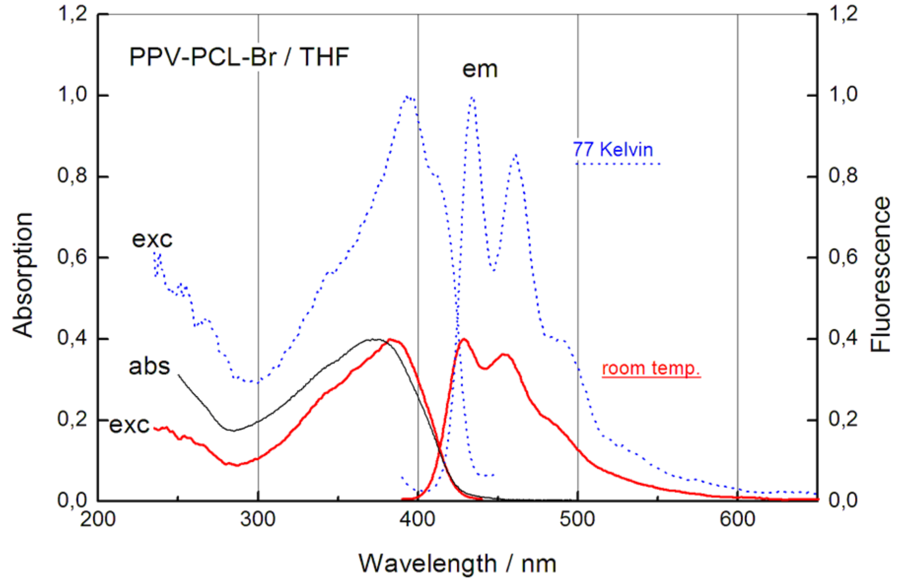


Figure 4.28 : Absorption, fluorescence excitation and fluorescence spectra of Br_2-DSB (**a**) and PPV-PCL-Br (**34**)(**b**) at room temperature and at 77 Kelvin.

As previously shown already (Fig. 4.25 and 4.26), there is a red shift of the absorption and emission spectra going from solution to thin solid films. Spin casted and inkjet printed films were obtained from a mixed toluene and *o*-chlorobenzene solution. The fluorescence spectra of the inkjet printed films of the polymers are depicted in Figure 4.29, the shape and position of the bands are similar to those already mentioned (Fig. 4.25 and 4.26).

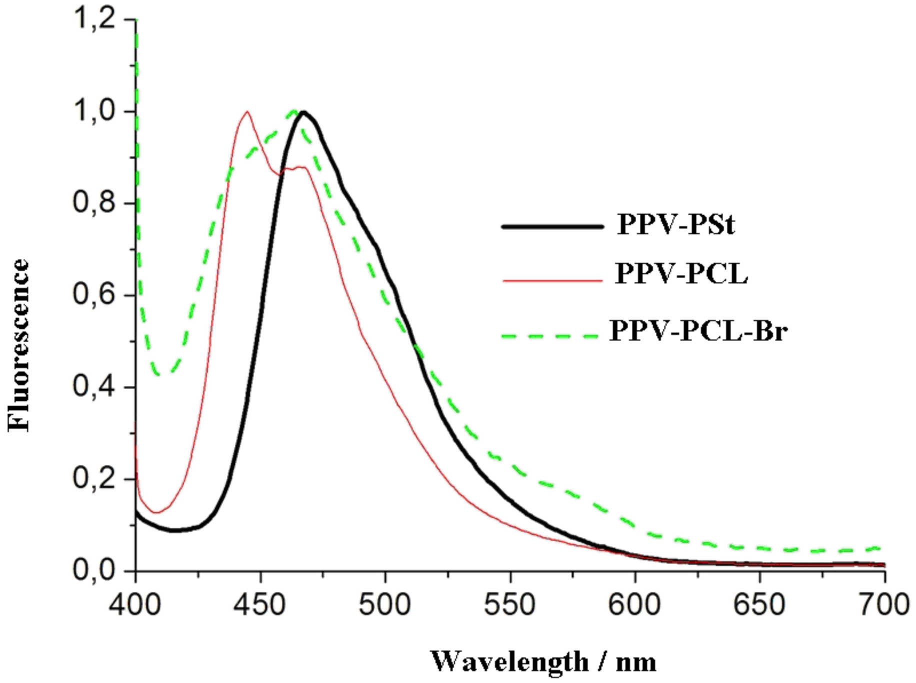


Figure 4.29 : Fluorescence spectra of inkjet printed films.

Absolute photoluminescence quantum yield of the bulk materials, thin films and their starting solution were measured using an *easy-to-handle* Hamamatsu PL system. The results are summarized in Table 4.7. The trend observed above in solution (Table 4.6), i. e. higher Φ_f-values for non Br-substituted compounds than for Br-substituted compound, was confirmed in the solid state. The relatively high solid state Φ_f-values are due to the presence of macro-substituents, which effectively hinder very strong π-π interactions and concomitant excimer formations, which are a source of fluorescence quenching in the solid state [322].

Table 4.7: Absolute quantum yields in solution, thin films and bulk polymer materials.

Compound	Bulk	Inkjet printed film	Spin coated film	Solution
PPV-PCL (33)	0.12	0.20	0.25	0.56
PPV-PCL-Br (34)	0.08	0.10	0.09	0.34
PPV-PSt (35)	0.43	0.48	0.52	0.89

Similar solution *relative* and *absolute* Φ_f values were obtained for the three PPV derivatives.

In summary, PPVs with well-defined PSt or PCL side chains were synthesized by combination of controlled polymerization methods (ATRP and ROP, respectively) and Wittig polycondensation. The structures of the complex macromolecules have been fully characterized as they had excellent solubility in common organic solvents at room temperature. The detailed photophysical investigations revealed that their photophysical behaviour is governed by the basic chromophore unit distyrylbenzene and steric effects caused by type and number of grafted macro-side chains. The polymers emit blue and exhibit very high relative and absolute photoluminescence quantum yield, $\Phi_{f,}$ in dilute solution, thin film (spin-coated and inkjet-printed) and bulk state. The relatively high solid state fluorescence quantum yields suggest minimized fluorescence deactivation channels due to the presence of the macro-substituents, an aspect which favours the use of the present macromolecules in the design of high efficient light-emitting-diodes.

4.4 Conclusions

In this thesis, mid- and end-chain functional telechelics, macromonomers and novel soluble and processable PPV derivatives bearing macromolecular side-chains have been synthesized by combination of controlled polymerization methods, namely ATRP and ROP, coupling processes and further condensation reactions.

The first step in the synthetic strategy of telechelics was the preparation of effective initiators bearing proper functionalities for both; controlled polymerization methods and Suzuki coupling reaction. Bifunctional initiator possessing hydroxymethyl functionalities initiated the ROP of ε-CL in the presence of $Sn(Oct)_2$ catalyst while the initiators having benzyl bromine moeities were used in ATRP of St in conjunction with CuBr/2,2'-bipyridine as catalyst. Thus, depending on the structure of the respective initiator, mid- or end-chain aromatic dibromo functional, well-defined PCL- and PSt-based polymers were obtained. The second step was the reaction of these polymers with amino- or aldehyde-functional monoboronic acids in Suzuki type couplings, which yielded the corresponding telechelics. Further functionalization with oxidable groups such as 2-pyrrolyl or 1-naphthyl was attained by condensation reactions of the amino or aldehyde groups with low molecular weight aldehydes or amines, respectively, with the formation of azomethine linkages. In this way, a variety of amino-, aldehyde-, 2-pyrrolyl, 1-naphthyl- or hydroxyl-functional telechelics were synthesized. These telechelics can be useful in the preparation of various macromolecular structures showing different characteristics. Moreover, polymers bearing pyrrolyl and naphthyl functions can be useful macromonomers for the synthesis of comb-like conjugated polymers by oxidative or electrochemical polymerizations. Fully conjugated poly(Schiff-base)s with polymeric substituents were also synthesized by oxidative polymerization of these macromonomers as preliminary attempts.

A similar strategy was followed for the synthesis of PPVs with well-defined PCL or PSt as lateral substituents. Macromonomers containing dialdehyde functionalities placed at the middle or at the end of the chains were synthesized in two reaction steps. First using ROP of ε-CL or ATRP of St in the presence of proper initiators provided well-defined low molecular weight precursor polymers with dibromobenzene moieties. In the second step, using Suzuki couplings of these dibromobenzene functions with 4-formylphenyl boronic acid, macromonomers possessing 4,4'-dicarbaldehyde terphenyl moieties were obtained. PPVs with PCL or PSt lateral substituents were synthesized by following a Wittig polycondensation in combination with bis-(triphenylphosphonium)salts in the presence of potassium *tert*-butoxide. The final PPVs were soluble in common organic solvents at room temperature as the starting macromonomers.

All of the synthesized polymers were characterized by using spectral methods (^{1}H- and ^{13}C-NMR, IR) and GPC measurements. Detailed photophysical investigations of the PPVs were studied by UV and fluorescence spectroscopy in dilute solutions, thin films and bulk state. The polymers behave as blue luminescent materials and exhibit very high relative and absolute photoluminescence quantum yield. The presence of the lateral macromolecules minimizes fluorescence deactivation channels. Thus, the optical properties and high solubility of the PPV graft copolymers imply that they are promising materials for the design of highly efficient light-emitting-diodes, and may find many applications in various areas.

The present research reveals new pathways for the synthesis of new materials for many high-tech applications. Further complex macromolecular structures based on poly(phenylene vinylene)s can readily be designed by the aforementioned synthetic strategy, using macromonomer technique.

REFERENCES

[1] **Yagci, Y., Nuyken, O. and Graubner, V.,** 2005. Telechelic polymers, in *Encyclopedia of Polymer Science and Technology*, **12**, p. 57-130, Eds. Kroschwitz, J.I., 3rd ed., Wiley, Newyork.

[2] **Goethals, E.J.**, 1989. *Telechelic polymers: Synthesis and Applications*, CRC Press., Boca Raton, FL.

[3] **Kato, M., Kamigaito, M., Sawamoto, M. and Higashimura, T.**, 1995: Polymerization of Methyl Methacrylate with the Carbon Tetrachloride/Dichlorotris(triphenylphosphine)ruthenium(II)/Methylaluminum Bis(2,6-di-*tert*-butylphenoxide) Initiating System: Possibility of Living Radical Polymerization, *Macromolecules*, **28**(5), 1721-1723.

[4] **Kamiagito, M., Ando, T. and Sawamoto, M.**, 2001: Metal-Catalyzed Living Radical Polymerization, *Chem. Rev.*, **101**, 3689-3746.

[5] **Percec, V. and Barboiu, B.**, 1995: "Living" Radical Polymerization of Styrene Initiated by Arenesulfonyl Chlorides and CuI(bpy)nCl, *Macromolecules*, **28**, 7970-7972.

[6] **Matyjaszewski, K.**, 1997. *Controlled Radical Polymerization*, ACS Symposium Series, **685**, American Chemical Soceity: Washington, DC.

[7] **Mishra, M.K. and Yagci, Y.**, 1998. *Handbook of Radical Vinyl Polymerization*, p.233, Dekker, New York.

[8] **Wang, J.S. and Matyjaszewski, K.,** 1995: Controlled Living Radical polymerization Atom Transfer Radical Polymerization in the Presence of Transition-metal Complexes, *J. Am. Chem. Soc.,* **117(20),** 5614-5615.

[9] **Gaynor, S.G., Edelman, S. and Matyjaszewski, K.,** 1996: Synthesis of Branched and Hyperbranched Polystyrenes, *Macromolecules*, **29(3)**, 1079-1081.

[10] **Meredith, P.L.**, 2000: Life Sciences and Materials: A Successful Marriage is Possible, *J. Polym. Sci.; Part A: Polym. Chem.*, **38(4)**, 667-678.

[11] **Stokheim, T.A., Elsenbaumer, R.L. and Reynolds, J.R.**, 1998. *Handbook of Conducting Polymers*, 2nd Ed., Marcel Dekker, New York.

[12] **Burroughes, J.H., Bradley, D.D.C., Brown, A.R., Marks, R.N., MacKay, K., Friend, R.H., Burn, P.L. and Holmes, A.B.,** 1990: Light-emitting Diodes Based on Conjugated Polymers, *Nature,* **347,** 539-541.

[13] **Heeger A.J.**, 2001: Semiconducting and Metallic Polymers: The Fourth Generation of Polymeric Materials, *Angew. Chem. Int. Ed.*, **40**, 2591-2611.

