<u>İSTANBUL TECHNICAL UNIVERSITY</u> ★ <u>INSTITUTE OF SCIENCE AND TECHNOLOGY</u>

PERFECTLY DESIGNED AMPHIPHILIC POLYPHENYLENES BY COMBINATION OF CONTROLLED POLYMERIZATION AND SUZUKI COUPLING PROCESSES

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KONTROLLÜ POLİMERİZASYON VE SUZUKİ KENETLENME PROSESİ İLE MÜKEMMEL DİZAYN EDİLMİŞ AMFİFİLİK POLİFENİLENLER

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ABBREVIATIONS

ATRP	:	Atom Transfer Radical Polymerization
RAFT	:	Reversible Addition Fragmentation Chain Transfer
NMP	:	Nitroxide Mediated Polymerization
CROP	:	Controlled Radical Opening Polymerization
PMDETA	:	*N, N, N',N'', N''*-Pentamethyldiethylenetriamine
AIBN	:	2,2'-Azobis-(isobutyronitrile)
Bpy	:	2,2-Dipyridyine
NBS	:	*N*-bromosuccinimide
PTHF	:	Poly(tetrahydrofuran)
PSt	:	Polystyrene
PVAc	:	Polyvinyl Acetate
PP	:	Polyphenylene
PEO	:	Poly(etyleneoxide)
$M_{n,th}$	:	Theoretical Molecular Weight
M_n	:	Number Average Molecular Weight
M_w	:	Molecular Weight
PD	:	Polydispersity
$MgSO_4$	:	Magnesium Sulfate
^{1}**H-NMR**	:	Nuclear Magnetic Resonance Spectroscopy
IR	:	Infrared Spectrophotometer
GPC	:	Gel Permeation Chromatography

x

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LIST OF SYMBOLS

R	: Radical
I	: Initiator
M	: Monomer
M_n	: The number average molecular weight
M_w	: The weight average molecular weight
M_w/M_n	: The molecular weight distribution
P_n^*	: Propagating species
M_{tn}	: Transition metal
P_n	: Polymer having a double bond at the chain end due to termination by disproportination
P_{n+m}	: Polymer terminated by chain combination
X	: Halide group
k_a	: Rate constant of activation
k_{da}	: Rate constant of deactivation
k_p	: Rate constant of propagation
k_t	: Rate constant of termination

PERFECTLY DESIGNED AMPHIPHILIC POLYPHENYLENES BY COMBINATION OF CONTROLLED POLYMERIZATION AND SUZUKI COUPLING PROCESSES

SUMMARY

Poly(phenylene) (PP) and its derivatives are a promising class of high-performance polymers because of their excellent thermal and mechanical properties. PP is used as a coating material in the packaging industry to protect integrated circuits from breakage, humidity, and corrosion.

As PPs are insoluble in many organic solvents, which limit their processability, attachment of conformationally mobile alkyl side chains to the backbone has been important because it has allowed the controlled synthesis of soluble and processable polymers with high molecular weight. On combining a stiff, insoluble, rod-like polymer such as PP with a soft coil, for example polystyrene (PSt), it is possible to form a new polymer with novel and interesting properties.

In this study, different types of new macromonomers were synthesized by using controlled polymerization methods. We have selected four different methods namely, Atom Transfer Radical Polymerization (ATRP), Reversible Additon-Fragmentation Chain Transfer (RAFT) polymerization, Controlled Ring Opening Polymerization (CROP) and etherification reaction, because of their versatility to prepare well-defined macromolecular structures. Among these macromonomers, the polyethylene oxide macromonomer, prepared by etherification reaction, was used as the representative polymer to demonstrate the macromolecular architecture to form conjugated polymers with alternating side chains. Independently, boronic ester type macromonomer of polystyrene was synthesized by ATRP. The two process allowed to link directly bromine atoms or boronic ester functionalities to a benzene ring of the polymer chain end, useful for the Suzuki type polycondesation.

In the final stage, the preparation amphiphilic polyphenylene possessing completely and perfectly alternating hydrophilic poly(ethylene oxide) and hydrophobic polystyrene side chains was performed. Experimentally, hydrophilic $Ar(Br_2)$-PEO type macromonomer and hydrophobic $Ar(BO_2C_3H_6)$-PSt macromonomer were reacted via for Suzuki-type polycondensation in the presence $Pd(PPh_3)_4$ as catalyst to form desired amphiphilic copolymer. The structure and molecular weight of the intermediates and the polymers formed at various stages were confirmed by spectral analysis and gel permeation chromatography.

KONTROLLÜ POLİMERİZASYON VE SUZUKİ KENETLENME PROSESİ İLE MÜKEMMEL DİZAYN EDİLMİŞ AMFİFİLİK POLİFENİLENLER

ÖZET

Polifenilenler ve türevleri, mükemmel termal ve mekanik özelliklerinden dolayı yüksek teknoloji polimerlerin önemli bir sınıfını oluştururlar. Polifenilenler elektrik devrelerini kırılma, nem ve korozyondan korumak için kaplama malzemesi olarak kullanılırlar.

Polifenilenlerin birçok organik çözücüde çözünmemesi işlenebilirliklerini kısıtlayıcı rol oynar. Bu yüzden, ana zincire hareketli alkil yan zincirlerinin eklenmesi, çözünür ve işlenebilir yüksek molekül ağırlıklı polimerlerin kontrollü sentezine izin vermesi yönünden önem kazanmıştır. Sert, çözünmez, çubuk şeklindeki Polifenilenlere yumuşak bir Polistiren grubunun eklenmesiyle tamamen yeni özelliklere sahip bir polimerin sentezi mümkün olabilir.

Bu çalışmada, kontrollü polimerizasyon metodları ile farklı, yeni makromonomerler sentezlenmiştir. İyi bilinen makromoleküler yapılar, çok yönlüdür. Bu sebeple dört farklı metod ile, sırasıyla atom transfer radikal polimerizasyonu, tersinir katılma-ayrılma transfer polimerizasyonu, katyonik zincir açılma polimerizasyonu ve eterifikasyon reaksiyonu ile hazırlanmıştır. Bu makromonomerler arasında, polietilenoksit makromonomeri eterifikasyon reaksiyonu ile hazırlanmış olup, makromoleküler yapıyı kanıtlamak için polimerde kullanılarak konjuge polimerler ile alterne yan zincirler oluşturuldu. Bağımsız olarak, polistirenin boronik ester tipli makromonomeri ATRP ile sentezlendi. İki proses, brom ve boronik ester fonksiyonalitelerin polimer zincirine benzen halkası ile doğrudan bağlanmasına izin vererek Suzuki polikondensazyon reaksiyonunda kullanıldı.

Finalde, hazırlanan amfifilik polifenilen tamamamen ve mükemmel alterne hidrofilik polietilenoksit ve hidrofobik polistiren yan zincirler olarak tanımlanmıştır. Deneysel olarak, hidrofilik $Ar(Br_2)$-PEO tipli makromonomer ve hidrofobik $Ar(BO_2C_3H_6)$-PSt makromonomer $Pd(PPh_3)_4$ kataliz varlığında reaksiyonuna girerek Suzuki polikondensazyon reaksiyonu ile amfifilik kopolimer oluşturuldu. Ara yapılar ve polimerlerin yapıları çeşitli evrelerde spektral analiz ve jel geçirgenlik kromatografisi ile onaylandı.

1. INTRODUCTION

Conjugated polymers are of considerable academic and industrial interest as active materials in devices such as waveguides, fluorescent chemical sensors, photoconductors, organic light-emitting diodes (OLEDs), and the most promising new applications such as flexible displays. Among the conjugated polymers, polythiophenes, polycarbazoles, poly(phenylene vinylene)s, and PPs have attracted particular interest as blue electroluminescent polymers due to their high quantum yield and good charge transport properties. In earlier studies, the low solubility of the PPs limited the processability for device fabrications. Introduction of substituents on the PP backbone is an alternative method to improve solubility; however, the repulsion of the side group forces the phenyl rings to a nonplanar conformation [1].

Amphiphilic polyphenylene have been synthesized via Suzuki polycondensation method in the presence of $Pd(PPh_3)_4$ as catalyst. In order to improve the solubility, by adopting this method to polymer synthesis, a series of functionalized PP has been reported by Wegner et al. Moreover, PPs containing hydrophilic $Ar(Br_2)$-PEO and hydrophobic $Ar(BO_2C_3H_6)$-PSt side chains in common organic solvents at room temperature were obtained, too.

New synthetic methods for introducing functional groups at specific location at either chain ends or along the backbone are emerging as powerful tools for the construction of these architectures. Considerable effort has recently been devoted to the controlled/'living' polymerization methods, which permitted to obtain nearly unlimited control of the polymer is composition, architecture and functionality. The methods of controlled/living radical polymerization (CRP) developed in the past decade allow the synthesis of not only copolymers with predetermined molecular weight and narrow molecular weight distribution but also with high functionality and desired microstructure. The most versatile methods of controlled radical polymerization are atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP), cationic ring opening polymerization (CROP) and reversible addition-fragmentation chain transfer polymerization (RAFT).

Our studies focused on the synthesis of amphiphilic PP by using macromonomers prepared by controlled polymerizations (ATRP, RAFT, CROP) and etherification reaction. These methods were elegantly combined with metal-catalyzed Suzuki polycondensation, specific to the obtainment of soluble conjugated polymers.

2. THEORETICAL PART

2.1 Controlled Polymerization Methods

Living polymerization was first defined by Szwarc [1] as a chain growth process without chain breaking reactions (transfer and termination). While such a polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition, it does not necessarily provide polymers with molecular weight (MW) control and narrow molecular weight distribution (MWD). Additional prerequisites to achieve these goals include that the initiator should be consumed at early stages of polymerization and that the exchange between species of various reactivities should be at least as fast as propagation [2-4]. It has been suggested to use a term "controlled polymerization" if these additional criteria are met. A controlled polymerization can be defined as a synthetic method for preparing polymers with predetermined molecular weights, low polydispersity and controlled functionality. Transfer and termination, which often occur in real systems, are allowed in a controlled polymerization if their contribution is sufficiently reduced by the proper choice of the reaction conditions such that polymer structure is not affected.

Among the controlled polymerization methods such as radical, cationic, group transfer, the former will be discussed in the following part, as the present thesis involves the use of controlled radical polymerization method in the experimental section.

2.1.1 Controlled radical polymerization (CRP)

Radical polymerization (RP) is a very convenient commercial process for the preparation of high molecular weight polymers since it can be employed for the polymerization of numerous vinyl monomers under mild reaction conditions, requiring an oxygen free medium, but tolerant to water, and can be conducted over a large temperature range (-80 to 250 ^{o}C) [5]. Furthermore, many monomers can easily be copolymerized through a radical route, and this leads to an infinite number of

copolymers with properties dependent on the proportion of the incorporated comonomers. One of the main disadvantages of RP is the poor control over the microstructure of the synthesized macromolecules. This includes the relatively high polydispersity index (PDI), 1.5 or 2.0, and also the practical impossibility to synthesize block copolymers, and other advanced structures.

Advanced structures can be synthesized via living polymerization techniques. Notable example of these techniques is anionic polymerization [6], which is known to allow the synthesis of low PDI materials as well as block copolymers. The main disadvantages of anionic polymerization are the limited choice of monomers, and the extremely demanding reaction conditions.

In order to overcome the disadvantages of RP without sacrificing the above-mentioned advantages, it was recognized that a living character had to be realized in conjunction with the free-radical mechanism. Thus, we have witnessed a real explosion of academic and industrial research on controlled/"living" radical polymerizations with over 4000 papers and hundreds of patents devoted to this area since the late 1990s. At present three main mechanisms exist that ensure this living character by establishing an equilibrium between active (radical) and dormant chains. These are atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP) and reversible addition-fragmentation chain transfer polymerization (RAFT). In either of these controlled radical polymerization methods (CRP), all chains are started early in the reaction, and are allowed to grow throughout the reaction. In general, the result of a successful CRP will be a polymer with low PDI, and predetermined (number-average) molar mass.

2.1.1.1 Atom transfer radical polymerization (ATRP)

The name atom transfer radical polymerization comes from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains. ATRP was developed by designing a proper catalyst (transition metal compound and ligands), using an initiator with an appropriate structure, and adjusting the polymerization conditions, such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process [7]. This allowed for an unprecedented control over the chain topology (stars, combs,

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branched), the composition (block, gradient, alternating, statistical), and the end functionality for a large range of radically polymerizable monomers [8, 9].

$$P_n\text{-}X + M_t^n\text{-}Y/\text{Ligand} \underset{k_{\text{deact}}}{\overset{k_{\text{act}}}{\rightleftharpoons}} P_n^* + X\text{-}M_t^{n+1}\text{-}Y/\text{Ligand}$$

$$\overset{(k_p)}{\underset{\text{monomer}}{}} \cdots k_t$$

$$\text{termination}$$

(2.1)

A general mechanism for ATRP is represented by **(2.1)**. The radicals, i.e., the propagating species P_n^*, are generated through a reversible redox process catalyzed by a transition metal complex (activator, $M_t^n -Y$ / ligand, where Y may be another ligand or a counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, P_n–X. Radicals react reversibly with the oxidized metal complexes, $X–M_t^{n+1}$ / ligand, the deactivator, to reform the dormant species and the activator. This process occurs with a rate constant of activation, k_a, and deactivation k_{da}, respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Elementary reactions consisting of initiation, propagation, and termination are illustrated below **(2.2a-e)** [10].

Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, the deactivators, which behave as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination at later stages [11]. A successful ATRP will have not only small contribution of terminated chains but also uniform growth of all the chains; this is accomplished through fast initiation and rapid reversible deactivation.

Initiation

$$R\text{-}X \; + \; M_t^n\text{-}Y/\text{Ligand} \; \underset{k_{\text{deact}}^{\,o}}{\overset{k_{\text{act}}^{\,o}}{\rightleftarrows}} \; R \; + \; X\text{-}M_t^{n+1}\text{-}Y/\text{Ligand} \tag{2.2a}$$

$$R \; + \; M \; \xrightarrow{k_i} \; P_1 \tag{2.2b}$$

Propagation

$$P_n\text{-}X \; + \; M_t^n\text{-}Y/\text{Ligand} \; \underset{k_{\text{deact}}}{\overset{k_{\text{act}}}{\rightleftarrows}} \; P_n^* \; + \; X\text{-}M_t^{n+1}\text{-}Y/\text{Ligand} \tag{2.2c}$$

$$P_n \; + \; M \; \xrightarrow{k_p} \; P_{n+1} \tag{2.2d}$$

Termination

$$P_n \; + \; P_m \; \xrightarrow{k_t} \; P_{n+m} \quad \text{or} \quad P_n^= \; + \; P_m^H \tag{2.2e}$$

As a multicomponent system, ATRP includes the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Both activating and deactivating components of the catalytic system must be simultaneously present. Sometimes an additive is used. Basic components of ATRP, namely, monomers, initiators, catalysts, ligands, and solvents are discussed as follows:

Monomers

A variety of monomers have been successfully polymerized using ATRP: styrenes, (meth)acrylates, (meth)acrylamides, dienes, and acrylonitrile, which contain substituents that can stabilize the propagating radicals [8]. In fact, all vinyl monomers are susceptible to ATRP except for a few exceptions. Notable exceptions are unprotected acids (eg (meth)acrylic acid). Some other monomers may be difficult to polymerize since they exhibit side reactions, which may be affected by the choice of reaction conditions, nature of the catalyst, etc. An example of such a monomer is 4-vinyl pyridine (4-VP), which can undergo quaternization by the (alkyl halide) initiator [12]. Nevertheless, successful polymerization of 4-VP has been reported.

The most common monomers in the order of their decreasing ATRP reactivity are methacrylates, acrylonitrile, styrenes, acrylates, (meth)acrylamides.

Initiators

The main role of the initiator is to determine the number of growing polymer chains. The initiation in ATRP may occur in one of two different ways. The common way to initiate is via the reaction of an activated (alkyl) halide with the transition-metal complex in its lower oxidation state. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, should rapidly and selectively migrate between the growing chain and the transition metal complex. Thus far, when X is either bromine or chlorine, the molecular weight control is best. Iodine works well for acrylate polymerizations in copper-mediated ATRP and has been found to lead to controlled polymerization of styrene in ruthenium and ruthenium-based ATRP [13, 14]. Many different types of halogenated compounds have the potential to initiate ATRP. Typical examples would be the use of ethyl 2-bromoisobutyrate and a Cu(I) complex for the initiation of a methacrylate polymerization [15], or 1-phenylethyl chloride for the initiation of a styrene polymerization [7]. In addition, there are initiators like 2,2,2-trichloro-ethanol [16] that appear to be very efficient, and that result in hydroxy-functional polymer chains. Percec and co-workers reported the use of sulfonyl chlorides as universal initiators in ATRP [17]. Also the use of di-, tri-, or multifunctional initiators is possible, which will result in polymers growing in two, three, or more directions. Besides, some pseudohalogens, specifically thiocyanates and thiocarbamates, have been used successfully in the polymerization of acrylates [18].

The alternative way to initiate ATRP is via a conventional free-radical initiator, which is used in conjunction with a transition-metal complex in its higher oxidation state. Typically one would use AIBN in conjunction with a Cu(II) complex. Upon formation of the primary radicals and/or their adducts with a monomer unit, the Cu(II) complex very efficiently transfers a halogen to this newly formed chain. In doing so the copper complex is reduced, and the active chain is deactivated. This alternative way of initiation was termed "reverse ATRP" [19].

Catalysts

Perhaps the most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the

dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst.

1. The metal center must have at least two readily accessible oxidation states separated by one electron.

2. The metal center should have reasonable affinity toward a halogen.

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

4. The ligand should complex the metal relatively strongly.

5. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system. To differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species [20].

A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The majority of work on ATRP has been conducted using copper as the transition metal. Apart from copper-based complexes, Fe [21], Ni [22], Ru [23], etc have been used to some extent. Recent work from Sawamoto and co-workers shows that the Ru-based complexes can compete with the Cu-based systems on many fronts. A specific Fe-based catalyst has also been reported to polymerize vinyl acetate via an ATRP mechanism [24].

Ligands

The main roles of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal. It should also allow expansion of the coordination sphere and should allow selective atom transfer without promoting other reactions.

