

166274

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

**SYNTHESIS AND CHARACTERIZATION OF
BENZOXAZINE-SUBSTITUTED MALEIMIDE POLYMERS
BY PHOTOINDUCED RADICAL POLYMERIZATION**

M. Sc. Thesis by

Burçin GACAL

515031006

Date of submission : 27 December 2004

Date of defence examination: 27 January 2005

Supervisor (Chairman): Prof. Dr. Yusuf YAĞCI

Members of the Examining Committee: Prof. Dr. Huceste GİZ (I.T.Ü.)

Asist. Prof. Dr. Havva Yağcı ACAR (K.U.)

JANUARY 2005

**BENZOKSAZİN GRUPLARI İÇEREN MALEİMİD
POLİMERLERİNİN SENTEZLENMESİ VE
KARAKTERİZASYONU**

YÜKSEK LİSANS TEZİ

Burçin GACAL

515031006

Tezin Enstitüye Verildiği Tarih : 27 Aralık 2004

Tezin Savunulduğu Tarih : 27 Ocak 2005

Tez Danışmanı : Prof. Dr. Yusuf YAĞCI

Diğer Jüri Üyeleri : Prof. Dr. Huçeste GİZ (İ.T.Ü.)

Yrd. Doç. Dr. Havva Yağcı ACAR (K.U.)

OCAK 2005

ACKNOWLEDGEMENTS

I would like to thank all the people who encouraged and supported me during my master education.

I would like to express my gratitude to my thesis supervisor, Prof. Dr. Yusuf YAĞCI for offering invaluable help in all possible ways, continuous encouragement and sharing his deep knowledge throughout my research.

I would like to thank Dr. Luminita CIANGA for her encouragement and helpful criticisms throughout this research.

It was great pleasure to work with Öner İZGİN, M. Atilla TAŞDELEN, Yasemin YÜKSEL DURMAZ, Hakan DURMAZ, Demet GÖEN ÇOLAK, Dr. Ioan CIANGA, Nihan YÖNET, Dr. Faruk YILMAZ, Binnur AYDOĞAN, Ali Ekrem MÜFTÜOĞLU, Dr. Senem KIRALP and Barış KIŞKAN.

I would also like to extend my gratitude to my friends; S. Erdem SÖNMEZ, Neslihan ZÖHRAP, Bingül BANCA, Hatice KOÇER and Enis BOZ.

I dedicated this thesis to my family; my father Adnan GACAL, my mother Gürsel GACAL and my brother Bahadır GACAL for their endless support during all stages of my life .

January 2005

Burçin GACAL

TABLE of CONTENTS

LIST of ABBREVIATIONS	vi
LIST of TABLES	viii
LIST of FIGURES	ix
LIST of SYMBOLS	x
SUMMARY	xi
ÖZET	xii
1. INTRODUCTION	1
2. THEORETICAL PART	3
2.1 Free Radical Polymerization	3
2.1.1 Initiators	3
2.1.1.1 Thermal Initiators (Intramolecular Bond Cleavage)	4
2.1.1.2 Redox Initiators	6
2.1.1.3 Photoinitiators	7
2.1.2 Monomers Fitted for Free Radical Polymerization	8
2.1.3 Mechanism of Free Radical Polymerization	10
2.2 Photoinitiated Polymerization	14
2.2.1 Photoinitiated Free Radical Polymerization	15
2.2.1.1 Absorption of Light	16
2.2.1.2 Radical Generation	17
2.3 Free Radical Chain Copolymerization	21
2.3.1 Copolymerization Models	22
2.3.1.1 Terminal Model	22
2.3.1.2 Penultimate Model	24
2.3.1.3 Complex Model	26
2.3.2 Principles of Alternating Copolymerization	27
2.3.2.1 Donor-Acceptor Complex Participation in Alternating Copolymerization	29
2.3.2.2 Donor-Acceptor Complexes in Radical Copolymerization	29
2.3.2.3 Monomer Orientation Control by Donor-Acceptor Complex in Alternating Copolymerization	33
2.3.2.4 Determination of the Equilibrium Constant for CTC Formation	34
	36

2.4 Maleimide Copolymers (<i>N</i>-Substituted)	
2.4.1 Copolymerization and Copolymers in <i>N</i> -Substituted Maleimides with Styrene and α -Methylstyrene	38
2.4.2 Copolymerization and Copolymers in <i>N</i> -Substituted Maleimides with Acrylic and Methacrylic Monomers	44
2.4.3 Copolymerization and Copolymers in <i>N</i> -Substituted Maleimides with Vinyl Acetate and Vinyl Ethers	48
2.4.4 Copolymerization and Copolymers in <i>N</i> -Substituted Maleimides with Other Monomers	50
2.4.5 Special Maleimide Copolymers	54
2.5 Polybenzoxazines (PBZ)	55
2.5.1 Features of Polybenzoxazines	57
3. EXPERIMENTAL WORK	59
3.1 Materials and Chemicals	59
3.1.1 Monomers	59
3.1.2 Solvents	59
3.1.3 Initiator	60
3.2 Equipments	60
3.2.1 Photoreactor	60
3.2.2 Infrared Spectrophotometer (IR)	60
3.2.3 Nuclear Magnetic Resonance Spectroscopy (NMR)	60
3.2.4 Gel Permeation Chromatography (GPC)	60
3.2.5 Differential Scanning Calorimetry (DSC)	60
3.3 Preparation Methods	61
3.3.1 Copolymerization of <i>N</i> -(<i>N</i> -4-cyanophenylbenzoxazine) Maleimide (BAMI) with Styrene (St) by Photoinitiated Radical Polymerization	61
3.3.2 Homopolymerization of <i>N</i> -(<i>N</i> -4-cyanophenylbenzoxazine) Maleimide (BAMI) with Styrene (St) by Photoinitiated Radical Polymerization	61
3.3.3 Thermal Ring-Opening Polymerization of Benzoxazine Moieties of BaMI-St Copolymer (Table 4.1., Run 3)	61
4. RESULTS and DISCUSSION	63
4.1 Homopolymerization and Copolymerization of <i>N</i>-(<i>N</i>-4-cyanophenylbenzoxazine) Maleimide (BAMI) with Styrene (St) by Photoinitiated Radical Polymerization	63
4.1.1 Characterization of the Polymers	65

4.1.2 Copolymerization Behavior	71
4.1.3 Feed-Copolymer Composition Profile	74
4.1.4 Structural Data for the Copolymers of St (1) and BaMI (2)	75
4.1.5 The Influence of the Reaction Conditions on the Characteristics of the Copolymers	77
4.1.6 Thermal Behavior	79
4.1.7 Thermal Ring-Opening Polymerization of Benzoxazine Moieties of BaMI-St Copolymer (Table 4.1., Run 3)	81
5. CONCLUSIONS	84
REFERENCES	86
AUTOBIOGRAPHY	102



LIST of ABBREVIATIONS

FRP	: Free Radical Polymerization
PI	: Photoinitiator
S	: Sensitizer
I	: Initiator
CTA	: Chain Transfer Agent
PPI	: Polymeric Photoinitiator
MWD	: Molecular Weight Distribution
PDI	: Poly Dispersity Index
CTC	: Charge Transfer Complex
D	: Electron-Donating Monomer
A	: Electron-Accepting Monomer
HOMO	: Highest Occupied Molecular Orbital
LUMO	: Lowest Occupied Molecular Orbital
Z	: Zusammen (cis)
E	: Entgegen (trans)
K_{CTC}	: Equilibrium Constant of CTC Complex Formation
RMI	: <i>N</i> -Substituted Maleimide
BMI	: Bismaleimide
BPO	: Benzoic Peroxide
ESR	: Electron Spin Resonance
DMF	: Dimethylformamide
PMI	: <i>N</i> -Phenylmaleimide
MA	: Maleic Anhydride
MSt	: α -Methylstyrene
CMI	: <i>N</i> -Carbamylmaleimide
CEMI	: <i>N</i> -Carbetoxymaleimides
EMI	: <i>N</i> -Ethylmaleimides
CPMI	: <i>N</i> -(2-chlorophenyl)maleimide
MOPMI	: <i>N</i> -(4-methoxyphenyl)maleimide
BPMI	: <i>N</i> -(4-bromophenyl)maleimide
MPMI	: <i>N</i> -(4-methylphenyl)maleimide
BPMI	: <i>N</i> -brominated phenyl maleimide
RPCMI	: <i>N</i> -4-substituted phenyl- α -chloromaleimide
THF	: Tetrahydrofuran
RCMI	: <i>N</i> -alkyl- α -chloromaleimide
AMI	: <i>N</i> -allylmaleimide
VBC	: Vinylbenzyl Chloride
TBSAMI	: <i>N</i> -thry- <i>n</i> -butyl-Sn-acetatemaleimide
RCIMI	: <i>N</i> -alkyl- or <i>N</i> -aryl- α -chloromaleimides
MPMI	: <i>N</i> -(4-methylphenyl)maleimide
DAEM	: <i>N,N</i> -dimethylaminoethylmethacrylate
VA	: Vinyl Acetate
CEVE	: 2-chloroethyl Vinyl Ether

CHVK	: Cyclohexyl Vinyl Ketone
AIBN	: α,α' -Azobisisobutyronitrile
PO	: Propylene Oxide
CHMI	: <i>N</i> -cyclohexylmaleimide
MPMI	: <i>N</i> -(4-methylphenyl) maleimide
DMPMI	: <i>N</i> -(2,4-dimethylphenyl) maleimide
IB	: Isobutene
IO	: Isooctene
CB	: <i>cis</i> -2-butene
TB	: <i>trans</i> -2-butene
NPMI	: <i>N</i> -(4-nitrophenyl)-maleimide
2MPMI	: <i>N</i> -(2-methyl phenyl)maleimide
ME	: Electrophilic Activity
MN	: Nucleophilic Activity
AOMI	: <i>N</i> -acetoxymaleimide
VOEIm	: <i>N</i> -(β -vinyloxyethyl) imidazole
BEMI	: <i>N</i> -(2-bromoethyl) maleimide
VOET	: 1-(2-vinyloxyethyl)thymine
ECPMI	: <i>N</i> -(2-ethyl-6-chloropurine)maleimide
PBZ	: Polybenzoxazines
GPC	: Gel Permeation Chromatography
IR	: Infrared Spectrophotometer
NMR	: Nuclear Magnetic Resonance Spectroscopy
UV	: Ultra Violet
DSC	: Differential Scanning Calorimetry
TGA	: Thermal Gravimetry Analysis
BaMI	: <i>N</i> -(<i>N</i> -4-cyanophenylbenzoxazine)
E-KT	: Extended Kelen–Tüdös
M	: Monomer
St	: Styrene
PSt	: Polystyrene
DMSO	: Dimethylsulfoxide
DMPA	: ω, ω -Dimethoxy- ω -phenylacetophenone

LIST of TABLES

	<u>Page No</u>
Table 2.1. Photosensitive Monomers.....	17
Table 4.1. Photoinduced Radical Polymerization of BaMI (M_2) with (St) (M_1) in Dimethylsulfoxide at Room Temperature ^a	68
Table 4.2. E-KT Parameters for Monomer BaMI and St Using ^1H NMR Spectroscopic Data.....	72
Table 4.3. Monomer Reactivity Ratios.....	73
Table 4.4. Structural Data for the Copolymers St (1) and BaMI (2).....	76
Table 4.5 The Influence of the Reaction Conditions on the Characteristics of the Copolymers.....	78
Table 4.6. Thermal Properties of Polymers.....	79



LIST of FIGURES

	<u>Page No</u>
Figure 4.1	: ^1H NMR spectrum of BaMI copolymer (Table 4.1., Run 3) in DMSO- d_6 67
Figure 4.2	: IR spectra of BaMI monomer, BaMI-St copolymers (Table 2.1., Run 1, Run 2, Run 3, Run 4, Run 5) and BaMI homopolymer (Table 4.1, Run 6)..... 69
Figure 4.3	: ^1H NMR spectrum of BaMI monomer in DMSO- d_6 70
Figure 4.4	: ^1H NMR spectrum of BaMI-St copolymer (Table 4.1., Run in DMSO- d_6 70
Figure 4.5	: Extended Kelen-Tüdös plots of ξ versus η for the photoinduced radical copolymerization of BAMI (M_2) with St (M_1). Tg $\alpha = (r_1 + r_2/\alpha)$, intercept r_2/α and $\alpha = 0.4178$ 72
Figure 4.6	: Copolymer composition curves : (\square) prediction by terminal model, using $r_1 = 0,111$, $r_2 = 0,083$; (\blacksquare) experimental points..... 74
Figure 4.7	: Diad monomer sequence fractions vs the BaMI mol fraction for the St -BaMI copolymers: 1-1, 2-2 and 1-2 diads..... 75
Figure 4.8	: DSC scans of Run 3 (scan rate 10 $^\circ\text{C}/\text{min}$)..... 80
Figure 4.9	: DSC scans of Run 8 (scan rate 10 $^\circ\text{C}/\text{min}$)..... 80
Figure 4.10	: DSC scans of Run 9 (scan rate 10 $^\circ\text{C}/\text{min}$)..... 81
Figure 4.11	: IR spectra of BaMI-St Copolymer (Table 4.1., Run 3) and crosslinked polymers obtained from thermal curing of BaMI-St Copolymer (Table 4.1., Run 3)..... 82

LIST of SYMBOLS

$\Phi_{R\cdot}$: Quantum Yield of Radical Formation
λ	: Wavelength
$h\nu$: Radiation
$R\cdot$: Radical
I	: Initiator
COI	: Coinitiator
M	: Monomer
S	: Sensitizers
M_n	: The Number Average Molecular Weight
M_w	: The Weight Average Molecular Weight
M_w/M_n	: The Molecular Weight Distribution
r_i	: Monomer Reactivity Ratio
D	: Electron-Donating Monomer
A	: Electron-Acceptor Monomer
CTC	: Charge Transfer Complex
ψ	: Wave Function
R_E	: Excited State of CTC
R_N	: Normal State of CTC
E_C	: Energy of Charge Transfer
I	: Potential Ionization of D-Monomer
E_A	: Resonance Energy
E_{cl}	: Culone Energy
K_{CTC}	: Equilibrium Constant of CTC Formation
A_{CTC}	: Absorbance of the Complex
ϵ_{CTC}	: Molar Absorbivity of the Complex
δ_{obs}	: Chemical Shift of the Acceptor protons
δ_f	: Chemical Shift of the Free Molecules
δ_{CTC}	: Chemical Shift of the Free Molecules
f_i	: Molar Fractions of the Monomers (M_1 or M_2) in the Copolymer
F_i	: Molar Fractions of the Monomers (M_1 or M_2) in the Feed
ξ_i	: Partial Molar Conversions
μ_i	: Molecular Weights of Monomer
w	: Total Fractional Conversion
X'	: Mol Fractions of the M_1 - M_1 Sequences
Y'	: Mol Fractions of the M_2 - M_2 Sequences
Z'	: Mol Fractions of the M_1 - M_2 Sequences
Φ_i	: Molar Fractions of the Monomers (M_1 or M_2) in the Feed
μ'_i	: Mean Sequence Length

SYNTHESIS AND CHARACTERIZATION OF BENZOXAZINE-SUBSTITUTED MALEIMIDE POLYMERS BY PHOTOINDUCED RADICAL POLYMERIZATION

SUMMARY

At the present there is considerable interest not only in synthesis of new types of plastic materials, but also in the modification of existing polymers in order to vary its properties to meet requirements for new applications. One of the existing methods of improving polymer properties is the copolymerization for effecting systematic changes in polymer properties. The incorporation of two different monomers, having diverse physical and/or chemical properties, in the same polymer molecule in varying proportions leads to the formation of new materials with great scientific and commercial importance.

Polymers of *N*-substituted maleimides and their derivatives can be classified as polyimides, important highperformance engineering plastics, being a class of rigid polymers because of the imide rings in the backbone. This provides the polymers with superior mechanical and thermal stability.

Recently, high performance polymeric materials have received considerable studies for their wide application in electronics, biomaterials, and other industrials. Among the developed materials, polybenzoxazines possess outstanding properties of small shrinkage in curing, low water absorption, good thermal stability, and high glass transition temperatures. These advantages of benzoxazines receive considerable increase on the studies of benzoxazines and their corresponding polymers.

In this study, photoinitiated radical homopolymerization of *N*-(*N*-4-cyanophenylbenzoxazine) maleimide (BaMI) and its copolymerization with styrene were performed at room temperature to give linear polymers containing pendant benzoxazine moieties. Monomer reactivity ratios for the studied monomer pairs were determined using extended Kelen-Tüdös method. Copolymers' compositions and the monomer reactivity ratios suggest an alternating nature of the copolymerization. In addition, different copolymerization conditions were examined to estimate the influence of the used solvents and comonomers' total molar concentration on the the number-average molecular weight (M_n), polydispersity index (M_w/M_n) and cis/trans ratio of the resulting polymers. The thermal behavior of the new synthesized polymers was investigated by differential scanning calorimetry (DSC). The ring-opening polymerization of pendant benzoxazine groups of BaMI-St copolymers were performed at a certain temperature and determined infrared spectroscopy (IR) measurements. These resulting polymers are expected to have higher thermal properties.

BENZOKSAZİN GRUPLARI İÇEREN MALEİMİD POLİMERLERİNİN SENTEZLENMESİ VE KARAKTERİZASYONU

ÖZET

Günümüzde, yeni tür plastik malzeme sentezlemeye karşı olan ilgi aynı zamanda yeni uygulamalar için varolan polimerlerin çeşitli modifikasyonlarla özelliklerini geliştirmesine karşı da gösterilmektedir. Kopolimerizasyon polimer özelliklerini geliştirme metodlarından bir tanesidir. Çeşitli fiziksel ve /veya kimyasal özelliklere sahip iki farklı monomerin değişen oranlarda aynı polimer molekülüne dahil edilmesi bilimsel ve ticari öneme sahip yeni materyallerin oluşumuna yol açmaktadır.

N- sübstitüye maleimidler ve onun türevleri ana zincirdeki halkalı imid yapıları sayesinde rijid (sert) polimerlerin önemli bir sınıfını oluştururlar. Ana zincirdeki halkalı imid yapıları üretilen polimerlere üstün mekanik ve termal dayanıklılık sağlar.

Son zamanlarda yüksek performanslı polimerik malzemelerin, elektronik, biyomalzeme ve diğer endüstriyel alanlarındaki geniş kullanım yelpazeleri sebebiyle önemli çalışmalara konu olmuştur. Benzoksazin polimerler, reçineleşme sırasındaki ufak hacim değişiklikleri (büzüşme), düşük miktarda su absorplamaları, ısıl dayanımları ve yüksek camı geçiş sıcaklıkları gibi göze çarpan özelliklere sahiptirler. Bu özellikler benzoksazin ve benzoksazin polimerleri hakkında yapılan çalışmaların önemli bir şekilde artmasına sebep olmuştur.

Bu çalışmada *N*-(*N*-4-siyanofenilbenzoksazin) maleimid (BaMI) monomerinin homopolimeri ve bu monomerin stirenle (St) olan kopolimeri fotokimyasal başlatılmış radikal polimerizasyonu ile oda sıcaklığında sentezlenerek benzoksazin yapısı içeren doğrusal polimerler elde edilmiştir. Monomerlerin reaktivite oranları geliştirilmiş Kelen-Tüdös metodu ile belirlenmiştir. Kopolimerlerin bileşimleri ve bulunan reaktivite oranları çalışılan sistemin ardışık kopolimerizasyon özelliğini göstermiştir. Ayrıca, kullanılan çözeltiler ve komonomerlerin toplam molar konsantrasyonu gibi farklı kopolimerizasyon koşullarının, polimerlerin sayıca-ortalama mol kütleleri (M_n), polidispersite indeksleri (M_w/M_n) ve cis/trans oranları üzerine etkileri incelenmiştir. Sentezlenen polimerlerin termal davranışları diferansiyel termal analiz ve yöntemiyle belirlenmiştir. BaMI-St kopolimerlerindeki benzoksazin gruplarının polimerizasyonu belirli bir sıcaklıkta halka-açılma polimerizasyonu ile gerçekleştirilmiş ve infrared spektroskopisi (IR) ölçümleriyle belirlenmiştir. Oluşan polimerlerin daha yüksek termal özelliklere sahip olabileceği düşünülmektedir.

1. INTRODUCTION

At the present there is considerable interest not only in synthesis of new types of plastic materials, but also in the modification of existing polymers in order to vary its properties to meet requirements for new applications. One of the existing methods of improving polymer properties is the copolymerization for effecting systematic changes in polymer properties. The incorporation of two different monomers, having diverse physical and/or chemical properties, in the same polymer molecule in varying proportions leads to the formation of new materials with great scientific and commercial importance.

Polymers of *N*-substituted maleimides and their derivatives can be classified as polyimides, important high performance engineering plastics, being a class of rigid polymers because five-member planar rings in the chain hinder the rotation of the imide residues around the backbone chain of the macromolecules. This provides the polymers with superior mechanical and thermal stability.

Maleimide-incorporated vinyl polymers have also gained current interest in several fields related to their dielectric [1] and nuclear magnetic relaxational characteristics [2], asymmetric induction polymerization [3], or Langmuir Blodgett film-forming properties [4]. Copolymers of *N*-substituted maleimides were synthesized and investigated for their use as positive photoresists [5], or for non-linear optical (NLO) applications [6].

The peculiar homo- and copolymerization characteristics of the electron-deficient maleimide group make it an attractive monomer for designing special vinyl polymers. Although maleimide undergoes homopolymerization with great difficulty, copolymerizes quite readily with a variety of vinyl monomers. Further, electron-deficient maleimides can form charge transfer complex (CTC) with many electron-rich monomers, thus being suitable model compounds for the mechanism investigation of alternating copolymerization involving the CTC participation into propagation.. Apart from enhancing the thermal stability and glass transition

temperature of the resultant copolymers, maleimide group can effectively serve as a vehicle for many functional group for their predefined distribution in a vinyl polymer backbone through free radical copolymerization.

Photopolymerization is one of the most rapidly expanding processes for materials production. Photopolymerization have gained prominence in recent years for the pollution-free curing of polymer films as well as emerging applications in dental materials, conformal coatings, electronic and optical materials and high-resolution rapid prototyping of 3D objects. Near to the excellent properties of the obtained polymers (adhesion, abrasion resistance, chemical resistance, etc.) photopolymerization process itself affords advantages such as very high reaction rates at room temperature and spatial control of polymerization.

In recent years the development of the benzoxazine-based family of phenolic resins has attracted significant attention. Various phenols and primary amines have been used to synthesize benzoxazine resins. As a result of the ring-opening polymerization, polybenzoxazines overcome many shortcomings associated with traditional phenolic resins such as releasing condensation by-products and using strong acids as catalysts, while retaining good thermal properties and flame retardance of phenolics [7]. Also, like epoxide based polymers and polyimide, polybenzoxazines have excellent mechanical properties and molecular design flexibility. Benzoxazine resins undergo near-zero volumetric changes or expansion upon polymerization [8]. By using particular types of amine and phenol, polybenzoxazines with char yield as high as 80% have recently been obtained [9]. These advantages of benzoxazines receive considerable increase on the studies of benzoxazines and their corresponding polymers.

This study describes the preparation of a new benzoxazine-substituted maleimide type monomer and its photoinitiated radical copolymerization with styrene (St). In addition, thermal behavior of the resulting polymers were examined. As it will be shown in the thesis these polymers can undergo thermal crosslinking.