[14] **MacDiarmid, A.G.**, 2001: Synthetic Metals: A Novel Role for Organic Polymers, *Angew. Chem. Int. Ed.*, **40**, 2581-2590.

[15] **Hu, B. and Karasz, F.E.**, 2003: Blue, green, red, and white electroluminescence from multichromophore polymer blends, *J. Appl. Phys.*, **93**, 1995-2001.

[16] **Akcelrud, L.**, 2003: Electroluminescent Polymers, *Prog. Polym. Sci.*, **28**, 875-962.

[17] **Kraft, A., Grimsdale, A.C. and Holmes A.B.**, 1998: Electroluminescent Conjugated Polymers - Seeing Polymers in a New Light, *Angew. Chem. Int. Ed.*, **37**, 402-428.

[18] **Friend, R.H., Gymer, R.W., Holmes, A.B., Burruoghes, J.H., Marks, R.N., Taliani, C., Bradley, D.D.C., Dos Santos, D.A., Bredas, J.L., Löglund, M. and Salaneck, W.R.**, 1999: Electroluminescence in conjugated polymers, *Nature*, **397**, 121-128.

[19] **Hadjichristidis, N., Pitsikalis, M., Iatrou, H. and Pispas, S.**, 2003: The Strength of the Macromonomer Strategy for Complex Macromolecular Architecture: Molecular Characterization, Properties and Applications of Polymacromonomers, *Macromol, Rapid Commun.*, **24**, 979-1013.

[20] **Szwarc, M.,** 1956: Living Polymers, *Nature.*, **178,** 1168-1169.

[21] **Szwarc, M. and Van Beylen M.,** 1993. *Ionic Polymerization and Living Polymers*, Chapman & Hall, New York-London.

[22] **Hsieh, H.L. and Quirk, R.P.**, 1996. *Anionic Polymerization: Principles and Practical Applications*, Marcel Dekker, New York.

[23] **Quirk, R. and Lee, B.,** 1992: Experimental Criteria for Living Polymerizations, *Polym. Int.,* **27(4),** 359-367.

[24] **Matyjaszewski, K.,** 1995: Introduction to Living Polymerization, Living and/or Controlled Polymerization, *J. Phys. Org. Chem.,* **8(4),** 197-207.

[25] **Litvinenko, G. and Muller, A.H.E.,** 1997: General Kinetic Analysis and Comparison of Molecular Weight Distributions for Various Mechanisms of Activity Exchange in Living Polymerizations, *Macromolecules,* **30(5),** 1253-1266.

[26] **Swarc, M.,** 1960: Termination of Anionic Polymerization, *Adv. Polym. Sci.,* **2,** 275-306.

[27] **Matyjaszewski, K.,** 2000. *Controlled / Living Radical Polymerization: Progress In ATRP, NMP, and RAFT,* Vol. 768, Ed. American Chemical Society, Washington DC.

[28] **Cianga, I., Cianga, L. and Yagci, Y.**, 2006. New Applications of Living/Controlled Polymerization Methods for Synthesis Copolymers with Designed Architectures and Properties, in *New Trends in Nonionic (Co)Polymers and Hybrids*, p.1-53, Ed. Dragan, E.S., Nova Science Publishers, New York.

[29] **Matyjaszewski, K. and Xia, J.,** 2001: Atom Transfer Radical Polymerization, *Chem. Rev.,* **101,** 2921-2990.

[30] **Hawker, C.J., Bosman, A.W. and Harth, E.,** 2001: New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations, *Chem. Rev.* **101,** 3661-3688.

[31] **Mayadunne, R.T.A., Rizzardo, E., Chiefari, J., Chong, Y.K., Moad, G. and Thang, S.H.,** 1999: Living Radical Polymerization with Reversible Addition-fragmentation Chain Transfer (Raft Polymerization) Using Dithiocarbamates as Chain Transfer Agents, *Macromolecules,* **32 (21),** 6977-6980.

[32] **Patten, T.E. and Matyjaszewski, K.,** 1998: Atom transfer radical polymerization and the synthesis of polymeric materials, *Adv. Mater.,* **10(12),** 901-915.

[33] **Patten, T.E. and Matyjaszewski, K.,** 1999: Copper(I)-catalyzed atom transfer radical polymerization, *Acc. Chem. Res.,* **32(10),** 895-903.

[34] **Wang, J.S. and Matyjaszewski, K.,** 1995: Controlled/"Living" Radical Polymerization. Halogen Atom Transfer Radical Polymerization Promoted by a Cu(I)/Cu(II) Redox Process, *Macromolecules,* **28,** 7901-7910.

[35] **Fischer, H.,** 1999: The persistent radical effect in controlled radical polymerizations, *J. Polym. Sci.; Part A: Polym. Chem.,* **37(13),** 1885-1901.

[36] **Matyjaszewski, K. and Xia, J.,** 2002. Fundamentals of Atom Transfer Radical Polymerization, in *Handbook of Radical Polymerization,*Chapter 11, Eds. Matyjaszewski, K. and Davis, T.P., John Wiley and Sons, Inc., New York.

[37] **Sonmez, H.B. and Bicak, N.,** 2002: Quaternization of poly(4-vinyl pyridine) beads with 2-chloroacetamide for selective mercury extraction, *React. Funct. Polym.,* **51(1),** 55–60.

[38] **Kotani, Y., Kamigaito, M. and Sawamoto, M.,** 2000: Living radical polymerization of para-substituted styrenes and synthesis of styrene-based copolymers with rhenium and iron complex catalysts, *Macromolecules,* **33(18),** 6746-6751.

[39] **Kotani, Y., Kamigaito, M. and Sawamoto, M.,** 1999: Re(V)-mediated living radical polymerization of styrene: $ReO_2I(PPh_3)(2)$/R-I initiating systems, *Macromolecules,* **32(8),** 2420-2424.

[40] **Destarac, M., Matyjaszewski, K. and Boutevin, B.,** 2000: Polychloroalkane initiators in copper-catalyzed atom transfer radical polymerization of (meth)acrylates, *Macromol. Chem. Phys.,* **201(2),** 265–272.

[41] **Percec, V., Kim, H.J. and Barboiu, B.,** 1997: Scope and limitations of functional sulfonyl chlorides as initiators for metal-catalyzed "living" radical polymerization of styrene and methacrylates, *Macromolecules,* **30(26),** 8526–8528.

[42] **Wang, J.S. and Matyjaszewski, K.,** 1995: Living controlled radical polymerization - transition-metal-catalyzed atom-transfer radical polymerization in the presence of a conventional radical initiator, *Macromolecules,* **28(22),** 7572-7573.

[43] **Singha, N.K. and Klumperman, B.,** 2000: Atom-transfer radical polymerization of methyl methacrylate (MMA) using CuSCN as the catalyst, *Macromol. Rapid Commun.,* **21(16),** 1116-1120.

[44] **Xia, JH. and Matyjaszewski, K.,** 1997: Controlled/"living" radical polymerization. Homogeneous reverse atom transfer radical polymerization using AIBN as the initiator, *Macromolecules,* **30(25),** 7692-7696.

[45] **Klumperman, B.,** 2004. Living Radical Polymerization, in *Encyclopedia of Polymer Science and Technology,* John Wiley & Sons, Inc., New York.

[46] **Teodorescu, M., Gaynor, S.G. and Matyjaszewski, K.,** 2000: Halide anions as ligands in iron-mediated atom transfer radical polymerization, *Macromolecules,* **33(7),** 2335-2339.

[47] **Moineau, G., Minet, M., Teyssie, P. and Jerome, R.,** 2000: Synthesis of fully acrylic thermoplastic elastomers by atom transfer radical polymerization (ATRP), 2 - Effect of the catalyst on the molecular control and the rheological properties of the triblock copolymers, *Macromol. Chem. Phys.,* **201(11),** 1108–1114.

[48] **Kato, M., Kamigaito, M., Sawamoto, M. and Higashimura, T.,** 1995: Polymerization of methyl-methacrylate with the carbon-tetrachloride dichlorotris (triphenylphosphine) ruthenium(ii) methylaluminum bis(2,6-di-tert-butylphenoxide) initiating system - possibility of living radical polymerization, *Macromolecules,* **28(5),** 1721–1723.

[49] **Wakioka, M., Baek, K.Y., Ando, T., Kamigaito, M. and Sawamoto, M.,** 2002: Possibility of living radical polymerization of vinyl acetate catalyzed by iron(I) complex, *Macromolecules,* **35(2),** 330–333.

[50] **Haddleton, D.M., Jasieczek, C.B., Hannon, M.J. and Schooter, A.J.,** 1997: Atom transfer radical polymerization of methyl methacrylate initiated by alkyl bromide and 2-pyridinecarbaldehyde imine copper (I) complexes, *Macromolecules,* **30 (7),** 2190-2193.

[51] **Matyjaszewski, K., Patten, T.E. and Xia, J.,** 1997: Controlled/"living" radical polymerization. Kinetics of the homogeneous atom transfer radical polymerization of styrene, *J. Am. Chem. Soc.,* **119(4),** 674-680.

[52] **Matyjaszewski, K., Davis, K., Patten, T. and Wei, M.,** 1997: Observation and analysis of a slow termination process in the atom transfer radical polymerization of styrene, *Tetrahedron,* **53(45),** 15321-15329.

[53] **Degee, P., Dubois, P. and Jerome, R.,** 1997: Bulk polymerization of lactides initiated by aluminium isopropoxide. 3. Thermal stability and viscoelastic properties, *Macromol. Chem. Phys.,* **198(6),** 1985-1995.

[54] **Albertsson A-C. and Varma I.K.**, 2003: Recent developments in Ring Opening Polymerization of lactones for biomedical applications, *Biomacromolecules*, **4**, 1466-1486.

[55] **Löfgren, A., Albertsson, A.C., Dubois, P. and Jerome, R.,** 1995: Recent advances in ring-opening polymerization of lactones and related-compounds, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.,* **C35(3),** 379-418.

[56] **Mecerreyes, D., Jerome, R. and Dubois, P.,** 1999: Novel macromolecular architectures based on aliphatic polyesters: relevance of the "coordination-insertion" ring-opening polymerization, *Adv. Polym. Sci.,* **147,** 1-59.

[57] **Kricheldorf, H.R. and Kreiser, S.I.,** 1996: Polylactides - synthesis, characterization and medical application, *Macromol. Symp.,* **103,** 85-102.

[58] **Saegusa, T., Kobayashi, S. and Hayashi, K.,** 1978: Polymerization via zwitterion 171 alternating copolymerization of 2-phenylimino-1,3-dioxolane with beta-propiolactone, *Macromolecules,* **11(2),** 360-361.

[59] **Penczek, S.,** 2000: Cationic ring-opening polymerization (crop) major mechanistic phenomena, *J. Polym. Sci. Polym. Chem.,* **38(11),** 1919-1933.

[60] **Kubisa, P. and Penczek, S.,** 1999: Cationic activated monomer polymerization of heterocyclic monomers, *Prog. Polym. Sci.,* **24(10),** 1409-1437.

[61] **Jedlinski, Z., Kurcok, P. and Kowalczuk, M.,** 1985: Polymerization of beta-lactones initiated by potassium solutions, *Macromolecules,* **18(12),** 2679-2683.

[62] **Lecomte, P.H. and Jerome, R.**, 2005. Ring Opening Polymerization, in *Encyclopedia of Polymer Science and Technology*, p. 547-565, Eds. Kroschwitz, J.I., 3rd ed., Wiley, New York.

[63] **Duda, A., Florjanczyk, Z., Hofman, A., Slomkowski, S. and Penczek, S.,** 1990: Living pseudoanionic polymerization of epsilon-caprolactone - poly(epsilon-caprolactone) free of cyclics and with controlled end groups, *Macromolecules,* **23 (6),** 1640-1646.

[64] **Bero, M., Czapla, B., Dobrzynski, P., Janeczek, H. and Kasperczyk.,** 1999: Copolymerization of glycolide and epsilon-caprolactone - 2 - random copolymerization ın the presence of tin octoate, *J. Macromol. Chem. Phys.,* **200 (4),** 911-916.

[65] **Dubois, P., Ropson, N., Jérôme, R. and Teyssie, P.,** 1996: Macromolecular engineering of polylactones and polylactides.19. Kinetics of ring-opening polymerization of epsilon-caprolactone initiated with functional aluminum alkoxides, *Macromolecules,* **29,** 1965-1975.

[66] **Kricheldorf, H.R. and Meier, H.J.,** 1993: Polylactones.22. ABA triblock copolymers of L-lactide and poly(ethylene glycol), *Macromol. Chem.* **194 (2),** 715-725.