The most common ligands for ATRP systems are 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). Examples of ligands used in copper-mediated ATRP are illustrated below [7, 25].

(2.3)

Bipy **dTBipy** **dHBipy** **dNBipy**

(2.4)

TMEDA **PMDETA** **HMTETA**
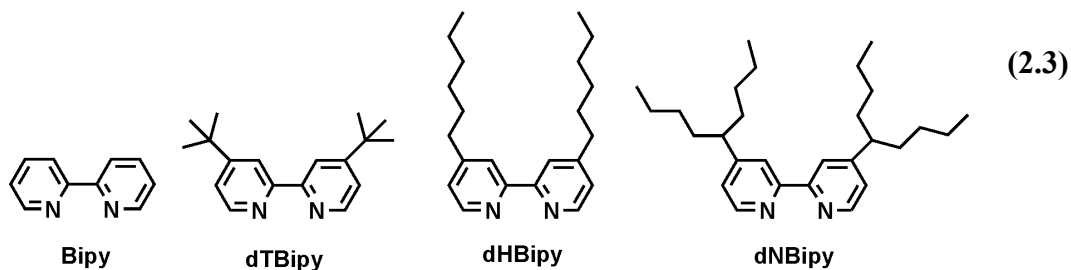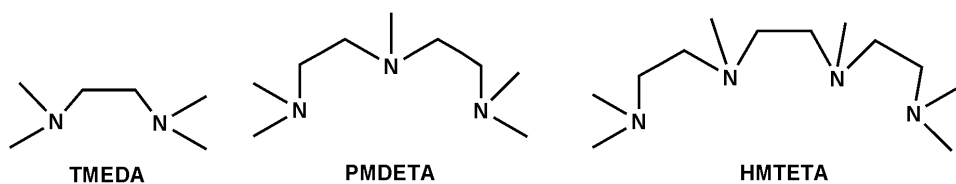
In addition to those commercial products, it has been demonstrated that hexamethyltriethylene tetramine (HMTETA) provides better solubility of the copper complexes in organic media and entirely homogeneous reaction conditions [26]. Since copper complexes of this new ligand are almost insoluble in water, ATRP technique can be employed in preparing poly(acrylate esters) in aqueous suspensions [27].

Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used in the polymerization of different monomers. A solvent is sometimes necessary, especially when the polymer is insoluble in its monomer (e.g., polyacrylonitrile). ATRP has been also successfully carried under heterogeneous conditions in (mini)emulsion, suspension, or dispersion. Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, potential interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP) [28] and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent [29], should be minimized.

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2.1.1.2 The reversible addition–fragmentation chain transfer polymerization (RAFT)

In terms of polymerizable monomers, RAFT is at present the most versatile technique for conducting CRP, that is, it can be applied to a larger range of monomers than SFRP and ATRP. In contrast to the previously described NMP and ATRP, this system relies on chain transfer for the exchange between active and dormant chains. The chain end of a dormant chain carries a thiocarbonylthio moiety, which is chain-transfer–active. Upon chain transfer, the thiocarbonylthio moiety is transferred to the previously active chain, which now becomes dormant, and the previously dormant chain carries the radical activity and is able to propagate.
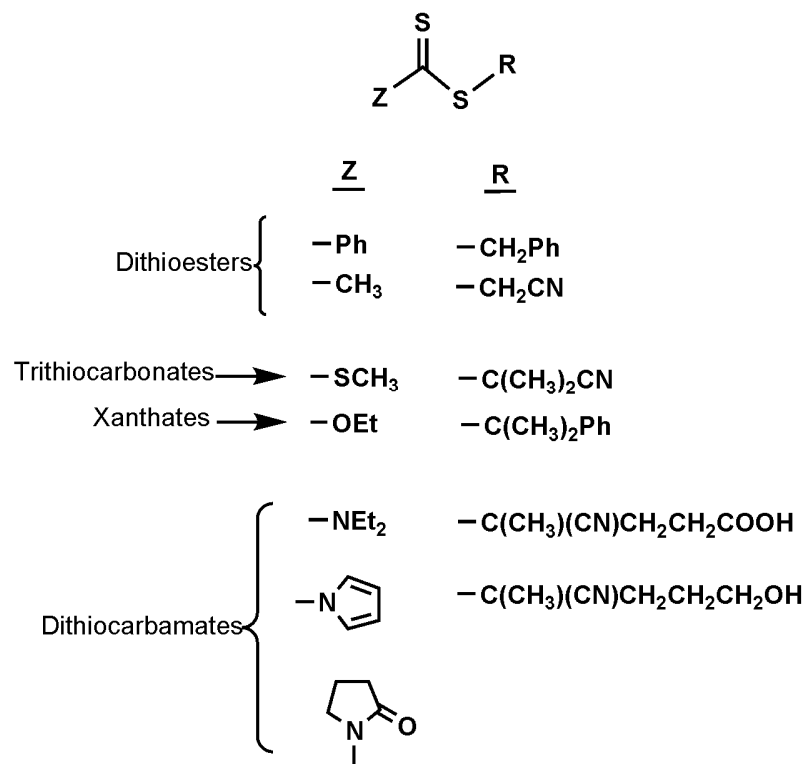
There are four classes of thiocarbonylthio RAFT agents, depending on the nature of the Z group: (1) dithioesters (Z = aryl or alkyl), (2) trithiocarbonates (Z = substituted sulfur), (3) dithiocarbonates (xanthates) (Z = substituted oxygen), and (4) dithiocarbamates (Z = substituted nitrogen). Representative examples of thiocarbonylthio RAFT agents are shown in Figure 2.1.

To some extent the choice of RAFT agent determines the degree of control obtained. The general structure of a RAFT agent is depicted in Figure 2.5, where the Z group is the activating group, and R is the homolytically leaving group. To a large extent, the Z group determines the rate of addition, and the R group determines the rate of fragmentation. The choice of Z and R groups is dependent on the nature of the monomer to be polymerized.

RAFT polymerization is performed by adding a chosen quantity of an appropriate RAFT agent Figure 2.1 to a conventional free radical polymerization mixture and yields polymers of predetermined chain length and narrow polydispersity. Polydispersity indices of less than 1.1 can be usually achieved under optimal conditions. The RAFT process offers the same versatility and convenience as conventional free-radical polymerization being applicable to the same range of monomers (e.g., (meth)acrylates, styrenes, acrylamides, vinyls), solvents, functional groups (e.g., OH, CO_2H, NR_2, NCO) and reaction conditions (e.g., bulk, solution, suspension and emulsion). The RAFT process yields thiocarbonylthio-terminated polymers (or 1,1-disubstituted alkene-terminated oligomers if macromonomers are

used as RAFT agents) that can be chain extended to yield a variety of copolymers (e.g., AB, ABA blocks, gradient).

	Z	R
Dithioesters {	−Ph	−CH$_2$Ph
	−CH$_3$	−CH$_2$CN
Trithiocarbonates →	−SCH$_3$	−C(CH$_3$)$_2$CN
Xanthates →	−OEt	−C(CH$_3$)$_2$Ph
Dithiocarbamates {	−NEt$_2$	−C(CH$_3$)(CN)CH$_2$CH$_2$COOH
	−N⟨⟩	−C(CH$_3$)(CN)CH$_2$CH$_2$CH$_2$OH

Figure 2.1 : Examples of the different classes of thiocarbonylthio RAFT agents.
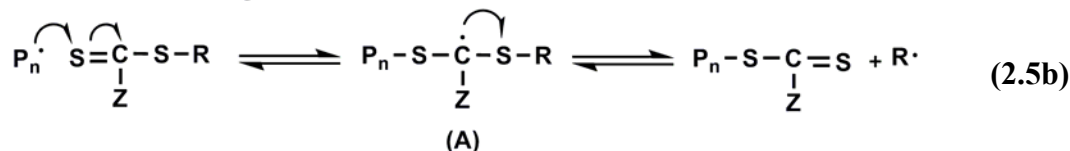
The mechanism of RAFT polymerization with the thiocarbonylthio-based RAFT agents involves a series of addition–fragmentation steps as depicted below **(2.5a-e)**. As for conventional free-radical polymerization, initiation by decomposition of an initiator leads to formation of propagating chains. In the early stages, addition of a propagating radical ($P_n·$) to the RAFT agent [S=C(Z)SR] followed by fragmentation of the intermediate radical gives rise to a polymeric RAFT agent and a new radical (R·). The radical R· reinitiates polymerization by reaction with monomer to form a new propagating radical ($P_m·$). In the presence of monomer, the equilibrium between the active propagating species ($P_n·$ and $P_m·$) with the dormant polymeric RAFT compound provides an equal probability for all the chains to grow. This feature of the RAFT process leads to the production of narrow polydispersity polymers. When the polymerization is complete, the great majority of the chains contain the thiocarbonylthio moiety as the end group **(2.5e)** which has been identified by ^{1}H-NMR and UV–vis spectroscopy [30]. Additional evidence for the proposed

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mechanism was provided by the identification of the intermediate thioketal radical ((A) and/or (B), **(2.5b,d)** by ESR spectroscopy [31, 32].
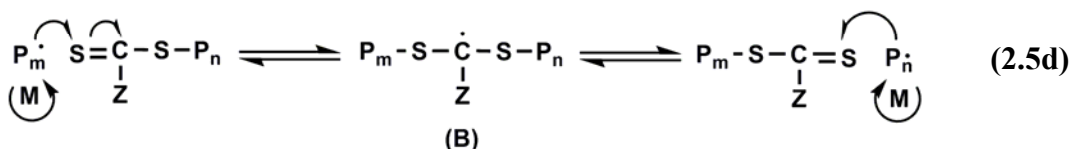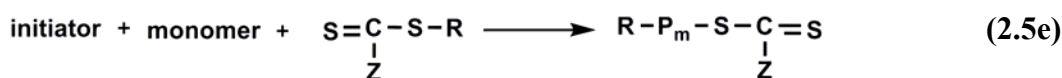
Initiation and propagation

$$\text{initiator} + \text{monomer} \longrightarrow P_n^{\bullet} \tag{2.5a}$$

Addition to RAFT agent

$$\tag{2.5b}$$

(A)

Reinitiation

$$R^{\bullet} + \text{monomer} \longrightarrow P_m^{\bullet} \tag{2.5c}$$

Chain equilibration by reversible addition fragmentation

$$\tag{2.5d}$$

(B)

Overall

$$\tag{2.5e}$$

2.1.2 Cationic ring-opening polymerization (CROP)

Among the cyclic esters, 4-, 6-, and 7- membered rings form polyesters when reacted with cationic catalysts [33]. The cationic ROP involves the formation of a positively charged species which is subsequently attacked by a monomer **(2.6)**. The attack results in a ring-opening of the positively charged species through an S_N2-type process.

$$\tag{2.6}$$
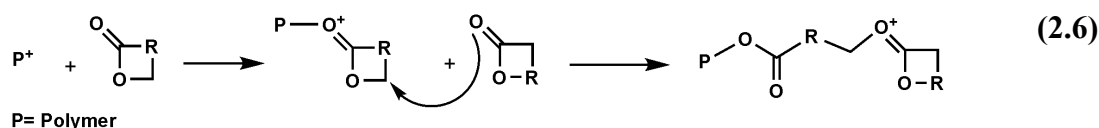
P= Polymer

The cationic polymerization is difficult to control and often only low-molecular weight polymers are formed. When the bulk and solution polymerization of 1,5-dioxepan-2-one (DXO) with cationic initiators were studied, the highest molecular weight achieved was about 10,000. More detailed reviews on cationic ROP have been published by Penczek and coworkers [34, 35].

2.2 Etherification Reaction (Williamson Ether Reaction)

The Williamson reaction, discovered in 1850, is still the best general method for the preparation of unsymmetrical or symmetrical ethers. The normal method involves treatment of the halide with alkoxide or aroxide ion prepared from an alcohol or phenol, although methylation using dimethyl carbonate has been reported. It is also possible to mix the halide and alcohol or phenol directly with Cs_2CO_3 in acetonitrile, or with solid KOH in Me_2SO. The reaction can also be carried out in a dry medium, on zeolite-HY or neat or in solvents using microwave irradiation [36].

$$RX \quad + \quad OR' \quad \longrightarrow \quad ROR' \quad\quad\quad\quad (2.7)$$
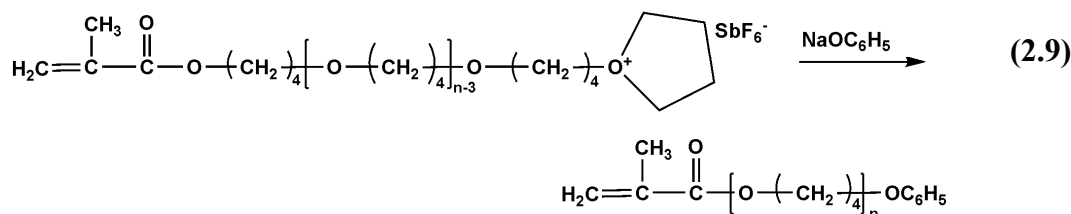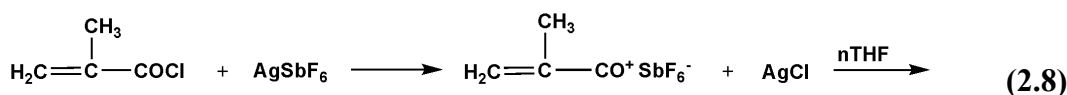
2.3 Macromonomers

Macromolecular monomers, called macromonomers or macromers, can be defined as oligomers or polymers with polymerizable end groups. Such groups may be vinyl, acrylic, or heterocyclic (ring-opening polymerization) or dicarboxylic or dihydroxylic (step-growth polymerization). The increasing interest in these materials stems from the growing need for well-defined graft copolymers for which macromonomers often are an ideal starting material [37, 38]. The length and number of branches of the graft copolymers can be controlled by the molar mass and feed ratio of macromonomers to comonomers.

There are basically three methods for preparing such reactive polymers:

1. On choosing an initiator containing a polymerizable group, macromonomers can be derived provided this reactive group is totally inert toward the active species generated by its carrier.

2. Macromonomers can also be obtained by functionalization of growing chains. Again, it is essential that the end-capping reaction does not involve the polymerizable group.

3. The last route consists in modifying o-functional polymers into macromonomers using post-functionalization methodologies. When chains are grown by free-radical polymerization, it is the easiest way to prepare macromonomers.

For example, telechelics were prepared through the first route from polytetrahydrofuran (PTHF) as illustrated in **(2.8)** and **(2.9)**.

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$$\text{(2.8)}$$

$$\text{(2.9)}$$

Oxiranes also polymerize under similar conditions **(2.10)**.

$$\text{(2.10)}$$
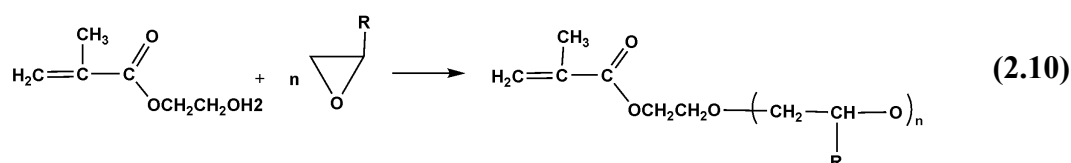
Termination of the cationic ring-opening polymerization of *N-t*-butylaziridine with methacrylic acid yields macromonomers [39], which is the case of functionalization of growing chains through end-capping **(2.11)**.

$$\text{(2.11)}$$
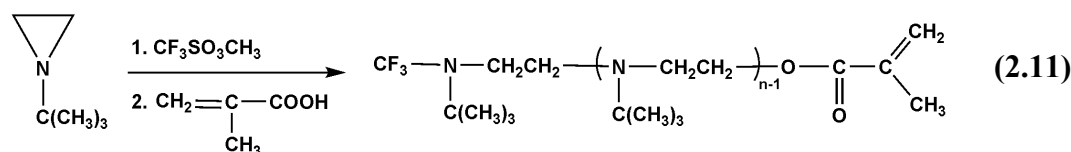
Another example to this type employs radical polymerization in the preparation of macromonomers as shown in **(2.12)** [40].

$$\text{(2.12)}$$
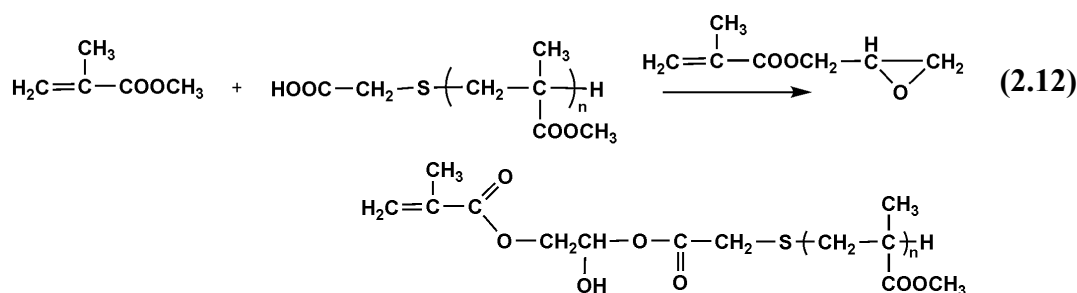
As for macromonomers derived by post-functionalization, an example was described by Haddleton and colleagues [41]. Starting from separately prepared o-bromo PMMA, they obtained o-unsaturated macromonomers on addition of methyl(2-bromomethyl)acrylate (MBrMA), a monomer known to undergo addition–fragmentation.

2.4 Polyphenylenes (PPs)

Polyphenylene (PP), one of the most structurally simple of all the linear, rigid-rod polymers, is arguably one of the potentially most useful engineering materials. Its primary properties include high mechanical strength, excellent thermal and thermal oxidative stability, insolubility in all solvents, intractability, and the ability to conduct electricity upon oxidative or reductive doping. Despite its deceptively simple structure and its unique combination of attractive materials properties, PP has traditionally been a very difficult polymer to synthesize and fabricate. The struggle to find efficient methods for producing PP with both a regioregular linear structure and high molecular weight, together with the inherent lack of processability of the material, have retarded the development of PP as a viable, useful material. Only within the past five to ten years has the problematic synthesis of high molecular weight, structurally regular PP been solved through a number of ingenious strategies. In addition, a number of methods have been recently found to overcome the processing difficulties commonly associated with this polymer. Furthermore, non-traditional roles have also been found for PPs of all qualities in applications far removed from the traditional roles of the polymer as a high-performance structural material and organic conductor [42].