2. THEORETICAL PART

2.1 Free Radical Polymerization (FRP)

The study of polymer science begins with understanding the methods in which these materials are synthesized. Polymer synthesis is a complex procedure and can take place in a variety of ways. Addition polymerization describes the method where monomers are added one by one to an active site on the growing chain. The most common type of addition polymerization is free radical polymerization (FRP) which involves the reaction of carbon-carbon double bonds with an unpaired electron on a species that is called a radical. A free radical is simply a molecule with an unpaired electron. FRP is used to make polymers from vinyl monomers, that is, from small molecules containing carbon-carbon double bonds. Polymers made by free radical polymerization include polystyrene, poly (methyl methacrylate), poly (vinyl acetate) and branched polyethylene.

FRP gains much attention in the field of industrial polymer synthesis due to its simplicity, compatibility and convenience. Polymers prepared by free-radical means are used in the manufacture of numerous products, such as fabrics, surface coatings and paints, plastics, packaging, spectacle and contact lenses and surgical devices. It has distinct advantages over other polymerization methods, such as tolerance to trace impurities, less stringent conditions, and also to be able to polymerize a wide range of monomers.

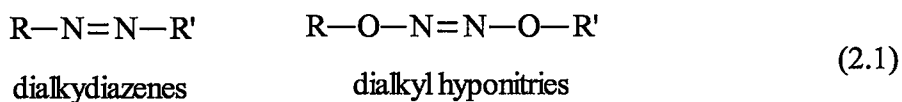
2.1.1 Initiators

Substances, which generate radicals when heated or irradiated or by any other means may initiate free radical polymerization under certain conditions. The free radical initiators can be classified into three basic groups as thermal, redox and photoinitiators. More commonly, the initiators are azo-compounds, peroxides or benzoin derivatives.

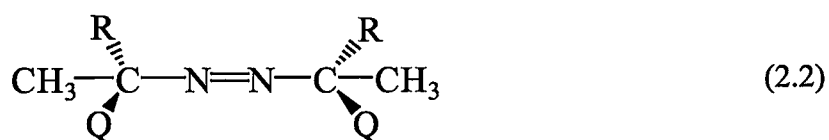
2.1.1.1 Thermal Initiators (Intramolecular Bond Cleavage)

Azo Initiators

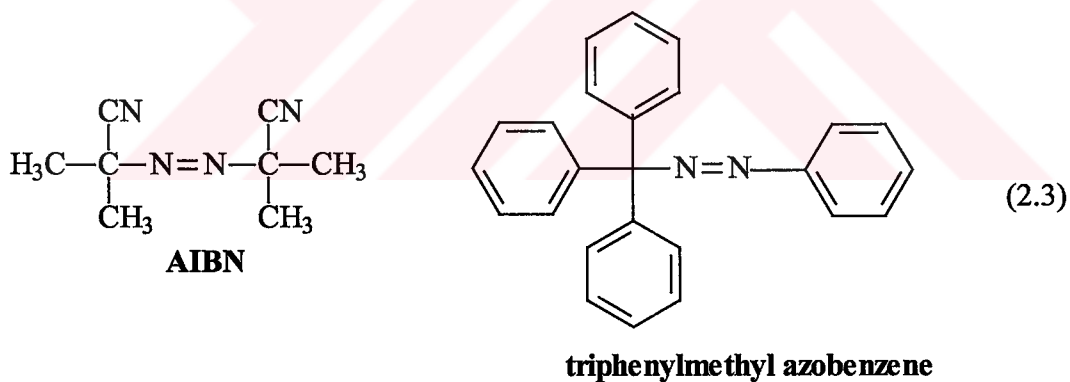
There are two general classes of azo-compounds namely, the dialkyldiazenes and the dialkyl hyponitries (2.1)



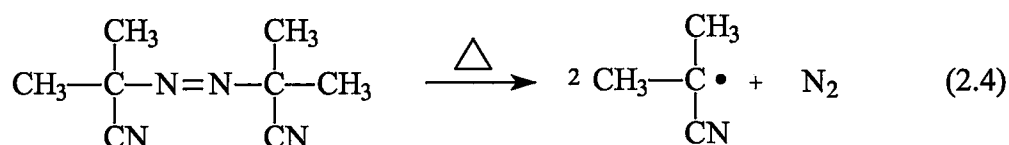
Most of the compounds are represented by the formula where R is an alkyl and Q is a simple carboxylic acid residue or a derivative (nitrile, ester) (2.2).



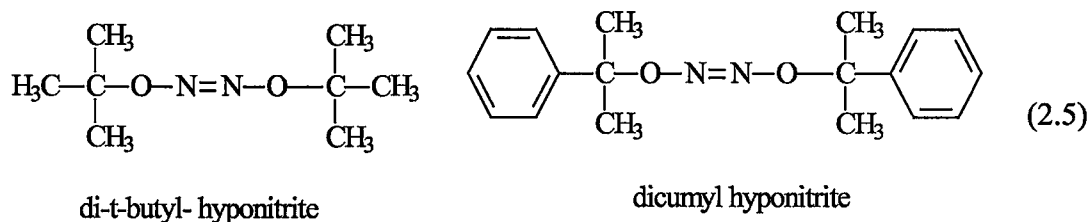
2, 2'-azobis (2-methylpropanenitrile) (better known as azobis (isobutyronitrile) or AIBN) is the most widely used initiator. Also, triphenylmethyl azobenzene is one of the unsymmetrical dialkyldiazenes (2.3).



Thermal decomposition of AIBN and its analogues is generally considered to produce cyanoisopropyl radicals (or analogues) according to the following reaction (2.4).

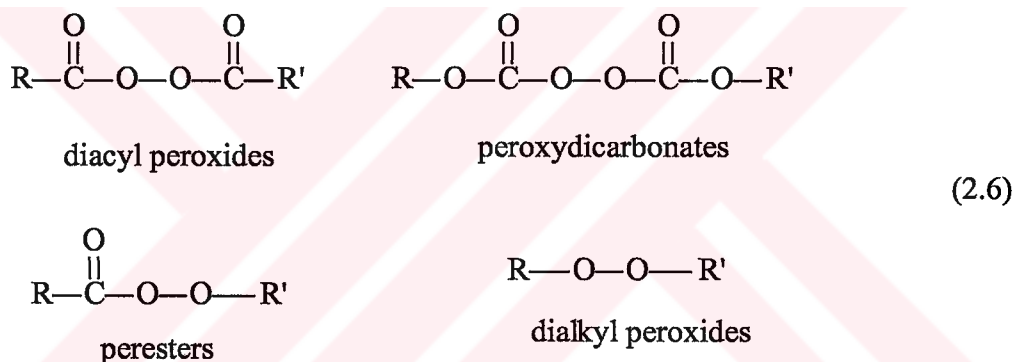


The hyponitrites, derivatives of hyponitrous acid (HO-N=N-OH), are low temperature sources of alkoxy or acyloxy radicals. Di-*t*-butyl and dicumyl hyponitrites have proved convenient sources of *t*-butoxy and cumyloxy radicals respectively in the laboratory (2.5).

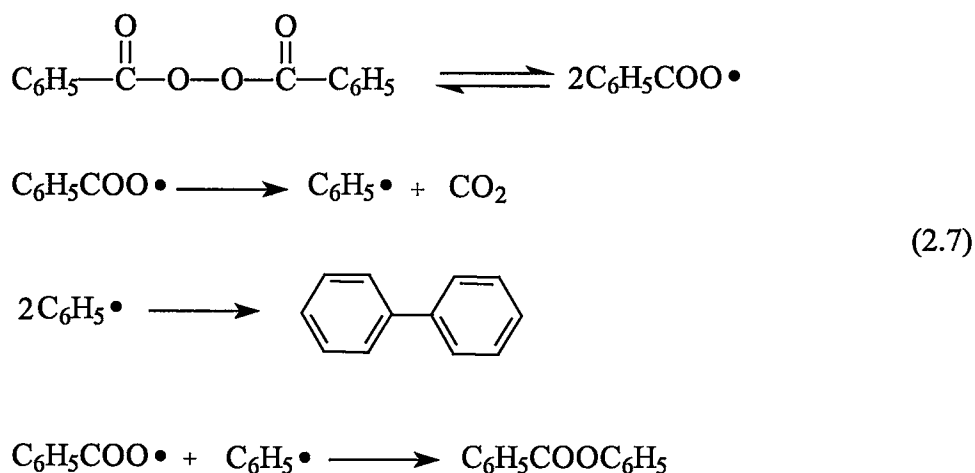


Peroxy Compounds

Many types of peroxides (R – O – O – R) are known. Those in common use as initiators include: diacyl peroxides, peroxydicarbonates, peresters, dialkyl peroxides, hydroperoxides, and inorganic peroxides (e.g. persulfate) (2.6) [10-15].



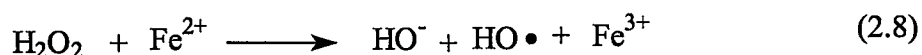
Benzoyl peroxide is a well-established initiator of polymerization. As with other peroxides, the primary step in the thermal decomposition is scission of the — O — O — bond to give two acyloxy radicals. A number of secondary processes may follow; in addition to reacting with monomer, benzoyloxy radicals may recombine or undergo β -scission to phenyl radicals and carbon dioxide. Further, recombination reactions giving biphenyl and phenyl benzoate may then occur (2.7).



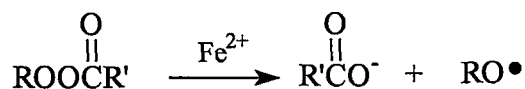
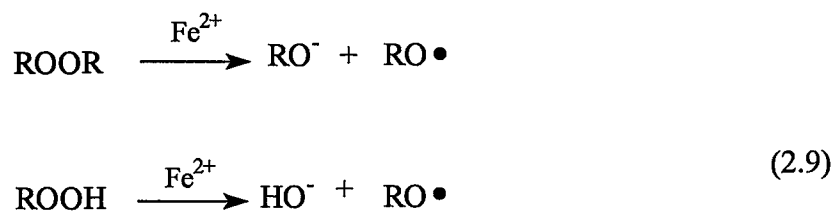
2.1.1.2 Redox Initiators

Radicals produced by many oxidation-reduction reactions can be used to initiate polymerization. This type of initiation is referred as *redox initiation*, *redox catalysis*, or *redox activation*. A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system, including initiation at moderate temperatures of 0-50 °C and even lower. This allows a greater freedom of choice of the polymerization temperature that is possible with the thermal homolysis of initiators [16].

Peroxides in the presence of a reducing agent are a common source of radicals, for example, the reaction of hydrogen peroxide with ferrous ion (2.8)



Ferrous ion also induces the decomposition of a variety of other compounds including various types of organic peroxides (2.9).



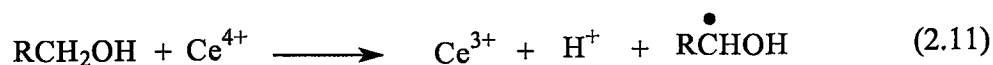
Also, Cr^{2+} , V^{2+} , Ti^{3+} , Co^{2+} , and Cu^+ can substitute ferrous ion in many instances.

The combination of a variety of inorganic reductants and inorganic oxidants initiates radical polymerization (2.10), for example,



Other redox systems include reductants such as HSO_3^- , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, and $\text{S}_2\text{O}_5^{2-}$ in combination with oxidants such as Ag^+ , Cu^{2+} , Fe^{3+} , ClO_3^- , and H_2O_2 .

Organic-inorganic redox pairs initiate polymerization, usually but not always by oxidation of the organic component, for example, the oxidation of an alcohol by Ce^{4+} or by V^{5+} , Cr^{6+} , Mn^{3+} (2.11).



There are some initiator systems in which the monomer itself acts as one component of the redox pair. Examples are thiosulfate plus acrylamide or methacrylic acid and *N,N*-dimethylaniline plus methyl methacrylate.

2.1.1.3 Photoinitiators

Photoinitiators for FRP fall into two classes: those which on irradiation undergo intramolecular bond cleavage with radical generation and those which form radicals

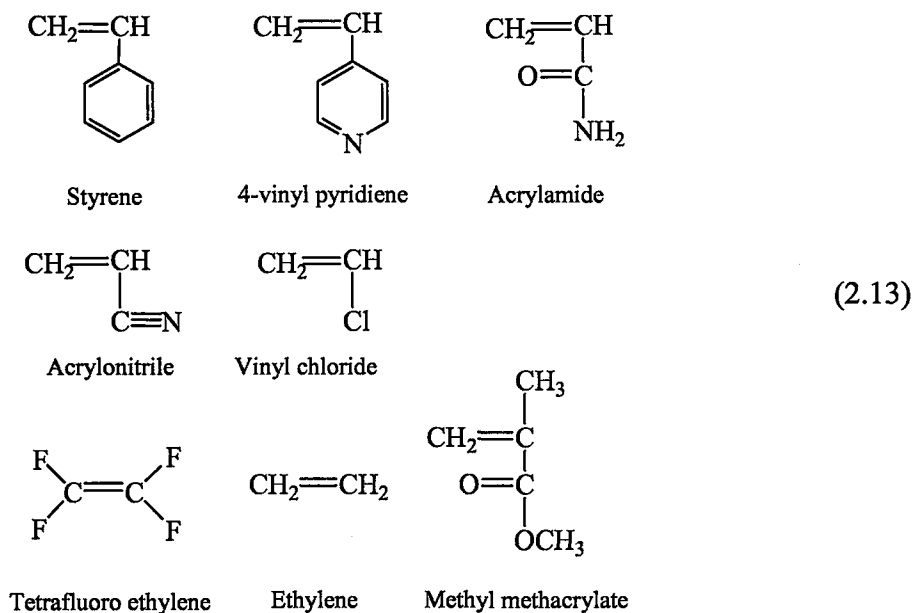
when photoexcited species abstract hydrogen atoms from H-donors. Detailed information will be given in part 2.2.1.

2.1.2 Monomers Fitted for Free Radical Polymerization

Commonly monosubstituted or unsymmetrically (1,1-) disubstituted ethylenes, $\text{CH}_2=\text{CHX}$ or $\text{CH}_2=\text{CXY}$ work in free-radical polymerization whereas symmetrically disubstituted (1,2-) ethylenes don't homopolymerize readily as a rule (2.12).

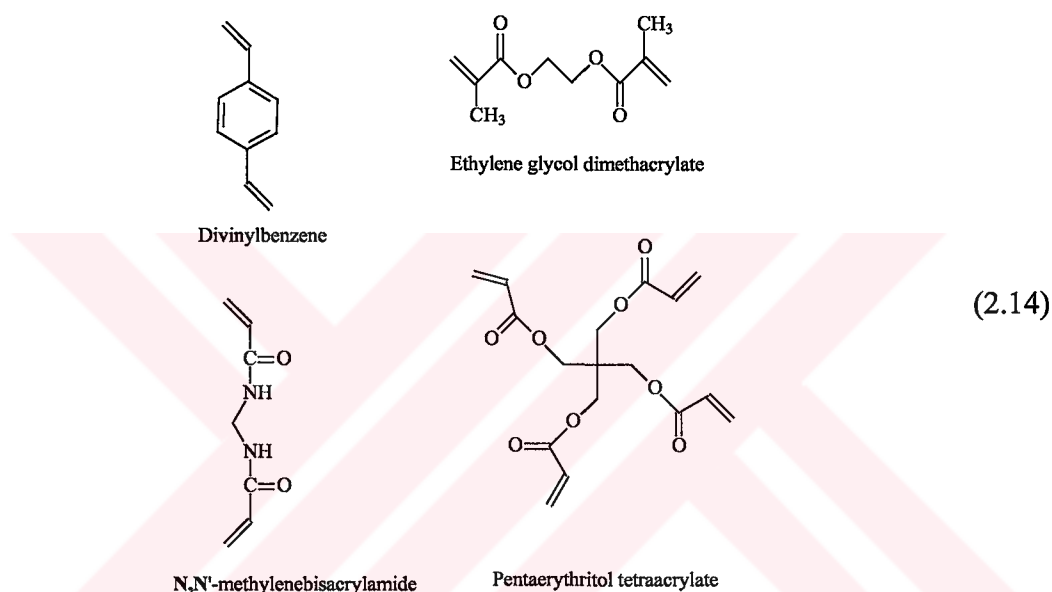
$\text{CH}_2=\text{CH}_2$	Unsubstituted (ethylene) Works fine.	
$\text{CH}_2=\underset{\text{R}}{\text{CH}}$	Monosubstituted Works fine.	
$\text{CH}_2=\underset{\text{R}}{\overset{\text{R}'}{\text{C}}}$	1,1-Disubstituted Usually works.	
$\underset{\text{R}'}{\text{CH}}=\underset{\text{R}}{\text{CH}}$	1,2-Disubstituted Seldom works.	(2.12)
$\underset{\text{R}'}{\text{C}}=\underset{\text{R}}{\overset{\text{R}''}{\text{C}}}\text{H}$	Trisubstituted Almost never works.	
$\underset{\text{R}'}{\text{C}}=\underset{\text{R}}{\overset{\text{R}''}{\text{C}}}\overset{\text{R}'''}{\text{C}}$	Tetrasubstituted Almost never works.	

The only exceptions to the unreactivity of tri- and tetra-substituted vinyl monomers are those with fluorine, like tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$). The main cause of this reactivity pattern is the steric size of the substituents.

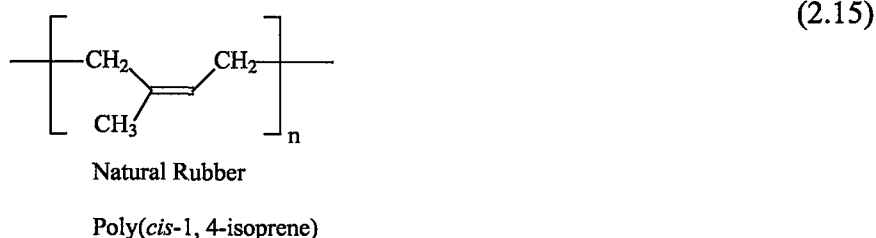
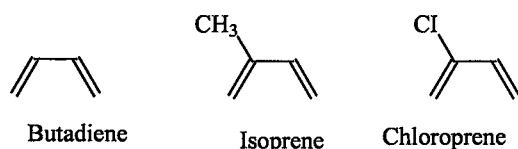


Most of vinylic, acrylic and diene monomers (2.13) can undergo free radical polymerization.

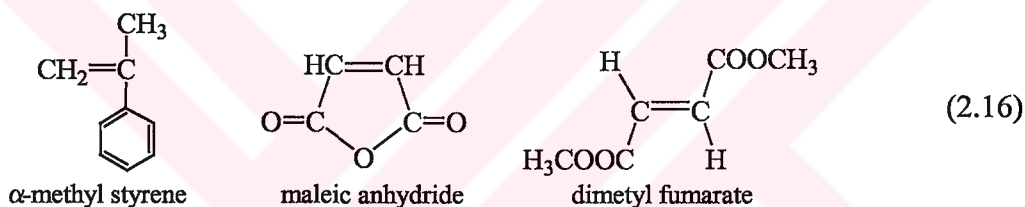
There are many monomers that have been developed containing more than one polymerizable vinyl group such as *p*-divinyl benzene, ethylene glycol dimethacrylate, *N,N'*-methylenebisacrylamide, and pentaerythritol tetraacrylate (2.14). When these groups are relatively far apart on the molecule, they react independently. Either one or both double bonds may participate in polymerization; when both react, cross-linked structures are generated and the polymer will be a thermoset, and cannot be dissolved or melted.



In contrast to the crosslinking monomers above, when the vinyl groups are adjacent and conjugated to each other (a "1, 3-dienes"), more complicated possibilities ensue. For example, the polymerization can occur through only one of the two double bonds, leaving the other one pendant. This is known as 1,2-propagation. In the second possibility, both double bonds get involved. The repeat unit winds up with a double bond within the backbone. This mechanism is known as 1,4-propagation. Examples of dienes containing conjugated double bonds are butadiene, isoprene, and chloroprene (2.15). These important monomers may react by 1,2 or 3,4 addition, or by 1,4 addition. In the former two cases polymerization gives chains with pendant vinyl groups, whereas 1,4 addition leads to unsaturation within polymer chains. Note that the double bond within the backbone can be *cis* or *trans*. Natural rubber is mostly poly(*cis*-1,4-isoprene).



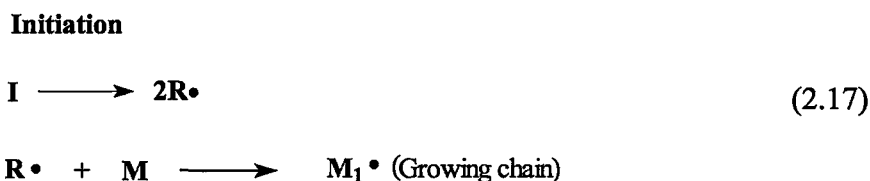
Some potential monomers do not form polymers under usual free radical polymerization conditions. Such as α -methyl styrene is involved in polymerization-depolymerization equilibrium above a ceiling temperature. Maleic anhydride and dimethyl fumarate (2.16) are symmetrically substituted ethylenes therefore; they can not be polymerized by free radical polymerization.



2.1.3 Mechanism of Free Radical Polymerization

A typical free-radical polymerization possesses four elementary steps: initiation, propagation, termination and chain transfer [17, 18]. These steps are *completely independent*. They are separate chemical reactions with different mechanisms, kinetics, and thermodynamics.

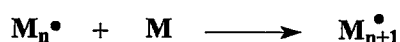
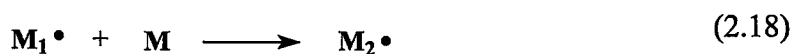
In *initiation*, a free radical R^\bullet derived from an initiator, the “primary radical”, adds to a monomer molecule to form an active center (2.17).



Propagation or growth reaction is just the repetitive addition of a radical to the vinyl group of the monomer, each time reproducing the reactive species at the growing chain end (2.18). Usually, it occurs in head-to-tail fashion, because the free radical

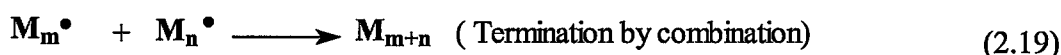
formed is more stable. However, as with initiation, alternatives are possible and head-to-head, tail-to-head, and tail-to-tail modes occur, usually to minor extents.

Propagation

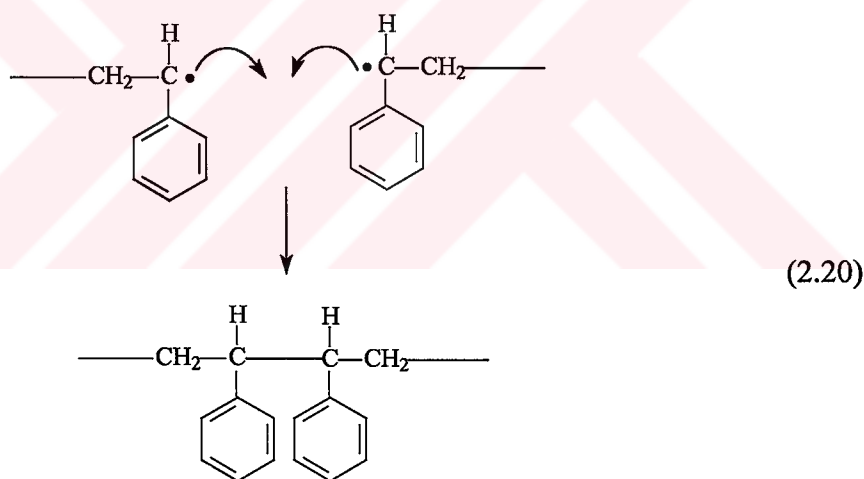


In *termination* of free radical polymerization, secondary reactions stop propagation by the destruction of propagating radicals. The two most common termination reactions are radical combination and disproportionation (2.19).