[67] **Kowalski, A., Duda, A. and Penczek, S.,** 1998: Kinetics and mechanism of cyclic esters polymerization ınitiated with tin(II) octoate, 1. Polymerization of epsilon-caprolactone, *Macromol. Rapid. Commun.* **19 (11),** 567-572.

[68] **Kowalski, A., Duda, A. and Penczek, S.,** 2000: Kinetics and mechanism of cyclic esters polymerization ınitiated with tin(II) octoate. 3. Polymerization of l,l-dilactide, *Macromolecules,* **33 (20),** 7359-7370.

[69] **Kricheldorf, H.R., Kreiser, S.I. and Stricker, A.,** 2000: Polylactones 48. Sn(Oct)$_2$-ınitiated polymerizations of lactide: a mechanistic study, *Macromolecules,* **33 (3),** 702-709.

[70] **Kricheldorf, H.R., Boettcher, C. and Tönnes, K.U.,** 1992: Polylactones.23. Polymerization of racemic and meso D,L-lactide with various organotin catalysts stereochemical aspects, *Polymer,* **33 (13),** 2817-2824.

[71] **Kowalski, A., Libiszowski, J., Duda, A. and Penczek, P.,** 2000: Polymerization of l,l-dilactide ınitiated by tin(II) butoxide, *Macromolecules*, **33 (6),** 1964-1971.

[72] **Ito, K.,** 1998: Polymeric design by macromonomer technique, *Prog. Polym.Sci.,* **23,** 581-620.

[73] **Ito, K. and Kawaguchi, S.,** 1999: Poly(macromonomers): Homo- and copolymerization, *Adv Polym. Sci., **142,*** 129-178.

[74] **Velichkova, R. S. and Christova, D. C.,** 1995: Amphiphilic Polymers from Macromonomers and Telechelics, *Prog. Polym. Sci.,* **20,** 819-887.

[75] **Yagci, Y. and Toppare, L.**, 2003: Electroactive macromonomers based on pyrrole and thiophene: a versatile route to conducting block and graft polymers., *Polym. Int.*, **52**, 1573-1578.

[76] **Coessens, V., Pintauer, T. and Matyjaszewski, K.,** 2001: Functional polymers by atom transfer radical polymerization, *Prog. Polym. Sci.,* **26,** 337-377.

[77] **Zhang, X. and Matyjaszewski, K.,** 1999: Synthesis of Functional Polystyrenes by Atom Transfer Radical Polymerization Using Protected and Unprotected Carboxylic Acid Initiators, *Macromolecules*, **32,** 7349-7353.

[78] **Percec, V., Kim, H.J. and Barboiu, B.,** 1997: Scope and limitations of functional sulfonyl chlorides as initiators for metal-catalyzed "living" radical polymerization of styrene and methacrylates, *Macromolecules,* **30,** 8526-8528.

[79] **Matyjaszewski, K., Coessens, V., Nakagawa, V., Xia, Y., Qiu, J., Gaynor, S. G. Coca, S. and Jaseczek, C.,** 1998. Functional polymers : modern synthetic methods and novel structures, *Am. Chem. Soc. Symp. Ser.*, **704**, 16-27.

[80] **Zhang, X., Xia, J. and Matyjaszewski, K.,** 2000: End-Functional Poly(tert-butyl acrylate) Star Polymers by Controlled Radical Polymerization. *Macromolecules,* **33(7)**, 2340-2345.

[81] **Moineau, G., Minet, M., Dubois, Ph., Teyssie, Ph., Senninger, T. and Jerome, R.,** 1999: Controlled Radical Polymerization of (Meth)acrylates by ATRP with NiBr$_2$(PPh$_3$)$_2$ as Catalyst, *Macromolecules*, **32(1)**, 27-35.

[82] **Hawker, C. J., Hedrick, J. L., Malmström, E. E., Trollsos, M., Mecerreyes, D., Moineau, G., Dubois, Ph. and Jerome, R.,** 1998: Dual Living Free Radical and Ring Opening Polymerizations from a Double-Headed Initiator, *Macromolecules,* **31**, 213-219.

[83] **Destarac, M., Matyjaszewski, K. and Boutevin, B.,** 2000: Polychloroalkane initiators in copper-catalyzed atom transfer radical polymerization of (meth)acrylates, *Macromol. Chem. Phys.*, **201(2)**, 265-272.

[84] **Destarac, M., Boutevin, B. and Matyjaszewski, K.,** 2000. Polychloroalkanes as ATRP initiators: Fundamentals and application to the synthesis of block copolymers from the combination of conventional radical polymerization and ATRP, in Controlled/Living Radical Polymerization: Progress in ATRP, NMP and Raft, K. Matyjaszewski, ed., (*ACS Symposium Series 768), American Chemical Society*, Washington, D.C., 234-247.

[85] **Haddleton, D. M., Waterson, C., Derrick, P. J., Jasieczek, C. B., Christina, B. and Shooter, A. J.,** 1997: Monohydroxy terminally functionalised poly(methyl methacrylate) from atom transfer radical polymerization, *Chem. Commun.*, **7,** 683-684.

[86] **Keul, H., Neumann, A., Reining, B. and Höcker, H.,** 2000: Synthesis of telechelics and block copolymers via "living" radical polymerization,. *Macromol. Symp*. **161(1)**, 63-72.

[87] **Coessens, V. and Matyjaszewski, K.,** 1999: Dehalogenation of polymers prepared by atom transfer radical polymerization, *Macromol.Rapid Commun*. **20(2)**, 66-70.

[88] **Xu, Y., Pan, C. and Tao, L.,** 2000: Block and star block copolymers by mechanism transformation. II. Synthesis of poly(DOP-b-St) by combination of ATRP and CROP, *J. Polym. Sci., Polym. Chem. Ed.,***38(3),** 436-443.

[89] **Matyjaszewski, K., Jo, S.M., Paik, H.J. and Gaynor, S. G.,** 1997: Synthesis of Well-Defined Polyacrylonitrile by Atom Transfer Radical Polymerization. *Macromolecules,* **30(20)**, 6398-6400.

[90] **Matyjaszewski, K., Wei, M., Xia, J. and McDermott, N.E.,** 1997: Controlled/"Living" Radical Polymerization of Styrene and Methyl Methacrylate Catalyzed by Iron Complexes, *Macromolecules,* **30(26)**, 8161-8164.

[91] **Mecerreyes, D., Athoff, B., Boduch, K. A., Trollsos, M. and Hedrick, J. L.,** 1999: Unimolecular Combination of an Atom Transfer Radical Polymerization Initiator and a Lactone Monomer as a Route to New Graft Copolymers, *Macromolecules,* **32(16)**, 5175-5182.

[92] **Haddleton, D. M., Heming, A. M., Kukulj, D., Duncalf, D. J. and Shooter, A. J.,** 1998: Atom Transfer Polymerization of Methyl Methacrylate. Effect of Acids and Effect with 2-Bromo-2-Methylpropionic Acid Initiation, *Macromolecules,* **31(6)**, 2016-2018.

[93] **Matyjazewski, K., Beers, K.L., Kern, A. and Gaynor, S.G.**, 1998: Hydrogels by Atom Transfer Radical Polymerization. I.Poly (N-Vinylpyrrolidinone-g-Styrene) via the Macromonomer Method, *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 823-830.

[94] **Zeng, F., Shen, Y., Zhu, S. and Pelton, R.**, 2000: Synthesis and Characterization of Comb-Branched Polyelectrolytes. 1. Preparation of Cationic Macromonomer of 2-(Dimethylamino)ethyl Methacrylate by Atom Transfer Radical Polymerization, *Macromolecules,* **33(5)**, 1628-1635.

[95] **Shen, Y., Zhu, S., Zeng, F. and Pelton, R.**, 2000: Synthesis of Methacrylate Macromonomers Using Silica Gel Supported Atom Transfer RadicalPolymerization, *Macromol. Chem. Phys.* **201(13)**, 1387-1394.

[96] **Haddleton, D.M. and Waterson, C.**, 1999: Phenolic ester-based initiators for transition metal mediated living polymerization, *Macromolecules,* **32(26)**, 8732-8739.

[97] **Matyjaszewski, K., Coessens, V., Nakagawa, V., Xia, Y., Qiu, J., Gaynor, S. G. Coca, S. and Jaseczek, C.**, 1998: Functional polymers : modern synthetic methods and novel structures, *Am. Chem. Soc. Symp. Ser.*, **704**, 16-27.

[98] **Zhang, X., Xia, J. and Matyjaszewski, K.**, 2000: End-Functional Poly(tert-butyl acrylate) Star Polymers by Controlled Radical Polymerization. *Macromolecules,* **33(7)**, 2340-2345.

[99] **Yurteri, S., Cianga, I. and Yagci, Y.**, 2003: Synthesis and Characterization of α-ω-Telechelic Polymers by Atom Transfer Radical Polymerization and Coupling Processes, *Macromol. Chem. Phys,* **204**, 1771-1783.

[100] **Malz, H., Komber, H., Voigt, D., Hopfe, I. and Pionteck, J.**, 1999: Synthesis of functional polymers by atom transfer radical polymerization,*Macromol. Chem. Phys.,* **200(3)**, 642-651.

[101] **Mecerreyes, D., Pompose, J.A., Bengoetxea, M. and Grande, H.**, 2000: Novel Pyrrole End-Functional Macromonomers Prepared by Ring-Opening and Atom-Transfer Radical Polymerizations, *Macromolecules,* **33(16)**, 5846-5849.

[102] **Alkan, S., Toppare, L., Hepuzer, Y. and Yagci, Y.**, 1999: Block copolymers of thiophene-capped poly(methyl methacrylate) with pyrrole, *J. Polym.Sci., Part A: Polym. Chem.,* **37(22)**, 4218-4225.

[103] **Erdogan, M., Hizal, G., Tunca, U., Hayrabetyan, D. and Pekcan, O.**, 2002: Molecular weight effect on swelling of polymer gels in homopolymer solutions: a fluorescence study, *Polymer,* **43(6)**, 1925-1931.

[104] **Ohno, K., Fujimoto, K., Tsujii, Y. and Fukuda, T.**, 1999: Synthesis of a Well-Defined Anthracene-Labelled Polystyrene by Atom-TransferRadical Polymerization, *Polymer*, **40(3)**, 759-763.

[105] **Korn, M.R. and Gagne, M. R.**, 2000: Simultaneous atom transfer and nitroxide mediated controlled free radical polymerization of styrene, *Chem. Commun.*, **18**, 1711-1712.

[106] **Erdogan, M., Hepuzer, Y., Cianga, I., Yagci, Y. and Pekcan, O.,** 2003: Diffusion of pyrene end-capped polystyrene prepared via atom transfer radical polymerization into polystyrene gels in the presence of toluene, *J. Phys. Chem.,* **107(40)**, 8363-8370.

[107] **Matyjaszewski, K., Nakagawa, Y. and Gaynor, S. G.,** 1997: Synthesis of well-defined azido and amino end-functionalized polystyrene by atom transfer radical polymerization, *Macromol. Rapid Commun.*, **18**, 1057-1066.

[108] **Coessens, V., Nakagawa, Y. and Matyjaszewski, K.,** 1998: Synthesis of azido end-functionalized polyacrylates via atom transfer radical polymerization, *Polym. Bull.,* **40**, 135-142.

[109] **Li, L., Wang, C., Long, Z. and Fu, S.,** 2000: Synthesis of C60 end-capped polymers from azide functional polystyrene via atom transfer radical polymerization, *J. Polym.Sci., Part A: Polym. Chem.,* **38**, 4519-4523.

[110] **Coessens, V., Pyun, J., Miller, P.J., Gaynor, S. G. and Matyjaszewski, K.,** 2000: Functionalization of polymers prepared by ATRP using radical addition reactions, *Macromol.Rapid Commun.*, **21**, 103-109.

[111] **Koulouri, E.G., Kallitsis, K. and Hadziionannou, G.,** 1999: Terminal Anhydride Functionalized Polystyrene by Atom Transfer Radical Polymerization Used for the Compatibilization of Nylon 6/PS Blends**,** *Macromolecules,* **32,** 6242-6248.

[112] **Ando, T., Kamigaito, M. and Sawamoto, M.,** 1998: Silyl Enol Ethers: End-Capping Agents for Living Radical Polymerization of Methyl Methacrylate with Ruthenium Complex[1]*, Macromolecules,* **31,** 6708-6711.