Mechanical properties of fabricated PP were compared to those of commercial polyimide and carbon graphite, and were found to fall between the properties of the two [43]. PP retains toughness over a wide range, but is inherently less tough than polyimide. In high-temperature air-aging studies, property retention was similar to that of polyimide, but the values were lower at the start. It seems that metal-containing impurities, probably mostly copper, accelerate the oxidative degradation of PP. High-temperature hydrolytic stability of the aromatic polymer was excellent, as would be expected.

A curious, unusual phenomenon was observed in the ablation-compaction of PP. When a compacted bar drilled with holes was heated at 590 $^{\circ}$C under hydrogen pressure, the recovered sample resembled the original very closely except that it was substantially smaller in all dimensions, including the holes. The overall reduction could be as much as 80 %. This can be regarded as the chemical counterpart of the aboriginal "shrunken heads". Apparently, as pore volume increases during ablation,

surface area increases, in conflict with thermodynamics which requires minimization of surface area. Contraction occurs in order to minimize the energy. No other polymer tested gave a similar result, suggesting that PP may be unique in this property.

PP is a thermally and thermooxidatively stable material. No significant decomposition occurs below 400 ^{o}C in air and only 7 % of the mass is lost when the polymer is heated in N_2 to 900 ^{o}C at a rate of 150 ^{o}C/h. Thermal loss of H and CH_4 from PP begins about 400 ^{o}C, whereas analogous decomposition of benzene occurs at approximately 600 ^{o}C. The decreased thermal stability of PP relative to benzene was attributed to structural irregularity and presence, in the polymer, of residual impurities such as Cl and O. PP has been reported to have a greater resistance to thermooxidative degradation than benzene and lower PP oligomers. The temperature at which thermal oxidation commenced was determined by defect structures in the polymer. The enhanced stability was attributed to coplanarity of rings, strong intermolecular interactions and high conjugation energy. Thermal and oxidative degradation of PP is a complex process which consists of bond cleavage and formation of a crosslinked carbon char. Upon further heating to 2800 ^{o}C, the char readily graphitizes. PP is also resistant to radiation. The strength of a compressed pellet of the material was essentially un-changed following exposure to 8.95 x 10^8 rads from a Co^{60} source.

Although PPs were first introduced as conducting materials, in recent years the other new applications have gained more importance. However, in order to give information of their initial usage, we would like to present a brief survey on their conductivity.

2.5 Organometallic Coupling

The cross-coupling reaction now accessible via a variety of organometallic reagents may provide a fundamentally common synthetic methodology **(2.13)**.

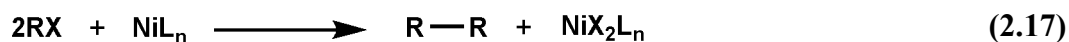$$R-M \ + \ R'-X \ \xrightarrow{\textbf{Pd-catalyst}} \ R-R' \tag{2.13}$$
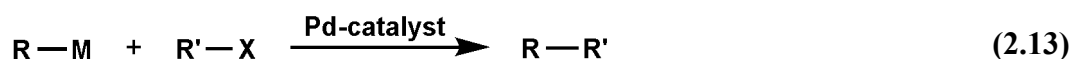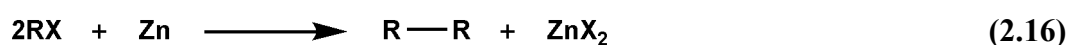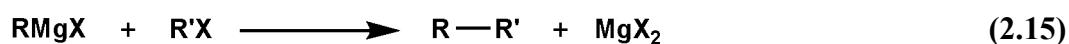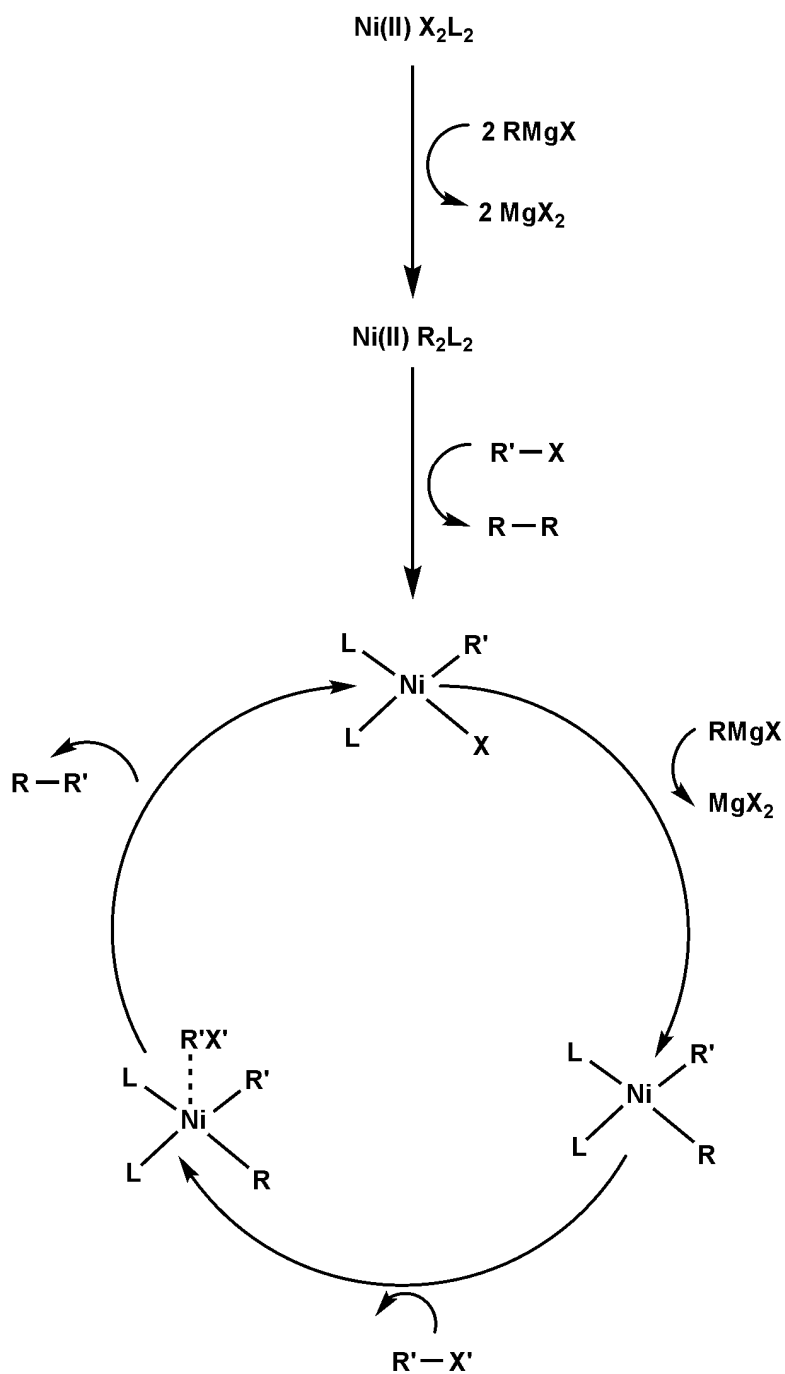
Kumada and Tamao [44] and Corriu [45] reported independently, in 1972, that the reaction of organomagnesium reagents with alkenyl or aryl halides could be markedly catalyzed by Ni(II) complex. Kochi [46]. found the efficiency of Fe(III)

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catalyst for the cross-coupling of Grignard reagents with 1-halo-1-alkenes and Li_2-$CuCl_2$ catalyst for haloalkanes. The palladium-catalyzed reaction of Grignard reagents was first reported by Murahashi [47], the synthetic utility of which was then amply demonstrated by Negishi [48] on the reactions of organoaluminum, zinc, and zirconium reagents. Afterwards, many other organometallic reagents such as organolithiums, organostannans, 1-alkenylcopper(I), have proven to be highly useful as nucleophiles for the cross-coupling reaction [49].

2.5.1 Ni-catalyzed Grignard coupling (Yamamoto Coupling)

Diorganonickel(II) complexes NiR_2L_n (neutral ligand,e.g.,$L=PPh_3$) undergo a reductive coupling reaction to give R-R [50-53] (2.14) and this coupling reaction has been utilized to carry out nickel-catalyzed C-C coupling between Grignard reagent and organic halide **(2.15)** [54] and dehalogenation coupling of organic halides with zinc **(2.16)** [55, 56].

$$L_nNiR_2 \longrightarrow R-R \tag{2.14}$$

$$RMgX + R'X \longrightarrow R-R' + MgX_2 \tag{2.15}$$

$$2RX + Zn \longrightarrow R-R + ZnX_2 \tag{2.16}$$

$$2RX + NiL_n \longrightarrow R-R + NiX_2L_n \tag{2.17}$$

Figure 2.2 : Ni-catalyzed Grignard coupling.

In addition to the coupling reactions expressed by **(2.15)** and **(2.16)**, Ulmann type coupling of organic halides using zerovalent nickel complex **(2.14)** itself as a dehalogenation reagent has been developed.

Among these organonickel-based coupling reactions, **(2.15)** and **(2.16)** have been developed for molecular design of electrically conducting π-conjugated poly(arylene)s **(2.18)** –(Ar)-, e.g., linear PP [57].

$$n \ X \text{---} Ar \text{---} X \ + \ n \ Mg \ \text{(or Zn)} \ \xrightarrow{\text{Ni complex}} \ \left(Ar \right)_n \qquad \text{(2.18)}$$

However, much less attention has been paid [58, 59] to application of coupling reaction **(2.17)** to the synthesis of the conjugated polymer. Since coupling reaction **(2.17)** proceeds under mild conditions, can be applied to a wide range of aromatic compounds (e.g., those with carbonyl and cyano groups) under various reaction conditions (e.g., in various solvents) and is the most direct and simple reaction among the Ni-based coupling reactions, **(2.17)** is expected to provide versitale means for molecular design and synthesis of electrically conducting π-conjugated polymers from haloaromatic compounds X-Ar-X **(2.19)**.

$$n \ X \text{---} Ar \text{---} X \ + \ n \ NiL_m \ \longrightarrow \ \left(Ar \right)_n \ + \ n \ NiX_2L_m \qquad \text{(2.19)}$$
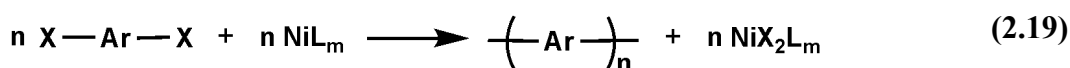
Unlike the established aromatic polyesters or polyamides, where the aromatic units are connected via carboxylic esters or amides and require CO-bond and CN-bond formations to synthesize, the synthesis of poly(arylene)s involves the formation of CC bonds, which is more difficult to achieve [60]. On the basis of a retrosynthetic analysis of PP, it was decided to connect the aromatic units directly to one another. Other possibilities for generating aromatic units sometime during the sequence [61] were considered disadvantageous. Consequently, instead of chain growth, a step-growth procedure had to be developed for which it was known that extremely high conversions per individual bond-formation step were a strict necessity if high molar mass polymer was to be obtained. The CC-bond-formation reaction, therefore, had to be chosen with the greatest care. The second aspect was solubility. From short, linearly (1,4-) connected oligophenylenes, it is known that the solubility already drops to negligibly small values after a few connected benzene rings. The solubility of all-para-linked nonaphenylene, for example, which is just a very short model for PP, is less than 10^{-8} g/L in toluene at room temperature [62]. Yamamoto's route was considered most interesting because it was the only one that guaranteed the straight, 1,4-connection of benzene rings. It is known that the solubility of rigid molecules increases drastically upon substitution with flexible side chains [63-65]. They render the dissolution of the molecules more attractive, mostly for entropic reasons. These considerations led us to believe that a simple decoration of 1,4-dibromobenzene, the Yamamoto monomer, with flexible alkyl chains may open a generally applicable route into PPs. Matthias synthesized 1,4-dibromo-2,5-dihexyl benzene (I) [66],

which turned out to be an extremely valuable compound for other purposes as well [67, 68], and applied the Yamamoto conditions **(2.20)** and **(2.21)**. The result, however, was quite disappointing [69]. Regardless of how he did the reaction and which catalyst precursors he used, exclusively oligomeric products were obtained. The only improvement was the excellent solubility of the oligomers, which enabled him to accurately determine their molar masses and chemical structures. It is determined that the steric hindrance imposed by the alkyl groups might have been responsible for termination at this early stage of growth, a view that was supported some time later by the successful Yamamoto-type synthesis of a sterically nonhindered polyarylene [70].

(2.20)

n=5-15

(2.21)

n=10-15
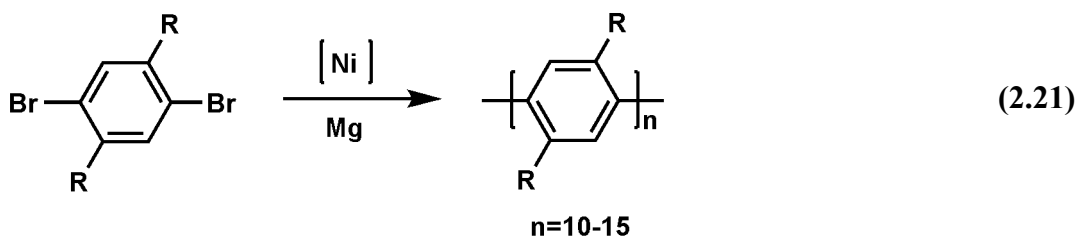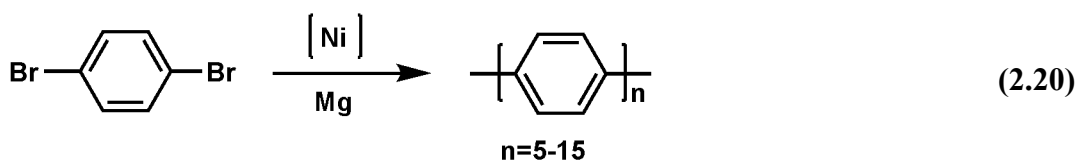
2.5.2 Palladium-catalyzed cross-coupling reactions of organoboron compounds (Suzuki coupling)

The palladium-catalyzed cross-coupling reaction between organoboron compounds and organic halides or triflates provides a powerful and general methodology for the formation of carbon–carbon bonds. Recently, this reaction has been called the Suzuki coupling, Suzuki reaction, or Suzuki–Miyaura coupling. The availability of the reagents and the mild reaction conditions all contribute to the versatility of this reaction. The coupling reaction offers several additional advantages, such as being largely unaffected by the presence of water, tolerating a broad range of functional groups, and proceeding generally regio- and stereoselectively. Moreover, the inorganic by-product of the reaction is non-toxic and easily removed from the reaction mixture thereby making the Suzuki coupling suitable not only for laboratories but also for industrial processes [71].

Organoboron compounds are highly electrophilic, but the organic groups on boron are weakly nucleophilic, thus limiting the use of organoboron reagents for the ionic

reactions. The coordination of a negatively charged base to the boron atom has been recognized to be an efficient method of increasing its nucleophilicity to transfer the organic group on boron to the adjacent positive center (1,2-migration reaction). However, intermolecular transfer reactions such as the Grignard-like reaction are relatively rare. Fortunately, organoboron compounds, even organoboronic acids and esters, have sufficiently enough reactivity for the transmetalation to other metals. In 1978, Negishi reported that iodobenzene selectively couples with the 1-alkynyl group on lithium l-hexynyl(tributy1)borate through a palladium-catalyzed addition-elimination sequence (Heck-type process); however, the cross-coupling reaction of organoboron compounds, which involves the transmetalation to palladium(II) halides as a key step, was found to proceed smoothly when these were activated with suitable bases and have proven to be a quite general technique for a wide range of selective carbon-carbon bond formation [72]. Many organometallic reagents undergo similar cross-coupling reactions, but much attention has recently been focused on the use of organoboronic acids in laboratories and industries since they are convenient reagents, which are generally thermally stable and inert to water and oxygen, thus allow their handling without special precautions.

2.5.2.1 Mechanism of Suzuki coupling reactions

A general catalytic cycle for the cross-coupling reaction of organometallics, which involves oxidative addition-transmetalation-reductive elimination sequences, is depicted in (Figure 2.3). Although each step involves further knotty processes including ligand exchanges, there is no doubt about the presence of those intermediates (1 and 2 in Figure 2.3) which have been characterized by isolation or spectroscopic analyses. It is significant that the great majority of cross-coupling reactions catalyzed by Ni(0), Pd(0), and Fe(I) are rationalized in terms of this common catalytic cycle.
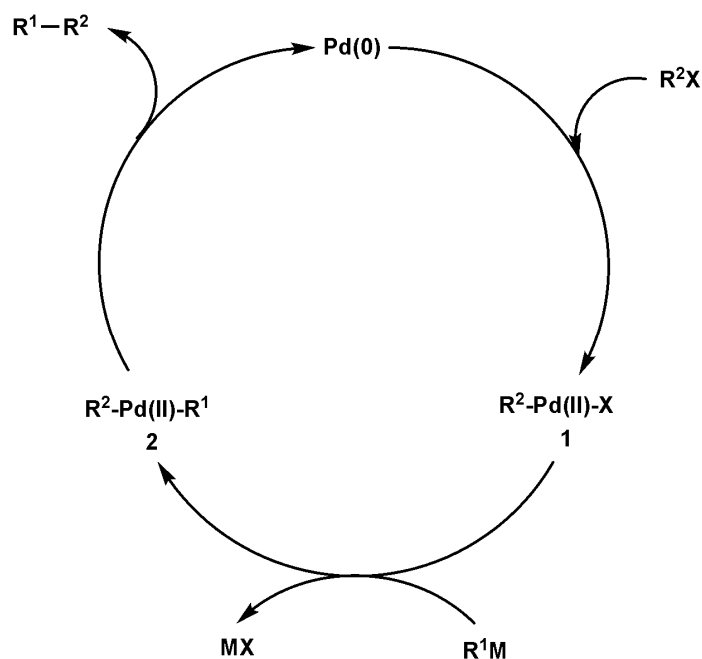
**Figure 2.3 :** A general catalytic cycle for cross-coupling.