Termination



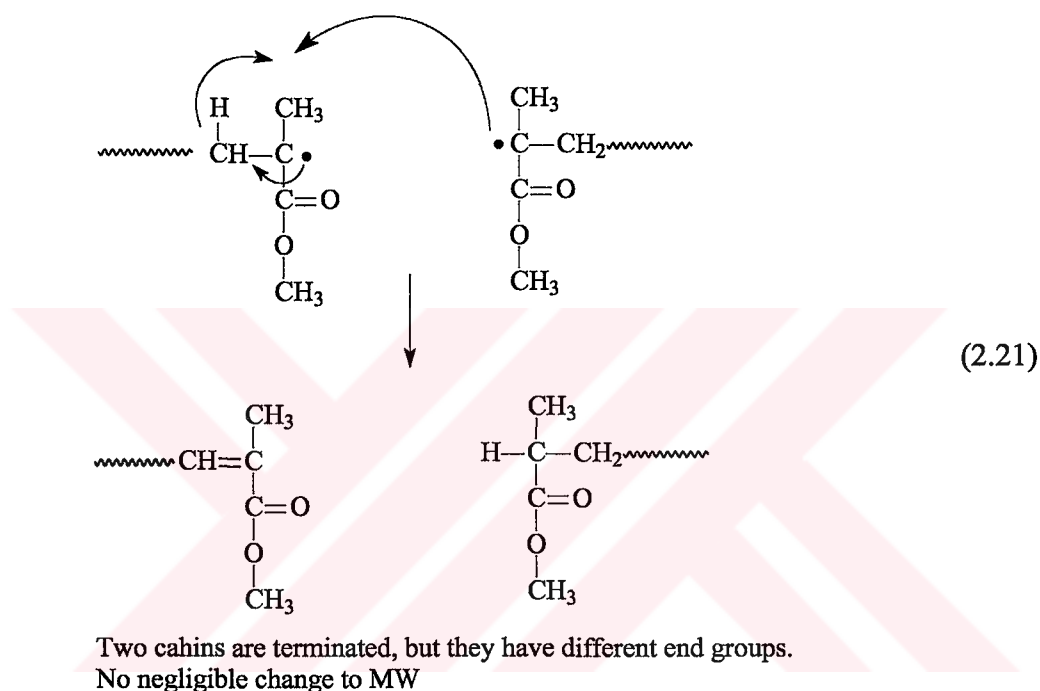
In termination by combination, two polymeric radicals couple and form a new polymer chain with higher molecular weight.



Creates one head to head link. Doubles MW

As for disproportionation, one chain reacts with the penultimate (second-to-last) carbon on the backbone by abstracting a hydrogen atom. In other words, the free radical removes a hydrogen atom with one of the two electrons in its former bond to produce a new (single) bond. Thus, the first chain is deactivated. The second chain is left with the other electron formerly part of the bond to the hydrogen (now removed), and its original propagating radical. These two electrons combine with the single bond to the last carbon atom on the chain to form a double bond. This double bond is rather crowded in most cases compared to the monomer, so it is essentially

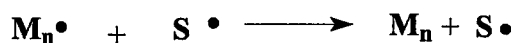
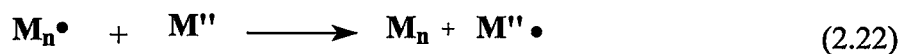
unreactive to radicals subsequently. In this way, the second chain is terminated as well. Because only a hydrogen atom is exchanged, the MW of the two chains is hardly affected by disproportionation. Each chain winds up with one original initiator fragment. The relative proportion of termination by the two mechanisms varies from monomer to monomer, and is also dependent on the solvent and temperature. For example, some polymers like polystyrene (2.20) terminate nearly exclusively by combination, while others such as PMMA (2.21) mostly by disproportionation, and still others by some of both mechanisms.



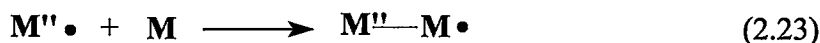
There is another type of termination, known as chain transfer, which stops one chain (2.22) and possibly starts another (2.23). Chain transfer is a kind of termination reaction. It differs from the “normal” termination reactions in that the growing chain radical reacts with chemical species that has an even number of electrons (that is, not another free radical, as is the case for normal termination). Atom (often hydrogen) abstraction from saturated molecules is a well-known reaction of free radicals and, as would be expected, is important in free-radical polymerization. It leads to the chain-transfer process, which brings about the cessation of growth of a propagating radical and at the same time produces a new small radical which may propagate. A great variety of species can participate in chain transfer, act as transfer agents. Chain transfer, therefore, occurs widely; it commonly involves reaction of growing chains with monomer or solvent or other additive and is well established for polymers and

some initiators. Atoms other than hydrogen, notably halogens (except fluorine), may be transferred.

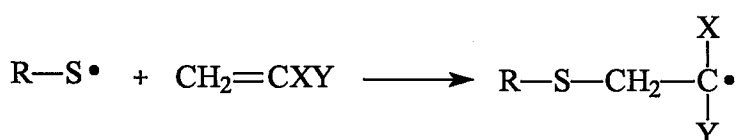
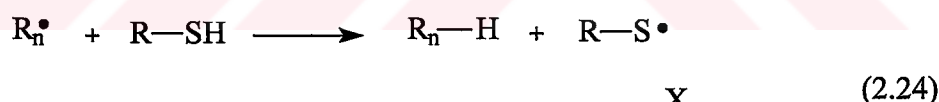
Chain transfer to monomer (M) or Solvent (S)



Reinitiation by transfer agent



There are many forms of chain transfer in vinyl free radical polymerization. They can be transfer to polymer, transfer to monomer, transfer to initiator, and transfer to solvent or impurities. In some circumstances, it is helpful to add deliberately a chain transfer agent (CTA). This is a compound with a weak bond, capable of terminating a growing chain. Various compounds can act as chain transfer agents, but the most common ones are structures with an S-H bond, known as mercaptans or thiols (2.24). Mercaptans have the unfortunate property that the smell is really bad. For example, a trace of mercaptan is added to natural gas to give it odor.



At the other extreme, the new free radical produced by chain transfer can be so unreactive that it does not start any new chains. In this circumstance, the chain transfer agent is better described as an inhibitor, that is, a substance that stops polymerization by reacting with free radicals. Hindered phenols are among the most commonly used inhibitors. Most commercial monomers are packaged with traces of inhibitor to prevent premature polymerization during shipping and storage. The inhibitor can be removed by distillation, extraction, or chromatography. Alternatively, one can simply use extra initiator to overwhelm the inhibitor. Molecular oxygen (O₂) is a particularly strong inhibitor of almost any vinyl free

radical polymerization reaction. Therefore, the reaction mixtures are thoroughly purged with inert gas such as nitrogen. Paradoxically, oxygen can also indirectly be an initiator of free radical polymerization, because it can react with some monomers or impurities to generate peroxides that are thermal initiators.

2.2 Photoinitiated Polymerization

Radical photopolymerization of vinyl monomers played an important role in the early development of polymerization. One of the first procedures for polymerizing vinyl monomers was the exposure of monomer to sunlight. Blyth and Hoffman [20] reported on the polymerization of styrene by sunlight more than 150 years ago. If polymerization is initiated by means of light and both the initiating species and growing chain ends are radicals, it is called *radical* photopolymerization. In the more general sense, photoinitiated polymerization means the increase of molecular weight caused by light and includes the photocrosslinking of preexisting macromolecules. Although vinyl polymerization can be initiated by ionic species as well as by free radicals, almost all examples of photoinitiated polymerization are of a free radical character.

It has to be pointed out that the *absorption* of incident light by one or several components of the polymerization mixture is the crucial prerequisite in the initiation step. If a photosensitive compound absorbs the photon energy directly it undergoes a homolytic bond rupture forming radicals, which may initiate the polymerization. However, the photon energy is absorbed by a compound that itself is not prone to radical formation in some cases. These so called sensitizers transfer their electronic excitation energy to reactive constituents of the polymerization mixture, which finally generate radicals. The radicals generated react with intact vinyl monomer starting a chain polymerization. Under favorable conditions, a single free radical can initiate the polymerization of a thousand molecules. The spatial distribution of initiating species may be arranged in any desired manner.

Comparing the thermally initiated polymerizations, photopolymerization can be carried out at room temperature. This is a basic advantage for both classical polymerization of monofunctional monomers and modern curing applications. Also photopolymerization of monofunctional monomers takes place without side reactions such as chain transfer whereas the probability of chain transfer is high which brings

about a high amount of branched macromolecules in thermal polymerization. Therefore, photopolymerization can be used successfully to obtain low-energy stereospecific polymeric species, namely of syndiotactic configuration. Another important use refers to monomers with low ceiling temperature. They can only be polymerized at moderate temperatures, otherwise depolymerization dominates over polymerization. By means of photopolymerization these monomers are often easily polymerizable. Furthermore, biochemical applications, such as immobilization of enzymes by polymerization, also usually need low temperatures.

Light induced free radical polymerization has enormous commercial use. Techniques related to curing of coatings on wood, metal and paper, adhesives, printing inks and photoresists are based on photoinitiated radical vinyl polymerization.

Photocurable formulations are mostly free of additional organic solvents; the monomer, which serves as reactive diluent, is converted to solid, environmentally safe resin without any air pollution. UV curing is often a very fast process, taking place as pointed out above without heating. If the polymerization mixture absorbs solar light and the efficiency of radical formation is high, photocuring can be performed with no light source but sun light. These features make photopolymerization an ecologically friendly and economical technology that has high potential for further development.

2.2.1 Photoinitiated Free Radical Polymerization

Photoinitiated free radical polymerization has four distinct steps:

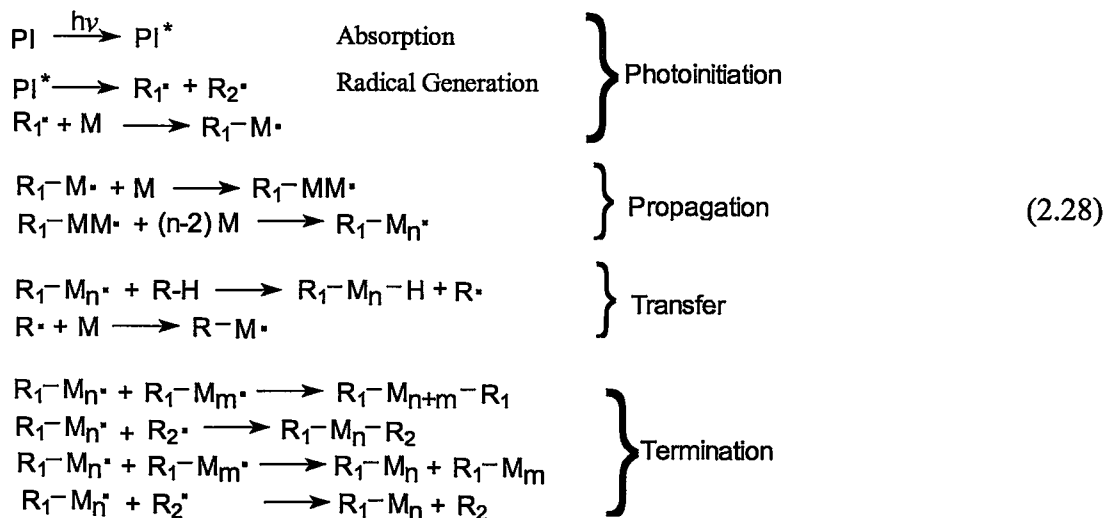
Photoinitiation: It is based on absorption of light by a photosensitive compound or transfer of electronic excitation energy from a light absorbing sensitizer to the photosensitive compound. Homolytic bond rupture results in the formation of a radical that reacts with one monomer unit. This step is the only difference between photopolymerization and thermal radical polymerization.

Propagation: It is repetitive addition of monomer units to the chain radical producing the polymer backbone.

Chain transfer: It is termination of growing chains via hydrogen abstraction from various species like solvent and accompanying production of a new radical capable of initiating another chain reaction.

Termination: Polymeric radicals are used up by coupling or disproportionation reactions.

Four steps of photopolymerization are summarized in reactions 2.28.



It should be pointed out that the role of light in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reaction of these radicals with monomer, propagation, transfer and termination are purely thermal processes and they are not affected by light.

2.2.1.1 Absorption of Light

When the light is absorbed by a molecule, its electrons are excited, what lessens the stability of a bond and can, under favorable circumstances, lead to its dissociation. Functional groups that have high absorbency, like phenyl rings or carbonyl groups, are referred to as chromophoric groups. Naturally, photoinduced bond dissociations do often take place in the proximity of the light absorbing chromophoric groups. In some examples, however, electronic excitation energy may be transferred intramolecularly to fairly distant, but easily cleavable bonds to cause their rupture.

If the monomer possesses chromophoric groups and is sensitive towards light (i.e., it undergoes photoinduced chemical reactions with high quantum yields) one can carry out photopolymerizations by just irradiating the monomer. In many cases, however, monomers are not efficiently decomposed into radicals upon irradiation. Furthermore, monomers are often transparent to light at $\lambda > 320$ nm, where commercial lamps emit. In these cases, photoinitiators are used. These compounds absorb light and bring about the generation of initiating radicals.

2.2.1.2 Radical Generation

a. Radical Generation by Monomer Irradiation

Some monomers can generate radical species via absorption of light. Studies carried out on various vinyl compounds show that a monomer biradical is formed (2.29).



These species can react with intact monomer molecules and thus leading to growing chains. Readily commercially available monomers which undergo polymerization and copolymerization through UV irradiation to some extent are listed in Table 2.1

Table 2.1 Photosensitive Monomers

Allyl methacrylate
Barium acrylate
Cinnamyl methacrylate
Diallyl phthalate
Diallyl isophthalate
Diallyl terephthalate
2-Ethylhexyl acrylate
2-Hydroxyethyl methacrylate
2-Hydroxypropyl acrylate
N,N'-Methylenebisacrylamide
Methyl methacrylate
Pentaerythritol
tetramethacrylate
Styrene
Tetraethylene glycol
dimethacrylate
Tetrafluoroethylene
N-Vinylcarbazole
Vinyl cinnamate
Vinyl 2-fuorate
Vinyl 2-furylacrylate

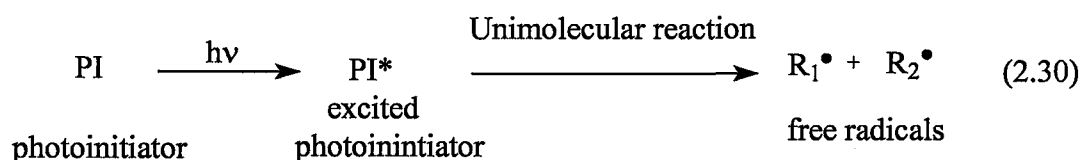
On the other hand, radical generation via irradiation of vinyl monomer does not play a role due to regarding technical applications such as very low efficiency of radical formation and usually unsatisfactory absorption characteristics.

b. Radical Generation by Initiators

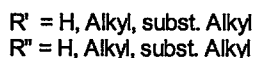
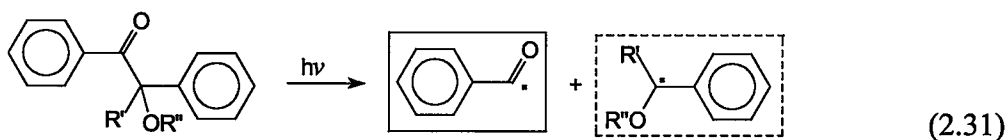
The function of initiators in the photoinduced polymerization applications is usually to generate radicals. Efficient photoinitiators find everyday usage. They are generally

divided into two classes based on process by which initiating radicals are formed [21].

1. Type I Photoinitiators: Initiators undergo a homolytic bond cleavage upon absorption of light. From the point of view of chemical kinetics, the fragmentation that leads to the formation of radicals is a unimolecular reaction (2.30). Although type I photoinitiators are highly reactive UV photoinitiators, they are less frequently used in visible light curing systems.

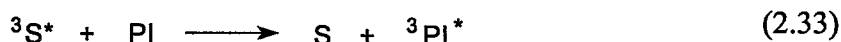


The number of initiating radicals formed upon absorption of one photon is termed as quantum yield of radical formation (Φ_R .) Theoretically, cleavage type photoinitiators should have a Φ_R value of two since two radicals are formed by the photochemical reaction. However, Φ_R values are much lower because of various deactivation routes of the photoexcited initiator other than radical generation. These routes include physical deactivation such as fluorescence or non-radiative decay and energy transfer from the excited state to other, ground state molecules, a process referred to as quenching. The reactivity of photogenerated radicals with polymerizable monomers is also to be taken into consideration. In most initiating systems, only one in two radicals formed adds to monomer thus initiating polymerization. The other radical usually undergoes either combination or disproportionation. Regarding the energy necessary, it has to be said that the excitation energy of the photoinitiator has to be higher than the dissociation energy of the bond to be ruptured. The bond dissociation energy, on the other hand, has to be high enough in order to ensure long term storage stability. The majority of Type I photoinitiators are aromatic carbonyl compounds with appropriate substituents, which spontaneously undergo α -cleavage generating free radicals (2.31). The benzoyl radical formed by the reaction depicted is very reactive towards the unsaturations of vinyl monomers [22].

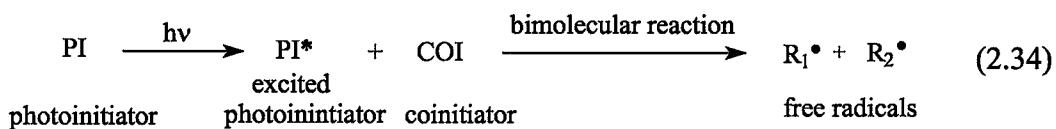


The α -cleavage often referred to as Norrish Type I reaction [23] of carbonyl compounds starts from the initiator's triplet state, which is populated via intersystem crossing. Notably, the excited triplet states are usually relatively short lived that prevents excited molecules to undergo side reactions with constituents of the polymerization mixture. While triplet quenching by oxygen can, in most cases, be neglected due to the short lifetime of the triplet states, quenching by monomer sometimes plays a role. However, this refers exclusively to monomers with low triplet energies, like, e.g., styrene ($E_T = 259 \text{ kJ mol}^{-1}$).

If the absorption characteristics of a cleavable compound are not meeting the requirements, i.e., the compound absorbs at too low wavelengths, the use of sensitizers (S) with matching absorption spectra is recommendable. Sensitizers absorb the incident light and are excited to their triplet state (2.32). The triplet excitation energy is subsequently transferred to the photoinitiator which forms initiating radicals (2.33). This process has to be exothermic, i.e., the sensitizer's triplet energy has to be higher than the triplet energy level of the initiator. Through energy transfer, the initiator is excited and undergoes the same reactions of radical formation as if it were excited by direct absorption of light. The sensitizer molecules return to their ground state upon energy transfer; they are therefore not consumed in the process of initiation.

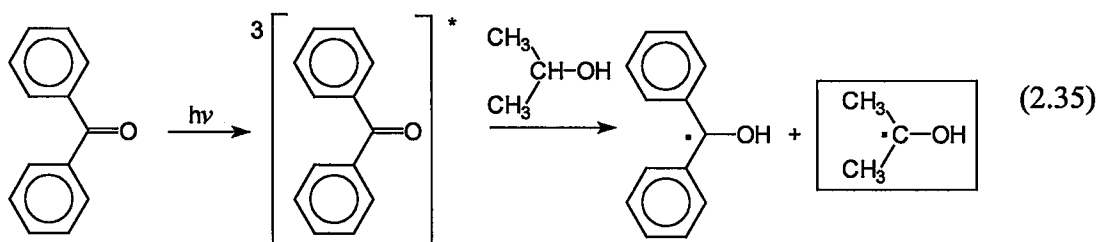


2. Type II Photoinitiator or PI₂-type initiator: They are the photoinitiators in the excited state interacting with a second molecule (a coinitiator) to generate radicals in a bimolecular reaction (2.34). Type II photoinitiators are versatile initiators for UV curing system and visible light photoinitiators belong almost exclusively to this class of photoinitiators.

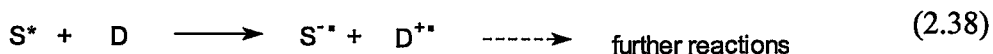
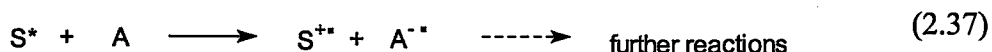


The excited states of certain compounds do not undergo Type I reactions because their excitation energy is not high enough for fragmentation, i.e., their excitation energy is lower than the bond dissociation energy. The excited molecule can, however, react with another constituent of the polymerization mixture, the so-called coinitiator (COI), to produce initiating radicals. There are two distinct pathways of radical generation by Type II initiating systems, namely *hydrogen abstraction*, *photoinduced electron transfer reaction and subsequent fragmentation*.

Hydrogen abstraction takes place from a suitable hydrogen donor. Photoinitiators of this group are generally aromatic ketones and include benzophenone, benzil, quinones, Michler's ketone, and thioxanthenes. When photoexcited these compounds do not dissociate but enter into bimolecular abstraction reactions with hydrogen donors such as alcohols, ethers, tertiary amines, and so on. As a typical example, the photoreduction of benzophenone by isopropanol is depicted (2.35). Bimolecular hydrogen abstraction is limited to diaryl ketones [23]. From the point of view of thermodynamics, hydrogen abstraction is to be expected if the diaryl ketone's triplet energy is higher than the bond dissociation energy of the hydrogen atom to be abstracted.



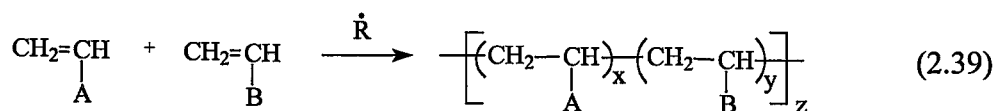
In electron transfer reactions, the photoexcited molecule, termed as sensitizer for the convenience, can act either as electron donor or electron acceptor according to the nature of the sensitizer and coinitiator (2.36). Fragmentation yields radical anions and radical cations (2.37), which are often not directly acting as initiating species themselves but undergo further reactions (2.38), by which initiating free radicals are produced.



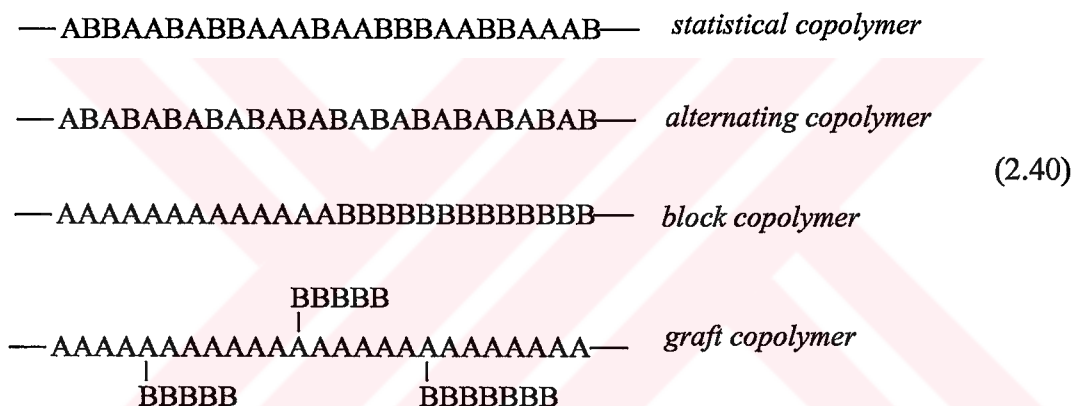
Electron transfer is often observed for aromatic ketone/amine pairs and always with dye/coinitiator systems.