[113] **Yurteri, S., Cianga, I. and Yagci, Y.,** 2003: Synthesis and characterization of Alpha, omega-telechelic polymers by atom transfer radical polymerization and coupling processes, *Macromol. Chem. Phys.,* 204(14), 1771-1783.

[114] **Durmaz, Y.Y., Cianga, I. and Yagci Y.,** 2006: Studies on the preparation of telechelic polymers by atom transfer radical polymerization and cross coupling processes, *E-Polymers,* no. 050.

[115] **Norman, J., Moratti, S.C., Slark, A.T., Irvine, D.J. and Jacson, A.T.,** 2002: Synthesis of Well-Defined Macromonomers by Sequential ATRP−Catalytic Chain Transfer and Copolymerization with Ethyl Acrylate**,** *Macromolecules,* **35,** 8954-8961.

[116] **Bielawski, C.W., Jethmalani, J.M. and Grubbs, R.H.,** 2003: Synthesis of telechelic polyacrylates with unsaturated end-groups, *Polymer,* **44,** 3721-3726.

[117] **Kamber, N.E., Jeong, W. and Waymouth, R.M.**, 2007: Organocatalytic ring opening polymerization, *Cem. Rev.*, **107**, 5813-5840.

[118] **King, C.,** 1968: *U.S. Patent,* No: 3418393.

[119] **Lenz, R.W., Dror, M. and Jorgensen, R.,** 1978: Polymerization of α,α-disubstituted β-propiolactones and lactams. 9. ABA block copolymers of α-methyl-α-butyl-β-propiolactone and pivalalactone, *Poly. Eng. Sci.,* **18(12),** 937-942.

[120] **Wilson, D.R. and Beaman, R.G.,** 1970: Cyclic amine initiation of polypivalolactone, *J. Polym. Sci., Poly. Chem. Ed.,* **8,** 2161-2170.

[121] **Ito, K., Hashizuka, Y. and Yamashita, Y.,** 1977: Equilibrium Cyclic Oligomer Formation in the Anionic Polymerization of iε-Caprolactone, *Macromolecules,* **10,** 821-824.

[122] **Hamitou, A., Ouhadi, T., Jerome, R. and Teyssie, P.,** 1977: Soluble bimetallic -oxoalkoxides. VII. Characteristics and mechanism of ring-opening polymerization of lactones, *J. Polym. Sci., Polm. Chem. Ed.,* **15,** 865-873.

[123] **Dubois, Ph., Degee, Ph., Jerome, R. and Teyysie, Ph.,** 1992: Macromolecular engineering of polylactones and polylactides. 8. Ring-opening polymerization of iε-caprolactone initiated by primary amines and trialkylaluminum, *Macromolecules,* **25,** 2614-2618.

[124] **Degee, Ph., Dubois, Ph., Jerome, R. and Teyysie, Ph.,** 1992: Macromolecular engineering of polylactones and polylactides. 9. Synthesis, characterization, and application of ι-primary amine poly(ε-caprolactone), *Macromolecules,* **25,** 4242-4248.

[125] **Trollsas, M., Hedrick, J.L., Dubois, Ph. and Jerome, R.,** 1998: Synthesis of acid-functional asymmetric aliphatic polyesters, *J. Polym. Sci., Part A: Polym. Chem.,***36,** 1345-1348.

[126] **Barakat, I., Dubois, Ph., Jerome, R. and Teyysie, Ph.,** 1991: Living polymerization and selective end functionalization of iε-caprolactone using zinc alkoxides as initiators, *Macromolecules,* **24,** 6542-6545.

[127] **Guo, Z., Wan, D. and Huang, Z.,** 2001: Synthesis and Characterization of Poly(-CL)-block-poly(MMA-co-St)-block-poly(-CL) by Combination of Coordination and Controlled Radical Polymerization, *Macromol. Rapid Commun.,* **22,** 367-371.

[128] **Kim, C., Lee, S.C. Kwon, I.C., Chung, H. and Jeong, S.Y.,** 2002: Complexation of Poly(2-ethyl-2-oxazoline)-*block*-poly(ε-caprolactone) Micelles with Multifunctional Carboxylic Acids, *Macromolecules,* **35,** 193-200.

[129] **Choi, Y.K., Bae, Y.H. and Kim, S.W.,** 1998: Star-Shaped Poly(ether−ester) Block Copolymers: Synthesis, Characterization, and Their Physical Properties, *Macromolecules,* **31,** 8766-8774.

[130] **Joziasse, C.A.P., Grablowitz, H. and Pennings, A.J.,** 2000: Star-shaped poly[(trimethylene carbonate)-co-(-capro-lactone)] and its block copolymers with lactide/glycolide: synthesis, characterization and properties, *Macromol.Chem. Phys.,* **201,** 107-112.

[131] **Dubois, P., Barakat, I., Jerome, R. and Teyssie, P.,** 1993: Macromolecular engineering of polyactones and polyactides. 12. Study of the depolymerization reactions of poly(.epsilon.-caprolactone) with functional aluminum alkoxide end groups*, Macromolecules,* **26,** 4407-4412.

[132] **Degirmenci, M., Hizal, G. and Yagci, Y.,** 2002: Synthesis and Characterization of Macrophotoinitiators of Poly(ε-caprolactone) and Their Use in Block Copolymerization*, Macromolecules,* **35,** 8265-8270.

[133] **Trollsas, M., Hawker, C.J., Hedrick, J.L., Garrot, G. and Hillborn, J.,** 1998: A Mild and Versatile Synthesis for the Preparation of Thiol-Functionalized Polymers*, Macromolecules,* **31,** 5960-5963.

[134] **Hoffman, V.R.**, 2004. *Organic Chemistry: an intermediate text*, 2nd Ed., John Wiley & Sons, Inc., Hoboken, New Jersey, USA.

[135] **Corbet, J-P. and Mignani, G.**, 2006: Selected Patented Cross-Coupling Reactions, *Chem. Rev.*, **106**, 2651-2710.

[136] **Sammelson, R.E. and Kurth, M.J.**, 2001: Carbon-carbon bond-forming solid-phase reactions. Part II., *Chem. Rev.*, **101**, 137-202.

[137] **Yin, L. and Liebscher, J**., 2007: Carbon-carbon coupling reactions catalyzed by heterogeneous palladium catalysts, *Chem. Rev.*, **107**, 133-173.

[138] **Roglans, A., Pla-Quintana, A. and Moreno-Manas, M.**, 2006: Diazonium salts as substrates in palladium-catalyzed cross-coupling reactions, *Chem. Rev.*, **106**, 4622-4643.

[139] **Suzuki, A.**, 1994: New synthetic transformations via organoboron compounds, *Pure Appl. Chem.*, **66(2)**, 213-222.

[140] **Miyaura, N. and Suzuki, A.**, 1995: Palladium-catalyzed cross-coupling reactions of Organoboron compounds, *Chem. Rev.*, **95**, 2457-2483.

[141] **Schlüter, A.D.**, 2001: The tenth anniversary of Suzuki polycondensation, *J. Polym. Sci.:Part A: Polym. Chem.*, **39**, 1533-1556.

[142] **Hall, D.G.**, 2005. *Boronic Acids: Preparation and applications in organic synthesis and medicine*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

[143] **Suzuki, A**., 1999: Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles: 1995-1998, *J. Organomet. Chem.*, **576**, 147-168.

[144] **Miyaura, N., Yamada, K., Suginome, H. and Suzuki, A.**, 1985: Novel and convenient method for the stereo- and regiospecific synthesis of conjugated alkadienes and alkenynes via the palladium-catalyzed cross-coupling reaction of 1-alkenylboranes with bromoalkenes and bromoalkynes, *J. Am. Chem. Soc.*, **107**, 972-980.

[145] **Beletskaya, I.P. and Cheprakov, A.V.**, 2000: The Heck reaction as a sharpening stone of palladium catalysis, *Chem. Rev.*, **100**, 3009-3066.

[146] **Kraft, A., Grimsdale, A.C. and Holmes, A.B.,** 2000: Electroluminescent Conjugated Polymers - Seeing Polymers in a New Light, Angew. Chem. Intl. Ed., **37,** 403-428.

[147] **Fink, J.K**., 2008. *High Performance Polymers*, William Andrew, Norwich, NY. USA.

[148] **Müllen, K. and Scherf, U**., 2006. *Organic Light Emitting Devices: Synthesis, Properties and Applications*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

[149] **Braun, D. and Heeger, A.J.,** 1991: Visible Light Emission From Semiconducting Polymer Diodes.*, Appl. Phys. Lett.,* **58,** 1982-1984.

[150] **Doi, S., Kuwabara, M., Noguchi, T. and Ohnishi, T.,** 1993: Organic electroluminescent devices having poly(dialkoxy-p-phenylene vinylenes) as a light emitting material, *Synth. Met.,* **57,** 4174-4179.

[151] **Pfeiffer, S. and Hörhold, H.H.,** 1999: Investigation of poly(arylene vinylene)s, 41. Synthesis of soluble dialkoxy-substituted poly(phenylene alkenylidene)s by applying the Horner-reaction for condensation polymerization, *Macromol. Chem. Phys.,* **200,** 1870-1878.

[152] **Karakaya, B., Claussen, W., Gessler, K., Saenger, W. and Schlüter, A.D.**, 1997: Toward Dendrimers with Cylindrical Shape in Solution, *J. Am. Chem. Soc.*, **119**, 3296-3301.

[153] **Kreyenschmidt, M., Uckert, F. and Müllen, K.**, 1995: A New Soluble Poly(pphenyl ene) with Tetrahydropyrene Repeating Units, *Macromolecules*, **28**, 4577-4582.

[154] **Halkyard, C.E., Rampey, M.E., Kloppenburg, L., Studer-Martinez, S.L. and Bunz, U.H.F.,** 1998: Evidence of Aggregate Formation for 2,5-Dialkylpoly(*p*-phenyleneethynylenes) in Solution and Thin Films*, Macromolecules,* **31,** 8655-8659.

[155] **Bunz, U.H.F.,** 2000: Poly(aryleneethynylene)s: Syntheses, properties, structures, and applications, *Chem. Rev.,* **100,** 1605-1644.

[156] **Weder, C. and Wrighton, M.S.,** 1996: Efficient Solid-State Photoluminescence in New Poly(2,5-dialkoxy-*p*-phenylene ethynylene)s*, Macromolecules,* **29,** 5157-5165.

[157] **Moroni, M., Le Moigne, M., Pham, T.A. and Bigot, J.Y.,** 1997: Rigid Rod Conjugated Polymers for Nonlinear Optics. 3. Intramolecular H Bond Effects on Poly(phenylene ethynylene) Chains*, Macromolecules,* **30,** 1964-1972.

[158] **Arnautov, S.A., Nechvolodova, E.M., Bakulin, A.A., Elizarov, S.G., Khodarev, A.N., Martyanov, D.S. and Paraschuk, D.Y.,** 2004: Properties of MEH-PPV films prepared by slow solvent evaporation, *Synth. Met.,* **147,** 287-291.

[159] **Nguyen, T.-Q., Yee, R.Y. and Schwartz, B.J.,** 2001: Solution processing of conjugated polymers: The effects of polymer solubility on the morphology and electronic properties of semiconducting polymer films, *J. Photochem. Photobiol.,***A, 144(1),** 21-30.

[160] **Tang, R., Tan, Z., Cheng, C., Li, Y. and Xi. F.,** 2005: Synthesis, electroluminescence, and photovoltaic properties of dendronized poly (*p*-phenylene vinylene) derivatives, *Polymer,* **46(14),** 5341-5350.

[161] **Wantz, G., Hirsch, L., Huby, N., Vignau, L., Silvain, J.F., Barriere, A.S. and Parneix, J.P.,** 2005: Correlation between the indium tin oxide mophology and performances of polymer light-emitting diodes, *Thin solid Films,* **485(1-2),** 247-251.

[162] **Tang, R., Xu, X., Cheng, C., Yu, G., Liu, Y. and Xi. F.,** 2005: Synthesis and luminescence properties of novel phenyl-substituted poly (*p*-phenylene vinylene) derivatives, *Synth. Met.,* **150(1),** 63-71.

[163] **Chen, L.X., Jager, W.J.H., Gosztola, D.J., Niemczyk, M.P. and Wasielewski, M.R.,** 2001: Effect of chemical modifications on photophysics and exciton dynamics of [pi]-conjugation attenuated and metal-chelated photoconducting polymers, *Synth. Met.,* **116(1-3),** 229-234.

[164] **Yang, C.Y., Heeger, A.J. and Cao, Y.,** 2000: Microstructure of gel-processed blends of conjugated polymer and ultrahigh moleculer weight polyethylene, *Polymer,* **41 (11),** 4113-4118.