Oxidative addition of 1-alkenyl, 1-alkynyl, allyl, benzyl, and aryl halides to a palladium(0) complex affords a stable trans-σ-palladium(II) complex (1). The reaction proceeds with complete retention of configuration for alkenyl halides and with inversion for allylic and benzylic halides. Alkyl halides having β-hydrogen are rarely useful because the oxidative addition step is very slow and may compete with β-hydride elimination from the σ-organopalladium-(II) species. However, it has been recently shown that iodoalkanes undergo the cross-coupling reaction with organoboron compounds [73].

Oxidative addition is often the rate-determining step in a catalytic cycle. The relative reactivity decreases in the order of I > OTf > Br >> Cl. Aryl and 1-alkenyl halides activated by the proximity of electron-withdrawing groups are more reactive to the oxidative addition than those with donating groups, thus allowing the use of chlorides such as 3-chloroenone for the cross-coupling reaction. A very wide range of palladium(0) catalysts or precursors can be used for cross-coupling reaction. $Pd(PPh_3)_4$ is the most commonly used, but $PdCl_2(PPh_3)_2$ and $Pd(OAc)_2$ plus PPh_3 or other phosphine ligands are also efficient since they are stable to air and readily reduced to the active Pd(0) complexes with organometallics or phosphines used for the cross-coupling.

Reductive elimination of organic partners from 2 reproduces the palladium(0) complex. The reaction takes place directly from *cis*-2, and the *trans*-2 reacts after its isomerization to the corresponding *cis*-complex **(2.22)**, **(2.23)** and **(2.24)**. The order of reactivity is diaryl- > (alkyl)aryl- > dipropyl- > diethyl- > dimethylpalladium(II), suggesting participation by the π-orbital of aryl group during the bond formation **(2.22)**.
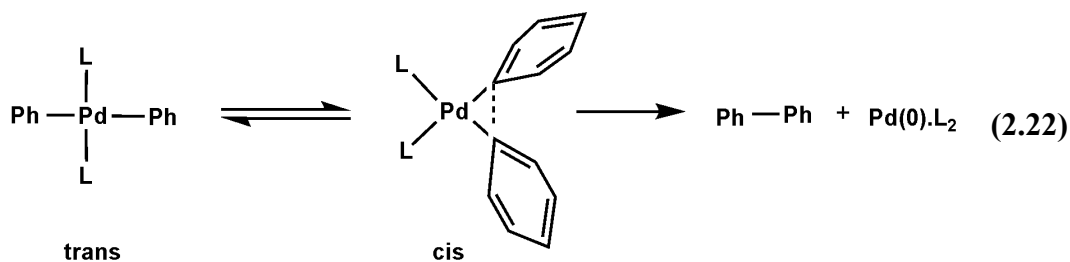
The thermolysis of *cis*-(dialkyl)palladium(II)·L_2, which is an intermediate on the alkyl-alkyl coupling, is inhibited by excess phosphine (L), hence it is considered to be initiated by the rate-determining dissociation of phosphine ligand (L) producing a three-coordinated *cis*-(dialkyl)palladium(II)·L complex (dissociative mechanism, **2.23** and **2.24**). Thus, the effect of phosphine ligands is comparable to the order of ease of their dissociation: dppe << PEt_3 < PEt_2Ph < $PMePh_2$ <. $PEtPh_2$ < PPh_3.
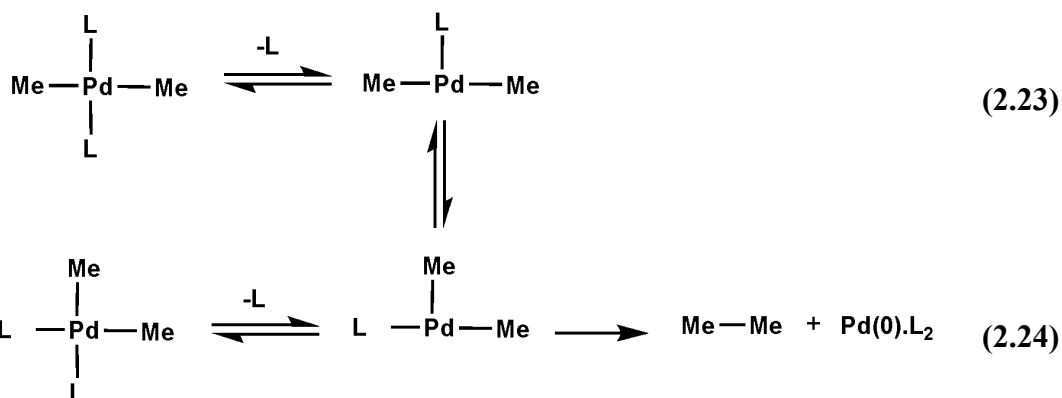
On the other hand, *cis*-alkenyl- and *cis*-arylpalladium(II) complexes, which are intermediates in most of cross-coupling reactions discussed here, directly eliminate organic partners from the four-coordinated complex (nondissociative-nonassociative mechanism, **2.22**).

Although the mechanism of oxidative addition and reductive elimination sequences are reasonably well understood and are presumably fundamentally common processes for all cross-coupling reactions of organometallics, less is known about the

transmetalation step because the mechanism is highly dependent on organometallics or reaction conditions used for the couplings.

The cross-coupling reaction of organoboron compounds with organic halides or triflates selectively reacts in the presence of a negatively charged base, such as sodium or potassium carbonate, phosphate, hydroxide, and alkoxides. The bases can be used as aqueous solution, or as suspension in dioxane or DMF. 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. The transmetalation of organoboron compounds with palladium halides under basic or neutral conditions can be considered to involve the following three processes illustrated by the **(2.25-2.27)**.

$$R'-\overset{|}{\underset{|}{B}}-OR \quad\quad\quad\quad (2.25)$$
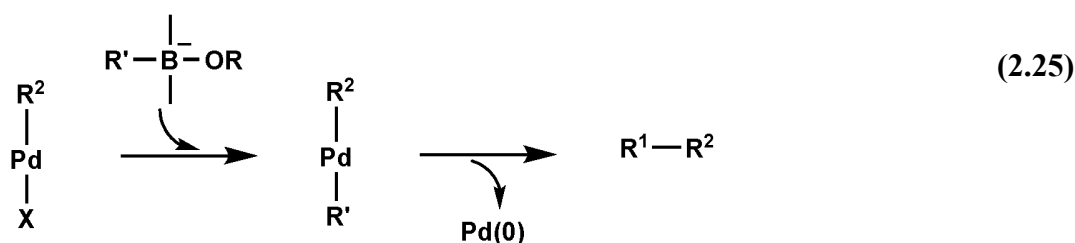
It is apparent that the transmetalation between organopalladium(II) halides and organoboron compounds does not occur readily due to the low nucleophilicity of organic group on boron atom. However, the nucleophilicity of organic group on boron atom can be enhanced by quaternization of the boron with negatively charged bases giving the corresponding "ate" complexes. The quaternization of trialkylboranes accelerates the transmetalation to the palladium(II) halides. Although there is no direct evidence that the boronate anions, such as $RB(OH)_3^-$, are capable of effecting the transmetalation, it is quite reasonable to assume the similar effect of base for the transmetalation of organoboronic acids. The cross-coupling reaction of arylboronic acids with aryl halides at pH = 7-8.5 is retarded relative to the reaction at pH = 9.5-11. The pK_A of phenylboronic acid is 8.8, thus suggesting the formation of the hydroxyboronate anion $[RB(OH)_3^-]$ at pH > pK_A and its transmetalation to the palladium(II) halides.

An alternative transmetalation process is that organoboron compounds readily transfer their organic groups to (alkoxo)-palladium(II) complexes under neutral conditions **(2.26)**.

24

$$(2.26)$$
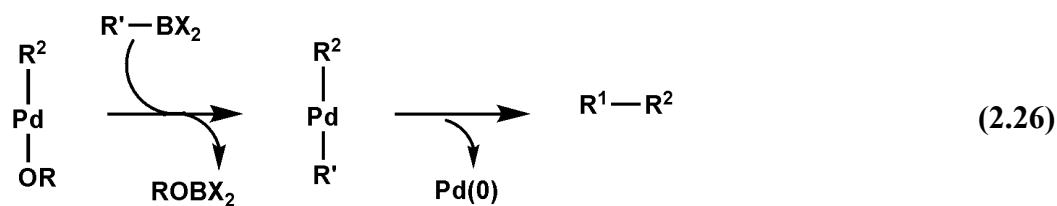
Finally, it is of interest to note the possibility of involvement of the (alkoxo) palladium intermediate 3 in the palladium/base-induced cross-coupling reaction (2.27). It is known that the halogen ligand on organopalladium(II) halide is readily displaced by alkoxy, hydroxy, or acetoxy anion to provide the reactive Pd-OR complexes (3), which have been postulated as reaction intermediates or isolated from the reaction of organopalladium(II) halides with sodium hydroxide or methoxide.

$$(2.27)$$
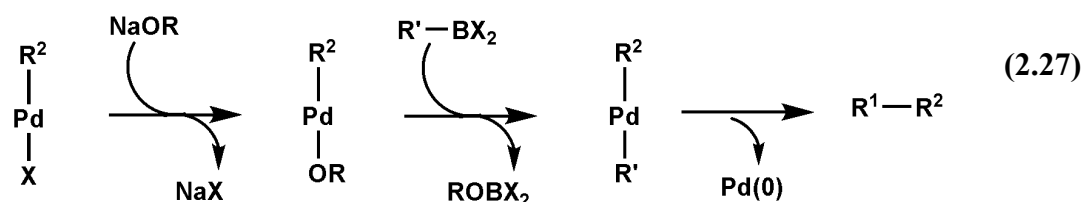
It is not yet obvious in many reactions which process shown in reaction (2.25) or (2.27) is predominant; however, the formation of alkoxo-, hydroxo-, or acetatopalladium(II) intermediate should be considered to be one of the crucial transmetalation processes in the base/palladium-induced cross-coupling reactions.

2.5.2.2 Suzuki polycondensation

AA/BB-approach

$$(2.28)$$

25
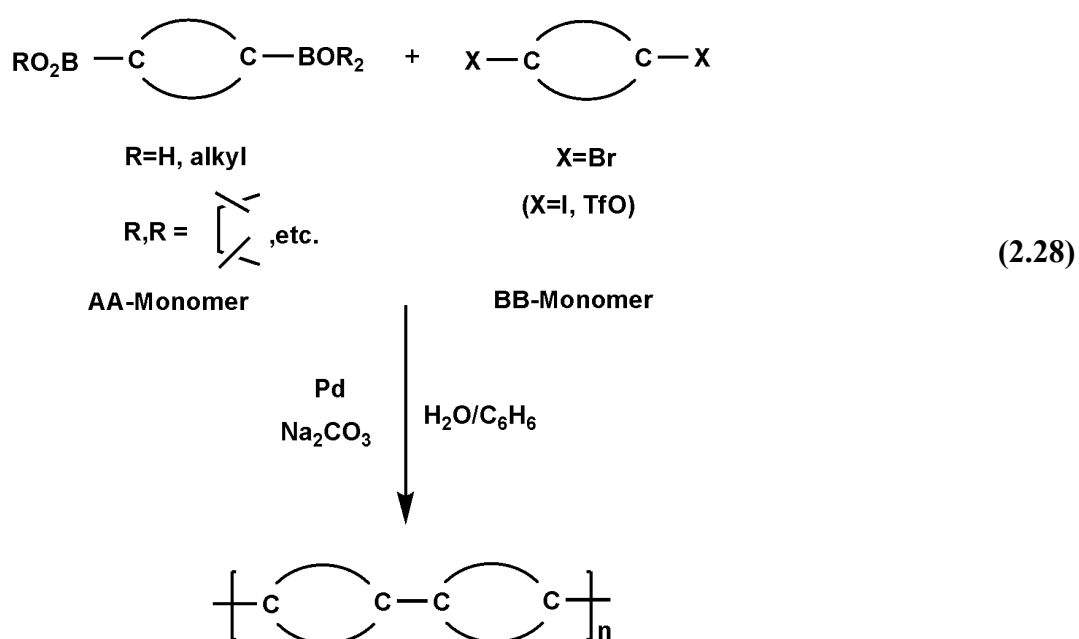
AB-approach

AB-Monomer

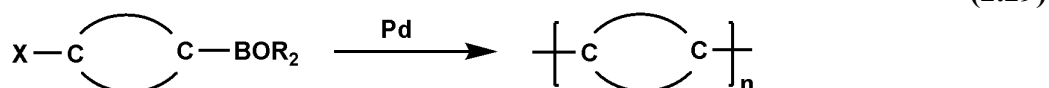Suzuki cross-coupling successfully transferred to Suzuki Polycondensation (SPC) reaction to polymer synthesis and give soluble and processable polyarylenes. SPC is a step-growth polymerization of bifunctional aromatic monomers to poly(arylene)s and related polymers **(2.28)** and **(2.29)** [74-76].

The required functional groups, boronic acid or esters on the one side and bromide, iodide, and so forth on the other, may be present in different monomers (AA/BB approach) or combined in the same monomer (AB approach). Both approaches have been successfully applied. AB-type monomers intrinsically have the stoichiometric balance between the two different functional groups that, according to Carother's equation [77], is a strict necessity in step-growth polymerizations when high molar mass polymer is concerned. There is a simple synthetic reason the AA/BB approach is nevertheless favored. Normally, it is easier to synthesize aromatic monomers with two identical substituents in opposite positions (for benzene, 1,4) than those with different ones. An additional factor is that once an aromatic dibromide is obtained, its conversion into the corresponding diboronic acid or ester can often be achieved in one simple step and on a large scale. The price to be paid for this, however, is the necessity of applying the AA and BB monomers in strictly equal molar amounts. Purities, methods of how to completely transfer mono-mers into the polymerization vessel, and losses of some of the functional groups during polymerization become important and, all of a sudden, even critical aspects when the molar mass difference between two monomers is very large [78]. The matter of purity is of real importance for SPC and should, therefore, be briefly addressed. Free boronic acid or one of the many cyclic boronic esters are used as boron-based functional groups. During polymerization, these esters may hydrolyze to the acids that then enter the normal cross-coupling or follow an independent mechanism [79]. Boronic acids always contain some water. Otherwise, they are partially or completely condensed to cyclic boroxines. This water content has to be precisely determined for the reasons mentioned previously [80]. Boronic esters, which do not have the problem with additional water, tend to partially hydrolyze on the column upon attempted

purification. This renders weighing and, thus, stoichiometry control also somewhat problematical. The boronic monomer counterparts in SPC are aromatic bromides, iodides, or triflates. The bromo group is by far the most often encountered coupling partner in SPC. Iodides [81] and triflates [82] were only seldom used, although iodo compounds may gain increasing attraction because they were recently found to furnish higher molar mass products than their bromo analogues (discussed later). Chloro aromatics, although successfully used in organic chemistry Suzuki Cross-Coupling (SCC) [83] have not been transferred to polymer chemistry yet.

The circles in **(2.28)** and **(2.29)** represent aromatic units, which are substituted benzenes in practically all cases but also include naphthalines, thiophenes, pyridines, and pyrroles (with an acceptor on nitrogen). When substituted with boronic acids, electron-rich aromatics tend to undergo deboronification reactions [84], which lead to stoichiometral misbalance with its detrimental impact on the achievable molar mass. This is why, for example, thiophenes in SPC are always used as dibromides and not as diboronic acids. These aromatic units are connected to one another to linear poly(arylene)s (for benzenes, PPs) in more than 95% of all publicized cases. In a few examples, regularly kinked poly(arylene)s or related conjugated polymers containing additional olefinic or acetylenic units or other functional groups as part of the main chain are generated. Linear poly(arylene)s, whose chemical constitution in principle allows the attainment of a totally straight conformation, are considered rigid-rod type polymers. Although they certainly have bent backbones and attain coiled conformations in solution, they have less conformational degrees of freedom, which are available at low energetic cost than, for example, saturated polymers such as polystyrene (PSt). As a result, these poly(arylene)s show poor solubility because they have little driving force to dissolve *molecularly dispers*.

This is why in most cases when SPC comes into play, it is applied to monomers that carry flexible chains of some sort. These chains help keep the growing (and final) polymer in solution and accessible to further growth until growth reaches its system's intrinsic limits.

These limits comprise termination through reduction of the bromo group or phosphorous incorporation through ligand scrambling channels (discussed later) or the removal of catalytically active Pd complexes through the precipitation of Pd(0) intermediates such as Pd black.

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The substituents on the poly(arylene)s are not only important for solubility (and processability) reasons.

They can also be used to incorporate function, a feature that has been increasingly and astoundingly successfully used in recent years. As far as the electronic properties of the backbones are concerned, substituents may, however, be disadvantageous, too. They normally lead to an increase of the dihedral angle of consecutive aromatic units, which reduces electronic conjugation and thus further increases the polymers' already quite large highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) gap.

As for SCC, SPC involves only the carbon atoms that carry the functional groups. Polymerizations proceed regiospecifically. This is important because some of the properties of poly(arylene)s depend on their backbone's ability to attain straight conformations without kinks. Also, the functional group compatibility of SPC is the same as for SCC. Aldehydes, nitro and cyano groups, sulfonic esters, ethers, various protected alcohols and amines, amides, and so forth can be present. Even free hydroxy and free amines have been reported, although they do not seem to work too well. The reaction conditions are like the ones Suzuki reported in his famous, original article of 1981 [49, 72, 85]. Other solvent systems were also applied whenever required by the solubility of the polymer. For example, SPC has even been done in water with both water-soluble monomers and catalyst precursors [86]. The mechanism of SPC is supposed to involve the same steps of oxidative addition, transmetallation, and reductive elimination as for SCC. The standard catalyst precursor is $Pd(PPh_3)_4$. Although SPC has not yet been developed into a reaction that is catalytic in an industrial sense, 0.5 mol % Pd complex is sufficient in many cases. Pd complexes with other phospine ligands have also been employed. For example, *ortho*- and *para*-tolyl ligands proved successful [87, 88]. Although the choice of the best catalyst precursor is still a matter of intuition, it is accepted knowledge that the complex used should be as pure as possible. Thus, the commercially available $Pd(PPh_3)_4$ should not be used as obtained but rather should be recrystallized and used directly thereafter (under nitrogen). Best results are normally obtained when the Pd complexes are self-prepared and used freshly.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Styrene (%99, Aldrich) : Styrene was purified by usual methods and distilled in vacuum from CaH_2 just before use.