2.3 Free Radical Chain Copolymerization

The demand for new and improved materials often can be achieved as a result of altering the properties of existing polymeric materials. For example, the use of additives can incorporate desirable properties into an existing polymer material that is to be used for specialized applications. Common additives include plasticizers, stabilizers, flame retardants, fillers, colorants, processing aids, and impact modifiers [24]. Another approach is to combine the beneficial properties of different known polymer structures. One known technique to achieve this is to simply blend two individual polymers to give a material whose mechanical properties exceed those of the individual blend components (*i.e.*, synergism). A few advantages of blending include reducing the cost of expensive high performance polymers, improving the processability of a high temperature material, and improving impact resistance of materials. However, because few polymers are miscible, their blends form immiscible phase separated materials. These immiscible blends often have poor physical properties due to inadequate interfacial strength between the phases [25]. A desirable alternative is to copolymerize different monomer structures into a single polymeric material (2.39) [26]. Prime examples include the important commercial materials produced from vinyl chloride/vinyl acetate and styrene/butadiene copolymers. Careful consideration of such factors as the selection of the comonomers and the copolymerization reaction conditions allows one to precisely tailor the properties of the resulting copolymer and provides a useful method of synthesizing an almost unlimited number of polymeric structures with a wide range of properties and applications.



Copolymer structures can be described in a variety of ways. Different types of copolymers include statistical, alternating, block, and graft copolymers (2.40). Statistical copolymers result from a single process where the incorporation of the comonomers follow some statistical law that is due solely to kinetic factors [27]. Alternating copolymerization, which will be focused in the preceding sections, is an example of chain copolymerization where each of the monomers adds preferentially to the other and homopropagation is effectively nonexistent [28]. Block and graft copolymers differ in that they contain long sequences of each comonomer either along the backbone or as side chains (grafts) and are often the result of a multi-step process [29].



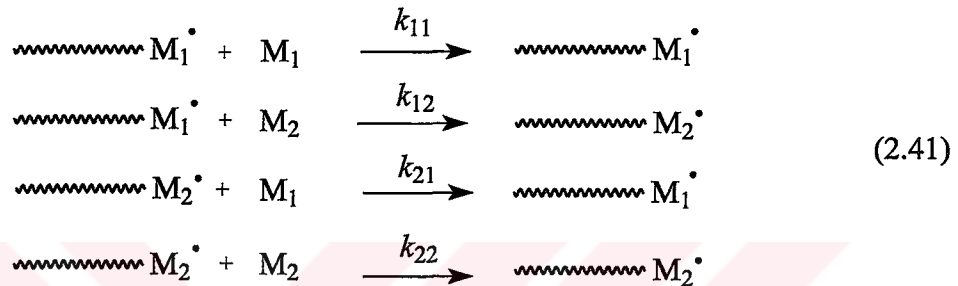
The manner in which comonomer repeat units are incorporated into the polymer backbone is determined from the reactivities of the monomers and radicals involved in the reaction. Reaction conditions such as solvent and temperature can also have a marked effect on the monomer reactivities and will contribute to the copolymer composition. Therefore, in only a few select cases of chain copolymerization will the copolymer composition be directly proportionate to the monomer feed. More typically, both the comonomer feed and instantaneous copolymer composition vary throughout the copolymerization, which results in heterogeneity.

2.3.1. Copolymerization Models

2.3.1.1. Terminal Model

The simplest quantitative statistical treatment for the determination of copolymerization composition, which is generally referred to as the terminal model,

was first hypothesized by Dostal [30] in 1936 and later elucidated by others [31]. The terminal model is based upon the assumption that the chemical reactivity of a propagating polymer chain is independent of the size or composition of the chain and is only influenced by the active end group [32]. Though the terminal model is dependent on several assumptions and may not be the most accurate model to describe a copolymer process, it is relatively simple to apply and provides a facile starting point when evaluating copolymerizations of various monomer pairs. When two monomers, M_1 and M_2 are copolymerized by free radical methods, four reactions are feasible according to the terminal model:



Where k_{11} is the rate constant for the addition of a propagating chain ending in M_1 adding to monomer M_1 , k_{12} is the rate constant for the addition of a propagating chain ending in M_1 adding to monomer M_2 , and so on. The rate constants can then be expressed in terms of the monomer reactivity ratios, r_1 and r_2 , where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. Monomer reactivity ratios may either be experimentally [33] determined or estimated [34] and for free radical polymerizations are generally independent of initiator and solvent with only slight temperature dependence. The different types of copolymerization behaviors can then be described based upon the values of the monomer reactivity ratios. “Random copolymerization” results when $r_1 = r_2 = 1$ due to the equal reactivity of the monomers toward both types of propagating chain ends and the resulting copolymer composition will directly reflect the comonomer feed. When $r_1 r_2 = 1$, the two different types of propagating chain ends both add preferentially to one of the monomers, and is described as “ideal copolymerization”. The case when r_1 and r_2 are much greater than one results in a tendency to form blocks of both monomers and is appropriately termed “block copolymerization”. The copolymerization behavior focused upon in this review, which describes the situation when $r_1 = r_2 = 0$, is referred to as “alternating copolymerization”. The mechanism of most typical copolymerizations fall somewhere between the extremes of “ideal copolymerization” and “alternating copolymerization”. The mechanism of becomes

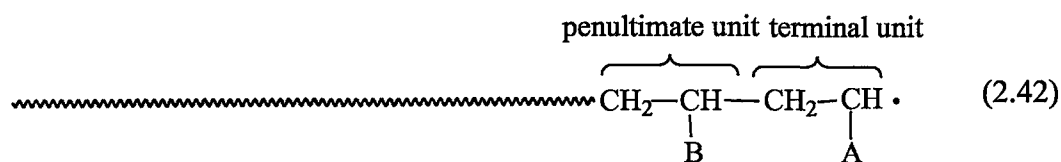
increasingly “alternating” as the $r_1 r_2$ product decreases from one toward zero. For polymerizations where the $r_1 r_2$ product lies somewhere between zero and one, the composition of the copolymer can be controlled to some extent by variation of the monomer feed ratio. However, as $r_1 r_2$ approaches very close to zero, the “alternating” behavior of the polymerization mechanism becomes the dominating factor and a 1:1 alternating copolymer can be formed independent of the monomer feed ratio. The terminal model also provides a useful means to approximate copolymer compositions that are dependent on such factors as the comonomer feed ratio and the reactivities of the comonomers according to the model. The Mayo-Lewis equation [35], which is derived from the terminal model using the assumption of the steady-state radical approximation, can be used to describe the instantaneous copolymer composition:

$$\frac{d [M_1]}{d [M_2]} = \frac{[M_1] (r_1 [M_1] + [M_2])}{[M_2] ([M_1] + r_2 [M_2])} \quad (\text{Eq.2.1})$$

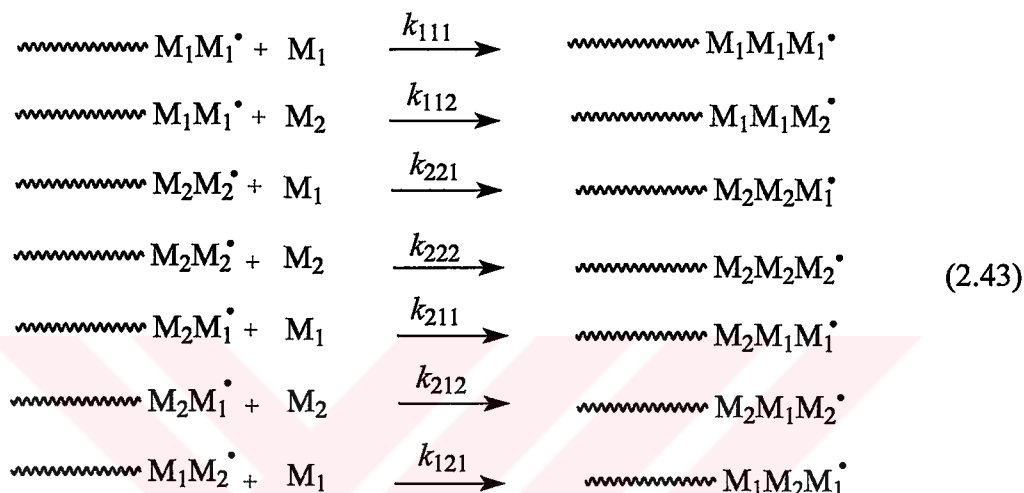
Where r_1 and r_2 are the respective monomer reactivity ratios. $[M_1]$ and $[M_2]$ describe the beginning concentrations in the comonomer feed. The instantaneous mole fractions of the two repeating units in the copolymer is then defined as $d[M_1]/d[M_2]$. The terminal model, therefore, allows one to predict the instantaneous copolymer composition for a given comonomer feed simply on the basis of the comonomer reactivity ratios. Although the terminal model relies on several assumptions and may not be the most reliable model to describe of a copolymerization process, it has the advantages of being simple to apply and very useful as a starting point to study a given copolymerization reaction.

2.3.1.2. Penultimate Model

It has been shown that the behavior of the propagating species of some comonomer pairs is significantly influenced by the penultimate monomer unit [36]. The principal feature of the penultimate model is that the penultimate unit (2.42) in a propagating polymer chain will affect the reactivity of the terminal reactive radical. The exact nature of the penultimate unit of the propagating species will determine the magnitude of this effect. For example, Tirrell and coworkers have reported that in copolymerizations of styrene and acrylonitrile, there is little effect of the terminal radical reactivity when the penultimate units is styrene unit, but there is an appreciable effect when the penultimate unit is acrylonitrile [37].



The effect of the penultimate unit on the kinetic of copolymerization was first reported by Merz et al. [38] and later by Ham [39] and Barb. [40] The mathematical model for the penultimate effect involves the use of eight propagating reactions (2.43) from which four reactivity ratios are defined (Eq.2.2):

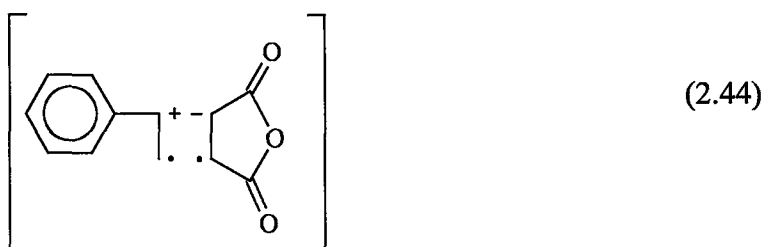


$$r_{11} = \frac{k_{111}}{k_{112}} \quad r_{12} = \frac{k_{122}}{k_{121}} \quad r_{22} = \frac{k_{222}}{k_{221}} \quad r_{21} = \frac{k_{211}}{k_{212}} \quad (\text{Eq.2.2})$$

Each monomer is thus characterized by two monomer reactivity ratios. One reactivity ratio (r_{11} and r_{22}) that represents the propagating species in which the penultimate and terminal monomer units are the same. The other represents the propagating species in which the penultimate and terminal units differ (r_{12} and r_{21}). Several copolymerization processes have been studied where the experimental data agreed better with the penultimate model than the terminal model. However, application of the penultimate model to study copolymerization behavior is significantly more complicated and time consuming than application of the terminal model. Consequently, the study of copolymerizations has been primarily limited to analysis in terms of the terminal model. Comonomers that have been studied using the penultimate model include acrylonitrile, [41] butadiene, [42] maleic anhydride [43], and vinyl chloride [44].

2.3.1.3. Complex Model

The complex model assumes that no free monomers are involved in the kinetic rate of the reaction, but rather the polymer chains propagate by the head-to-tail homopolymerization of comonomer complexes. Copolymerization mechanisms involving complexed comonomers were first introduced to help explain the high degree of alternation observed for some copolymerization reactions [45]. One proposed mechanism is that there is a charge-transfer-complex (CTC) that exists between electron poor/electron rich comonomer pairs and propagation of the copolymer then proceeds via the polymerization of the CTC and not of the individual comonomers [46]. The most studied system is that of styrene-maleic anhydride. The idealized structure of the proposed CTC of the styrenemaleic anhydride comonomer pair is illustrated in (2.44) [47]. The validity of complex copolymerization models has been thoroughly debated over the years. The existence of complexes between certain comonomer pairs using spectroscopic techniques has been well documented and accepted. Donor-accepter interactions between monomer pairs can lead to highly colored complexes and the appearance of new absorption bands in the UV-visible spectrum are observed [48]. In addition, charge transfer complexes have been characterized by small chemical shifts in the NMR spectra [49]. However, evidence for the involvement of these complexes in the actual propagation step has been less conclusive and thus undeniable proof for a copolymerization mechanism via a CTC has not been presented [50].



Complex copolymerization models have been applied to the study of many electron donor-acceptor comonomer pairs [51]. Electron donating monomers studied include linear dienes, heterocyclic dienes, vinylbenzenes, vinyl esters, vinyl ethers, and vinyl sulfides. Electron accepting monomers include maleic anhydride, maleimides, acrylate esters, cinnamate esters, cyanoethylenes, and fumarate esters. Characteristic features of copolymerizations involving electron donor-accepter pairs include high degrees of alternation, faster copolymerization rates than either homopolymerization

rate, and in many cases the strongly electron donating or accepting monomers will not undergo homopolymerization to an appreciable extent. Several complex copolymerization models have been reported to help explain the behavior of copolymerizations involving donor-acceptor comonomer pairs. For example, the complex participation model assumes that the comonomer complex that is formed is much more reactive than the uncomplexed monomers and as a result the comonomers are incorporated into the chain as pairs and result in perfectly alternating sequences [52]. The complex participation model considers both propagation of complexed comonomer pairs and also competing propagation of uncomplexed monomers. An alternative model is called the complex dissociation model [53], which also considers propagation of uncomplexed monomers. However, where the complex dissociation model differs is that it assumes the complexed monomer pairs dissociate upon addition to a growing polymer chain and as a result only a single monomer unit is incorporated into the polymer chain. These complex models have been successful in describing the copolymerization behavior of certain donor-acceptor comonomer pairs. However, it is often difficult to differentiate between these models and other higher order models such as the penultimate model, which do not consider the existence of comonomer complexes [54]. In addition, application of complex copolymerization models have been further complicated due to the feature that many of these donor-acceptor pairs undergo spontaneous initiation [55].

2.3.2. Principles of Alternating Copolymerization

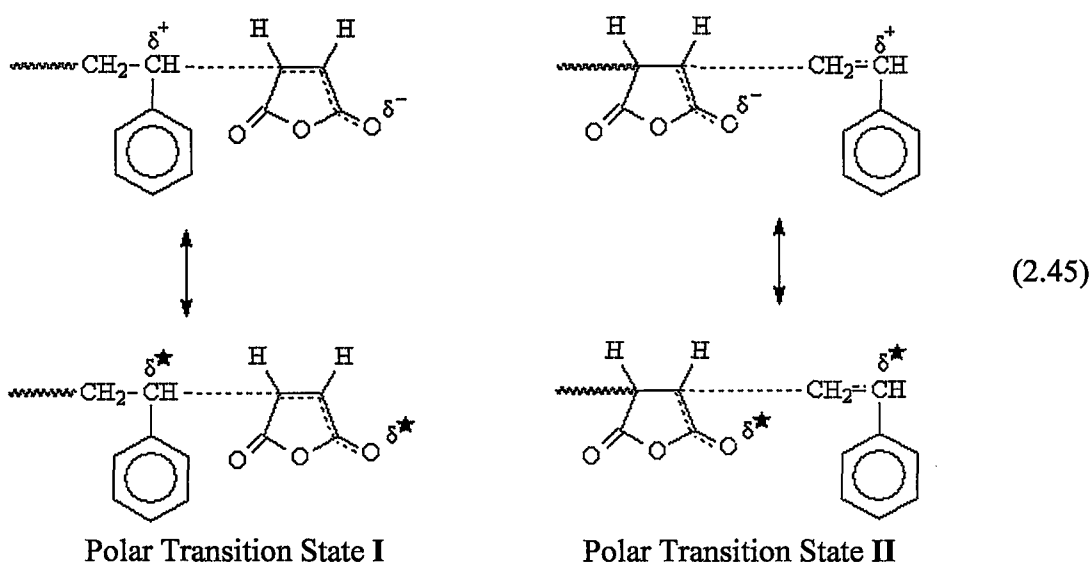
When two monomers are mixed together in the presence of an initiator there are several ways that the monomers may combine to form a copolymer. In general, the composition of the product rarely follows the monomer feed ratio. Furthermore, the composition resulting from a copolymerization reaction cannot directly be predicted from knowledge of the homopolymerization rates of the monomers [56]. Therefore, the factors that determine the incorporation of repeating units into a copolymer chain are not as trivial as those in homopolymerization reactions. Not only does the homopolymerization rate of the comonomers have an effect, but the rate at which comonomers react with each other is also a determining factor.

Alternating copolymerization is an example of chain copolymerization where each of the monomers adds preferentially to the other, which results in an alternating monomer sequence distribution along the backbone [57]. Monomers that are difficult to homopolymerize are often found to be capable of alternating copolymerization. For example, if a strong electron acceptor is added together with a strong electron donor, regular alternating copolymers may result from either spontaneous initiation or a free radical source [58].

Alternating copolymerization of certain pairs of vinyl monomers has been known for many years, and debate and disagreement about the mechanism of this process have been extensive [59, 60].

The probability of formation of such regularly alternating copolymers via a random process is very low. However, one set of properties invariably associated with monomer pairs that exhibit this alternating tendency is the complementary electron-donor/electron-acceptor character of the pair. A strongly electron-donating monomer (D) tends to undergo alternating copolymerization with a strongly electron-accepting monomer (A). Thus, two independent theories have been advanced to account for this result. The first postulate [61] was that polarity differences between the radical chain end and the incoming monomer would lower the energy of activation of cross-propagation, as opposed to a homopropagation reaction, thus producing strictly alternating copolymers when the comonomers have widely different polarities.

The first explanation assumes the a transitions state in which the electron-poor maleic anhydride accepts charge from the electron-rich styrene donor [61,62]. This can occur when either monomer is present at the growing end of the macroradical thereby leading to either polar transition state **I** or **II** (2.45). Thus, the transition state for the addition of a styrene-terminated growing chain radical to maleic anhydride can be presented by **I**, while the transition state for the addition of a maleic anhydride-terminated macroradical to a styrene can be presented by **II**. Both of these are highly polar.



Polarization in the transition state should be greater than in the individual monomers because the electron-poor and electron-rich monomers interact and extend the distance and magnitude of charge separation. In this rational, alternation occurs because transition states I and II are stabilized by charge attraction, thereby lowering the activation energies and enhancing k_{12} and k_{21} relative to k_{11} and k_{22} . This polar stabilization is not present when a styrene-terminated macroradical adds to styrene or when a maleic anhydride macroradical attempts to add to maleic anhydride. Thus, the rate constants k_{12} and k_{21} are increased relative to k_{11} and k_{22} by such polar factors. The net effect is that r_1 and r_2 become very small and an alternating copolymer forms.

2.3.2.1 Charge Transfer Complex (CTC) Participation in Alternating Copolymerization

The second postulate was that an electron-donating/ electron-accepting monomer pair formed a charge transfer complex (CTC) that, due to an inherently higher reactivity of the complex relative to the free monomers, preferentially added to the chain end [63-67].

Charge Transfer Complex in Radical Copolymerization

In general, depending on the type of conjugation of double bond and functional groups, all functional monomers can be categorized into two major groups: electron-acceptor (A) monomers and electron-donor (D) monomers. Functional substituted ethylenes, containing primary carboxyl, anhydride, ester, amide, imide and nitril fragments, include a wide range of A-monomers such as: (1) maleic anhydride and

its a,b-substituted derivatives (citroconic, dimethylmaleic and halogen-substituted maleic anhydrides), itaconic anhydride and etc.; (2) imides and *N*-substituted imides of unsaturated dicarboxylic acids (maleic and a,b-substituted maleic acids, itaconic acid, etc.); (3) unsaturated mono- and dicarboxylic acids (crotonic, *trans*-cinnamic, maleic, fumaric acids, etc.) and their esters, nitrils and amides and (4) tetrahalogen-substituted ethylenes. Sulfur dioxide (SO₂) can be also included in the abovementioned group of A-monomers which easily copolymerize with vinyl and allyl D-monomers and form the alternating copolymers.

Geometry and structure of molecular A–D complexes and their relationship with mechanism of reactions were considered by Andrews and Keefer [68] and Briegleb [69], where mechanism about alternating copolymerization of some monomers also was mentioned. It is known that molecular complex with equimolar composition is A–D system which has wave function (ψ) in the basis state [69, 70]:

$$\psi_N \approx a\psi_0(D \cdot A) + b\psi_1(D^+ - A^-) \quad (\text{Eq.2.3})$$

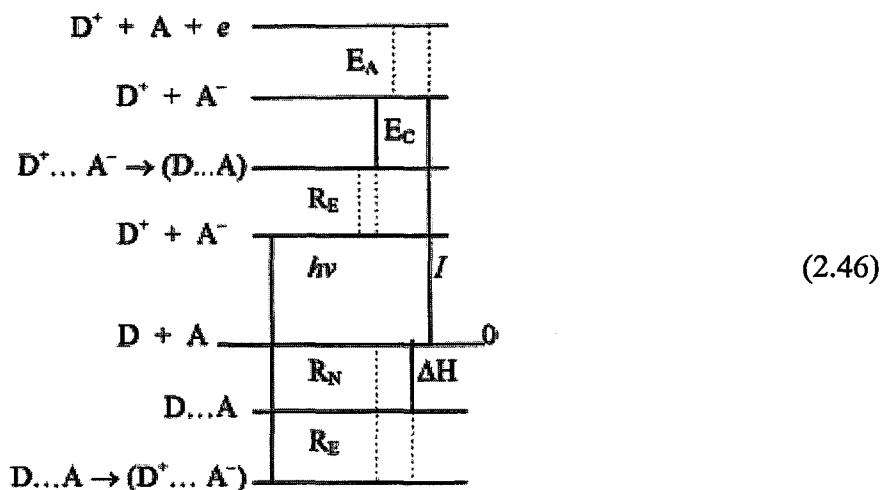
Molecular complex with weak bond ($a^2 \gg b^2$) is considered as resonance hybrid. E-complex in the excited state is described by following equation:

$$\psi_E = a^* \psi_1(D^+ - A^-) - b^* \psi_0(D \cdot A), \text{ where } a^* \approx a, b^* \approx b \text{ and } a^2 \gg b^2 \quad (\text{Eq.2.4})$$

$N \rightarrow E$ transfer is accompanied by visible or UV absorption which corresponds to the electron transfer from D-monomer to A-monomer.

π -electrons of double bond and/or functional group (COOH, COOR, C=O, CN, etc.) of A-monomers can be take part in complex-formation depending on the nature of second component (X) of $A \cdot \cdot X$ complex, where X can be: (1) D-monomers; (2) organic compounds with electron-acceptor or electron-donor functional groups or bonds; (3) polar organic solvents and (4) acids, inorganic and organometallic compounds of Lewis-acid-type. On the other hand, D-monomers at the same time can take part in complex-formation through other functional groups.