[165] **Dridi, C., Blel, N., Chaieb, A., Majdoub, M., Roudesli, M.S., Davenas, J., Ouada, H.B. and Maaref, H.,** 2001: The effect of synthesis procedure of on physical properties of poly (*p*-phenylene vinylene) derivatives, *Eur. Polym. J.,* **37(4),** 683-690.

[166] **Samal, G.S., Biswas, A.K., Singh, S. and Mohapatra, Y.N.,** 2005: Electroabsorption spectroscopic study of cyano-substituted phenylene vinylene polymer (CN-PPV), *Synth. Met.,* **155(2),** 303-305.

[167] **Courric, S. and Tran, W.H.,** 1998: the electromagnetic properties of poly (*p*-phenylene vinylene) derivatives, *Polymer,* **39 (12),** 2399-2408.

[168] **Hwang, D.-H., Kim, S.T., Shim, H.-K., Holmes, A.B., Moratti, S.C. and Friend, R.H.,** 1997: Highly efficient green light-emitting diodeswith aluminium cathode, *Synth. Met.,* **84(1-3),** 615-618.

[169] **Huang, H.-C., Huang, G.L., Chen, H.L. and Lee, Y.-D.,** 2006: Immobilization of TiO_2 nanoparticles on carbonnanocapsules for photovoltaic applications, *Thin solid Films,* **511-512,** 203-207.

[170] **Yang, S.-H., Chen, J.-T., Li, A.-K., Huang, H.-C., Chen, K.B., Hsieh, B.-R. and Hsu, C.-S.,** 2005: New soluble poly(2,3-diphenylphenylene vinylene) derivatives for light-emitting diodes, *Thin solid Films,* **477(1-2),** 73-80.

[171] **Cheng, M., Xiao, Y., Yu, W.L., Chen, Z.K., Lai, Y.H. and Huang, W.,** 2000: Synthesis and characterization of a cyano-substituted electroluminescent polymer with well defined conjugation lenght, *Thin solid Films,* **363(1-2),** 110-113.

[172] **Talaie, A., Lee, Y.K., Huh, G., Kim, K.M., Jeong, H.Y., Choo, D.J., Lee, J.Y. and Jang, J.,** 2001: Improvement of photoluminescence properties of MEH-PPV by means of copolymerization, *Mater. Sci. Eng.,* **B, 85(2-3),** 199-202.

[173] **Brabec, C.J., Sariciftci, N.S. and Hummelen, J.C.,** 2001: Plastic solar cells, *Adv. Funct. Mater.* **11(1),** 15-26.

[174] **Wu, Z.K., Wu, S.X., Liao, J.H., Fu, D.G. and Liang, Y.Q.,** 2002: Two-dimensionel ordered array of poly(2-methoxy,5-(*n*-hexadecyloxy)-*p*-phenylene vinylene) in monolayer by langmuir-blodgett technique, *Synth. Met.,* **130(1),** 35-38.

[175] **Ramachandran, G., Smith, T.A., Gomez, D. and Ghiggino, K.P.,** 2005: Fluorescence studies on the conjugated polyelectrolyte DPS-PPV [poly (2,5-di-propoxy sulphonato *p*-phenylene) vinylene] in aqueous solution, *Synth. Met.,* **152(1-3),** 17-20.

[176] **Wang, Z., Chen, X., Yang, S. and Xu, X.,** 2000: Electronic states in conjugated polymers probed by excimers, *Displays,* **21(2-3),** 73-77.

[177] **Breselge, M., Van Severen, I., Lutsen, L., Adriaensens, P., Manca, J., Vanderzande, D. and Cleij, T.,** 2006: Comparison of the electrical characteristics of four 2,5-subtituted poly (*p*-phenylene vinylene) derivatives with different side chains, *Thin solid Films,* **511-512,** 328-332.

[178] **Wilking, J.N., Hsieh, B. and Arbuckle-Keil, G.A.,** 2005: Chlorine precursor route to poly(2-phenoxy *p*-phenylene vinylene) Synthesis and characterization, *Synth. Met.,* **149(1),** 63-72.

[179] **Huo,L., Hou, J., He, C., Han, M. and Li, Y.,** 2006: Synthesis and characterization and photovoltaic properties of poly[1', 4'-bis-(thienyl-vinyl)]-2-methoxy-5-(2'-ethylhexyloxy)-2,4-phenyl-vinylene, *Synth. Met.,* **156(2-4),** 276-281.

[180] **Gedelian, C.A., Ten Eyck, G.A. and Lu, T.M.,** 2007: Onset of thermal degradation in poly (*p*-phenylene vinylene) films deposited by chemical vapor deposition, *Synth. Met.,* **157(1),** 48-52.

[181] **Qu, G. Jiang, F., Zhang, S. and Usuda, S.,** 2007: A novel poly (*p*-phenylene vinylene)-b-poly(methyl methacrylate) rod-coil diblock copolymer, *Mater. Lett.,* **61(16),** 3421-3424.

[182] **Ohnishi, T., Murase, I., Noguchi, T. and Hirooka, M.,** 1986: Highly conductive graphite film prepared from pyrolysis of poly (*p*-phenylene vinylene), *Synth. Met.,* **14(3),** 207-213.

[183] **Ohnishi, T., Murase, I., Noguchi, T. and Hirooka, M.,** 1987: Preparation of graphite film by pyrolysis of polymers, *Synth. Met.,* **18(1-3),** 497-502.

[184] **Jin, J.-I., Kim, J.-H., Lee, Y.-H., Lee, G.-H. and Park, Y.W.,** 1993: Carbonization of poly(1,4-phenylene ethynylene), *Synth. Met.,* **57(1),** 3742-3747.

[185] **Nguyen, T.P.,** 2006: Defect analysis in organic semiconductors, *Mater. Sci. Semicond. Process.,* **9(1-3),** 198-203.

[186] **Stalinga, P., Gomes, H.L., Rost, H., Holmes, A.B., Harrison, M.G. and Friend R.H.,** 2001: Minority effects in poly (phenylene vinylene) as studied by electrical characterization, *J. Appl. Phys.,* **89(3),** 1713-1724.

[187] **Kim, T.-H., Park,J.H., Park, O.O., Yu, J.-W., Kim, J.K. and Kim, Y.C.,** 2006: Effect of hole transporting layer doped with organic salts on performance of polymer electroluminescent devices, *Curr. Appl. Phys.,* **6(4),** 616-619.

[188] **Zeng, Q.G., Ding, Z.C., Tang, X.D. and Zhang, Z.M.,** 2005: Pressure effect on photoluminescence and Raman spectra of PPV, *J. Lumin.,* **115(1-2),** 32-38.

[189] **Gourley, K.D., Lillya, C.P., Reynolds, J.R. and Chien, J.C.W.,** 1984: Electrically conducting polymers: arsenic pentaflluoride-doped poly (*p*-phenylene vinylene) and its analogs, *Macromolecules,* **17(5),** 1025-1033.

[190] **Fernandes, M.R., Garcia, J.R., Schultz, M.S. and Nart, F.C.,** 2005: polaron and bipolaron transitions in doped poly (*p*-phenylene vinylene) films, *Thin solid Films,* **474(1-2),** 279-284.

[191] **Tanigaki, N., Mochizuki, H., Mo, X., Mizokuro, T., Hiraga, T., Taima, T. and Yase, K.,** 2006: Moleculer doping of poly (*p*-phenylene vinylene) under vacuum for photovoltaic application, *Thin Solid Films,* **499(1-2),** 110-113.

[192] **Gustafsson, G., Cao, Y., Tracey, G.M., Klavetter, F., Colaneri, N. and Heeger, A.J.,** 1992: Flexible light-emitting diodes made from soluble conducting polymers, *Nature,* **357(6378),** 477-479.

[193] **Cao, Y.,** 2001: Electrically active polymer compositions and their use in efficient, low operating voltage, polymer light-emitting diodes with air-stable cathodes, *US Patent, No:* 6284435, assigned to Uniax Corp.

[194] **Dreuth, H. and Heiden, C.A.,** 1998: Method for local application of thin micropatterned structures, *Mater. Sci. Engng.,* **C5,** 227-231.

[195] **Adachi, C., Kwong, R. and Forest, S.R.,** 2001: Efficient electrophosphorescence using a doped ambipolar conductive molecular organic thin films, *Org. Electron,* **2,** 37-43.

[196] **Guo, T.F., Chang, S.C., Yang, Y., Kwong, R.C., Thompson M.E.,** 2001: Highly efficient electrophosphorescencent polymer light-emitting devices, *Org. Electron,* **1,** 15-20.

[197] **Lee, C.L., Lee, K.B., Kim, J.J.,** 2001: Highly efficient polymer phosphorescencent light-emitting devices, *Mater. Sci. Engng.,* **B5,** 228-231.

[198] **Bradley, D.D.C. and Friend, R.H.,** 1989: Light-induced luminescence quenching in precursor-route poly (*p*-phenylene vinylene), *J. Phys. Condens. Matter.,* **1(23),** 3671-3678.

[199] **Ziemelis, K.E., Hussain, A.T., Bradley, D.D.C., Friend, R.H., Ruhe, J. and Wegner, G.,** 1991: Optical spectroscopy of field-induced charge in poly(3-hexyl thienylene) metal-insulator-semiconducter structures: evidence of polarons, *Phys. Rev. Lett.,* **66(17),** 2231-2234.

[200] **Wang, C., Jung, G.Y., Hua, Y., Pearson, C., Bryce, M.R., Petty, M.C., Batsanov, A.S., Goeta, A.E. and Howard, J.A.K.**, 2001: An efficient pyridine and oxadizole-containing hole-blocking material for organic light-emitting diodes: synthesis, crystal structure, and device performance, *Chem. Mater.*, **13**, 1167-1173.

[201] **Tamada, M., Koshikawa, H., Suwa, T., Yoshida, T., Usui, T. and Sato, H.**,: 2000, Thermal stability and EL efficiency of polymer thin film prepared from TPD-acrylate, *Polymer*, **41(15)**, 5661-5667.

[202] **Xiao, S.S., Qiu, C. and Qiu, C.X.,** 2006: Organic semiconductor devices and methods of fabrication including forming two parts with polymerisable groups and bonding the parts, *US Patent,* No: 7063994, assigned to Organic vision Inc.

[203] **Gettinger, C.L., Heeger, A.J., Drake, J.M. and Pine, D.J.,** 1994: A photoluminescence study of poly (*p*-phenylene vinylene) derivatives: the effect of intrinsic persistence length, *J. Chem. Phys.,* **101,** 1673-1678.

[204] **Hsieh, B.R., Yu, Y., Forsythe, E.W., Schaaf, G.M. and Felt, W.A.,** 1998: A new family of higly emissive soluble poly (*p*-phenylene vinylene) derivatives: a step toward fully conjugated blue-emitting poly (*p*-phenylene vinylenes), *J. Am. Chem. Soc.,* **120,** 231-232.

[205] **Vaidyanathan, S., Dong, H. and Galvin, M.E.,** 2004: The role of side chains in luminescence of an electroactive polymer, *Synth. Met.,* **142(1-3),** 1-6.

[206] **Dinakaran, K., Hsiao, S.-M., Chou, C.-H., Shu, S.-L. and Wei, K.-H.,** 2005: Synthesis and characterization of an efficiency fluorescent poly (*p*-phenylene vinylene) possessing pendant dendritic phenyl groups, *Macromolecules,* **38,** 10429-10435.

[207] **Wantz, G., Dautel, O., Vignau, L., Serein-Spirau, F., Lere-Porte, J.P., Hirsch, L., Moreau, J.J.E. and Parneix, J.P.,** 2006: polymer light-emitting diodes with a phenyleneethynylene derivative as novel hole blocking layer for efficiency enhancement, *Synth. Met.,* **156(9-10),** 690-694.

[208] **Shin, D,-C., Kim, Y.-H., You, H., Jin, J.G. and Kwon, S.K.,** 2004: Intramoleculer energy transferable (2,2-diphenylvinyl)phenyl substituted fluorescent poly (*p*-phenylene vinylene) derivative with efficient photoluminescence and electroluminescence, *J. Polym. Sci.,Part A: Polym. Chem.,* **42,** 5636-5646.

[209] **Jin, Y., Jee, J., Kim, K., Kim, J., Song, S., Park, H., Lee, K. and Suh, H.,** 2007: Synthesis and electroluminescent properties of copolymers based on PPV with fluoro groups in vinylene units, *Polymer,* **48(6),** 1541-1549.