Vinyl acetate (Aldrich) : Vinyl acetate was dried over calcium hydride and distilled under nitrogen.

3.1.2 Solvents

Methanol (Technical) : Methanol was used for the precipitation of polymers without further purification.

Tetrahydrofuran (THF) (99.8%, J.T.Baker) : Predried over magnesium sulfate followed by sodium wire and then distilled from sodium wire and benzophenone immediately before use.

Diethylether (Sigma-Aldrich) : Diethylether was used as recieved.

Dichloromethane (99.8%, J.T.Baker): Dichloromethane was dried with P_2O_5.

Chloroform (Sigma) : Chloroform was used without further purification.

Hexane (Sigma) : Hexane was used without further purification.

Benzene (Sigma) : Benzene was used without further purification.

Carbontetrachloride (J. T. Baker) : Carbontetrachloride was used without further purification.

Petroleum Ether (Sigma) : Petroleum Ether was used without further purificaition.

3.1.3 Other chemicals and reagents

Copper(I) Bromide (CuBr) (98%, Acros) : Copper(I) bromide was used as received.

N, N, N', N", N"–Pentametyldiethylenetriamine (PMDETA) (99%, Aldrich) :

PMDETA was used as a ligand, was distilled before used.

2,5-Dibromotoluene (Aldrich) : It was used as received.

N-Bromomsuccinimide (NBS) (Fluka) : It was used as received.

Benzoyl Peroxide (Aldrich) : It was used as received.

Magnesium Sulfate (Aldrich) : It was used as received.

O-Ethylxanthic Acid Potassium Salt (Aldrich) : It was used as received.

AIBN (Aldrich) : It was used as received.

AgSbF$_6$ (Aldrich) : It was used as received.

PEO (Aldrich) : It was used as received.

Sodium Hydride (Aldrich) : It was used as received.

n-Butyl Lithium (Aldrich) : It was used as received.

Trimethylborate (Aldrich) : It was used as received.

Hydrochloric Acid (HCl) (Sigma-Aldrich) : It was used as received.

1,3-Propanediol (Aldrich) : It was used as received.

2.2'-Bipyridine (bpy) (Aldrich) : It was used as received.

Sodium bicarbonate (NaHCO$_3$) (Aldrich) : It was used as received.

Pd(PPh$_3$)$_4$ (Aldrich) : It was used as received.

3.2 Equipments

3.2.1 ^{1}H Nuclear magnetic resonance spectroscopy (^{1}H-NMR)

^{1}H-NMR spectra of 5–10 % (w/w) solutions in CDCl$_3$ with Si(CH$_3$)$_4$ as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer.

3.2.2 Infrared spectrophotometer (IR)

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

3.2.3 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns (G2000H$_{HR}$, G3000H$_{HR}$ and G4000H$_{HR}$), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456–42,800, 1050–107,000, and 10,200–2,890,000, respectively. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30°C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were calculated with the aid of polystyrene standards.

3.3 Preparation Methods

3.3.1 Preparation of 1,4-diboromo-2-(bromomethyl)benzene

2,5-dibromotoluene, (4.99 g, 20 mmol), NBS (3.92 g, 22 mmol), and benzoyl peroxide (0.1g, 0.4 mmol) was heated under reflux in 20 mL CCl$_4$ under nitrogen for 4 hours. The reaction mixture was filtered to remove succinimide, the succinimide was washed with a supplementary amount of CCl$_4$ and finally with a little quantity of CH$_2$Cl$_2$. 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 silica gel column using diethylether as eluent. Finally, the product was obtained as white crystals after recrystallizing twice from petroleum ether. (Yield: 38%)

3.3.2 General procedure for the ATRP of styrene

A Schlenk tube was charged with CuBr (0.062 g, 43.3 mmol), (PMDETA) (0.075 g, 43.3 mmol), initiator (1,4-diboromo-2-(bromomethyl)Benzene) (0.14 g, 0.433 mmol), and styrene (4.51 g, 43.3 mmol). Three freeze-pump-thaw cycles were performed and the tube was stirred in oil bath at 110 °C for 50 min. After the given time, the mixture was diluted with THF. Then the copper complex was removed out by passing through a neutral alumina column, and THF was removed by rotary evaporation. The mixture was precipitated in methanol and the solid was collected after filtration and dried at room temperature in a vacuum overnight.

3.3.3 General procedure for RAFT agent

1,4-dibromo-2-(bromomethyl)benzene (1,33 g, 4 mmol) was dissolved in chloroform (100 mL) and stirred with 10-fold excess of *O*-ethylxanthic acid potassium salt (6.41 g, 40 mmol) for 3 days. The suspended remaninig sodium (*O*-ethyl) xanthate was filtered off and washed several times with chloroform. After evaporation of the solvent the product was purified using column chromatography on silica gel (hexane:dichloromethane 80/0.5).

3.3.4 General procedure for the RAFT polymerization of VAc

RAFT agent (0.24 g, 0.66 mmol), vinyl acetate (4 g, 46.5 mmol), AIBN (0.02 g, 0.13 mmol) was degassed by three freeze-pump-thaw cycles, sealed under nitrogen, and heated at 60 °C for 4h. The polymerization was stopped by cooling and the polymer was isolated by evaporating off the residual monomer and solvent.

3.3.5 General procedure for the cationic polymerization of THF

The polymerization was carried out under nitrogen atmosphere. 0.4 g of 1,4-dibromo-2-(bromomethyl)benzene (1.22 mmol) and 0.47 g (1.35 mmol) of $AgSbF_6$ were dissolved in 1 mL THF under efficient stirring at 0 °C. After 15 min, 9 mL THF was added as a monomer. The reaction was continued for 15 min. The product was pericipitated in cold methanol/water (3/1) for removing AgBr. Additional purification is passing through a silica gel column using CH_2Cl_2 as eluent. CH_2Cl_2 was removed by rotary evaporation. The mixture was precipitated in methanol and cooled to -30 °C. The prepicipitated polymer was filtered off and dried a vacuo.

3.3.6 General procedure for the etherification reaction (Ar(Br$_2$)-PEO)

Sodiumhydride (97 %) was added to PEG (2 g, 1 mmol) in dry 25 mL of THF (0.0264 g, 1,1 mmol) and the reaction mixture was stirred at 0 °C under nitrogen for 30 min. 1,4-diboromo-2-(bromomethyl)benzene (0.657 g, 2 mmol) in dry 10 mL THF was added portion wise to the solution. The mixture was kept stirring at room temperature for 24h. The solution was extracted with water, and the organic layer was dried over anhydrous $MgSO_4$ and CH_2Cl_2 was removed by rotary evaporation.

The mixture was precipitated in diethyl ether and the solid was collected after filtration and dried at room temperature in a vacuum overnight.

3.3.7 Synthesis of 2-methyl-1,4-phenylenediboronic acid

2,5-Dibromotoluene, (21.8 g, 87 mmol) heated under reflux in 140 mL n-hexane under nitrogen for 2 hours. The solution was allowed to warm to room temperature for 30 min. The reaction mixture was then cooled to $-78\ ^{o}C$, and n-BuLi (96 mL, 238 mmol) was added at that temperature. The solution was stirred 1 hour at 80, and then was allowed to warm to room temperature for 3 hours. After stirring at room temperature for 12 hours, the solution heated to reflux temperature under nitrogen for 2 hours. The solution was allowed to warm to room temperature for 30 min. The reaction mixture was then cooled to $-78\ ^{o}C$, and $B(OCH_3)_3$ (100 mL, 870 mmol) was added. The solution was allowed to warm to room temperature for 3 hours before the reaction was quenched with the addition of 2M HCl. The two phases were separated, and the water phase was extracted with four portions of diethyl ether and then dried over $MgSO_4$ and evaporated to yield the boronic acid as a white solid, which was used without further purification. (Yield: 50%)

3.3.8 Synthesis of bis(1,3-propanediol) ester of 2-methyl-1,4-phenylenediboronic acid

1,3-propanediol (10.5 mL, 144 mmol) and 10.85 g boronic acid in were refluxed in dry benzene (200 mL) for 6 h under nitrogen using a Dean-Stark trap. The reaction mixture were washed several times with water and then dried over $MgSO_4$. The solvent was removed in vacuo to afford a light yellow solid. Recrystallization from hexane (Yield: 18%).

3.3.9 Preparation of 2,2'-(2-bromomethyl)-1,4-phenylene) bis(1,3,2-dioxaborinane)

Bis(1,3-propanediol) ester of 2-methyl-1,4-phenylenediboronic acid (1.8 g, 6.93 mmol) NBS (1.48 g, 8.31 mmol), and benzoyl peroxide (0.03 g, 0.14 mmol) was heated under reflux in 15 mL CCl_4 under nitrogen for 4 hours. The reaction mixture was filtered to remove succinimide, 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 then dried

over MgSO$_4$. The solvent was removed by rotary evaporator. The product was purified by passing through a silica gel column using diethylether as eluent. Finally, the product was obtained as white crystals after recrystallizing twice from diethyl ether . (Yield: 30%)

3.3.10 ATRP of styrene using 2,2'-(2-bromomethyl)-1,4-phenylene) bis(1,3,2-dioxaborinane) as an initiator

A Schlenk tube was charged with CuBr (0.0397g, 0.277 mmol), bpy (0.129 g, 0.831 mmol), initiator (2) (0.09 g, 0.277 mmol), and styrene (4.51 g, 23.8 mmol). Three freeze-pump-thaw cycles were performed and the tube was stirred in oil bath at 110 °C for 50 min. After the given time, the mixture was diluted with THF. Then the copper complex was removed out by passing through a neutral alumina column, and THF was removed by rotary evaporation. The mixture was precipitated in methanol and the solid was collected after filtration and dried at room temperature in a vacuum overnight.

3.3.11 Suzuki coupling of Ar(BO$_2$C$_3$H$_6$)-PSt based macromonomer with Ar(Br$_2$)-PEO based macromonomer

A 100 mL three necks round bottom flask equipped with a condenser, a septum, nitrogen inlet-outlet, and magnetic stirrer, was charged with 20 mL 1M NaHCO$_3$ solution and 30 mL THF. The solvents were previously degassed by bubbling nitrogen over a period of 30 minutes. The mixture was refluxed under nitrogen, 3 hours. A 20 mL three necks round bottom flask equipped in the same way as the previous one was charged under inert atmosphere with 0.25 g (0.028 mmol) PSt, 0.069 g (0.028 mmol) Ar(Br$_2$)- PEO and (0.66 mg 5.74 x 10^{-4} mmol) Pd(PPh$_3$)$_4$, 3 mL of the mixture of solvents were introduced with a syringe through the septum. The reaction was maintained ender vigorously stirring and with the exclusion of oxygen and light at reflux. After 48h a supplementary amount of 5 mL of mixture of solvents was added through the septum and stirred 1 day more. After that the polymer was obtained by prepicipitation in methanol.

4. RESULTS AND DISCUSSION

In this study, amphiphilic PP was synthesized via the Suzuki type polycondesation. The synthetic strategy followed involves several steps. Firstly, different types of new macromonomers were synthesized by using controlled polymerization methods. Among these macromonomers, the $Ar(Br_2)$-PEO macromonomer and boronic ester type macromonomer of polystyrene were reacted via Suzuki polycondensation reaction in the presence of $Pd(PPh_3)_4$ as catalyst to form the desired amphiphilic copolymer. The various steps of the procedure will be described below.

4.1 Synthesis of Designing Macromonomer

Different types of new macromonomers were synthesized by using the below-mentioned initiator (1,4-dibromo-2-(bromomethyl)benzene), (2) **(4.1)** in controlled polymerization of common monomers such as styrene, vinylacetate, tetrahydrofuran and the commercially available monohydroxy poly(ethylene oxide) was directly used in the etherification reaction. Well-defined macromonomers with low molecular weights and narrow polydispersities, preserving the functionalities needed for PP formation, were obtained. The details of each macromonomer synthesis were described below.

4.1.1 Preparation of dual-functional initiator for ATRP

It is well established that benzylbromides are efficient initiators for ATRP. On the other hand, arylhalides does not initiate ATRP. In fact, this behavior is an advantage to obtain the polymers with bromine functional groups directly attached to the benzene ring. Obivously, these groups are the crucial reactive sites for the subsequent Suzuki coupling. (2) was synthesized by bromination of methyl groups of commercially available 2,5-dibromotoluene (1) with NBS in CCl_4 **(4.1)**.

(4.1)
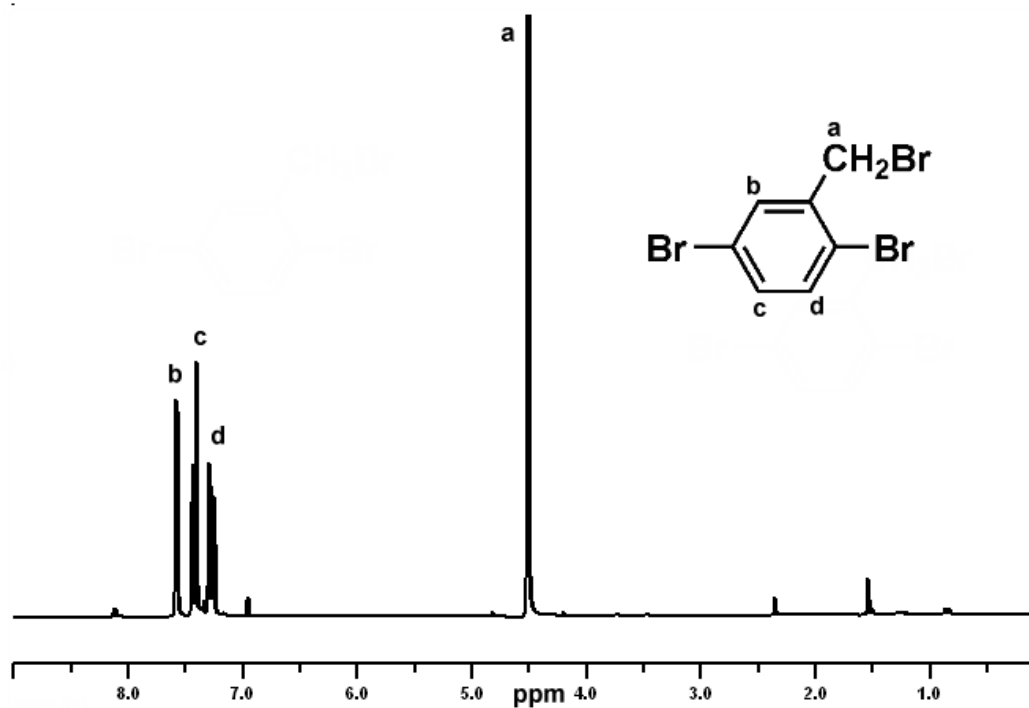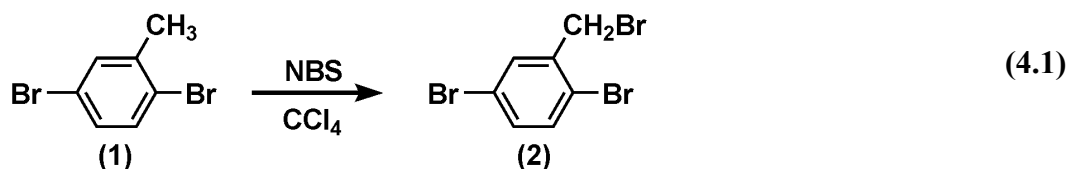
Figure 4.1 : ^{1}H-NMR (CDCl$_3$) spectrum of initiator (2).

The structure of the initiator was confirmed by ^{1}H-NMR analysis. As can be seen from Figure 4.1, the ^{1}H NMR (CDCl$_3$) spectrum of (2) contains characteristic bands of CH$_2$ and aromatic protons at 4.51 ppm and 7.25-7.58 ppm, respectively.

4.1.2 Preparation of PSt macromonomer by ATRP

The ATRP of Styrene using (2) as initiator and the CuBr/PMDETA catalytic system provided precursor polymers (3), containing dibromo-substituted benzene group at one end (4.2).

Br + n styrene → PMDETA , CuBr, 110 °C → (3) (4.2)

(2)
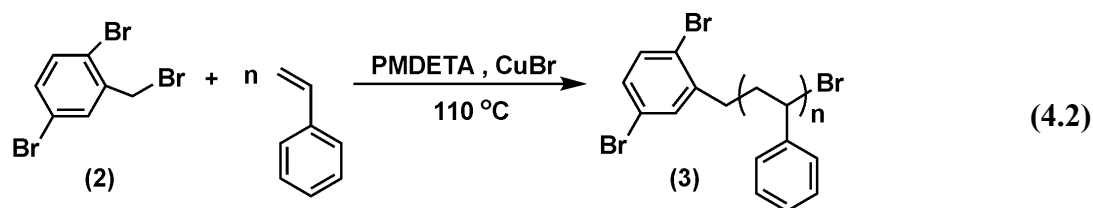
As these polymer was intended to be used in further polymerization reactions, the efforts were directed toward obtaining a low molecular weight and low polydispersity along with a convenient yield. Some conditions and results of the ATRP experiments for styrene are given in Table 4.1.

Table 4.1 : Results of ATRP of styrene by using 1,4-dibromo-2-(bromomethyl) (2) benzene as an initiator.

Macromonomers	Conversion (%)	Time (min)	M_{ntheo} (g/mol)	M_{nNMR}[b] (g/mol)	M_{nGPC}[c] (g/mol)	$M_{\text{w}}/M_{\text{n}}$[c]
PSt-1[a]	6.5	50	1000	1700	2100	1.26
PSt-2	24	60	2816	3100	2690	1.12

Polymerization conditions; $[M]_0/[CuBr]_o / [L]_o = 100/1/1$ in toluene at 110 °C. PMDETA used as a ligand.
[a] Bulk.
[b] Determined by ^{1}H-NMR spectra.
[c] Determined by GPC based on polystyrene standards.