The phenomenon of charge transfer in D–A monomer system from the point of view of interaction energy levels and their mutual transfers can be presented by the following scheme [71]:



where R_E —excited state, R_N —normal state, E_C —energy of charge transfer, $h\nu$ —bond energy, I —potential ionization of D-monomer, E_A —affinity of A-monomer to electron and ΔH —enthalpy of CTC formation.

CTC formation reaction is accompanied by the initiation of two new level energies: (1) more stable lower level corresponding to R_N state and (2) less stable excited level in R_E state. When light is absorbed by a CTC an electron in a definite orbit is excited and is transferred to a lower molecular orbit. The energy of this transfer as usually has an insignificant value (2–10 kcal/mol) and absorption is carried out in the visible field of spectra. As a result, the formed complexes acquire a visible color due to this reason in spite of their individual components being colorless. For transfer of electron from D-monomer orbit to orbit of A-monomer molecules of these monomers must approach each other sufficiently near and must take one's bearings so as to provide a maximum floor of corresponding orbits. Spontaneous charge transfer can be carried out in case of more active D-monomers having small value of potential ionization. Evidently, extreme case, i.e. formation of two ion-radical as a result of Culone interaction cannot be realized in monomer CTC systems. Formation of monomer CTC can be considered from the point of view of theory of valence as a resonance hybrid of inert and charge forms, which are transferred from one form to another as a result of interchange of charge, as shown in above-mentioned scheme. CTC have nearly non-bonded structure with insignificant conversion of donor–acceptor structure ($D^+ \cdot \cdot A^-$). In normal state (R_N), E_C depends on potential ionization of D-monomer as well as on affinity of A-monomer for electron. Increase of I

decreased force of charge transfer at $E_A = \text{const}$: Energy of band in CTC depend on I , E_A , E_r (resonance energy) and E_{cl} (Culone energy):

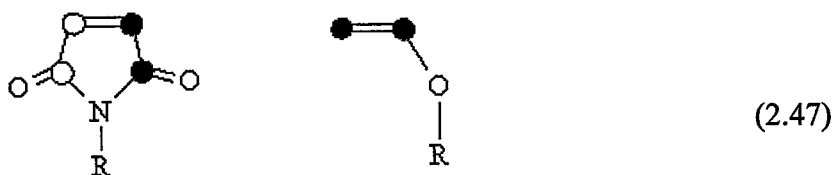
$$h\nu = I + E_A + E_r + E_{cl} \quad (\text{Eq.2.5})$$

$R_N \rightarrow R_E$ transfer accompanied by increasing of ΔH of complex-formation. Decrease of complexformation constant (K_c) of $A \cdot \cdot D$ complex depends on the nature of A and D monomers and ΔH becomes more negative (maximum increase of ΔH). Use of potential curves representing plot of $E_c \rightarrow R$ (internucleusdistance) also is convenient method for elucidation of charge transfer phenomenon in the D–A monomer systems [71].

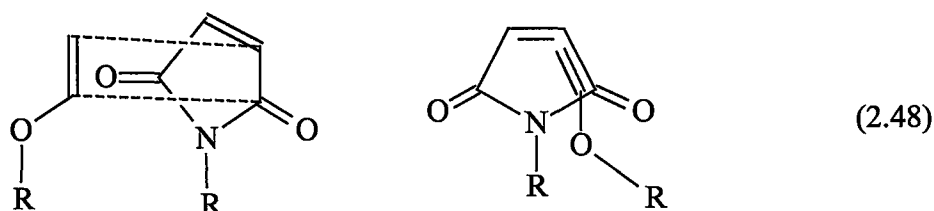
2.3.2.3 Monomer Orientation Control by Charge Transfer Complex Participation in Alternating Copolymerization

CTC is expected to have a preferred geometry; thus, a CTC may add to the chain end in a concerted manner (as opposed to stepwise addition of D and A), introducing controlled stereoregularity. If the "free" monomers add to the chain end, random stereochemistry would be expected [72].

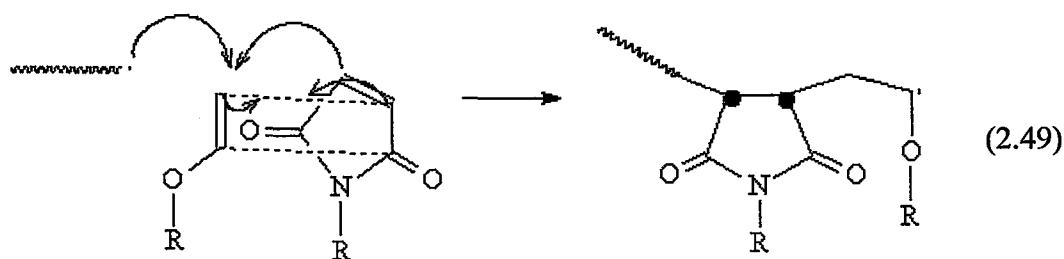
Mulliken theory [73] predicts that the most probable geometry of a charge-transfer complex is that in which there is maximum overlap between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor. The LUMO of maleimide monomers [74] and the HOMO of vinyl ethers are depicted below.



Thus, the expected geometry of the complex may be visualized as

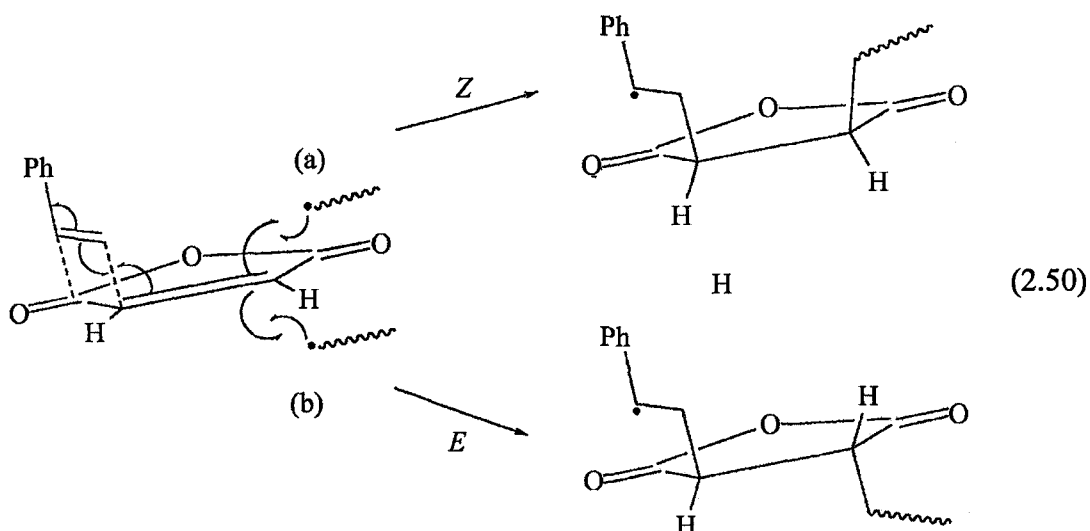


The stereochemical results discussed above may be rationalized by involving attack of the radical chain end on the side of the complex that is *syn* to the vinyl ether.



This mechanism is, in effect, a concerted addition of the complex to the chain end. The next complex could conceivably add to either side of the vinyl ether radical, thus explaining the random relative stereochemistry between the vinyl ether methine carbon and the methines of adjacent succinimide units observed in the copolymers.

If EDA complex participation is largely responsible for the formation of alternating sequences as described above, the stereochemistry of complex addition needs further investigation if the formation of a predominance of *zusammen* (*cis*) *Z*-MA units in the completely alternating copolymer samples is to be explained when the *entgegen* (*trans*) *E* form is more thermodynamically favourable [75,76]. In addition, workers studying rigidly alternating copolymers in the past have suggested that complex addition should lead to rigidly stereoregular alternating copolymers, not ones in which a mixture of configurations exist [77-79]. Butler and coworkers [80,81] have proposed a mechanism based on the maximum orbital overlap theory of Mulliken [73], for the formation of *cis*(*erythro*) succinimide units in copolymer of *N*-substituted maleimides with vinyl ethers, that may provide an explanation for the result. The mechanism, adapted to the present case, is presented (2.50). This shows that addition of the growing radical chain to the side of the complex that is *syn* to the styrene unit leads to the addition of MA unit in the *Z* configuration (a), while attack from the opposite side (b), yields the *E* configuration. EDA complex participation following this mechanism can therefore lead to addition of both *Z*- and *E*-MA units to the growing radical chain. As the addition of free comonomers to the chain could normally be expected to result in MA units in the *E* configuration. CTC complex addition via can be hence seen as the main source of *Z*-MA units in the copolymers (2.51).



The stereoregularity of this type of copolymers varies with copolymerization conditions as temperature, solvent, total concentration of the co-monomers, co-monomer concentration ratio at fixed total monomers' concentration and the donor-acceptor character of the co-monomers' pair.

2.3.2.4 Determination of the Equilibrium Constant for CTC Formation

A measure for the strength of the donor-acceptor interaction is the equilibrium constant of CTC complex formation (K_{CTC}). The interaction of the donor and acceptor can be described by the equilibrium equation (2.51).



The magnitude of the equilibrium constant, K_{CTC} , was determined as a measure of the interaction between two molecules by several methods. Ultraviolet spectrophotometry and NMR spectroscopy are most often used, but other techniques such as calorimetry, vapor pressure measurement, and dielectric constant determination have been applied. The UV spectroscopic measurements utilize the Benesi-Hildebrand [82] equation for determining the charge-transfer equilibrium constant. The equilibrium constant for the CTC equilibrium can be written as (Eq.2.6) where D and A stand for donor and acceptor, respectively and $[A]_0$ and $[D]_0$ are the initial concentrations:

$$K_{CTC} = \frac{[CTC]}{[A][D]} = \frac{[CTC]}{([A]_0 - [CTC])([D]_0 - [CTC])} \quad (\text{Eq.2.6})$$

The formation constant of the complex was determined by the following Benesi-Hildebrand equation (Eq.2.7),

$$[A]_0 \cdot 1/A_{CTC} = 1/\epsilon_{CTC} + 1/K_{CTC} \epsilon_{CTC} \cdot (1/[D]_0) \quad (\text{Eq.2.7})$$

where A_{CTC} and ϵ_{CTC} are the absorbance and molar absorptivity of the complex, K_{CTC} is the equilibrium constant for complex formation and $[D]_0$ and $[A]_0$ are the initial concentrations of the donor and acceptor. This method takes the advantage of the fact that most π -complex that CTC represents have a new absorption band in the visible or ultraviolet region which is characteristic of the complex. From an appropriate plot observed optical density vs. donor concentration, the molar absorptivity index of the complex can be calculated.

An expression analogous to the Benesi-Hildebrand equation is derived by Hanna and Ashbough [83] for use with ^1H NMR data. Consider the chemical shift of protons on acceptor molecules which are undergoing rapid exchange [84] between the complexed and the uncomplexed state. ^1H NMR spectroscopy for the determination of the equilibrium constant has been shown by Hanna and Ashbough to be the preferred method for determination of EDA equilibrium constants, particularly when there is clearly visible olefinic hydrogen.

The chemical shift (δ_{obs}) the acceptor protons is a weighted average of the shift due to the free molecules (δ_f) and those due to the CTC formed (δ_{CTC}) since equilibration is rapid on NMR scale. This leads the following equation (Eq.2.8):

$$\delta_{\text{obs}} = \delta_f \left[\frac{[A]}{[A] + [CTC]} \right] + \delta_{CTC} \left[\frac{[CTC]}{[A] + [CTC]} \right] \quad (\text{Eq.2.8})$$

During polymerization the donor molecules are present in large excess over donor molecules. When this is the case the Hanna-Ashbough relation [85,83] can be obtained and employed (Eq.2.9):

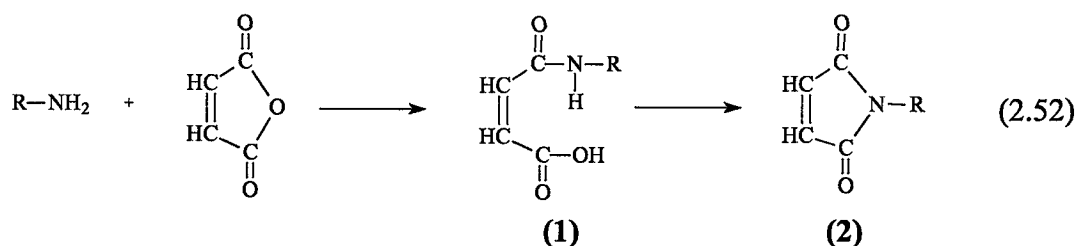
$$\frac{1}{\Delta_{\text{obs}}} = \frac{1}{K \cdot \Delta_{CTC}} \times \frac{1}{[D]_0} + \frac{1}{\Delta_{CTC}} \quad (\text{Eq.2.9})$$

where $\Delta_{\text{obs}} = \delta_{\text{obs}} - \delta_f$ and $\Delta_{CTC} = \delta_{CTC} - \delta_f$. Thus, the equilibrium constant for CTC formation can be measured from the intercept of a plot of $1/\Delta_{\text{obs}}$ versus $1/[D]_0$.

2.4 Maleimide Copolymers (N-Substituted)

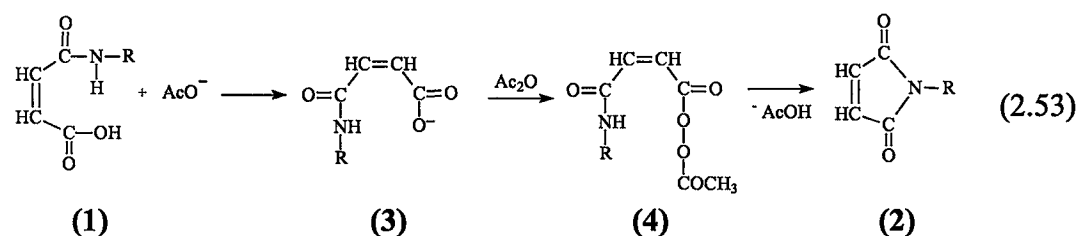
Polymaleimides are a new class of polymers obtained on the basis of N-substituted maleimides (RMI) or bismaleimides (BMI). RMIs are derivatives of maleic anhydride (MA).

The syntheses of differently structured RMI substituents are realized by Searle's and Ivanov's methods mainly in interaction with primary aliphatic and aromatic amines with MA (2.52) where R is H, OH, Alkyl, Aryl, etc.



The adequate maleamic acid (1) is obtained in the first phase of the acetylenizing reaction. A dehydrocyclization of the maleamic acid to the respective RMI (2) flows during the heating of solution (1) in the presence of a dehydrating agent in the second phase. A number of other dehydrating agents (e.g., NR_3 , thionyl chloride, chloroformates, acid chlorides, PCl_3 , P_2O_5 , dicyclohexylcarbodiimide, etc.) have been tried. Using Searle's sodium acetate acetic anhydride usually gives a good RMI yield.

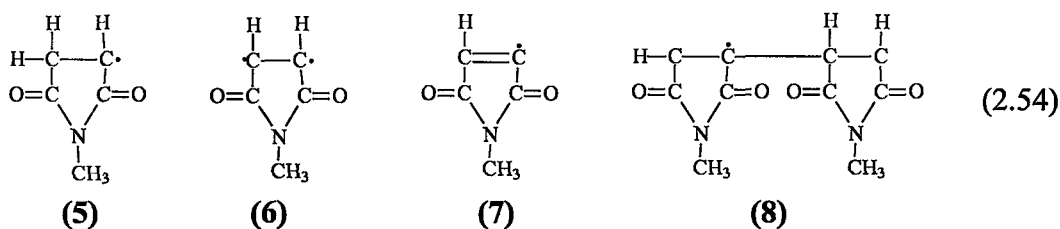
Yang and Wang determined during an imidization study that an intermediate product is constituted at the second phase-anhydride of maleamic acid [86]. Optimal results are reached with a molecular proportion (1) : NaAc = 1.0:0.1. The acetate ion acts as catalyst separating a proton from (1) and forming the maleamic ion (3). It undergoes a nucleophilic attack and contributes to formation of the anhydride (4) (2.53).



The cyclization of (4) flows by inner molecular nucleophilic reaction. The imidization rate increases with increase in temperature.

The RMIs have a higher polymerization capacity than MA. The polymerization is conducted in radicals by azobis-isobutyronitrile (AIBN), benzoic peroxide (BPO), UV, or Co initiating irradiation ; anionic ($n\text{-C}_4\text{H}_9\text{Li}$; $\text{tert-C}_4\text{H}_9\text{Li}$; $\text{tert-C}_4\text{H}_9\text{OK}$; $\text{C}_2\text{H}_5\text{MgBr}$) ; or zwitterionic mechanisms ; or by retro-Diels-Alder reaction, and Michael's addition polymerization.

Using electron spin resonance (ESR) during a free-radical homopolymerization of *N*-methylmaleimide (MMI), Sandreczki and Brown determined the structure of the initial (5), the propagating (6), the vinyl (7), and the penultimate (8) radicals [87].



Nakayama and Smets obtained a rather unusual rate expression for *N*-maleimide (MI) polymerization [95]:

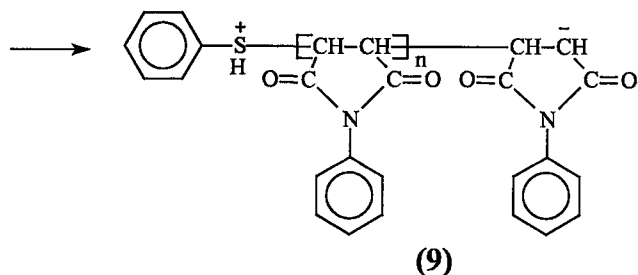
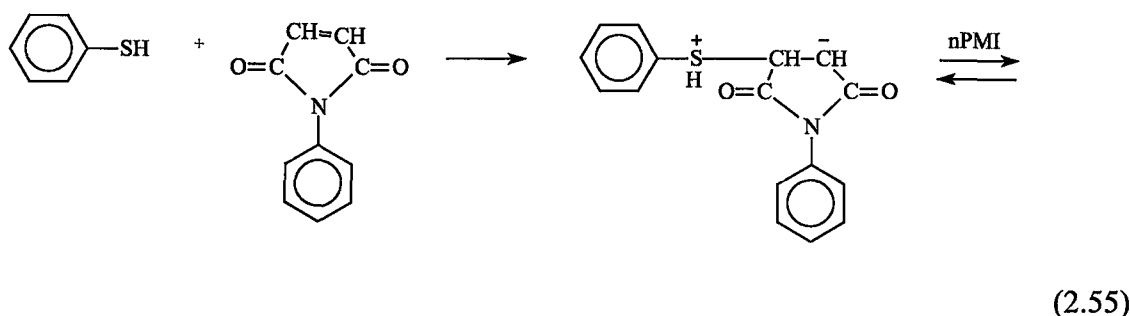
$$R_p = k[I]^{0.8}[M]^{1.1-1.3} \quad (\text{Eq.2.10})$$

The activation energy for MI radical polymerization is 21 kcal/mol. The activation energy is determined to be about 5 kcal/mol for MI polymerization with triphenylphosphine as an initiator in DMF (dimethylformamide) .

Elsabee and Mokhtar determined that the polymerization rate of *N*-(2-chlorophenyl) maleimide (2CPMI) and (or) *N*-(2-methylphenyl) maleimide (2MPMI) in dioxane increases ZnCl_2 [89] :

$$R_p = k[\text{AIBN}]^{0.5}[\text{RMI}]^{1.1} \quad (\text{Eq.2.11})$$

For the homopolymerization of *N*-phenylmaleimide (PMI) with thiophenol, Takeishi et al. discuss Michael's addition polymerization shown (2.55) [90].



Matsumoto et al. report *N*-alkylphenyl- and *N*-alkyloxymaleimides polymerization from both an anionic, free-radical initiation, and a self-photoinitiation [91]. They obtained high yield and high molecular weight polymaleimides by anionic polymerization and oligomeric products by free-radical polymerization.

N-arylmaleimides are crystal substances with a high melting point [92]. Many *N*-alkylmaleimides are oily liquid products. RMIs are used as comonomers for the maleimide copolymers. Free-radical copolymerization generally uses vinyl monomers such as styrene, α -methyl styrene, vinyl acetate, methyl methacrylate, olefins, vinyl chloride, and so forth. The maleimide copolymers are characterized by high glass transition temperature (T_g) and they are thermostable in high temperatures

2.4.1 Copolymerization and Copolymers in *N*-Substituted Maleimides with Styrene and α -Methylstyrene

Several alternating copolymers are derived by the radical copolymerization of RMI with styrene and α -methylstyrene (MSt). The monomer reactivity ratios r_1 and r_2 for all monomer pairs are smaller than one and incline to zero. They prove the copolymerization alternating character. Many researchers offer explanations of the alternating copolymerization character with the CTC between the donor monomer St and the acceptor RMI. The great difference between the St ($e = -0.8$) and RMI ($e = 1.1$ to 2.2) polarities favors electron donor-acceptor interactions, although they form a weak CTC. Abayasekara and Ottenbrite studied RMI complex formations of *N*-

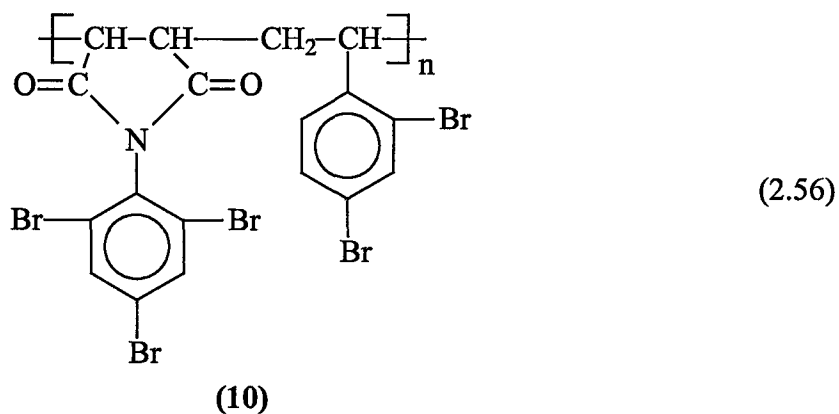
carbonylmaleimide (CMI), *N*-carboxymaleimides (CEMI), *N*-ethylmaleimides (EMI), and *N*-phenylmaleimide, with electron-donor monomer [93]. They found that the electron-acceptor substituents of RMI favor to a great degree the complex formation of St, because of the change of the maleimide ring electronic consistency and of the functional CH=CH group. Alternating copolymers with maximum yield are obtained by the CEMI and CMI copolymerizations with St that have equimolecular monomer proportions in the reaction mixture.

Complex formation and copolymerization character can be influenced by the selection of suitable solvents. The reactivity copolymerization ratios of *N*-(2-chlorophenyl) maleimide (CPMI) with St in dioxane ($r_1 = 0.0415$ and $r_2 = 0.0305$) are higher than those with chloroform ($r_1 = 0.0126$ and $r_2 = 0.0169$). The copolymerization rate increases with increase of CPMI concentration and it maximizes at approximately 80-90 mol% 2CPMI [94].

The copolymerization of *N*-(4-methoxyphenyl) maleimide (MOPMI) and *N*-(4-bromophenyl)maleimide (BPMI) with St in dioxane, chloroform, and DMF solution passes under homogeneous conditions, whereas conditions are heterogeneous in benzene solution. The copolymer obtained in equimolar feed composition of MOPMI-St in benzene solution gives the lowest yield and contains 72 mol% St units. The competition between the donor monomer St and the solvent in the donor-acceptor interactions with the maleimide monomer explains this fact.