[210] **Lee, R.-H., Lin, K.-T. and Huang, C.-Y.,** 2006: High red, green, and blue color purity electroluminescence from MEH-PPV and Polyalkylfluorenes-based bright white polymer light emitting displays, *J. Polym. Sci., Part B: Polym. Phys.* ,**45,** 330-341.

[211] **Huang, J., Li, G., Wu, E., Xu, Q. and Yang, Y.,** 2006: Achieving high-efficiency polymer white-light-emitting devices, *Adv. Matter.,* **18,** 114-117.

[212] **Salafsky, J.,** 2005: Solid-state device, *US Patent,* No: 7115434, assigned to The Trustees of Colombia University in the city of New York.

[213] **Andriessen, H.,** 2005: Layer configuration comprising an electron-blocking element, *US Patent,* No: 6977390, assigned to Agfa Gevaert (Mortsel, BE.)

[214] **Shaheen, S., Brabec, C., Fromherz, T., Padinger, F., Sariciftci, S. and Gloetzl.,** 2005: Photovoltaic cell, *US Patent,* No: 6993436, assigned to Konarka Austria Forschungs und Entwicklungs GmbH (AU).

[215] **Bertho, S.,Haeldermans, Swinnen, A., Moons, W., Martens, T., Lutsen, L., Vanderzande, D., Manca, J., Senes, A. and Bonfiglio, A.,** 2007: Influence of thermal ageing on the stability of polymer bulk heterojunction solar cells, *Sol. Energ. Matter. Sol. Cell,* **91(5),** 385-389.

[216] **Huang,S.-P., Liao, J.-L., Tseng, H.-E., Jen, T.-H., Liou, J.-Y. and Chen, S.-A.,** 2006: Enhanced photovoltaic cells efficiency via incorporation of high electron-deficient oxadiazole moieties on side chains of poly (*p*-phenylene vinylene)s and poly(fluorine)s, *Synth. Met.,* **156(14-15),** 949-953.

[217] **Egbe, D.A.M., Nguyen, L.H., Carbonnier, B., Muhlbacher, D. and Sariciftci, N.S.,** 2005: Thiophene-containing poly(arylene-ethynylene)-*alt*-Poly(arylene-vinylene)s: Synthesis, characterization and optical properties, *Polymer,* **46(23),** 9585-9595.

[218] **Burroughes, J.H.,** 2006: Optoelectronic devices, *US Patent,* No: 7091516 assigned to Cambridge display Technology Limited (Cambridg, UK)

[219] **Dennler, G., Lungenschmied, C., Neugebauer, H., Sariciftci, N.S.,Latreche, M., Czeremuszkin, G. and Wertheimer, M.R.,** 2006: A new encapsulation solution for flexible organic solar cells, *Thin Solid Films,* **511-512,** 349-353.

[220] **Zhang, W., Huang, Z., Yan, E., Wang, C., Xin, Y., Zhao, Q. and Tong, Y.,** 2007: Preparation of poly (*p*-phenylene vinylene) nanofibers by electrospinning, *Mater. Sci. Eng.,* **A, 443(1-2),** 292-295.

[221] **Zhang, W., Yan, E., Huang, Z., Wang, C., Xin, Y., Zhao, Q. and Tong, Y.,** 2007: Preparation and study of PPV/PVA nanofibers via electrospinning PPV precursor alcohol solution, *Eur. Polym. J.,* **43(3),** 802-807.

[222] **Zhao, Q., Huang, Z., Wang, C., Zhao, Q., Sun, H. and Wang, D.**, 2007: Preparation of PVP/MEH-PPV composite polymer fibers by electrospinning and study of their electrochromic character, *Mater. Lett.*, **61(11-12)**, 2159-2163.

[223] **Joo, S.-H., Lee, C.-Y., Kim, K., Lee, K.-R. and Jin, J.-I.,** 2006: Chemical vapor decomposition polymerization of poly(arylenevinylene)s and applications to nanoscience, *Bull. Korean Chem. Soc.,***27,** 169-184.

[224] **Kim, K., Lee, S.-H., Yi, W., Kim, J., Choi, J.W., Park, Y. and Jin, J.-I.,** 2003: Efficient field emission from highly aligned, graphitic nanotubes embedded with gold nanoparticles, *Adv. Mater.,* **15,** 1618-1622.

[225] **Pistor, P., Chu, V., Prazeres, D.M.F. and Conde, J.P.,** 2007: pH sensitive photoconductor based on poly(*p*-phenylene vinylene), *Sens. Actuators,* **B, 123(1),** 153-157.

[226] **Babudri, F., Farinola, G.M., Giancane, S., Naso, F., Rella, R., Scarpa, A. and Valli, L.,** 2002: deposition and application in gas sensors of thin films of a bridged chain dialkoxy PPV derivative, *Mater. Sci. Eng.,* **C, 22(2),** 445-448.

[227] **Peres, L.O. and Gruber, J.,** 2007: The use of block copolymers containing PPV in gas sensors for electronic noses, *Mater. Sci. Eng.,* **C, 27(1),** 67-69.

[228] **Wessling, R.A.,** 1985: The polymerization of xylylene bisdialkyl sulfonium salts, *J.Polym. Sci. Polym. Symp.,* **72,** 55-66.

[229] **Denton, F.R., Lahti, P.M. and Karaz, F.E.,** 1992: The effect of radical trapping reagents upon formation of poly(-tetrahydrothiophenio para-xylylene) polyelectrolytes by the wessling soluble precursor method, *J.Polym. Sci.Part A: Polym. Chem.,* **30,** 2223-2231.

[230] **Padmanaban, G. and Ramakrishnan, S.,** 2000: Conjugation Length Control in Soluble Poly[2-methoxy-5-((2‘-ethylhexyl)oxy)-1,4-phenylenevinylene] (MEHPPV): Synthesis, Optical Properties, and Energy Transfer, *J. Am. Chem. Soc.,* **122,** 2244-2251.

[231] **Louwet, F., Vanderzande, D., Gelan, J. and Mullens, J.,** 1995: A New Synthetic Route to a Soluble High Molecular Weight Precursor for Poly(p phenylenevinylene) derivatives, *Macromolecules,* **28,** 1330-1331.

[232] **De Kok, M.M., van Breeman, J.J.M., Corlear, R.A.A., Adriaensens, P.J., Gelan, J.M. and Vanderzande, D.,** 1999: The elimination process of sulfinyl-precursor polymers towards poly(*p*-phenylene vinylene). Methods for monitoring elimination, *Acta Polym.,* **50,** 28-34.

[233] **Lutsen, L., Adriaensens, P.J., Becker, H., van Breeman, A.J., Vanderzande, D. and Gelan, J.,** 1999: New Synthesis of a Soluble High Molecular Weight Poly(arylene vinylene): Poly[2-methoxy-5-(3,7-dimethyloctyloxy)-p-phenylene vinylene]. Polymerization and Device Properties, *Macromolecules,* **32,** 6517-6525.

[234] **Issaris, A., Vanderzande, D. and Gelan, J.,** 1997: Polymerization of a p-quinodimethane derivative to a precursor of poly(*p*-phenylene vinylene)—indications for a free radical mechanism, *Polymer,* **38,** 2571-2574.

[235] **Van Breeman, A.J.J.M., Vanderzande, D.J.M, Adriaensens, P.J., and Gelan, J.M.J.V.,** 1999: Highly Selective Route for Producing Unsymmetrically Substituted Monomers toward Synthesis of Conjugated Polymers Derived from Poly(*p*-phenylene vinylene), *J. Org. Chem.,* **64,** 3106-3112.

[236] **Van Der Borgth, M., Vanderzande, D., Adriaensens, P.J. and Gelan, J.,** 2000: Scope and Limitations of a New Highly Selective Synthesis of Unsymmetrical Monomers for the Synthesis of Precursors toward Poly(arylenevinylene)s, *J. Org. Chem.,* **65,** 284-289.

[237] **Lutsen, L., van Breeman, A.J., Kreuder, W., Vanderzande, D. and Gelan, J.M.J.V,** 2000: Highly Selective Route to Unsymmetrically Substituted 1-{2-[(Butylsulfanyl)methyl]-5-(chloromethyl)-4-methoxyphenoxy}-3,7-dimethyloctane and Isomers toward Synthesis of Conjugated Polymer OC1C10 Used in LEDs: Synthesis and Optimization, *Helv. Chim. Acta.,* **83,** 3113-3121.

[238] **Van Severen, I., Motmans, F., Lutsen, L., Cleij, T.J. and Vanderzande, D.**, 2005: Poly(*p*-phenylene vinylene derivatives with ester and carboxy-functionalized substituents: a versatile platform towards polar functionalized conjugated polymers, *Polymer*, **46(15)**, 5446-5475.

[239] **Gilch, H.G. and Wheelwright, W.L.,** 1996: Polymerization of -halogenated *p*-xylenes with base, *J. Polym. Sci.:A-1,* **4,** 1337-1349.

[240] **Hsieh, B.R., Yu, Y., Van Laeken, A.C. and Lee, H.,** 1997: Figure 1 of 2. General Methodology toward Soluble Poly(*p*-phenylenevinylene) Derivatives, *Macromolecules,* **30,** 8094-8095.

[241] **Neef, C.J. and Ferraris, J.P.,** 2000: MEH-PPV: Improved Synthetic Procedure and Molecular Weight Control, *Macromolecules,* **33,** 2311-2314.

[242] **Hontis, L., Vrindts, V., Lutsen, L., Vanderzande, D., and Gelan, J.,** 2001: The Gilch polymerisation towards OC1C10-PPV: indications for a radical mechanism, *Polymer,* **42,** 5793-5799.

[243] **Hontis, L., Lutsen, L., Vanderzande, D., and Gelan, J.,** 2001: Mechanistic study on the Gilch and the Sulfinyl polymerisation routes, *Synth. Met.,* **119,** 135-136.

[244] **Wiesecke, J. and Rehahn, M.,** 2007: The effect of persistent TEMPO radicals on the Gilch polymerization, *Macromol. Rapid Commun.,* **28,** 78-83.

[245] **Raabe, D. and Hörhold, H.-H.,** 1992: Investigation of poly(arylene vinylenes), 39. Synthesis of functionalized poly(1,4-phenylene-1,2-diphenylvinylenes) by dehydrochlorination of unsymmetric p-xylene dichlorides, *Acta Polymer,* **43,** 275-278.

[246] **Weitzel, H.-P., Bohnen, A. and Müllen, K.,** 1990: Polyarylenes and poly(arylenevinylene)s, 3. Oligomeric model compounds for poly(9,10-anthrylenevinylene), *Makromol. Chem.,* **191,** 2815-2835.

[247] **Garay, R.O., Sarimalis, M.N., Maontni, R.S. and Hernandez, S.A.,** 2000: Synthesis of conjugated polymers. Polymerizability studies of bis-sulfonium salts , *Des. Monomers* Polym., **3,** 231-244.

[248] **Capistran, J.D., Gagnon, D.R., Antoun, S., Lenz, R.W. and Karasz, F.E.,** 1984: Synthesis and electrical conductivity of high molecular weight poly(arylene vinylenes), *Polym. Prepr.,* **25(2),** 282-283.

[249] **Becker, H., Spreitzer, H., Ibrom, K. and Kreuder, W.,** 1999: New Insights into the Microstructure of Gilch-Polymerized PPVs, *Macromolecules,* **32,** 4925-4932.

[250] **Becker, H., Gelsen, O., Kluge, E., Kreuder, W., Schenk, H. and Spreitzer, H.,** 2000: Development of high performance PPVs: implications of the polymer-microstructure, *Synth. Met.,* **111-112,** 145-149.

[251] **Becker, H., Spreitzer, H., Kreuder, W., Kluge, E., Westweber, H., Schenk, H. and Treacher, K.,** 2001: Advances in polymers for PLEDs: from a polymerization mechanism to industrial manufacturing, *Synth. Met.,* **122,** 105-110.

[252] **McDonald, R.N. and Campbell, T.W.,** 1960: Synthesis of hydrocarbon derivatives by Wittig reaction, III. Wittig reaction as a polymerization method, *J. Am. Chem. Soc.,* **82,** 4669-4671.

[253] **Brandon, K.L., Bentley, P.G., Bradley, D.D.C. and Dunmer, D.A.,** 1997: Electroluminescent properties of a family of dialkoxy PPV derivatives, *Synth. Met.,* **91,** 305-306.

[254] **Drury, A., Maier, S., Davey, A.P., Dalton, A.B., Coleman, J.N., Byrne, H.J. and Blau, W.J.,** 2001: Systematic trends in the synthesis of (meta-phenylene vinylene) copolymers, *Synth. Met.,* **119,** 151-152.