As can be seen from Table 4.1, (2) is effective initiator for ATRP of styrene and the theoretical molecular weights ($M_{\text{n,th}}$), calculated with equation **(2)**, fit with the measured ones very well:

$$\overline{M}_{\text{n,th}} = \frac{[M_0]}{[I_0]}(M_W)\,(\text{conversion}) + M_I \qquad (2)$$

Where $[M_0]$ and $[I_0]$ are the initial molar concentrations of the monomer and initiator, and M_w and M_I are the molecular weights of the monomer and initiator, respectively.

Due to the low molecular weights of the polymer, the results could be verified by ^{1}H-NMR analyses (Figure 4.2). The peak from the final CH-Br protons appears very clear at about 4.4 ppm. The molecular weights of the polymers were also calculated by ^{1}H-NMR spectra and the results were consisted with theoretical and GPC measured molecular weight.
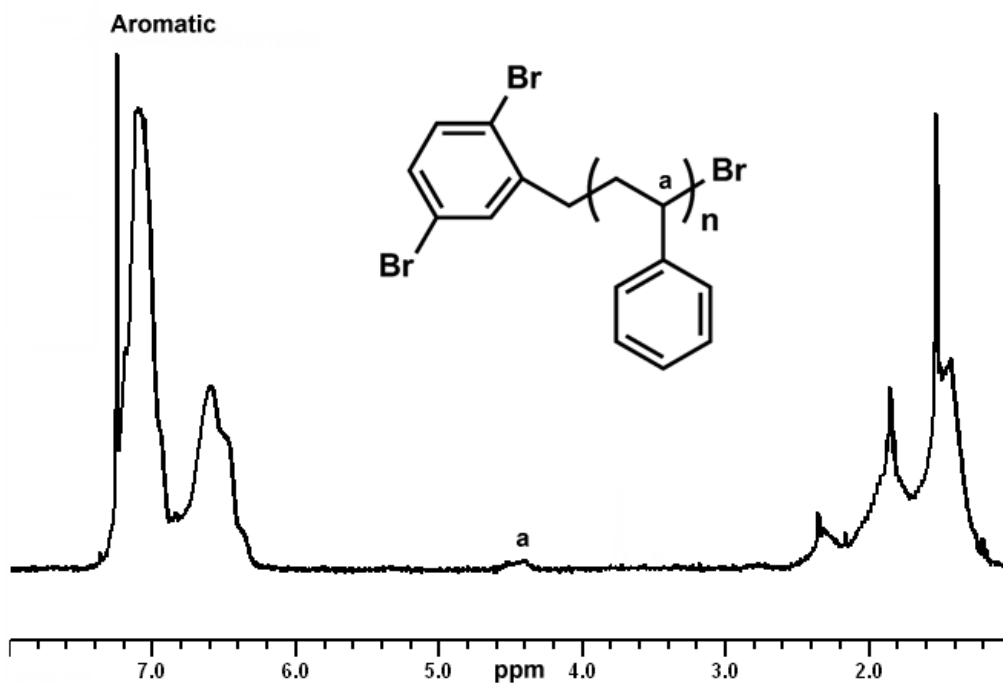
Figure 4.2 : ^{1}H-NMR (CDCl$_3$) spectrum of macromonomer (3).

4.1.3 Preparation of dibromo-xanthate agent

Xanthates are good transfer agents to mediate the radical polymerization of VAc. Therefore, xanthate derivative (4) was prepared in two steps by conventional substitution reactions, from the commercially available 2,5-dibromotoluene **(4.3)**. These xanthate agent was intended to be used in further polymerization reaction.


(4.3)
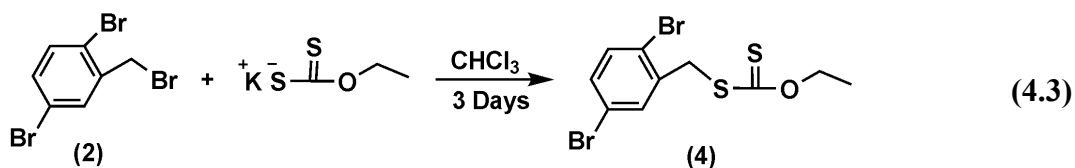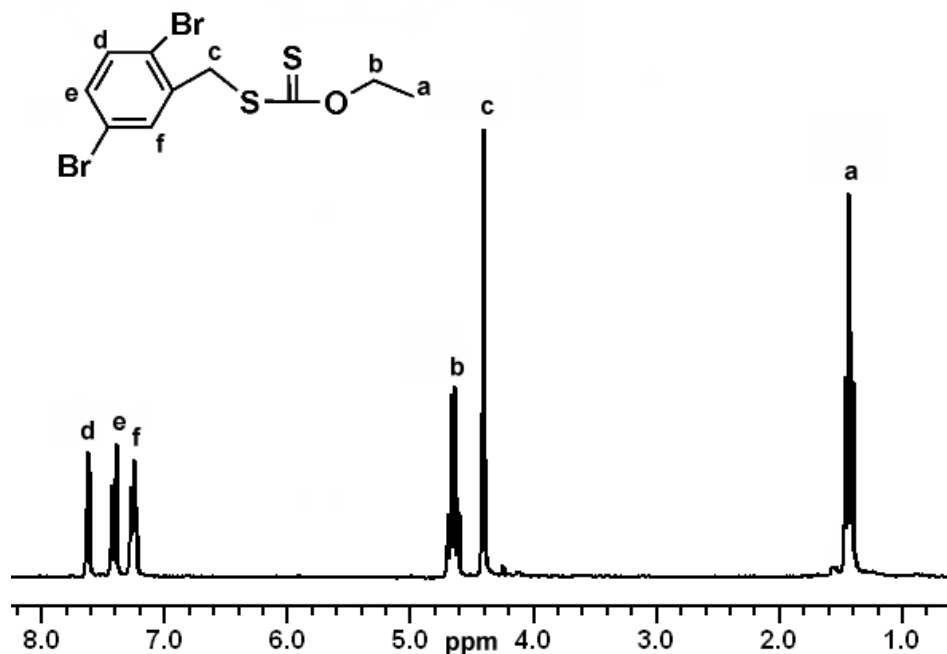
Figure 4.3 : ^{1}H-NMR (CDCl$_3$) spectrum of RAFT agent (4).

The structure of RAFT agent (4) was confirmed by spectral analysis. ^{1}H-NMR (CDCl$_3$) spectrum of (4) exhibits the signals at 7.23-7.63 ppm, 1.42 ppm, 4.41 ppm and 4.7 ppm corresponding to the aromatic protons, methyl protons, methylene protons and methylene sulfur, respectively.

4.1.4 Preparation of PVAc macromonomer by RAFT

(4) was used to polymerization of VAc. RAFT polymerization of vinyl acetate was subsequently carried out in bulk at 60 °C in the presence of mediating (4) **(4.4)**.
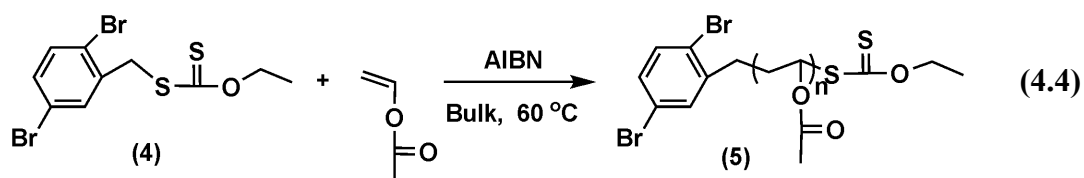

Typical results were summarized in Table 4.2. Low polydispersity and molecular weights PVAc were obtained.

Table 4.2 : Results of RAFT polymerization of VAc.

Macromonomers	Conversion (%)	Time (h)	M_{ntheo} (g/mol)	M_{nNMR} [b] (g/mol)	M_{nGPC} [c] (g/mol)	M_w/M_n [c]
PVAc-1	82	45	5250	3300	5400	1.14
PVAc-2	95	40	5725	3440	5750	1.11

[b] Determined by ^{1}H-NMR spectra.
[c] Determined by GPC based on polystyrene standards.
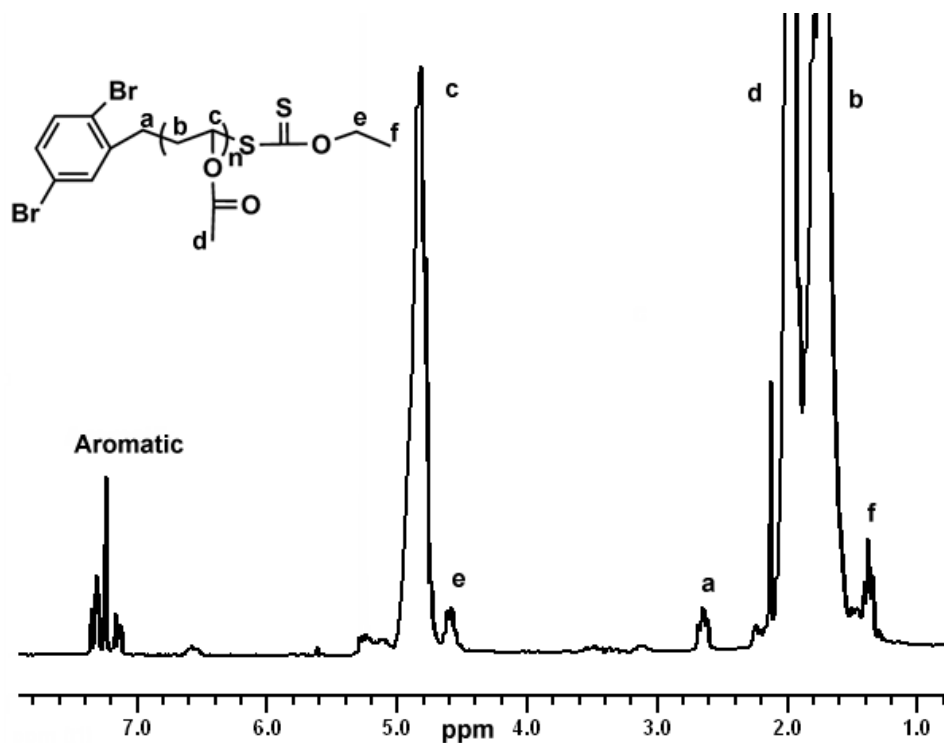

Figure 4.4 : ^{1}H-NMR (CDCl₃) spectra of macromonomer by RAFT polymerization (5).

The structure of PVAc was confirmed by ^{1}H-NMR (CDCl₃) analysis. The characteristic backbone proton (c) of PVAc as observed at 4.8 ppm. Other PVAc protons, (COCH₃) (d) and (CHCH₂) (b) were located at 1.9 and 1.7 ppm, respectively. (CH₂CH)(a) , (CH₂CH₃) (e), and (CH₂CH₃) (f) protons which come from RAFT agent were appeared 2.6, 4.6 and 1.41 ppm, respectively. Moreover, the aromatic protons of central benzene ring from 7.13 at 7.35 ppm can be seen very clearly.

4.1.5 Preparation of PTHF macromonomer by CROP

THF is a cyclic monomer which undergoes CRP with various initiators. For our convenience, we used (2), as an initiator in combination with $AgPF_6$ **(4.5)**. The silver salt reacts only with the benzylic bromide and thus forms corresponding carbocations capable of initiating cationic polymerization of THF. It is expected that the aromatic bromides preserved in the polymerization and can successfully be used in the following Suzuki step. The results of polymerization and ^{1}H-NMR spectral characterization are shown in Table 4.3 and Figure 4.5, respectively. The relatively, higher molecular weight values obtained with GPC may be due to the high solubility of the low molecular weight polymers under precipitation conditions. However, relatively low polydispersity was attained.
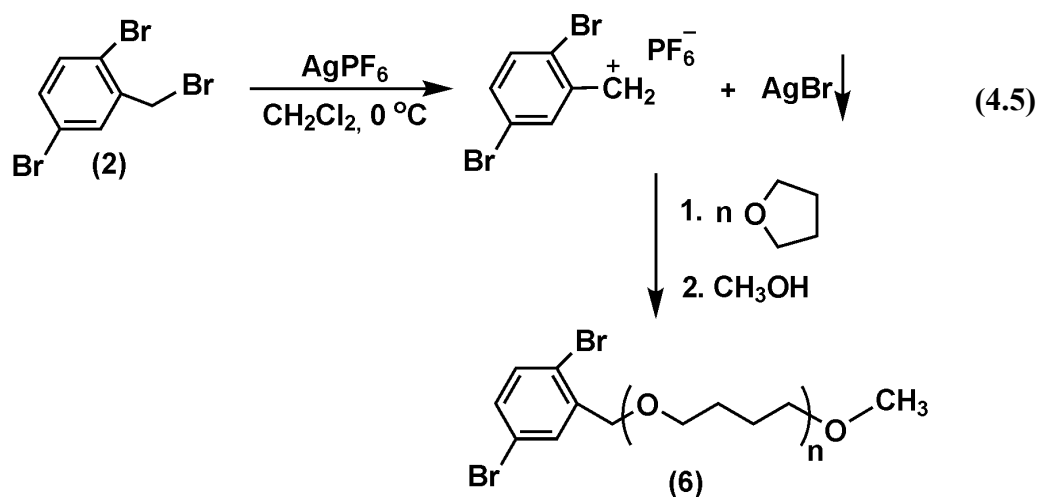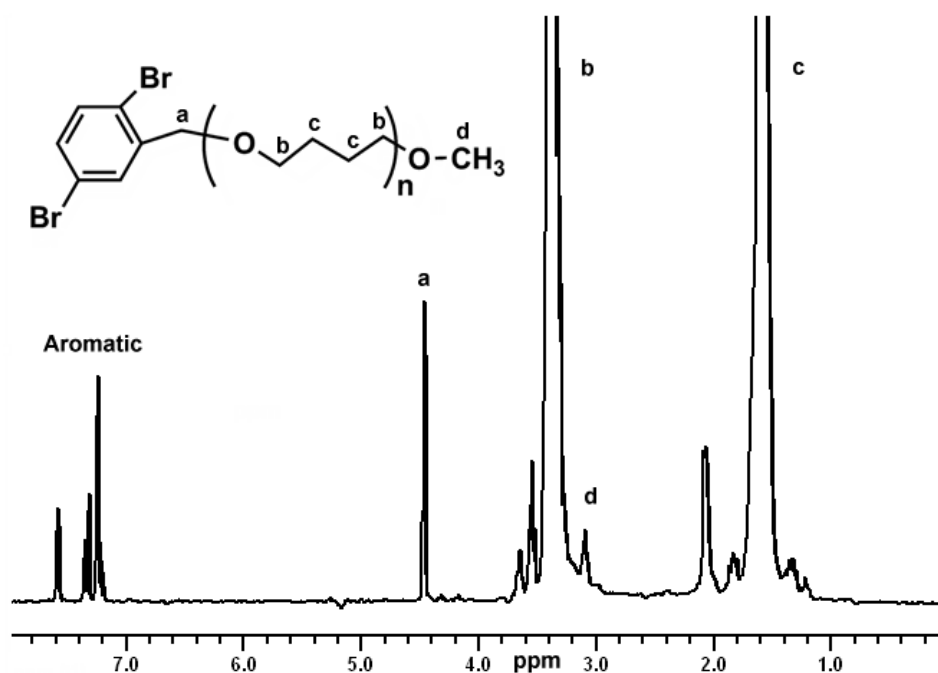

Table 4.3 : Result of ROP of THF by using 1,4-dibromo-2-(bromomethyl) benzene (2) as an initiator.

Macromonomer	Conversion (%)	Time (min)	M_{ntheo} (g/mol)	M_{nNMR}[b] (g/mol)	M_{nGPC}[c] (g/mol)	M_w/M_n[c]
PTHF (6)	11	15	1100	2300	3600	1.32

[b] Determined by ^{1}H-NMR spectra.
[c] Determined by GPC based on polystyrene standards.

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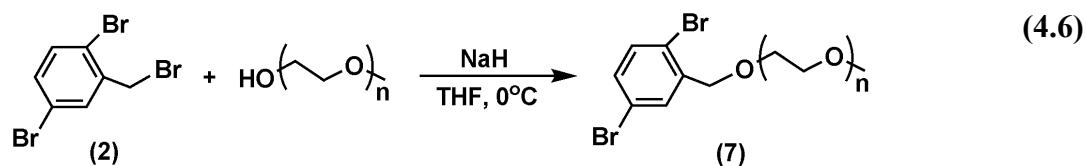
Figure 4.5 : ^{1}H-NMR (CDCl$_3$) spectrum of macromonomer by CROP (6).

The structure of the macromonomer was confirmed by ^{1}H-NMR (CDCl$_3$) . As can be seen from Figure 4.5, ^{1}H-NMR (CDCl$_3$) spectrum of (2) contains characteristic bands contains at 1.58 ppm (CH$_2$), 3.37 ppm (O-CH$_2$) and the aromatic protons of central benzene ring at 7.35 ppm. Due to the implied mechanism, the aromatic CH$_2$ groups are in the vicinity of O atoms of the first THF repeating unit and the corresponding protons give a clear signal at 4.46 ppm. As the reaction was stopped by adding CH$_3$OH, the final OCH$_3$ protons appear as a signal at 3.1 ppm.

4.1.6 Preparation of Ar(Br$_2$)-PEO macromonomer by etherification reaction

(2) was used as the reactive component in etherification reaction of PEO, in combination with NaH **(4.6)**. At the end of the reaction, the aromatic bromide groups are expected to remain for the Suzuki coupling step. As can be seen from Table 4.4, the molecular weight of the polymer was slightly increased by the etherification reaction. The observed increase is due the incorporation of the aromatic group at the chain end. The polydispersity remained unchanged indicating that there was no degradation or coupling during the etherification reaction.
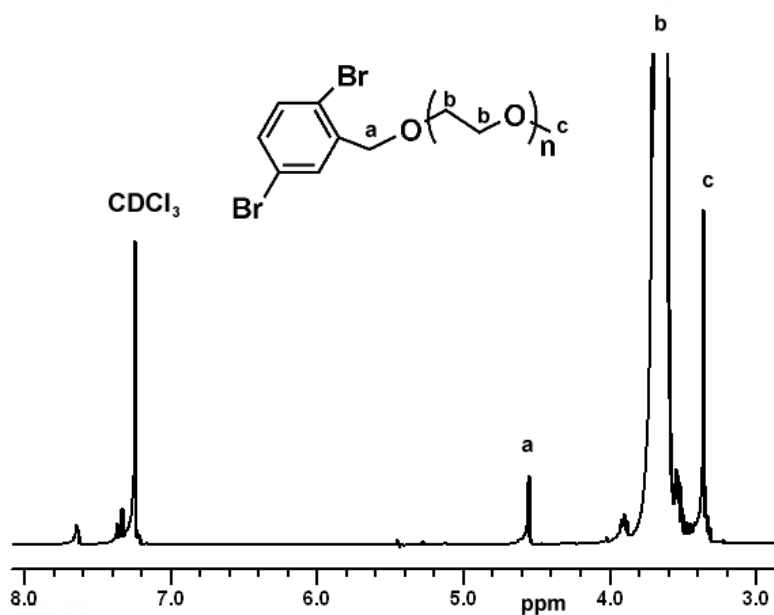
(4.6)

Table 4.4 : Preperation of Ar(Br$_2$)-PEO (7) macromonomer.