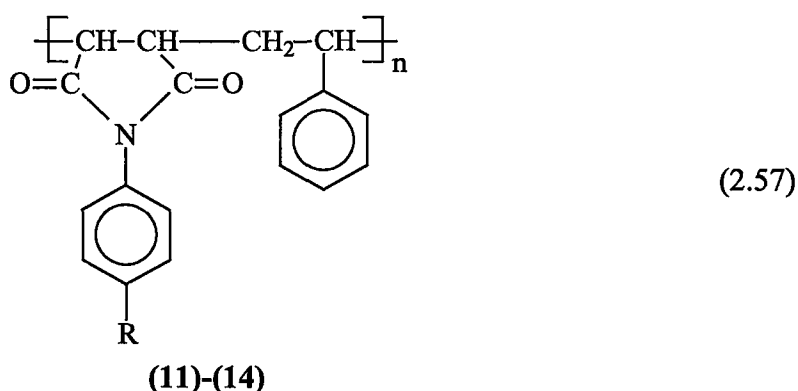
Rittel prepared copolymers containing from 20 to 77 mol% maleimide units by *N*-(4-methylphenyl)maleimide (MPMI) copolymerization with St in benzene initiated by benzoic peroxide (BPO) at 90 °C [95, 96]. Analogous results were seen in *N*-(chlorophenyl)maleimide copolymerization in a solution of dioxane initiated by AIBN with great conversion degrees (60-90%) in 65 °C has [97]. A connection is found between the Cl-atom position in the CPMI aromatic nucleus and the copolymerization rate, which decreases in the studied monomer pairs in the following order: 4CPMI-ST, 3CPMI-ST, and 2CPMI-ST.

Halogen-containing maleimide copolymers evoke considerable interest. Younes suggests a method for the preparation of alternating copolymer *N*-brominated phenyl maleimide (BPMI) with brominated styrene (2.56) [98].



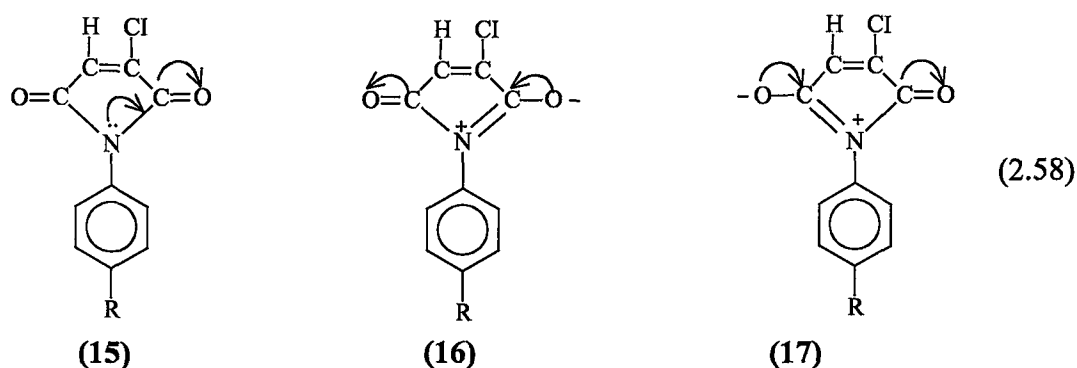
The copolymerization of *N*-(2,4,6-tribromophenyl)maleimide with dibromostyrene is held in methyl ethyl ketone solution initiated by the radical initiator BPO. The reactor is purged with nitrogen after it is heated to 80 °C and the polymerization is allowed to continue for 23 hours. The resulting alternating copolymer (10) has an average molecular weight of 150,000 and a glass transition temperature of 244 °C. These brominated maleimide copolymers can be used to produce flame-retardant compositions such as polystyrene, polystyrene copolymers, polycarbonates, polypropylene, polybutadienes, polyamide resins, and their mixtures.

Oishi synthesized alkyl- and aryl-substituted chloromaleimides by Pyriadi method [99, 100]. Alternating copolymers are prepared by radical copolymerization of *N*-4-substituted phenyl- α -chloromaleimide (RPCMI) with St in tetrahydrofuran (THF) with AIBN as an initiator at 60 °C [99], as (2.57) shows where (11), R = H; (12), R = Cl; (13), R = OCH₃, and (14), R = COOC₂H₅.

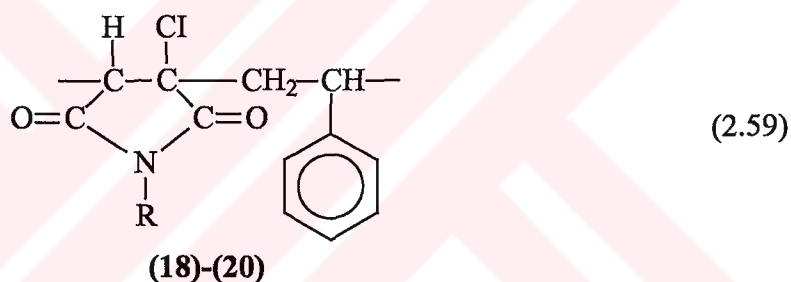


RPCMI do not homopolymerize under these conditions. Their copolymerization with styrene proceeds homogeneously in the initial solution throughout the whole monomer composition interval. Maximal conversion is obtained with equimolar proportions of comonomers RPCMI/ST = 1. The alternating character of the copolymerization can be attributed to the formation of CTC between RPCMI and St

although it is not yet proved experimentally. The relative reactivity ($1/r_2$) of RPCMI to a polystyryl radical correlates only with the polar-substituent constant (σ). It does not correlate with the resonance-substituent constant (E_R). However, this can be attributed to the conjunction of the double bond with the substituent R, as illustrated (2.58):

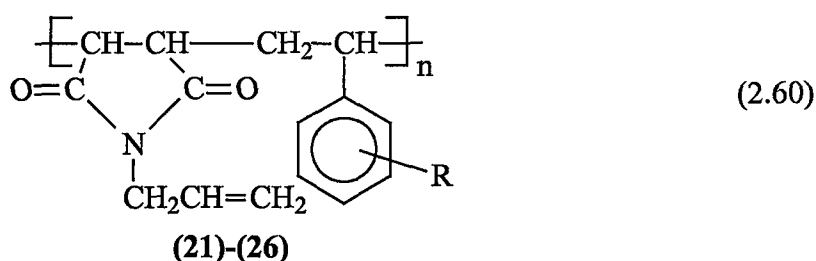


Oishi et al. describe *N*-alkyl- α -chloromaleimide (RCMI) copolymer synthesis with styrene (2.59) where (18), R = CH₃; (19), R = C₂H₅; and (20), R = CH₂CH₂Cl [100]



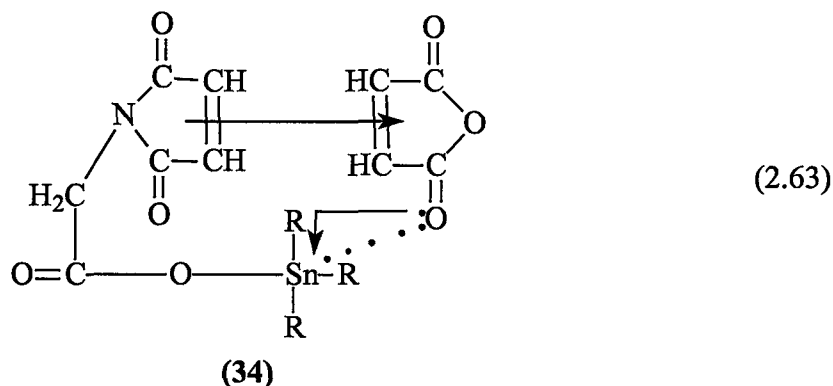
The copolymerization of RCMI with ST is performed in benzene with AIBN as an initiator at 60 °C. The maleimide monomers do not homopolymerize under these conditions ($r_1 = 0$). The resultant copolymers are polydispersive in molecular weight ($M_w/M_n = 6.4$ to 15.8). They are soluble in organic solvents such as THF, DMF, chloroform, dimethyl sulfoxide and *N,N*-dimethylacetamide.

Turner et al. suggest an original method for obtaining new reactive copolymers by an alternating copolymerization of *N*-allylmaleimide (AMI) with vinylbenzyl chloride (VBC) or other substituted styrene (2.60) [101].



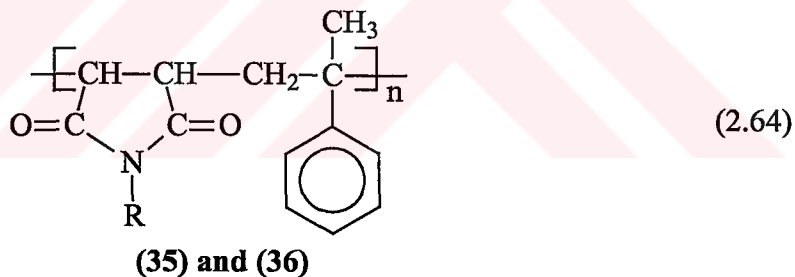
contrast to this, the alternating copolymer (33) is formed from the model *N*-acetylmaleimide compound with St.

Rzaev et al. analyzing BSAMI-MA mixtures, prove the formation of a weak CTC ($K = 0.005 \text{ L mol}^{-1}$) with (2.63) [105]:



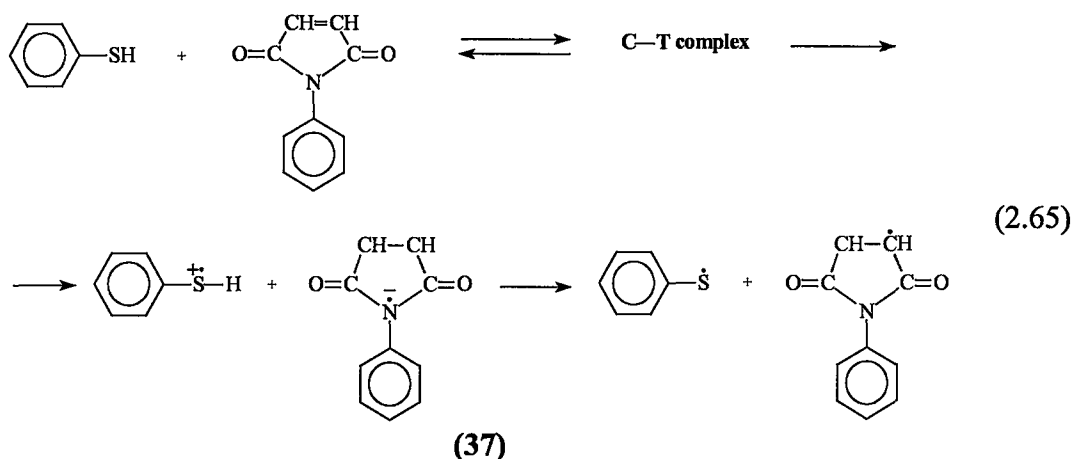
An alternating maleimide copolymer containing Sn is obtained by a radical copolymerization of the two monomers in benzene at 70 °C. These studies reveal a potential maleimide terpolymer with St and MA.

Fles et al. report alternating maleimide copolymers with *a*-methyl styrene (MSt) (2.64) [106, 107] where (35), R = CH₃; and (36), R = C₆H₅.

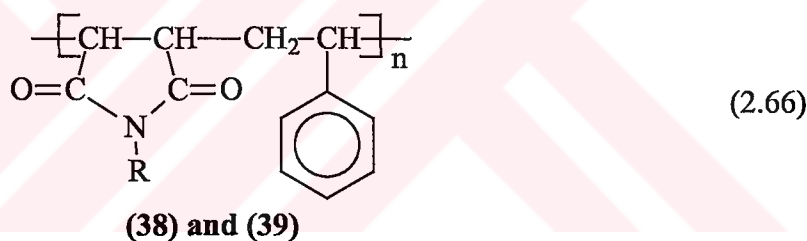


The maleimide copolymer (35) is synthesized by a radical copolymerization of *N*-methylmaleimide (MMI) with MSt in chloroform at 60 °C. The maleimide copolymer (36) is synthesized by the PMI copolymerization with MSt in toluene at 70 °C with the radical initiator AIBN. The CTC of the studied PMI and MSt ($K = 0.02 \text{ L mol}^{-1}$) influences the alternating character of the copolymerization. The alternating copolymer (36) is obtained by equimolar comonomer proportions and it has a glass transition temperature of 264 °C.

Takeishi et al. use a new method for RMI radical copolymerization with St [90]. They initiate it with CTC, formed between thiophenol and *N*-PMI, as figure (2.65) illustrates.



The generated radical (37) initiates a radical polymerization which is inhibited by hydroquinone. *N*-substituted maleimides EMI and PMI ($T = 40\text{ }^{\circ}\text{C}$) are polymerized by thiophenol. Copolymers with equimolar compositions are obtained by copolymerization with styrene (2.66):



where (38), $R = \text{C}_2\text{H}_5$, and (39), $R = \text{C}_6\text{H}_5$.

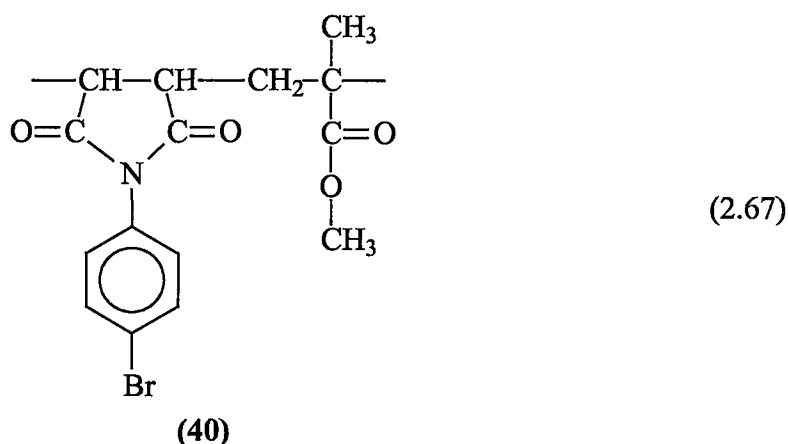
This thiophenol-initiated copolymerization is useful for the polymerization of monomers with unsaturated carbonyl groups, and especially for the preparation of copolymers with relatively low molecular weight and narrow molecular weight distribution. M_n is 6500 in copolymer (38) and 12,600 in (39). M_w/M_n are 1.92 and 2.34 respectively.

2.4.2 Copolymerization and Copolymers of *N*-Substituted Maleimides with Acrylic and Methacrylic Monomers

Several functional maleimide copolymers with acrylic and methacrylic monomers are obtained by radical polymerization. PMI copolymerizations with methyl methacrylate (MMA) in benzene solution, dioxane, THF, and tetrachloromethane are

the most fully studied. Regardless of the solution the methacrylic radicals are more reactive than the maleimide ones.

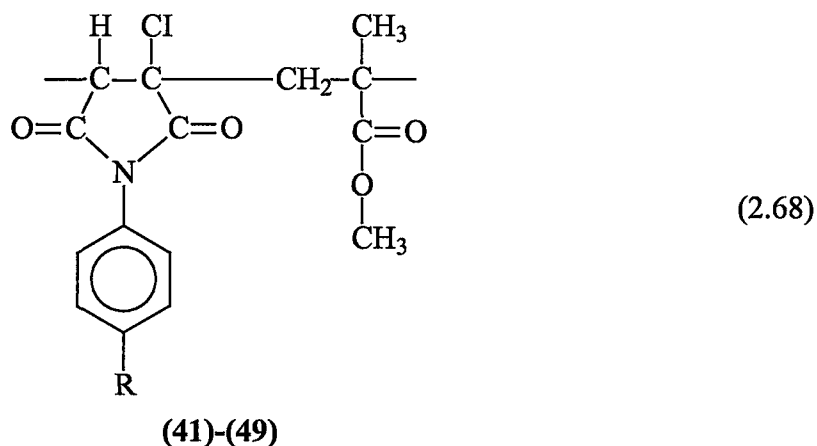
A new functional copolymer poly[N-(4-bromophenyl) maleimide-co-methyl methacrylate] is synthesised in dioxane at 60 °C with AIBN as radical initiator [108] (2.67).



The copolymers (40) obtained with different monomer proportions in the primary reaction mixture contain a greater amount of MMA units.

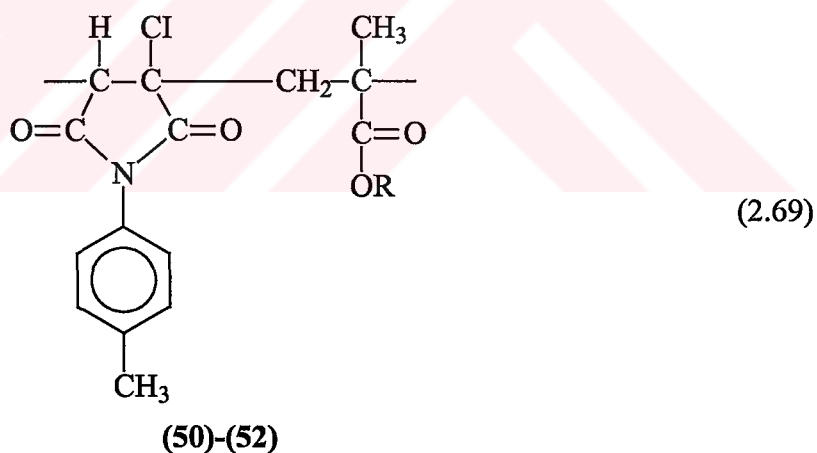
The maximal content of maleimide units (BPMI units) in the copolymers is 72.6 mol%. The thermostability of the MMA maleimide copolymers depends on the amount of BPMI units. The glass transition temperature of the copolymers with different compositions was measured by differential scanning calorimetry (DSC). The linear correlation of increase from 128 to 210 °C is determined in the studied BPMI contents interval [109].

Oishi et al. investigated the copolymerization of *N*-alkyl- or *N*-aryl-*a*-chloromaleimides (RCIMI) with MMA in benzene or THF, respectively at 60 °C. They obtained a number of new maleimide copolymers with MMA exhibiting (2.68) [99, 100] where (41), R = CH₃; (42), R = C₂H₅; (43), R = CH₂CH₂Cl; (44), R = CH₂C₆H₅; (45), R = C₆H₅; (46), R = C₆H₄Cl; (47), R = C₆H₄O CH₃; (48), R = C₆H₅CH₃; and (49), R = C₆H₄COO C₂H₅.



The RCIMI radical copolymerization proceeds homogeneously throughout. The copolymerization rates in the RCIMI-MMA systems are much lower than those in the RCIMI-ST systems. The amount of maleimide units in the copolymers increases with increase of *N*-phenyl- α -chloromaleimide (PCIMI) concentration in the reaction mixture and it does not differ essentially in (41), (42), and (43). The copolymer (44) contains considerably fewer maleimide units.

Ryttel obtained thermostable maleimide copolymers by a radical copolymerization of *N*-(4-methylphenyl) maleimide (MPMI) with alkyl acrylates (2.69) [95, 96]:

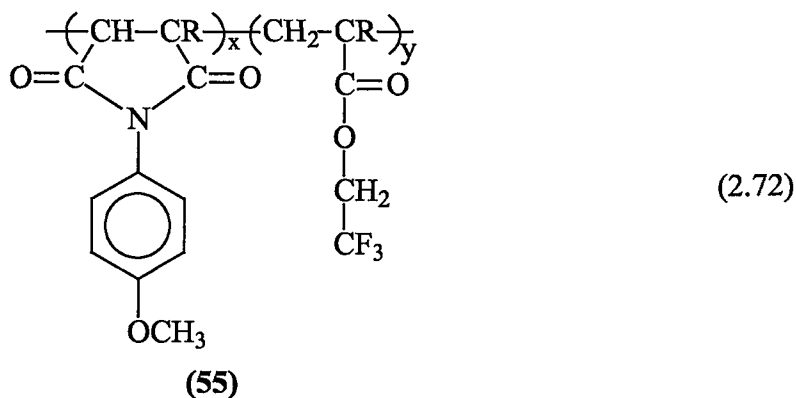


where (50), R = CH₃; (51), R = C₂H₅; and (52), R = n-C₄H₉.

The copolymerization in methyl acrylate, ethyl acrylate and n-butyl acrylate with MPMI is performed in bulk or in benzene solution at high conversion degrees with BPO as a radical initiator at 90 °C. The acrylate radical reactivity depends on R. The maleimide copolymer (51) with an azeotropic composition is obtained with the monomer proportion 50/50 mol%, and the copolymer (52) is obtained with 80/20 mol%. The values ($r_1 > 1$ and $r_2 < 1$) indicate that the obtained copolymer is enriched with acrylate units.

and 495 nm respectively. The functional group interaction in the copolymers is observed in solution as well as in hard state.

The trifluoroethylmethacrylate copolymers with different *N*-(4-methoxyphenyl) citraconimide contents (from 10 to 34 mol %), synthesized by Gong and Chien, are suggested as high Tg E-leans resist (2.72) [112] :

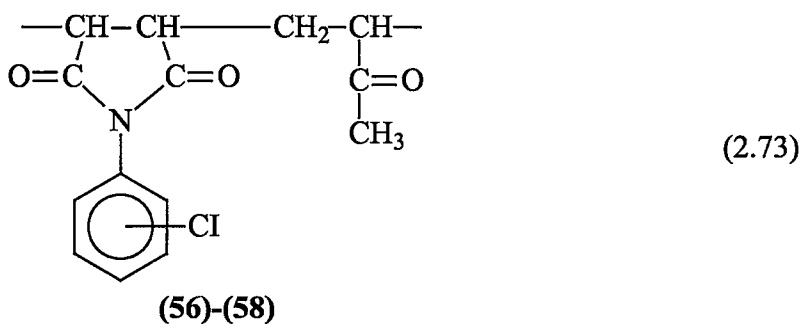


The polymerization process is held in 85-110 °C (1 mas% AIBN) or in 110-130 °C (1 mas% tert-butyl peroxybenzoate) depending on the initiator used. The imide monomer does not homopolymerize. A copolymer with more than 34 mol% imide units is not obtained. The material sensitivity and the glass transition temperature of copolymers (55) with different compositions increase from 95 to 150 °C with the increase of imide units.

2.4.3 Copolymerization and copolymers of *N*-Substituted Maleimides with Vinyl Acetate and Vinyl Ethers

It is known that the *N*-substituted maleimides are electron acceptors and that the vinyl acetate (VA) is a donor monomer. This favors their copolymerization. VA copolymers with *N*-acetoxyethylmaleimide, *N*-(2-propionyloxyethyl)maleimide, *N*-(3-acetoxypropyl)maleimide, *N*-*n*-butylmaleimide, *N*-chloroethylmaleimide and other RMIs have all been obtained. Elsabee et al. proved the influence of the solvent-maleimide interaction, the total monomer concentration, the solution nature, and the ZnCl₂ supplement in the reaction mixture on the reactivity ratios, the compositions, and the capacities of the obtained copolymers [113, 114].