[255] **Dalton, A.B., Coleman, J.N., in het Panhuis, M., McCarthy, B., Drury, A., Blau, W.J., Nunzi, J.M. and Byrne, H.J.,** 2001: Controlling the optical properties of a conjugated co-polymer through variation of backbone isomerism and introduction of carbon nanotubes, *J.Photochem. Photobiol.A: Chem,* **144,** 31-41.

[256] **Pfeiffer, S. and Hörhold, H.-H.,** 1999: Investigation of poly(arylene vinylene)s, 41. Synthesis of soluble dialkoxy-substituted poly(phenylene alkenylidene)s by applying the Horner-reaction for condensation polymerization, *Macromol. Chem. Phys.,* **200,** 1870-1878.

[257] **Staring**, **E.G.J., Demandt, R.C.J.E., Braun, D., Rikken, G.L.J., Kessener, Y.A.R.R., Venhuizen, A.H.J., van Knippenberg, M.M.F. and Bouwmans, M.,** 1995: Electroluminescence and photoluminescence efficiency of poly(*p*-phenylene vinylene) derivatives, *Synth. Met.,* **71(1-3),** 2179-2180.

[258] **Greenham, N.C., Moratti, S.C., Bradley, D.D.C., Friend, R.H. and Holmes, A.B.,** 1993: Efficient light-emitting diodes based on polymers with high electron affinities, *Nature,* **365,** 628-630.

[259] **Kannoo, S., Saruhashi, T., Ishibe, S., Nakagawa, K. and Tomita, I.**, 2006: Synthesis of poly(*p*-phenylene vinylene derivative having amphiphilic substituents by palladium-catalyzed three-component coupling polymerization of *p*-bromophenylallene and nucleophile containig oligooxyethylene units, *Polym. Bull.*, **57(6)**, 843-848.

[260] **Liu, Y., Lahti, P. and La, F.,** 1998: Synthesis of a regiospecific, soluble poly(2-alkoxy-1,4-phenylenevinylene), *Polymer,* **39,** 5241-5244.

[261] **Xu, B., Zhang, J., Pan, Y. and Peng, Z.,** 1999: Syntheses and optical properties of poly(*o*-phenylene vinylene)s, *Synth. Met.,* **107,** 47-51.

[262] **Peng, Z. and Galvin, M.E.,** 1998: Polymers with High Electron Affinities for Light-Emitting Diodes, *Chem. Mater.,* **10,** 1785-1788.

[263] **Li, X., Zhang, Y., Yang, R., Huang, J., Yang, W. and Cao, Y.**, 2005: Novel saturated red-emitting poly(*p*-phenylene vinylene copolymers with narrow-band-gap units of 2,1,3-benzothiadiazole synthesized by a palladium-catalyzed Stille coupling reaction, *J. Polym. Sci.: Part A: Polym. Chem.*, **43**, 2325-2336.

[264] **Babudri, F., Cicco, S.R., Chiavarone, L., Farinola, G.M., Lopez, L.C., Naso, F. and Scamarcio, G.**, 2000: Synthesis and optical investigations of low molecular weight alkoxysubstituted poly(*p*-phenylenevinylene)s , *J. Mater. Chem.*, **10**, 1573-1579.

[265] **Babudri, F., Cicco, S.R., Farinola, G.M., Lopez, L.C., Naso, F., Bolognesi, A. and Porzio, W.**, 1996: Synthesis, characterization and properties of a soluble polymer with a poly(phenylenevinyl1ene) structure, *Macromol. Rapid. Commun.*, **17**, 905-911.

[266] **Thorn-Cśanyi, E. and Kraxner, P.,** 1997: All-trans oligomers of 2,5-dialkyl-1,4-phenylenevinylenes-metathesis preparation and characterization, *Macromol. Chem. Phys.,* **198,** 3827-3843.

[267] **Reetz, R., Norwark, O., Herzog, O., Brocke, S. and Thorn-Cśanyi, E.,** 2001: Ring substituted PV oligomers synthesized via olefin metathesis; Fluorescence properties of monodisperse products, *Synth. Met.,* **119,** 539-540.

[268] **Conticello, V.P., Gin, D.L. and Grubbs, R.H.,** 1992: Ring-opening metathesis polymerization of substituted bicycle[2.2.2]octadienes: a new precursor route to poly(1,4-phenylenevinylene, *J. Am. Chem. Soc.,* **114,** 9708-9710.

[269] **Miao, Y,-J. and Bazan, G.C.,** 1994: Paracyclophene route to poly(*p*-phenylene vinylene), *J. Am. Chem. Soc.,* **116,** 9379-9380.

[270] **Pu, L., Wagaman, M. and Grubbs, R.H.,** 1996: Synthesis of Poly(1,4-naphthylenevinylenes): Metathesis Polymerization of Benzobarrelenes, *Macromolecules,* **29,** 1138-1143.

[271] **Utley, J.H.P. and Gruber, J.,** 2002: Electrochemical synthesis of poly(*p*-xylylenes) (PPXs) and poly(*p*-phenylene vinylene) (PPVs) and the study of xylylene(quinodimethane) intermediates; an underrated approach, *J. Mater. Chem.,* **12,** 1613-1624.

[272] **Utley, J.H.P. and Smith, C.Z.,** 2000: Electroorganic reactions. Part 53. The electrosynthesis of novel water-soluble poly(*p*-xylylenes) (PPX) and poly(*p*-phenylene vinylene) (PPV) polymers and copolymers, *J. Mater. Chem.,* **10,** 2642-2646.

[273] **Iwatsuki, S., Kubo, M. and Kumeuchi, T.,** 1991: New method for preparation of poly(*p*-phenylene vinylene) films, *Chem. Lett.,*1071-1074.

[274] **Vaeth, K.M. and Jensen, K.F.,** 2000: Blue electroluminescent copolymers by parylene-based chemical vapor deposition, *Macromolecules,* **33,** 5336-5339.

[275] **Tung, N.T., Yu, Y.-J., Kim, K., Joo, S.-H., Park, Y. and Jin, J.-I.,** 2005: Versatile preparation of poly(1,4-phenylenevinylene-co-1,4-phenylene-1,2-ethanediyl) by CVD polymerization of *p-(*methoxymethyl)benzyl chloride, *J. Polym. Sci.Part:A Polym. Chem.* **43,** 742-751.

[276] **Egbe, D.A.M., Roll, C.P., Birckner, E., Grummt, U.W., Stockmann, R. and Klemm E.**, 2002: Side-chain effects in hybrid PPV/PPE polymers, *Macromolecules*, **35**, 3825-3837.

[277] **Egbe, D.A.M., Bader, C., Nowotny, J., Gunther, W. and Klemm, E.**, 2003: Investigation of the Photophysical and Electrochemical Properties of Alkoxy-Substituted Arylene−Ethynylene/Arylene−Vinylene Hybrid Polymers, *Macromolecules*, **36**, 5459-5469.

[278] **Egbe, D.A.M., Bader, C., Klemm, E., Ding, L., Karasz, F.E., Grummt, U.W. and Birckner, E.**, 2003: Influence of the Conjugation Pattern on the Photophysical Properties of Alkoxy-Substituted PE/PV Hybrid Polymers, *Macromolecules*, **36**, 9303-9312.

[279] **Ding, L., Lu, Z., Egbe, D.A.M. and Karasz, F.E.**, 2004: Structure−Morphology−Electroluminescence Relationship for Hybrid Conjugated Polymers, *Macromolecules*, **37**, 10031-10035.

[280] **Nguyen, T.-Q., Doan, V., and Schwartz, B.J.**, 1999: Conjugated polymer aggregates in solution: control of interchain interactions, *J. Chem. Phys.*, **110**, 4068-4078.

[281] **Nguyen, T.-Q., Martini, I.B., Liu, J. and Schwartz, B.J.**, 2000: Controlling Interchain Interactions in Conjugated Polymers: The Effects of Chain Morphology on Exciton-Exciton Annihilation and Aggregation in MEH-PPV Films, *J. Phys. Chem. B.*, **104**, 237-255.

[282] **Zyung, T., Kim, J.-J., Hwang, W.-Y., Hwang, D.H. and Shim, K.H.**, 1995: Electroluminescence from poly(*p*-phenylene vinylene) with monoalkoxy substituent on the aromatic ring, *Synth. Met.*, **71**, 2167-2169.

[283] **Martin, R.E., Geneste, F., Riehn, R., Chuah, B.S., Cacialli, F., Friend, R.H. and Holmes, A.B.**, 2000: Efficient blue–green light emitting poly(1,4-phenylene vinylene) copolymers, *Chem. Commun.*, 291-292.

[284] **Martin, R.E., Geneste, F., Fischmeister, C., Ma, Y., Holmes, A.B. and Riehn, R.**, 2001: Versatile synthesis of various conjugated aromatic homo- and copolymers, *Synth. Met.*, **122**, 1-6.

[285] **Andersson, M.R., Yu, G. and Heeger, A.J.**, 1997: Photoluminescence and electroluminescence of films from soluble PPV-polymers, *Synth. Met.*, **85**, 1275-1276.

[286] **Vestweber, H., Greiner, A., Lemmer, U., Mahrt, F.R., Richert, R., Heitz, W. and Bässler, H.**, 1992: Progress towards processible materials for light-emitting devices using poly(*p*-phenylphenylenevinylene), *Adv. Mater.*, **4**, 661-662.

[287] **Feast, W.J., Millichamp, I.S., Friend, R.H., Horton, M.E., Phillips, D. and Rughooputh, S.D.D.V.**, 1985: Optical absorption and luminescence in poly(4,4'-diphenylene diphenylvinylene), *Synth. Met.*, **10**, 181-191.

[288] **Feast, W.J. and Millichamp, I.S.**, 1983: The synthesis of poly(4,4'-diphenylene diphenylvinylene) via condensation polymerization of 4,4'-dibenzoylbiphenyl, *Polym. Commun.*, **24**, 102-103.

[289] **Kim, S.T., Hwang, D.-H., Li, X.-C., Grüner, J., Friend, R.H., Holmes, A.B. and Shim, H.-K.**, 1996: Efficient Green Electroluminescent Diodes Based on Poly(2-dimethyloctylsilyl-1,4-phenylenevinylene), *Adv. Mater.*, **8**. 979-982.

[290] **Ahn, T., Jang, M.S., Shim, H.-K., Hwang, D.-H. and Zyung, T.**, 1999: Blue Electroluminescent Polymers: Control of Conjugation Length by Kink Linkages and Substituents in the Poly(*p*-phenylenevinylene)-Related Copolymers, *Macromolecules,* **32,** 3279-3285.

[291] **Carter, J.C., Grizzi, I., Hecks, S.K., Lacey, D.J., Latham, S.G., May, P.G., Ruiz de los Panos, O., Pichler, K., Towns, C.R. and Wittmann, H.F.,** 1997: Operating stability of light-emitting polymer diodes based on poly(*p*-phenylene vinylene), *Appl. Phys. Lett.,* **71,** 34-36.

[292] **Burn, P.L., Holmes, A.B., Kraft, A., Bradley, D.D.C., Brown, A.R., Friend, R.H. and Gymer, R.W.**, 1992: Chemical tuning of electroluminescent copolymers to improve emission efficiencies and allow patterning , *Nature*, **356**, 47-49.

[293] **Remmers, M., Neher, D., Grüner, J., Friend, R.H., Gelinck, G.H., Warman, J.M., Quattrocchi, C., dos Santos, D.A. and Bredas, J.L.,** 1996: The Optical, Electronic, and Electroluminescent Properties of Novel Poly(*p*-phenylene)-Related Polymers, *Macromolecules,* **29,** 7432-7445.

[294] **Baigent, D.R., Hamer, P.J., Friend, R.H., Moratti, S.C. and Holmes, A.B.,** 1995: Polymer electroluminescence in the near infra-red, *Synth. Met.,* **71,** 2175-2176.

[295] **Mülher, R., Cravino, A., Williams, J., Stelzer, F., Jakopic, G. and Leising, G.,** 2001: Poly(2-hexyl-9,10-anthrylene vinylene)–A new class of soluble poly(anthrylene vinylene)s, *Synth. Met.,* **119,** 193-194.

[296] **Onoda, M., Ohmori, Y., Kawai, T. and Yoshino, K.,** 1995: Visible-light electroluminescent diodes using poly(arylene vinylene), *Synth. Met.,* **71,** 2181-2182.