Macromonomer	$M_w{}^a$ (g/mol)	$M_n{}^a$ (g/mol)	$M_w/M_n{}^a$
PEO-OH	2280	2200	1.03
Ar(Br$_2$)- PEO	2470	2400	1.03

[a] Determined by GPC based on polystyrene standards

**Figure 4.6 :** ^{1}H-NMR (CDCl$_3$) spectrum of macromonomer by etherification reaction (7).

The structure of the macromonomer was confirmed by ^{1}H-NMR (CDCl$_3$). As can be seen from Figure 4.6, ^{1}H-NMR (CDCl$_3$) spectrum of (7) contains characteristic bands contains at 3.34 ppm (CH$_3$), 3.70 ppm (O-CH$_2$CH$_2$-O), and the aromatic protons of central benzene ring at 7.24-7.64 ppm. Due to the implied mechanism, the

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aromatic-CH_2 groups are in the vicinity of O atoms of the first PEO repeating unit and the corresponding protons give a clear signal at 4.55 ppm.

4.1.7 Preparation of 2-methyl-1,4-phenylenediboronic acid

2-methyl-1,4-phenylenediboronic acid (8) was synthesized from 2,5-dibromotoluene by using *n*-BuLi followed by reaction with trimethylborate at -78 $^{\circ}$C and acidic working **(4.7)**.

(4.7)
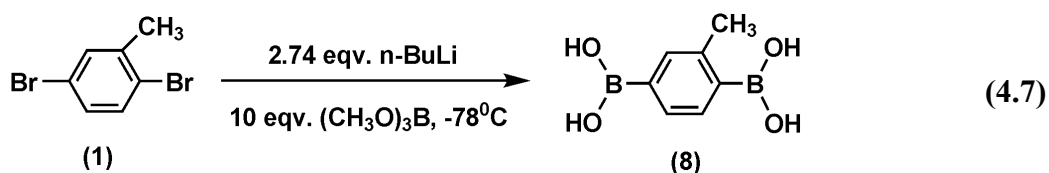
4.1.8 Preparation of bis(boronic ester) for esterification reaction

Refluxing of (8) with 1,3-propanediol using a Dean-Stark trap afforded bis(boronic ester) (9) **(4.8)**. The esterification reaction of the diboronic acid was made for solubility reasons, as compound (8) is not soluble in CCl_4, the apporiate solvent for bromination of methyl groups with NBS.

(4.8)
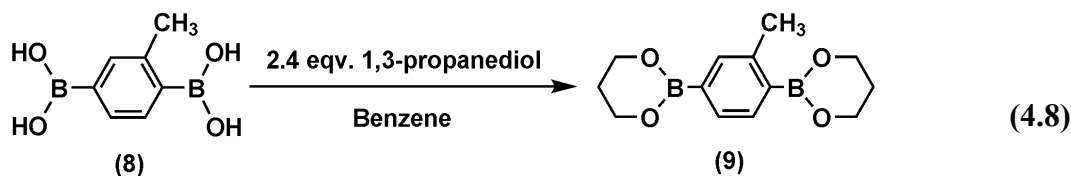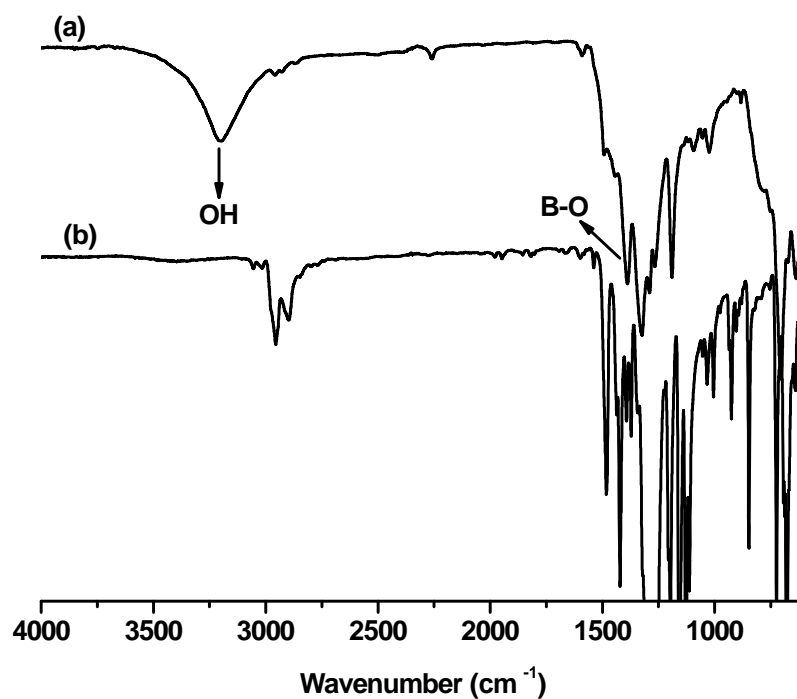
Figure 4.7 : IR spectra of boronic acid (a) and boronic ester (b).

The IR spectra of boronic acid and boronic ester are given in Figure 4.7. The peak from 3200 cm^{-1} attributed to –OH stretch from spectra of boronic acid is not present in that of boronic ester (Figure 4.7b). As can be seen from Figure 4.7a, in addition to the band corresponding to the B-O stretching band at 1390 cm^{-1} from boronic acid was noted.
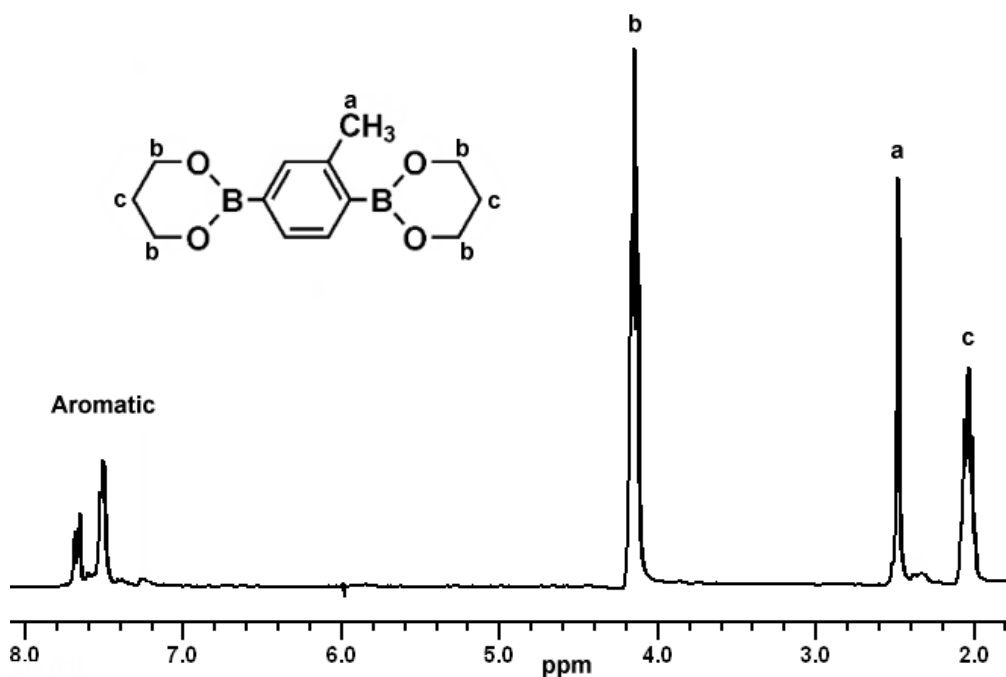
Figure 4.8 : ^{1}H-NMR (CDCl$_3$) spectrum of boronic ester (9).

The structure of Boronic ester agent was confirmed by spectral analysis. ^{1}H-NMR (CDCl$_3$) spectrum of (9) exhibits the signals at 4.2 and 2.0 ppm corresponds to methylene protons of ester group. The aromatic protons of compound 9 was observed at 7.25-7.68 ppm. 2.4 ppm corresponding to the methyl protons were also noted.

4.1.9 Preparation of monofunctional initiator for ATRP

Benzene-2-bromomethyl-1,4-bis(boronic acid propanediol diester) (10) was synthesized by bromination of methyl groups of bis(boronic ester) (9) with NBS in CCl$_4$ **(4.9)**. These initiaor was intended to be used in further polymerization reaction. Intermediate (10) has a pair CH$_2$Br groups and is expected to be effective as a monofunctional initiator in ATRP.


(4.9)

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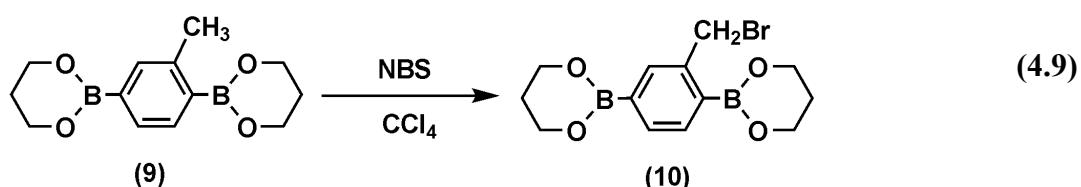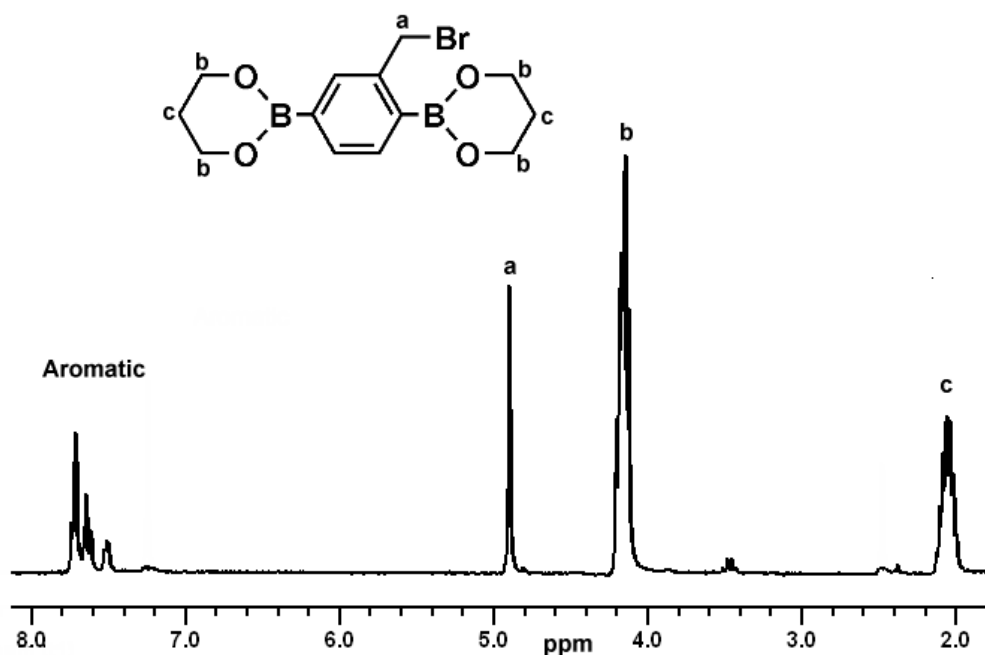
Figure 4.9 : ^{1}H-NMR (CDCl$_3$) spectrum of monofunctional initiator (10).

The structure of boronic ester agent was confirmed by ^{1}H-NMR (CDCl$_3$) spectral analysis. The shifting of the peak from 2.4 ppm (a protons in Figure 4.8) to 4.8 ppm (a proton in Figure 4.9) is a clear indication of bromination. The aromatic protons of 10 appeared at 7.25-7.73 ppm. Notably, methylene protons (c) adjacent to ester linkage were disapered at 2.0 ppm.

4.1.10 Preparation of PSt macromonomer by ATRP

(10) has a pair of CH$_2$Br groups and is expected to be effective as a monofunctional initiator in ATRP. Moreover, boronic ester functionalities, useful for Suzuki coupling in combination with Ar(Br$_2$)-PEO macromonomer are present in this structure. The ATRP using the CuBr/bpy catalytic system provide a precursor polymer with a central benzene group substituted with macromolecular chain of styrene and preserving also the two ester boronic functionalities **(4.10)**. As the functionalized Ar(BO$_2$C$_3$H$_6$)-PSt was intended to be used in a further polymerization reaction. The result of polymerization is shown in Table 4.5. The relatively, higher molecular weight values obtained with GPC may be due to expected boronic ester functionality cannot observe from ^{1}H-NMR (CDCl$_3$). However, relatively low polydispersity was attained.

$$(4.10)$$
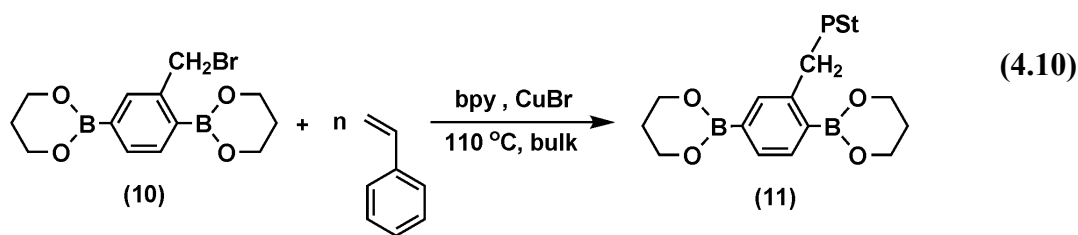
Table 4.5 : Result of ATRP of styrene by using benzene-2-bromomethyl-1,4-bis(boronic acid propanediol diester) (10) as an initiator.

Macromonomer	Conversion (%)	Time (min)	M_{ntheo} (g/mol)	M_{nNMR}[b] (g/mol)	M_{nGPC}[c] (g/mol)	$M_{\text{w}}/M_{\text{n}}$[c]
Ar(BO$_2$C$_3$H$_6$)-PSt (11)	32	50	3200	8250	9150	1.4

Polymerization conditions; [M]$_0$/[CuBr]$_o$ / [L]$_o$ = 86/1/3 at 110 ^{o}C. bipyridine used as a ligand.
[a] Bulk
[b] Determined by ^{1}H -NMR spectra.
[c] Determined by GPC based on polystyrene standards.

4.1.11 Preparation of PP by Suzuki polycondensation

Hydrophilic Ar(Br$_2$)-PEO type macromonomer (7) and hydrophobic Ar(BO$_2$C$_3$H$_6$)-PSt (11) type macromonomer were reacted via for Suzuki-type polycondensation in the presence Pd(PPh$_3$)$_4$ as catalyst to form desired amphiphilic copolymer **(4.11)**.

$$(4.11)$$
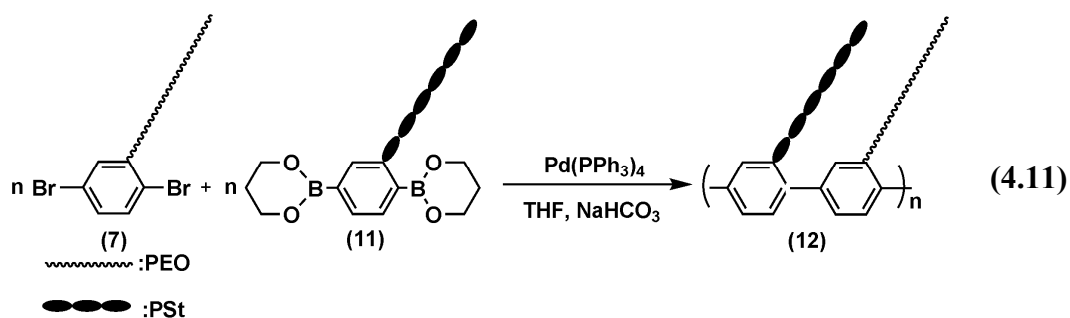
Table 4.6 : Result of polyphenylene by Suzuki polycondensation using (7) and (11) as macromonomers.