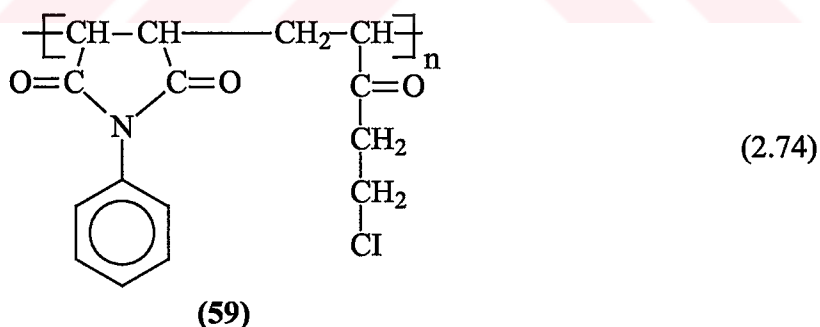
N-chlorophenylmaleimide (CPMI) radical copolymerization with VA in different organic solvents (THF, CHCl₃, 1,4-dioxane) are synthesised [115]. The copolymer structures (2.73) are proved by ¹H and ¹³C NMR:



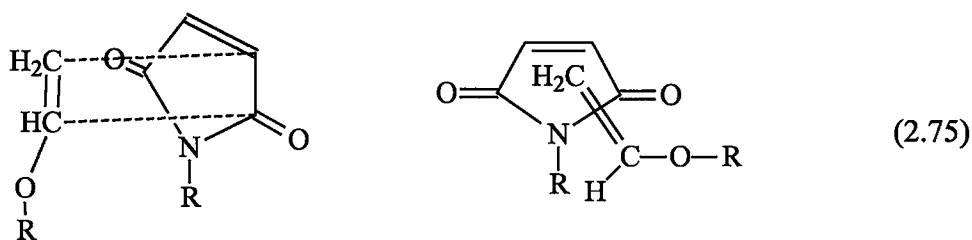
where (56), *o*-Cl(2CPMI); (57), *m*-Cl(3CPMI); and (58), *p*-Cl(4CPMI).

The nature of the solvents influences the polymerization ratio and the copolymer compositions to a certain degree. The Cl-atom position in the aromatic nucleus influences the maleimide radical reactivity and the r_1 values increase in the following order: 2CPMI, 3CPMI, and 4CPMI. The copolymer (56) has a better expressed alternating structure, whereas the VA units vary from 15 to 50 mol% in the copolymer (58), obtained with different monomer proportions.

The alternating copolymer (59) (2.74) is obtained by the radical copolymerization of *N*-phenylmaleimide with 2-chloroethyl vinyl ether (CEVE) in CH₂Cl₂ solution at 60 °C.



The vinyl ether radical is less active than the maleimide radical ($r_1 = 0.275$ and $r_2 = 0$). Olson and Butler prove the complex stereoregular structure that is due to the CTC participation in the act of the chain increase (2.75) [80]:

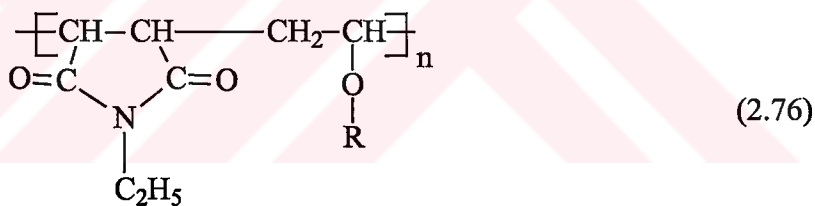


(60)

The copolymer *cis*-unit contents are proportional to the PMI concentration. It is connected with the complex (60) and it decreases with the temperature increase.

Extra data confirming the CTC participation in stereo-regular structure formation are obtained in studies of CEVE copolymerization with *p*-substituted *N*-maleimides. The *cis*-unit contents in the macromolecule increase linearly with the increase of the σ -constant of the *p*-positioned substituent of the maleimide phenyl nucleus. A linear correlation is found between the values for K (constants of the complex formation) and the copolymer *cis*-unit contents.

Alternating copolymers of *N*-ethylmaleimide (EMI) with vinyl ethers are synthesized by a copolymerization in bulk that occurs with acylperoxide/tertiary amine as an initiator (2.76) [116]:



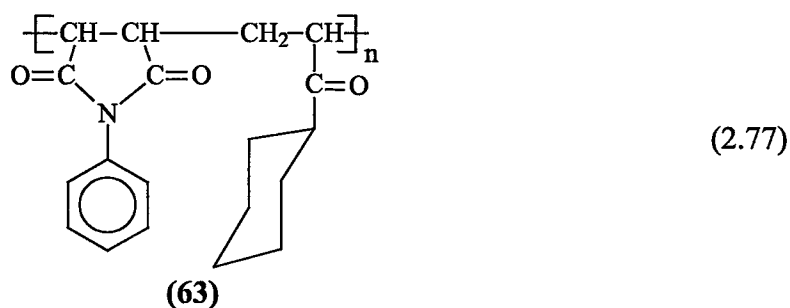
(61) and (62)

where (61), $R = n\text{-C}_4\text{H}_9$; and (62), $R = i\text{-C}_4\text{H}_9$.

The nature and the amount of the initiating system influence the EMI units in the copolymers.

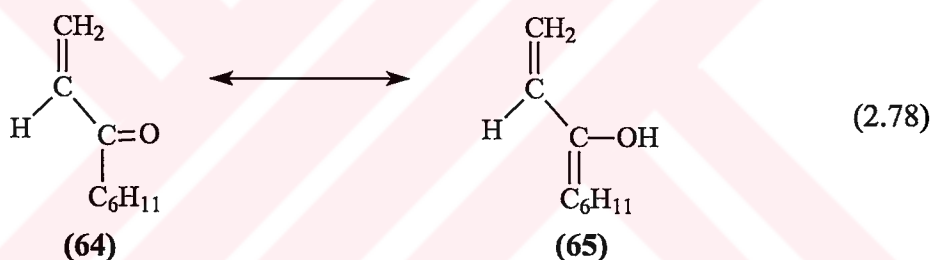
2.4.4 Copolymerization and copolymers of *N*-Substituted Maleimides with Other Monomers

Zubov, Rzaev et al. report a synthesis of PMI alternating copolymer with cyclohexyl vinyl ketone (CHVK) (2.77) [117].



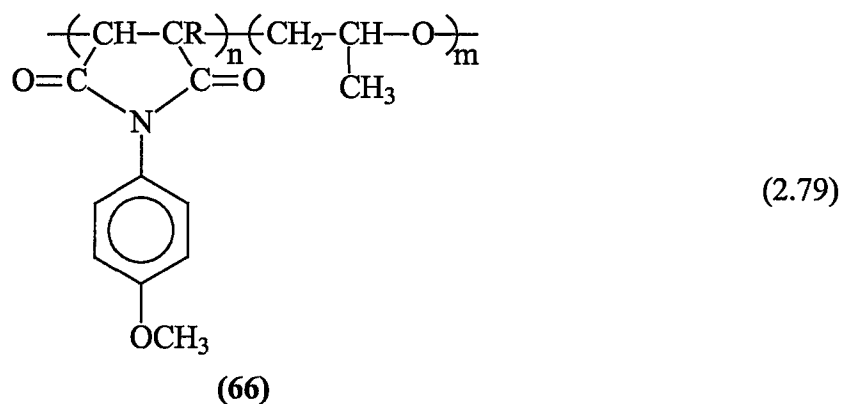
The copolymerization is held in a solution of methyl ethyl ketone with BPO as an initiator at 60 °C. The copolymers (63) with permanent compositions are obtained in all monomer proportions. The polymerization ratio increases with the monomer concentration increase and the kinetic maximum moves aside to CHVK 0.6 mole part in the reaction mixture.

It is proved that the system PMI-CHVK forms CTC complex ($K = 0.021 \text{ L mol}^{-1}$) with an equimolar composition composition 1:1. CHVKs do not show electro-donor capacities, but in keto-enol tautomerism the enol form (65) is a donor, as (2.78) illustrates.



The balance is drawn back to the enol (65) in the presence of PMI, which favors CTC formation and alternating polymerization.

PMI copolymerization with propylene oxide (PO) initiated with organozinc compounds is carried out in THF at 80 °C [118] The PO mole fraction of the obtained copolymers (66) (2.79) is 20 mol%:



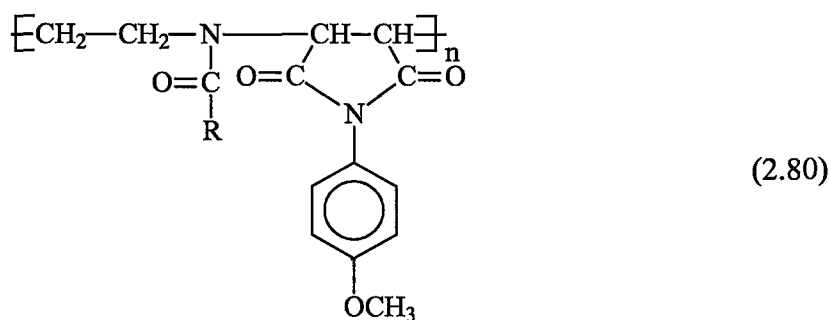
The number-average molecular weight (calculated from standardized polystyrene calibration) is 5×10^3 and the molecular weight distribution (Mw/Mn) is 1.5.

Maleimide copolymers can be obtained by the radical copolymerization of *N*-substituted maleimides with vinyl chloride (VC) [119-122]. The copolymerizations of *N*-cyclohexylmaleimide (CHMI), *N*-phenylmaleimide (PMI), *N*-(4-methylphenyl) maleimide (MPMI), and *N*-(2,4-dimethylphenyl) maleimide (DMPMI) are carried out in solution (DMF, THF, CHCl₃), in bulk or suspension at 50 °C. It is determined that RMIs form more reactive radicals and greater contents in the copolymers regardless of polymerization method. The maleimide reactivity decreases at homogeneous copolymerization in solution in the following order: CHMI, DMPMI, MPMI. The copolymerization reactivity ratios for the studied RMIs are higher in solution copolymerization than bulk copolymerization.

Thermostable maleimide copolymers with olefins are obtainable. CHMI copolymerizations with isobutene (IB), isooctene (IO) and *cis*- and *trans*-2-butene (CB,TB) are held in benzene at 60 °C [122]. The yield, the molecular weight, and the olefin unit contents depend on the olefin structure (alkyl residuum) and they decrease in the following order: IB, IO, CTB. The copolymerization reactivity ratio values are $r_{IB} = 0.41$, $r_{IO} = 0.72$ and $r_{CHMI} = 0$ for all monomer pairs. An alternating copolymer is obtained at PMI copolymerization with ethylene.

The reactivity ratio values r_2 show a reduction of the alternating tendency with increase of the substituent steric factor influence in the olefin monomers. The obtained olefin maleimide copolymers have a high thermostability up to 335-340 °C. The CHMI copolymer glass transition temperature with IB is 180 °C; 157 °C for the PMI copolymer with ethylene [123].

Rivas and Pizarro suggest a method for *N*-(4-nitrophenyl)-maleimide (NPMI), *N*-(2-methyl phenyl)maleimide (2MPMI), and *N*-(4-methyl phenyl)maleimide copolymer syntheses with oxazoline derivatives (2-methyl-2-oxazoline and 2-ethyl-2-oxazoline) [124, 125] (2.80):



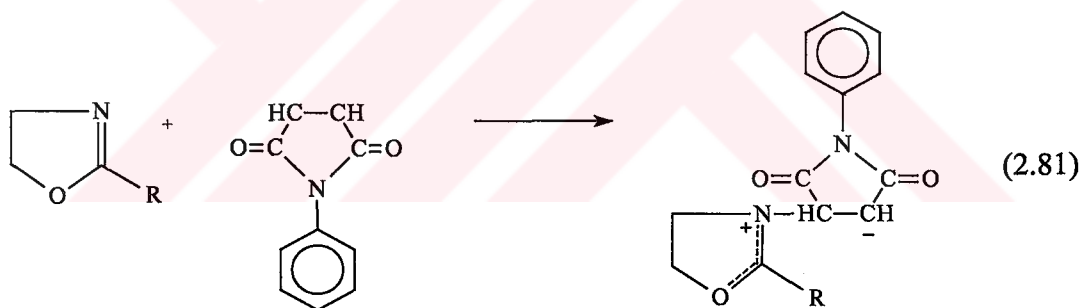
(67)–(70)

where (67), R = CH₃, X = H, and Y = NO₂; (68), R = CH₃, X = *o*-CH₃, and Y = H; (69), R = C₂H₅, X = H, and Y = *p*-CH₃; (70), R = CH₃, X = H, and Y = *p*-CH₃.

Specific monomer combinations are used: the maleimides have electrophilic activity (ME) and the oxazolines have nucleophilic activity (MN). The interaction of these monomers leads to the formation of an intermediate caused by the initiation and the propagation (Equation 2.12).

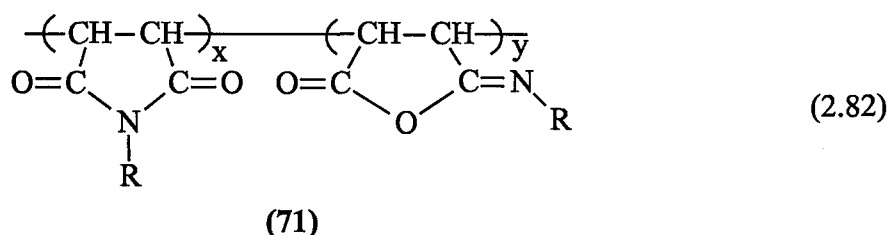
$$R_p = k[I]^{0.8}[M]^{1.1-1.3} \quad (\text{Eq.2.12})$$

The copolymerization is held in organic solvents (acetonitrile, methylpropionate, or benzene) at 50-70 °C and it proceeds via zwitterionic mechanism (2.81).



Copolymer yield, viscosity, and structure alternating tendency increase with the solvent polarity increase.

Copolymers containing maleimide and isomaleimide units are obtained during anionic polymerization of different isomaleimides with *n*-butyl-Li (2.82) [126].

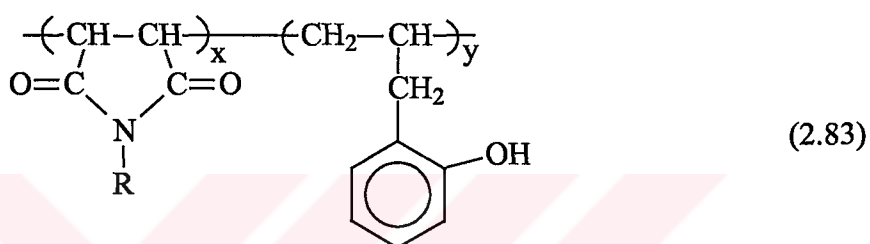


where R is C₆H₅, C₆H₄Cl, C₆H₄Br, C₆H₄CH₃, C₆H₄OCH₃, and so on.

2.4.5 Special Maleimide Copolymers

Syntheses of functional polymers provoke considerable interest as models of the enzymes (synzymes) and nucleic acids that are similar to the natural macromolecules such as nucleic acids, enzymes, and so forth. The alternating copolymers give a greater active capacity for the mutual action of the macromolecular functional groups.

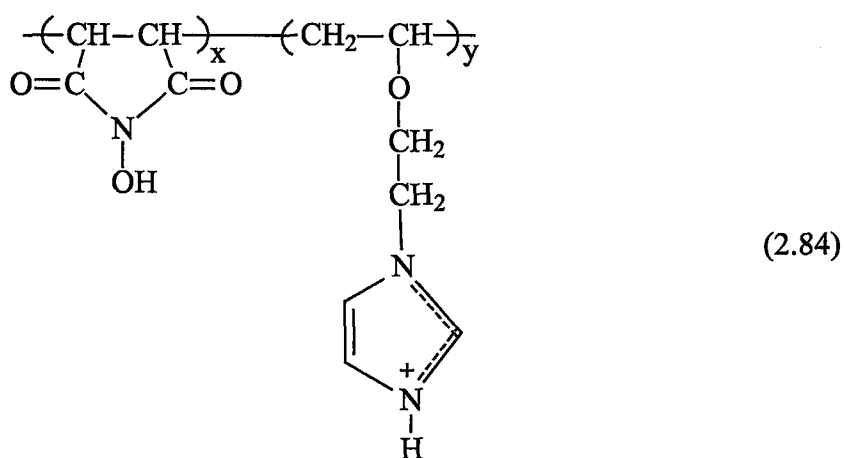
Water-soluble copolymers with a higher maleimide unit content are obtained by the copolymerization of a maleimide or *N*-phenylmaleimides with methallylphenol in a solution of 1,2-dichloroethane or 2-butanone solution in 80 °C (2.83) [127] where (72), R = H; (73), R = C₆H₅ and x/y 1.



(72) and (73)

The molecular weights of these copolymers range from 4000 to 10,000. Observe that CTC with $K = 0.02 \text{ L mol}^{-1}$ in CDCl_3 is formed between PMI and 2-allylphenol.

Vanderbilt and Butler suggest an original method for a bifunctional synzyme synthesis by an alternating copolymerization of *N*-acetoxymaleimide (AOMI) with *N*-(β -vinyloxyethyl) imidazole (VOEIm) [128] (2.84).

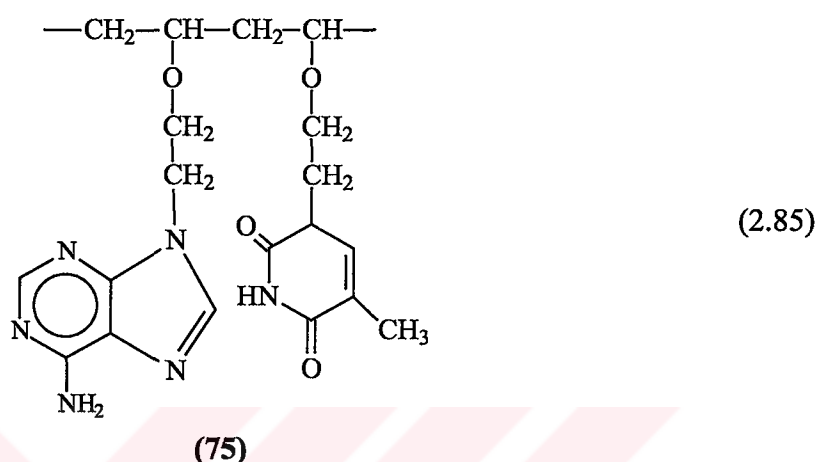


(74)

The comonomers AOMI and VOEIm copolymerize very successfully when the pyridine-like nitrogen of the VOEIm imidazole group is blocked. The alternating

copolymer (74) is obtained when VOElm is pretreated with HCl and it copolymerizes with AOMI that has a redox initiating system $K_2S_2O_4/Fe(II)$ at 30 °C. The copolymer (74) shows hydrophilic characteristics of a polyampholyte that is water-soluble at a higher pH.

Aponte and Butler report syntheses of alternating copolymers containing nucleic acid bases adenine and thymine as pendant groups [129] (2.85).



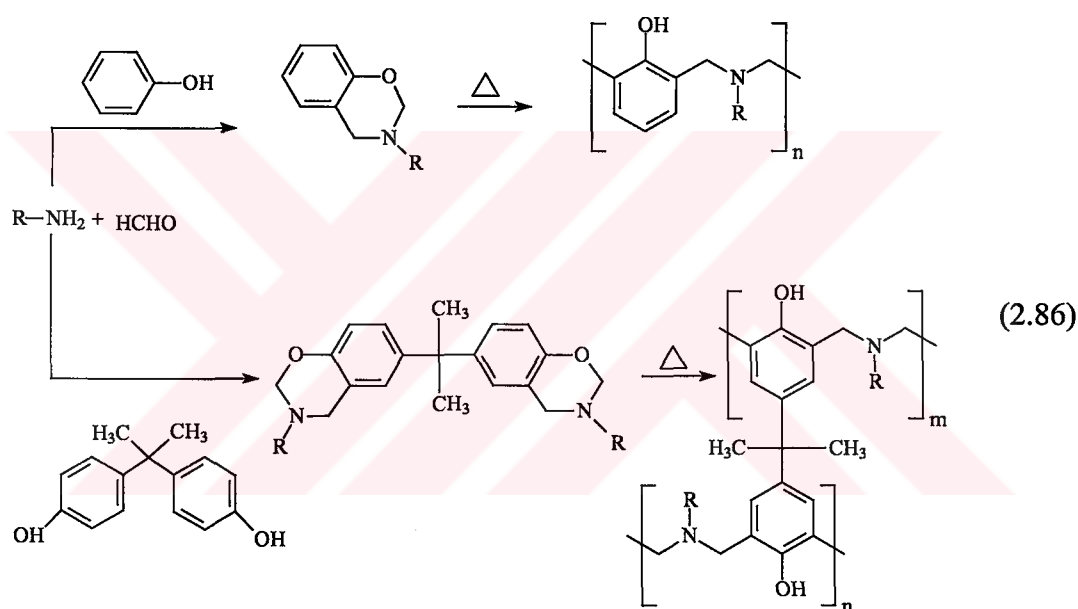
Two methods for synthesis of the alternating copolymer (75) are suggested: The first one consists of *N*-(2-bromoethyl) maleimide (BEMI) copolymerization with 1-(2-vinyloxyethyl) thymine (VOET) and the inclusion of adenine in the alternating copolymer macromolecule. But better results are obtained by the second method, the treatment of the VOET alternating copolymer with *N*-(2-ethyl-6-chloropurine) maleimide (ECPMI) with ammonia in methanol. The alternating copolymer (75), containing adenine and thymine as pendant groups, is obtained in the last phase. Note the formation of complementary H-bonds among the functional groups (nitrogen bases).

2.5 Polybenzoxazines (PBZ)

In recent years the development of the benzoxazine-based family of phenolic resins has attracted significant attention. Oxazine-modified phenolic resin undergoes a ring-opening polymerization to give polybenzoxazine, which is effectively a poly(aminophenol). The precursors are formed from phenol and formaldehyde in the presence of amines. The choice for phenol and amine permits design flexibility and polymer property tailoring.

The typical method of obtaining polybenzoxazines is to polymerize the corresponding monomers at elevated temperatures without catalysts. Some work has been done involving the catalyst-assisted benzoxazine curing and the results show that by adding certain catalyst, the induction time for the benzoxazine precursor curing can be reduced and the reaction rate can be accelerated [130]. However, the reduction of the maximum exotherm temperature was modest and no significant polymerization has been observed under 100 °C.

In the presence of acidic catalysts (e.g. phenols), the cure temperature window can be reduced from 160–220 °C to about 130–170 °C (i.e. a decrease of 30–50 °C). The synthesis and polymerization benzoxazine and benzoxazine based on bisphenol A are depicted (2.86).



The benzoxazine ring is a six-membered heterocyclic ring with N and O as two of the constitutive elements. Molecular modeling results show that the oxazine ring in a benzoxazine molecule assumes a distorted semichair structure in terms of minimum energy model [131].

The resulting ring strain makes it possible for this kind of molecule to undergo ring-opening polymerization under certain reaction conditions. Moreover, the strong basicity of the N and O atoms by Lewis definition makes the ring very likely to be opened via a cationic mechanism.

2.5.1 Features of Polybenzoxazines

These new materials, belonging to the additioncure phenolics family were developed to combine the thermal properties and flame retardance of phenolics and the mechanical performance and molecular design flexibility of advanced epoxy systems [132].