[297] **Van Der Borght, M., Vanderzande, D. and Gelan, J.,** 1998: Synthesis of high molecular weight poly(4,4′-bisphenylene vinylene) and poly(2,6-naphthalene vinylene) via a non-ionic precursor route, *Polymer,* **39,** 4171-4174.

[298] **Miao, Y,-J. and Bazan, G.C.,** 1994: Paracyclophene route to poly(*p*-phenylene vinylene), *J. Am. Chem. Soc.,* **116,** 9379-9380

[299] **Yurteri, S., Cianga, I., Degirmenci, M. and Yagci, Y.,** 2004. Synthesis and Characterization Of Poly(*p*-phenylene)-graft-Poly(ε-caprolactone) Copolymers By Combined Ring-Opening Polymerization and Cross-Coupling Processes, *Polym. Int.,* **53(9),** 1219-1225.

[300] **Colak, D., Cianga, I., Muftuoglu, A.E. and Yagci, Y.,** 2006: Synthesis and characterization of mid- and end-chain functional telechelics by controlled polymerization and coupling processes, *J. Polym. Sci Part A: Polym. Chem.*, **44**, 727-743.

[301] **Yurteri, S., Cianga, I., Yagci, Y.,** 2005: Synthesis and characterization of poly(epsilon-caprolactone)-b-polystyrene macromonomer by combined ring-opening and atom transfer radical polymerizations and its use for the preparation of grafted polyphenylenes by Suzuki polycondensation, *Designed Monomers and Polymers*, **8(1),** 61-74.

[302] **Morgan, P.W., Kwolek, S.L. and Pletcher, T.C.**, 1987: Aromatic azomethine polymers and fibers, *Macromolecules*, **20**, 729-739.

[303] **Simionescu, C.I., Cianga, I., Ivanoiu, M., Duca, A., Cocarla, I. and Grigoras, M.**, 1999: Synthesis and electrochemical polymerization of some monomers with Schiff base or vinylene structures and thiophene moieties, *Eur. Polym. J.*, **35**, 587-599.

[304] **Simionescu, C.I., Cianga, I., Ivanoiu, M., Airinei, A., Grigoras, M. and Radu, I.**, 1999: Oxidative polymerization of some monomers with pyrrole moieties—an UV–vis absorption spectroscopy study, *Eur. Polym. J.*, **35**, 1895-1905.

[305] **Muftuoglu, A.E.; Cianga, I.; Colak, D.; Yagci, Y.**, 2004: Synthesis of A(2)B and A(2)B(2) type miktoarm star co-polymers by combination of ATRP or ROP with photoinduced radical polymerization, *Designed Mon. Polym.*, **7(6)**, 563-582.

[306] **Kiskan, B.; Colak, D.; Muftuoglu, A.E.; Cianga, I.; Yagci, Y.**, 2005: Synthesis and characterization of thermally curable benzoxazine-functionalized polystyrene macromonomers., *Macromol. Rapid. Commun.*, **26(10)**, 819-824.

[307] **Tarkuc, S., Sahin, E., Toppare, L., Colak, D., Cianga, I. and Yagci Y.,** 2006: Synthesis, characterization and electrochromic properties of a conducting copolymer of pyrrole functionalized polystyrene with pyrrole, *Polymer,* **47(6)**, 2001-2009.

[308] **Colak, D.G., Cianga, I., Yagci, Y., Cirpan, A. and Karasz, F.E.,** 2007: Novel poly(phenylene vinylene)s with well-defined poly(ε-caprolactone) or polystyrene as lateral substituents: Synthesis and Characterization, *Macromolecules*, **40**, 5301-5310.

[309] **Cianga,I., Yagci, Y.**, 2002: Synthesis and characterization of comb-like polyphenylenes via Suzuki coupling of polystyrene macromonomers prepared by atom transfer radical polymerization, *Eur. Polym. J.*, **38(4)**, 695-703.

[310] **Cianga, I., Hepuzer, Y. and Yagci, Y.**, 2002: Poly(p-phenylene) graft copolymers with polytetrahydrofuran/polystyrene side chains, *Polymer*, **43(8)**,2141-2149.

[311] **Cianga, I. and Yagci, Y.**, 2004: New polyphenylene-based macromolecular architectures by using well defined macromonomers synthesized via controlled polymerization methods, *Prog. Polym. Sci.*, **29(5)**,387-399.

[312] **Yurteri, S., Cianga, I., Demirel, A.L. and Yagci Y.**, 2005: New polyphenylene-g-polystyrene and polyphenylene-g-polystyrene/ poly(epsilon-caprolactone) copolymers by combined controlled polymerization and cross-coupling processes, *J. Polym. Sci.: Part A:Polym. Chem.*, **43(4)**,879-896.

[313] **Demirel, A.L., Yurteri, S., Cianga, I. and Yagci, Y.**, 2005: Layered morphology of poly(phenylene)s in thin films induced by substitution of well-defined poly(epsilon-caprolactone) side chains, *Macromolecules*, **38(15)**, 6402-6410.

[314] **Zheng, M., Bai, F., Li, Y., Yu, G. and Zhu, D.**, 1999: Synthesis and characterization of a high-efficiency light-emitting alternating copolymer, *J. Polym. Sci.: Part A:Polym. Chem.*, **37**, 2587-2594.

[315] **Grisoiro, R., Mastrorilli, P., Nobile, C.F., Romanazzi, G. and Surana, G.P.**, 2005: A novel synthetic protocol for poly(fluorenylenevinylene)s: a cascade Suzuki–Heck reaction, *Tetrahedron Lett.*, **46**, 2555-2558.

[316] **Yurteri, S., Cianga, I., Degirmenci, M. and Yagci, Y.**, 2004: Synthesis and characterization of poly(p-phenylene)-graft-poly(epsilon-caprolactone) copolymers by combined ring-opening polymerization and cross-coupling processes, *Polym. Int.*, **53(9)**,1219-1225.

[317] **Yamamoto, T., Xu, Y., Inoue, T. and Yamaguchi, I.**, 2000: Preparation of poly(biphenylene vinylene) type polymers by Ni-promoted polycondensation and their basic optical properties, *J. Polym. Sci.: Part A: Polym. Chem.*, **38**, 1493-1504.

[318] **Nur, Y., Colak, D.G., Cianga, I., Yagci, Y. and Hacaloglu, J.**, 2008: Pyrolysis of poly(phenylene vinylene)s with polycaprolactone side chains, *Polym. Degrad. Stab.*, **93(5)**, 904-909.

[319] **Nur, Y., Colak, D.G., Cianga, I., Yagci, Y. and Hacaloglu, J.**, 2008: Direct Pyrolysis Mass Spectrometry Studies on Thermal Degradation Characteristics of Poly(phenylene vinylene) with Well-Defined PSt Side Chains, *J. Therm. Anal. and Calorim.*, **94(1)**,157-162.

[320] **Colak, D.G., Egbe, D.A.M., Birckner, E., Yurteri, S., Cianga, I., Tekin, E., Schubert, U.S. and Yagci, Y.,** 2009: Photophysical properties of PPP and PPV derivatives bearing polystyrene or polycaprolactone as side groups, *Eur. Polym. J.*, **45(3)**,940-945.

[321] **Egbe, D.A.M., Nguyen, L.H., Schmidtke, K., Wild, A., Gunes, S., Sieber, C. and Sariciftci, N.S.**, 2007: Combined effects of conjugation pattern and alkoxy side chains on the photovoltaic properties of thiophene-containing PPE-PPVs, *J. Polym. Sci. Part A: Polym. Chem.*, **45(9)**, 1619-31.

[322] **Weder, C. and Wrighton, M.S.**, 1996: Efficient solid-state photoluminescence in new poly(2,5-dialkoxy-*p*-phenylene ethynylene)s, *Macromolecules*, **29**, 5157-65.

CURRICULUM VITAE

Candidate's full name: Demet GÖEN ÇOLAK

Place and date of birth: İSTANBUL, 01.12.1976

Permanent Address: Çubuklu Engürü Bağı Cad. Yazgı Sok. No:7 Daire:2
Beykoz, İstanbul/Turkey.

Universities and Colleges attended:

2001-2009	Philosophy of Doctorate, Chemistry Istanbul Technical University, Istanbul, Turkey
1998-2001	Master of Science, Chemistry Istanbul Technical University, Istanbul, Turkey
1994-1998	Bachelor of Science, Chemistry Istanbul Technical University, Istanbul, Turkey
1987-1994	İstek Private Bilge Kağan College, Istanbul, Turkey

Professional Experience:

1999-	Research and Teaching Assistant, Chemistry Istanbul Technical University, Istanbul, Turkey

Publications:

- Synthesis of A_2B and A_2B_2 type miktoarm star co-polymers by combination of ATRP or ROP with photoinduced radical polymerization. Muftuoglu AE, Cianga M, **Colak D**, Yagci Y. *Designed Monomers and Polymers,* 7(6), 563-582, (2004).
- Synthesis and characterization of thermally curable benzoxazine-functionalized polystyrene macromonomers. Kiskan B, **Colak D**, Muftuoglu AE, Cianga I, Yagci Y. *Macromolecular Rapid Communications*, 26(10), 819-824, (2005).
- Synthesis and characterization of mid- and end-chain functional telechelics by controlled polymerization methods and coupling processes. **Colak D,** Cianga I, Muftuoglu AE, Yagci Y. *Journal of Polymer Science Part A-Polymer Chemistry,* 44(2), 727-743, (2006).

- Synthesis, characterization and electrochromic properties of a conducting copolymer of pyrrole functionalized polystyrene with pyrrole. Tarkuc S, Sahin E, Toppare L, **Colak D**, Cianga I, Yagci Y. *Polymer,* 47(6), 2001-2009, (2006).

- Design and Synthesis of Thermally Curable Polymers with Benzoxazine Fuctionalities, B. Kiskan, B. Gacal, M. A. Tasdelen, **D. Colak**, Y. Yagci, *Macromolecular Symposia*, 245-246, 27-33, (2006).

- Block copolymers of N-vinyl carbazole and α,ω -dihydroxy polydimethylsiloxane, Akar A, Kizilcan N, Ustamehmetoglu Belkis, **Colak D,** Sarac A.S, Colak, C, *Journal of Applied Polymer Science,* 106(6), 3694-3702, (2007).

- Novel poly(phenylene vinylenes) with well-defined poly(ε-caprolactone) or polystyrene as lateral substituents: Synthesis and characterization. **Colak DG***,* Cianga I, Yagci Y, Cirpan A, Karasz FE. *Macromolecules,* 40(15), 5301-5310, (2007).

- Pyrolysis of poly(phenylene vinylene)s with polycaprolactone side chains. Nur Y, **Colak DG**, Cianga I, Yagci Y, Hacaloglu J. *Polymer Degradation and Stability,* 93(5), 904-909, (2008).

- Direct Pyrolysis Mass Spectrometry Studies on Thermal Degradation Characteristics of Poly(phenylene vinylene) with Well-Defined PSt Side Chains. Nur Y, **Colak DG**, Cianga I, Yagci Y, Hacaloglu J. *Journal of Thermal Analysis and Calorimetry,* 94(1), 157-162, (2008).

- Photophysical properties of PPP and PPV derivatives bearing polystyrene or polycaprolactone as side groups, **D.G. Colak**, D.A.M Egbe, E. Birckner, S. Yurteri, I. Cianga, E. Tekin, U.S. Schubert, Y. Yagci. *European Polymer Journal*, 45, 940-945, (2009).

- High temperature pyrolysis of poly(phenylene vinylene)s with poly(ε-caprolactone) or polystyrene side chains. Nur Y, **Colak DG**, Cianga I, Yagci Y, Hacaloglu J. *Journal of Thermal Analysis and Calorimetry*, 98(2): 527–532, (2009).

Chapters in Books:

- Addition-Fragmentation Type Reactions in Photoinitiated Cationic Polymerization, **D. Colak**, S.Yurteri, B. Kiskan, Y. Yagci, *Photochemistry and UV Curing : new trends* (Ed J.P. Fouassier) Photochemistry and Photobiology Research Signpost., Trivandrum, , Ch. 16, pp 175-185, (2006).

- New Polymers with Optoelectronic Properties by Combination of ATRP, ROP and Coupling Processes, **D.G. Colak**, I. Cianga, S. Yurteri, Y. Yagci, *New Smart Materials via Metal Mediated Macromolecular Engineering* (Eds E. Khosravi, Y. Yagci, Y. Savelyev) *NATO Science for Peace and Security Series-A: Chemistry and Biology*, Springer, Ch. 4, pp.49-73, (2009).