Macromonomer	Macromonomer	Method of Polymerization	M_{nGPC} (g/mol)	$M_{\text{w}}/M_{\text{n}}$
Ar(BO$_2$C$_3$H$_6$)-PSt (11)	Ar(Br$_2$)-PEO (7)	Suzuki	32400	2.28

The structure of PP (12), carrying $Ar(BO_2C_3H_6)$-PSt and $Ar(Br_2)$-PEO, was investigated by ^{1}H-NMR, GPC analysis, FT-IR, UV and fluorescenece.
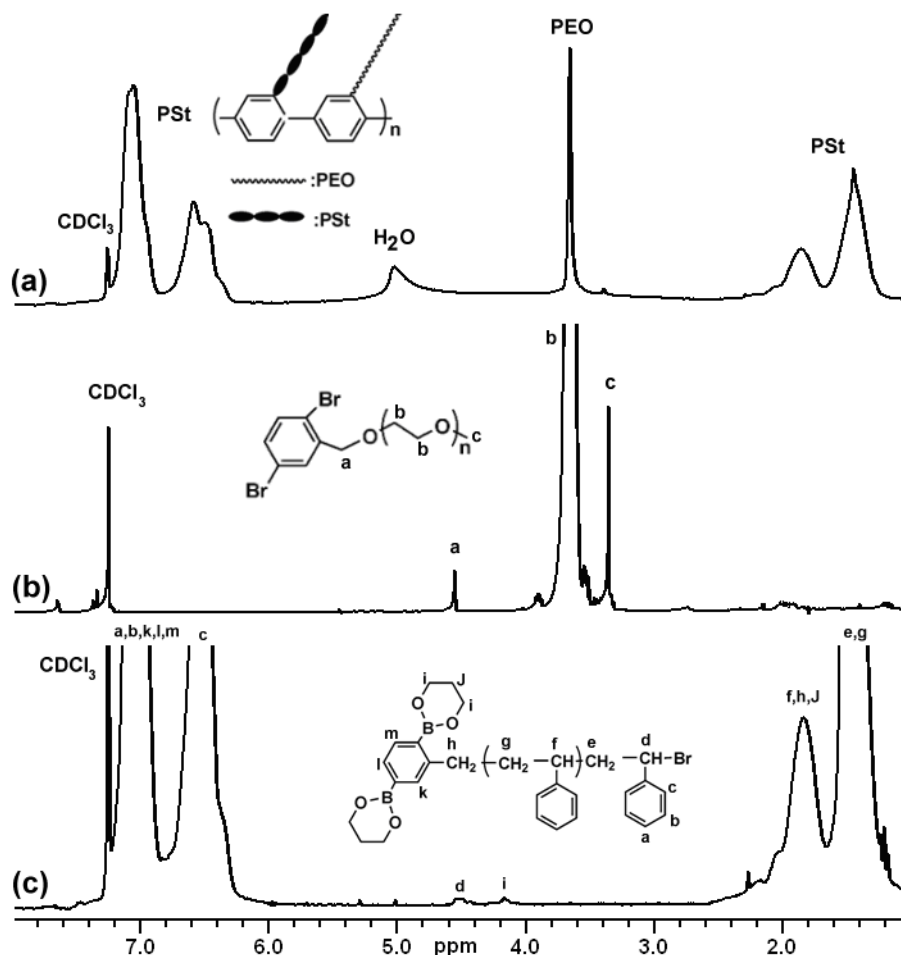
Figure 4.10 : ^{1}H-NMR (CDCl$_3$) spectra of functionalized $Ar(BO_2C_3H_6)$-PSt (11) and $Ar(Br_2)$-PEO (7) and finalcopolymer (12).

Figure 4.10 shows ^{1}H-NMR spectra of PP and its precursors $Ar(BO_2C_3H_6)$-PSt (11) and $Ar(Br_2)$-PEO (7). Even if the protons of the backbone of PP (12) appear together with aromatic PSt ones in the ^{1}H-NMR (CDCl$_3$) spectrum in Figure 4.10a, by comparing with that of precursor polymer (7) (Figure 4.10b), one can observe the disappearance of the boronic ester functionality (protons i), due to its consuming in Suzuki reaction.

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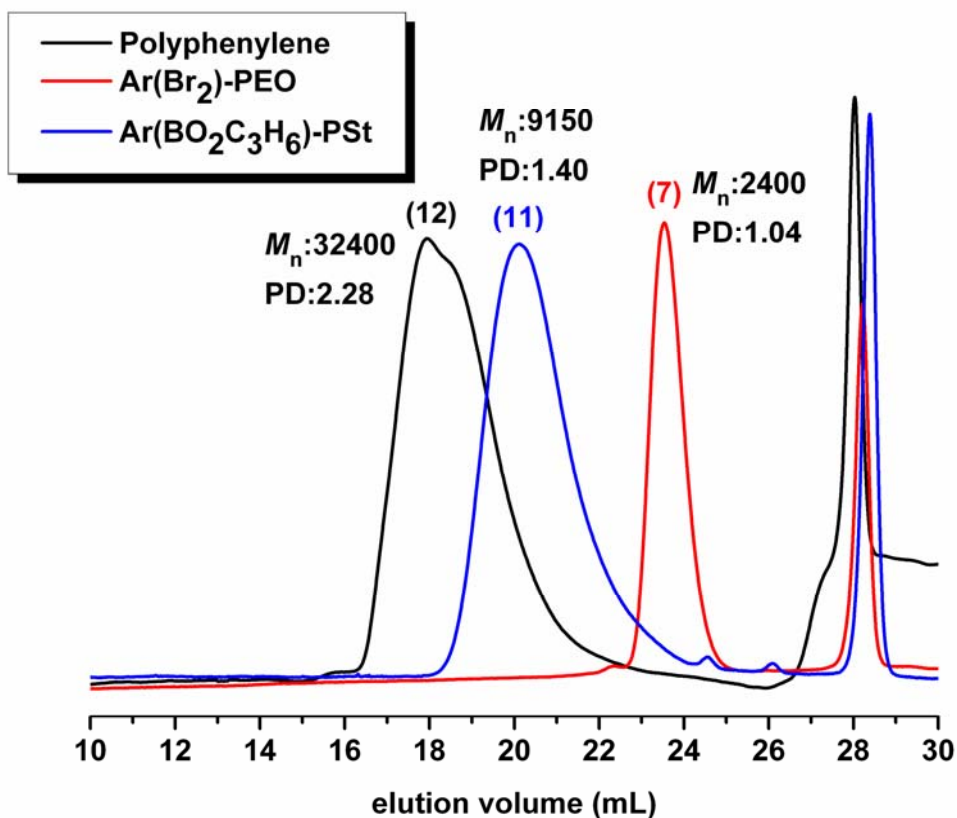
Figure 4.11 : GPC traces of macromonomers Ar(Br$_2$)- PEO (7), Ar(BO$_2$C$_3$H$_6$)-PSt (11) and the resulted PP(12).

Figure 4.11 shows that the GPC trace of the new polymer (curve 12) is shifted to higher molecular weights, as comparing with that of starting Ar(Br$_2$)-PEO (curve 7) and Ar(BO$_2$C$_3$H$_6$)-PSt (curve 11). It is also interesting to notice that the GPC trace of PP, even broader, is also symmetrical. GPC measurement of PP was performed after the reprecipitation from diethylether for removing the unreacted PEO macromonomer (7). But, unreacted PSt macromonomer could not removed by precipitation due to the high polystyrene character of PP.
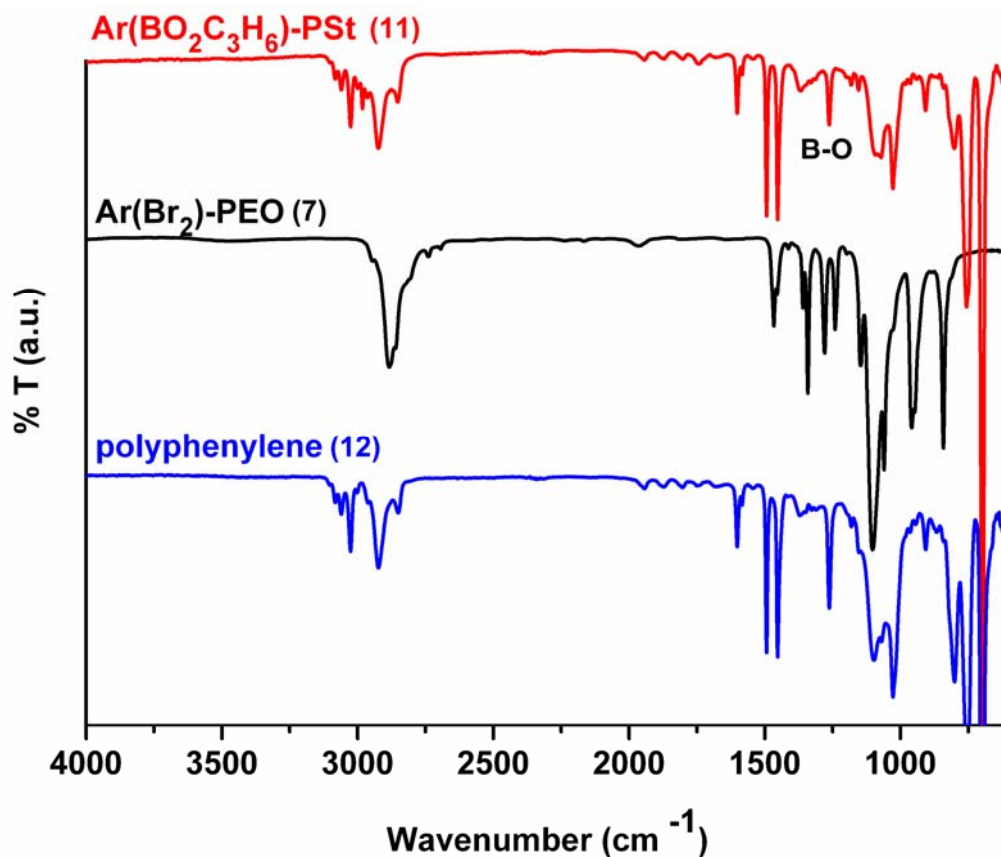
Figure 4.12 : IR spectra of macromonomers (7) and (11) and copolymer (12).

The IR spectra of macromonomers (7) and (11) and copolymer (12) are given in Figure 4.12. The PP IR spectra also show the presence of both components $Ar(BO_2C_3H_6)$-PSt and $Ar(Br_2)$-PEO) in the structure of (12). The peak from 1262 cm^{-1} attributed to B-O stretch from the spectra of macromonomer is not present in that of PP, in aggrement with ^{1}H-NMR result. Other absorptions are found in both spectra due to the high content of styrene units, that usually covers the peaks of PP rings from the main chain: 3059 cm^{-1}, 3025 cm^{-1} (aromatic CH stretching), 2923 cm^{-1}, 2849 cm^{-1} (aliphatic CH stretching), 1937 cm^{-1}, 1867 cm^{-1}, 1798 cm^{-1}, 1665 cm^{-1} , 760 cm^{-1} (out of plane hydrogen deformation), 1583 cm^{-1}, 1492 cm^{-1}, 1452 cm^{-1} (in plane bend stretching vibrations of phenyl ring).
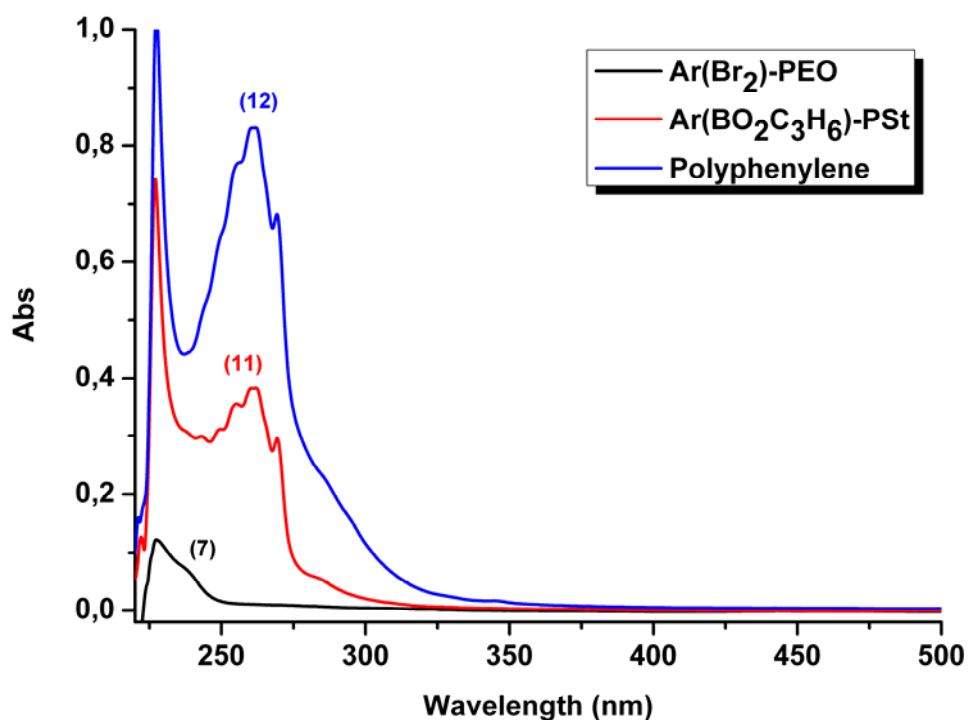
Figure 4.13 : UV spectra of macromonomers (7) and (11) and copolymer (12).

Moreover, UV absorption spectra of macromonomers (7) and (11) and copolymer (12) registered in CH_2Cl_2 solutions with same concentrations are shown in Figure 4.13. The PSt macromonomer had an absorption at 240 nm and a smaller one at 262 nm, whereas PEO macromonomer had an absorption at 227 nm. PP UV spectra also present two maxia of absorption at wavelengths close to that of macromonomer (11). Both peaks have a higher intensity than that of (11), but a more accentuated difference can be noticed in second one. The second strong absorption band of each PP was due to the presence of suplamentary phenylene rings in the main chain.
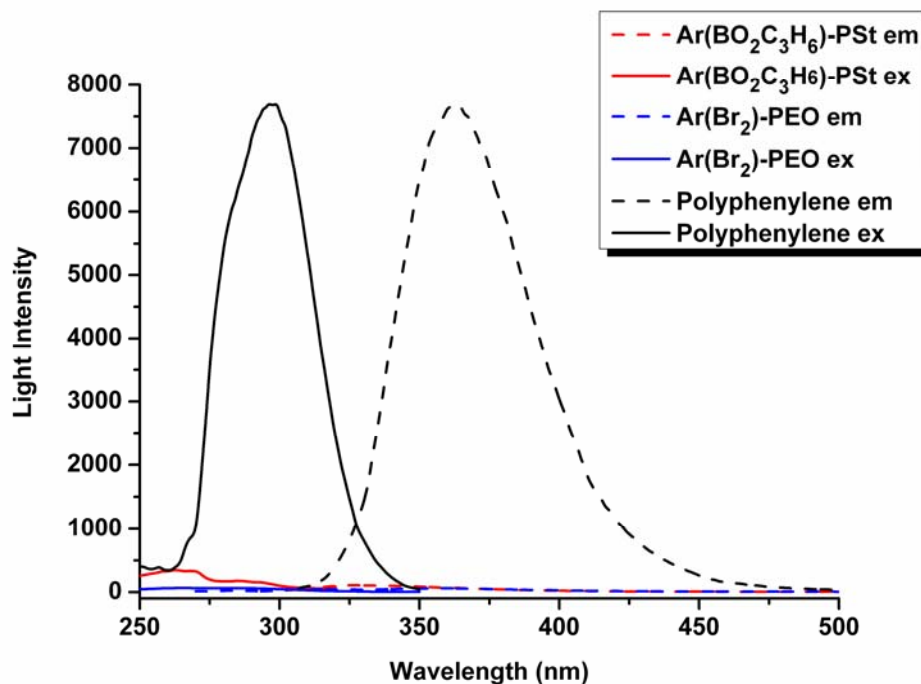
Figure 4.14 : Fluoresence spectra of macromonomers (7) and (11), and the PP obtained by the Suzuki method (12).

Furthermore, fluorescence properties of PP and macromonomers were investigated in Figure 4.14. The measurements were performed in CH_2Cl_2 solutions at the same concentration. Whereas PEO and PSt macromonomer does not show any fluorescenece properties, PP shows the strong fluorescence properties. The excitation spectrum of (12) had the maximum at 299 nm, and emission spectrum obtainedfor the excitation wavelength at this value had a maximum at 366 nm.
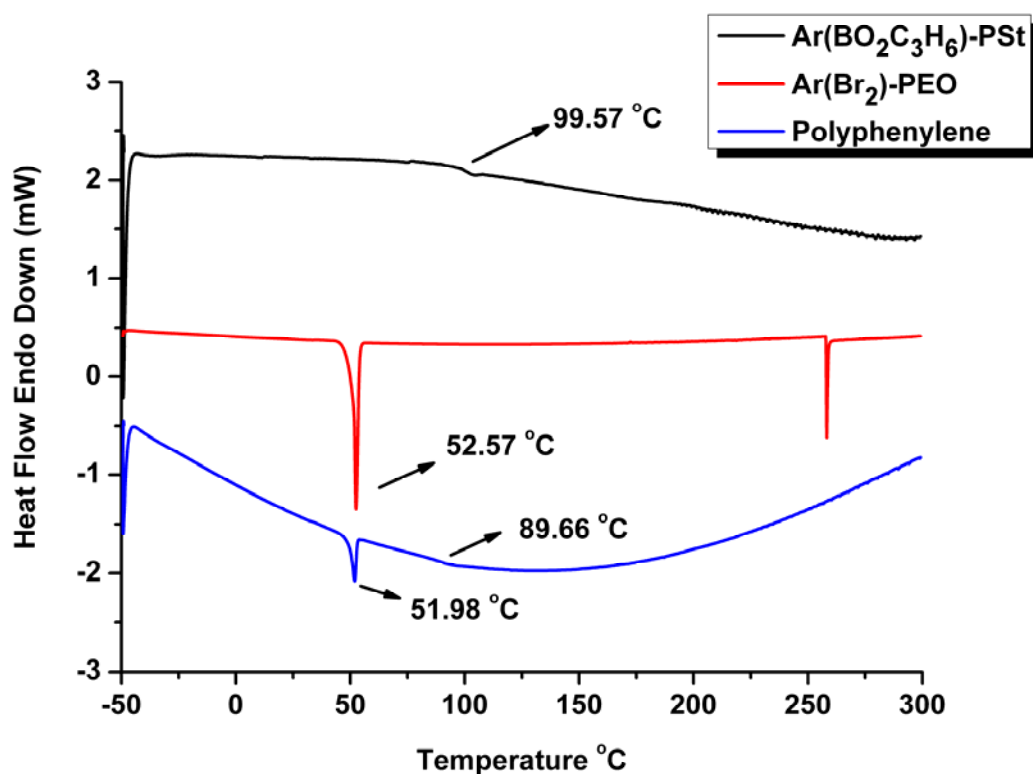
Figure 4.15 : DSC traces of macromonomers (7) and (11), and the PP obtained by the Suzuki method (12).

Also, the thermal behaviour of the polymers was followed by differential scanning calorimetry under nitrogen, with a heating rate of 10 ^{o}C/min (Figure 4.15). A first run was performed until 150 ^{o}C (lower than the well known intial degradation temperature of polystyrene), cooled down at 30 ^{o}C and than reheated until 300 ^{o}C (second run), for macromonomers and PP. The Pst and PP has close glass transition temperatures (around 89.9 ^{o}C and 99.57 ^{o}C) characteristic for PSt. The PEO and PP has close melting temperatures (around 52.57 ^{o}C and 51.98 ^{o}C) characteristic for PEO.

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