The polybenzoxazines overcome several shortcomings of conventional novolac and resole-type phenolic resins, while retaining their benefits. PBZ resins are expected to replace traditional phenolics, polyesters, vinyl esters, epoxies, BMI, cyanate esters and polyimides in many respects. The molecular structure of PBZ offers superb design flexibility that allows properties of the cured material to be controlled for specific requirements of a wide variety of individual requirements. The physical and mechanical properties of these new polybenzoxazines are shown to compare very favorably with those of conventional phenolic and epoxy resins. The resin permits development of new applications by utilizing some of their unique features such as [133,134]:

- Near zero volumetric change upon polymerization
- Low water absorption
- Tg much higher than cure temperature
- Fast mechanical property build-up as a function of degree of polymerization
- High char-yield
- Low coefficient of thermal expansion
- Low viscosity
- Excellent electrical properties

PBZ present a resin system with the highest tensile properties, and Tg can be boosted to as much as 340 °C through proper choice of the precursor phenol. This new family of phenolic resin features a wide range of mechanical and physical properties that can be tailored to various needs. Dynamic mechanical analysis reveals that these candidate resins for composite applications possess high moduli and glass transition temperatures, at low cross-link densities. Long-term immersion studies indicate that these materials have a low rate of water absorption and low saturation content. Impact, tensile, and flexural properties are also good. Results of the

dielectric analysis on these polybenzoxazines demonstrate their suitability for electrical applications [135].

BZs are cured usually in the temperature window of 160–220 °C. The polymers exhibit T_g in the range 170–340 °C depending on the structure, and have higher thermal stability. The high TGA decomposition onset temperature (for dihydroxy benzophenone –aniline system, it is, 400 °C) is attributed to the very strong intramolecular H-bonding between phenolic OH and the Mannich bridge. Char-yield as high as 82% has been claimed. Their composites are comparable to polyimides and other high performance polymers, but are easily processable [136].

The ring-opening polymerization of these new materials occurs with either near-zero shrinkage or even with a slight expansion upon cure. It is proposed that the volumetric expansion of the BZ resin is mostly due to the consequence of molecular packing influenced by inter- and intramolecular hydrogen bonding. The role of hydrogen bonding on the volumetric expansion has been studied by systematically changing the primary amine used in the BZ monomer synthesis. In comparison to the other known expanding monomers and spiro ortho compounds, this resin has been shown to have a high potential for structural/engineering applications [137].

Properties sensitive to network structure, however, are affected. The incorporation of the monofunctional BZ reduces cross link density and produces a looser network structure, while the difunctional epoxy increases cross link density and leads to a more connected network structure. Regulation of the viscosity of a difunctional BZ resin is achieved by addition of a monofunctional BZ monomer or a difunctional epoxy monomer as reactive diluents to further improve processibility [138].

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Styrene (St) (Fluka)

It was washed with aq. 5% NaOH to remove inhibitors, then water, dried with CaH₂ several hours and distilled under reduced pressure (50 °C/25 mm Hg). Middle fraction was collected and immediately used.

N-(*N*-4-cyanophenylbenzoxazine) Maleimide (BaMI)

It was kindly supplied by Professor Tsutomu Takeichi and used without further purification.

mp (DSC): 244 °C.

¹H NMR[δ , ppm from tetramethylsilane (TMS) in dimethyl sulfoxide (DMSO-*d*6)]: 4.82 (s, CH₂, oxazine), 5.6 (s, CH₂, oxazine), 6.87–7.70 (9H, -CH=CH- and Ar).

3.1.2 Solvents

Dichloromethane (CH₂Cl₂) (Lab-scan)

Methylene chloride was used as solvent for dissolving bulky polymer formations, It was first washed with conc. H₂SO₄ until the acid layer remained colourless, then washed with water, aq. %5 NaOH and then water again. It was pre-dried with CaCl₂ and distilled from CaH₂ kept over activated molecular sieve (type 4 A⁰).

Dimethyl sulfoxide (DMSO)

Distilled over CaH₂ before use.

Methanol (Technical)

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

3.1.3 Initiator

ω,ω -Dimethoxy- ω -phenylacetophenone (DMPA) (Ega-Chemia)

It was used as a photoinitiator without further purification.

3.2 Equipments

3.2.1. Photoreactor

RayonetTM photoreactor equipped with 16 Philips 8W / O6 lamps emitting light nominally at 350 nm was used.

3.2.2 Infrared Spectrophotometer (IR)

IR spectra were recorded on a Perkin Elmer Spectrum One B infrared spectrophotometer.

3.2.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

¹H-NMR analyses were recorded on a Bruker 250 MHz NMR Spectrometer.

3.2.4 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) analyses were performed on Waters 515 instrument with a set up consisting of an Waters 996TM RI dedector equipped with three Waters ultrastyrigel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min. Molecular weights were calculated by using monodisperse polystyrene standards.

3.2.5 Differential Scanning Calorimetry (DSC)

A Du Pont modular thermal analyzer system in conjunction with 910 differential scanning calorimeter was used to perform thermal analysis. A constant heating rate of 10 °C/min was using during DSC experiments.

3.3 Preparation Methods

3.3.1 Copolymerization of *N*-(*N*-(4-cyanophenylbenzoxazine) Maleimide (BaMI) with Styrene (St) by Photoinduced Polymerization

Copolymer of maleimide monomer (BaMI) with St was synthesized as follows: The monomer BaMI was solved in dry dimethyl sulfoxide, and the solution was introduced into a Pyrex polymerization tube. For copolymerization the appropriate amount of St and DMPA were also added to the tube. After degassing the solution with the purified N₂ gas, the tube was sealed and placed in Rayonet^{T.M} photoreactor equipped with 16 Philips 8W/06 lamps emitting light nominally at $\lambda = 350$ nm. The reactions were carried out at 25 °C for 92 hours. Then the polymer was precipitated in methanol. The obtained polymer was filtered, washed with acetone to remove the unreacted maleimide monomer, and dried under vacuum. The product was purified by reprecipitation from dimethylsulfoxide solution in methanol.

3.3.2 Homopolymerization of *N*-(*N*-(4-cyanophenylbenzoxazine) Maleimide (BaMI) by Photoinduced Polymerization

Homopolymer of maleimide monomer (BaMI) as follows: The monomer BaMI was solved in dry dimethyl sulfoxide, and the solution was introduced into a Pyrex polymerization tube. After degassing the solution with the purified N₂ gas, the tube was sealed and placed in Rayonet^{T.M} photoreactor equipped with 16 Philips 8W/06 lamps emitting light nominally at $\lambda = 350$ nm. The reactions were carried out at 25 °C for 92 hours. Then the polymer was precipitated in methanol. The obtained polymer was filtered, washed with acetone to remove the unreacted maleimide monomer, and dried under vacuum. The product was purified by reprecipitation from dimethyl sulfoxide solution in methanol.

3.3.3 Thermal Ring-Opening Polymerization of Benzoxazine Moieties of BaMI-St Copolymer

The thermal polymerization behavior of BaMI-St was monitored with a DSC. BaMI-St copolymer showed a glass transition temperature at 230 °C and an exothermic peak centered at 280 °C in its DSC heating scan. This exothermic peak was assigned to be from the ring-opening polymerization of benzoxazine moieties of BaMI-St copolymer. The same amount of BaMI-St copolymer (Run 3) samples was further

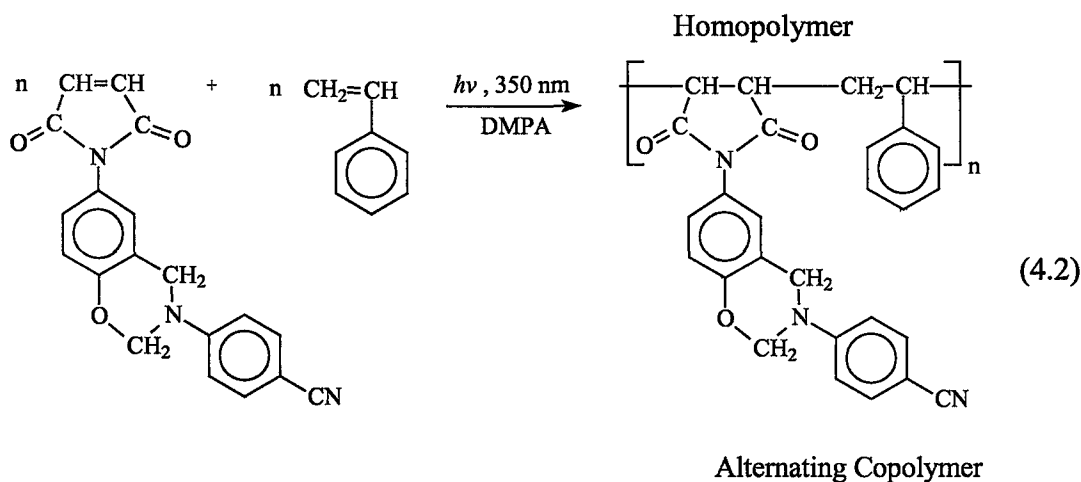
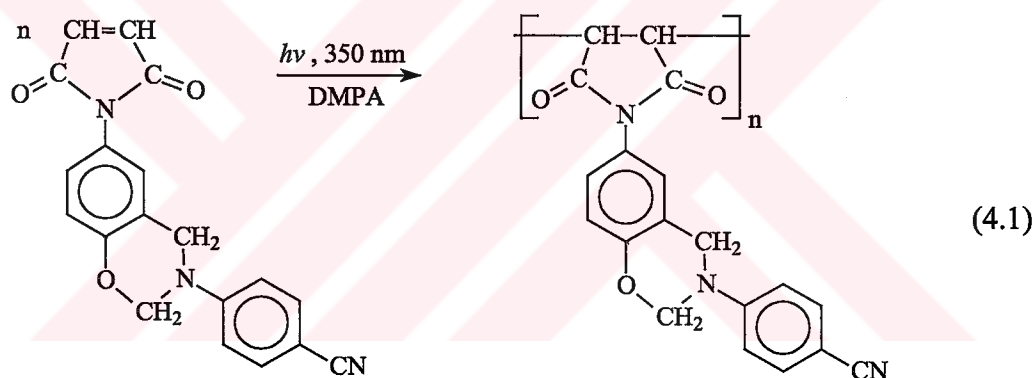
polymerized isothermally at 280 °C for 15 min., 30 min., 45 min.,60 min. in an oven to give a cured polymer and reddish brown, phenolic-resin like product was obtained.



4. RESULTS and DISCUSSION

4.1 Homopolymerization and Copolymerization of *N*-(*N*-4-cyanophenyl benzoxazine) Maleimide (BaMI) with Styrene (St) by Photoinitiated Polymerization

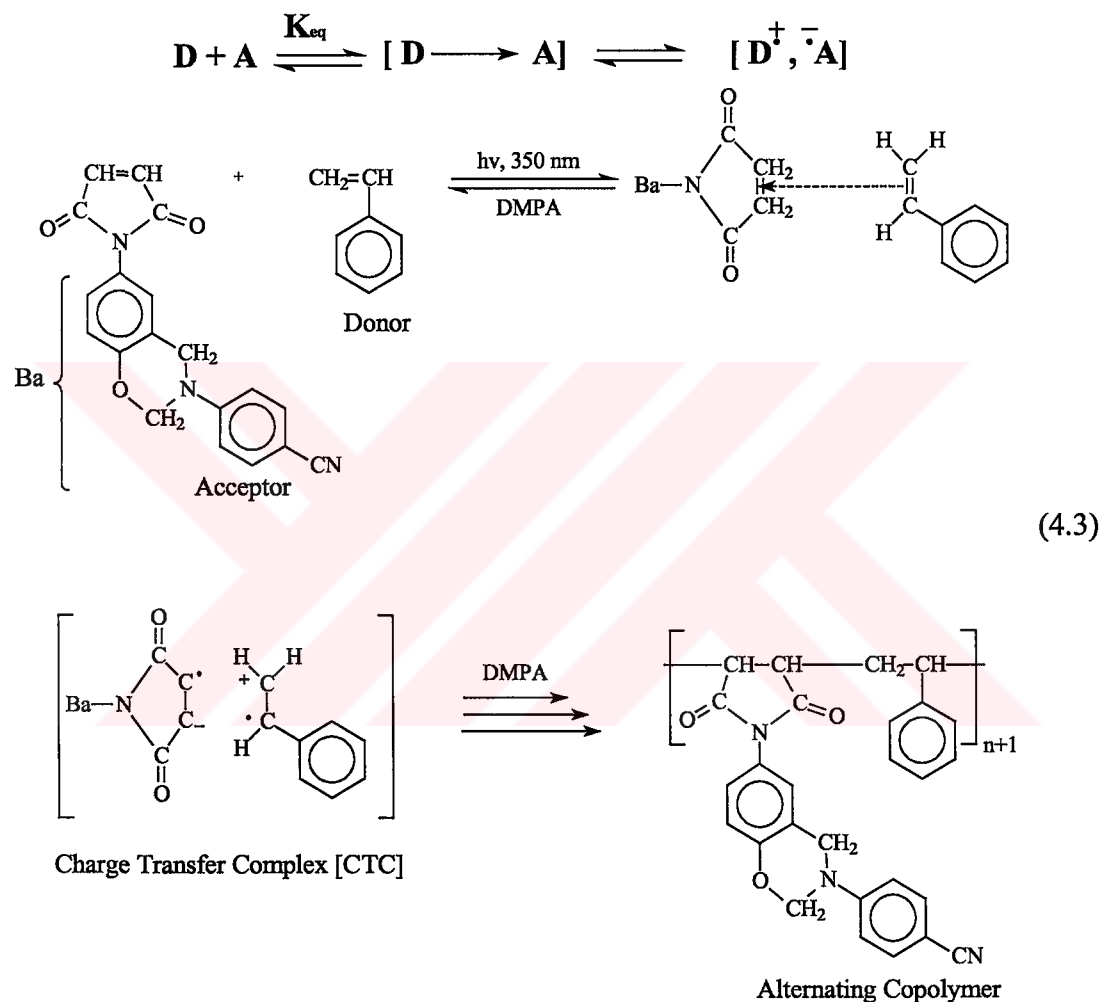
Photoinduced radical homopolymerization of *N*-(*N*-4-cyanophenylbenzoxazine) maleimide (BaMI) and its copolymerization with styrene were performed at room temperature to give linear polymers containing pendant benzoxazine moieties using ω , ω -dimethoxy- ω -phenylacetophenone as an initiator (4.1 and 4.2).



Free radical polymerization and copolymerization of styrene as electron-rich monomer with various *N*-substituted maleimides as electron-deficient monomers

have been reported in many papers [139-144, 145, 146] and a nearly alternating copolymer was obtained through the formation of charge transfer complexes (CTCs).

An equilibrium exists between styrene (St), an electron donor (D), and maleimide (MI), an electron acceptor (A) to form St→MI charge-transfer complex (CTC). If the growing macroradical react with this CTC instead of reacting with styrene or maleimide both monomers will incorporated into the polymer (4.3). This generates an alternating copolymer.



A measure for the strength of the donor (D) – acceptor (A) interaction is the equilibrium constant of CTC complex formation, (K) (4.3). Weak complex formation is generally slightly exothermic and disfavored entropically and an increase in temperature would decrease the complex concentration [147]. Lower temperature is also expected to lead to a higher equilibrium constant for the complex formation [182] and increase of (K) will lead to an increase in copolymer stereoregularity [181]. We have, therefore, chosen photopolymerization at room temperature as a

method for the synthesis the homopolymer of BaMI and the alternating copolymers of BaMI with St. Although it was claimed that only *N*-alkylmaleimides undergo polymerization under UV irradiation, but not *N*-phenyl maleimide,[49] to our knowledge there are few reports on the preparation of polymers by photopolymerization of *N*-phenylmaleimide-type monomers [150–151]. Our attempt was also successful. The results of photoinduced radical homopolymerization of BaMI and its copolymerization with St are summarized in Table 4.1.

All the polymerizations were conducted in dimethylsulfoxide (DMSO) and the concentration of photoinitiator (DMPA) being constant as the total concentration of monomers. Generally, the choice of a solvent for the polymerization of the maleimides is limited by the poor solubility of both monomeric and polymeric materials as in our experiments. Consequently, polar solvents are often used for the polymerizations, many of which are undesirable as solvents for free radical polymerization. It is, therefore, of interest to produce maleimide based polymers of improved solubility in common solvents and of high molecular weight, both of which extend their use in industrial applications.

4.1.1. Characterization of the Polymers

The structure of the homopolymer and copolymers was analyzed by ¹H NMR and IR spectroscopies. The polymerization of *N*-substituted maleimides (RMI) proceeds via stereoregularity of *cis* and *trans* addition. Although Cubbon [154] reported that the polymerization of RMI cannot proceed through *cis* addition because of steric hindrance, the *cis* forms (*erythro*-diisotactic and *disyndiotactic*) were found in both radical and anionic polymerizations of this type of monomer (4.4). CT complex during the polymerisation of styrene-maleimide copolymers and the corresponding polymerization mechanism leading to *zusammen* (*Z*) and *entgegen* (*E*) configurations and an alternating character (4.4). This shows that addition of the growing radical chain to the side of the complex that is *syn* to the styrene unit leads to the addition of MI unit in the *Z* configuration (a), while attack from the opposite side (b), yields the *E* configuration. CTC complex participation following this mechanism can therefore lead to addition of both *Z*- and *E*- MI units to the growing radical chain. As the addition of free comonomers to the chain could normally be expected to result in MI

units in the *E* configuration. CTC complex addition via can hence be seen as the main source of *Z*-MI units in the copolymers.

The effect of varying reaction conditions on the stereochemistry of alternating copolymers of *N*-substituted maleimides with electron-donor comonomers has been already studied [147, 80, 155]. So, it is well known that the stereoregularity of this type of copolymers varies with copolymerization conditions as temperature, solvent, total concentration of the co-monomers, co-monomer concentration ratio at fixed total monomers' concentration and the donor–acceptor character of the co-monomers' pair.

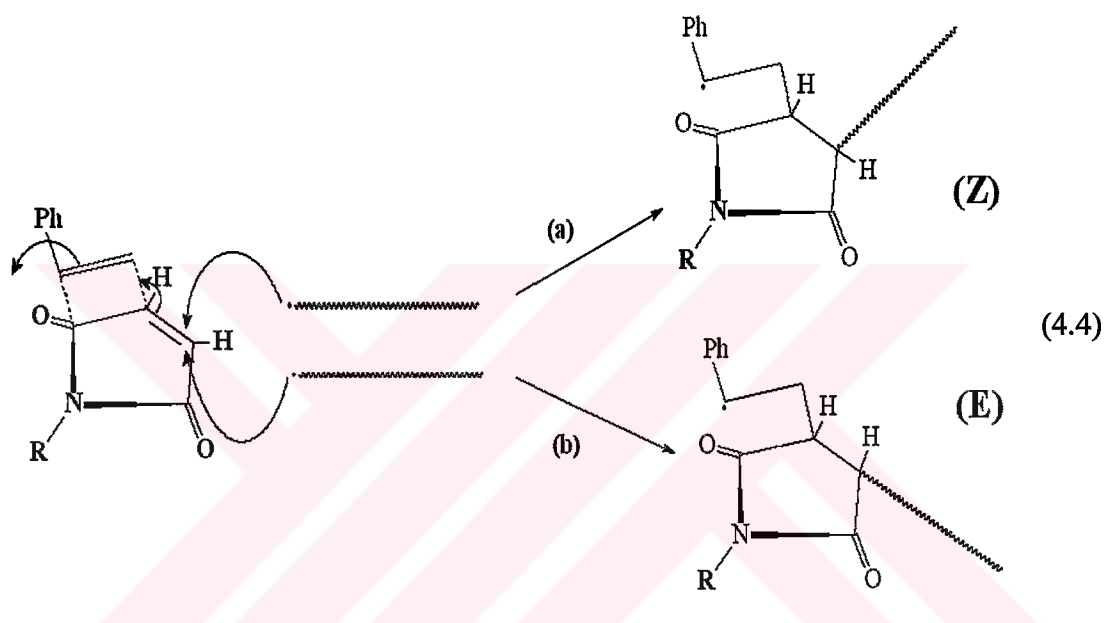


Figure 4.1 depicts the ^1H NMR spectrum of BaMI-St copolymer (Run 3 in Table 4.1).

In the ^1H NMR spectrum at 4.17 and 3.18 ppm could be assigned to the methine protons in the succinimide moiety in the *trans* and *cis* form, respectively [156].

The composition of the copolymers was calculated on the basis of the ^1H NMR results, comparing the values of the integrals of the peaks appearing after 7.48 ppm, characteristic to aromatic protons of maleimide monomer ortho to the cyano group (Figure 4.1) and other aromatic protons in the range of 6,2–7,48 ppm belonging to the maleimide and styrene structural units. The ratios between *cis* and *trans* configurations for the synthesized copolymers are presented in Table 4.1 and were calculated from the corresponding integrals in their ^1H -NMR spectra.

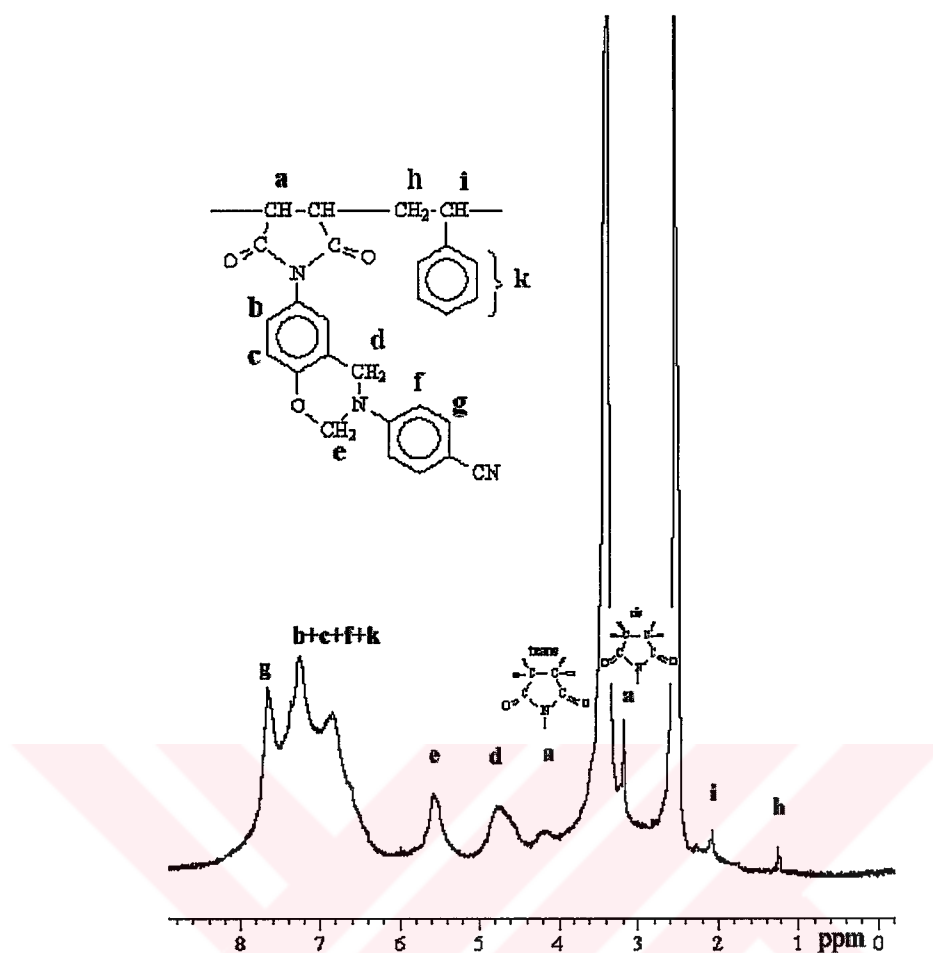


Figure 4.1 ^1H NMR spectrum of copolymer BaMI-St (Table 4.1, Run 3) in $\text{DMSO-}d_6$.

The *cis/trans* ratios of the copolymers synthesized in DMSO showed in Table 4.1., where it can be seen that *cis* contents of the copolymers increases progressively with molar fraction of BaMI monomer in the feed (F_2) except for the last run in Table 4.1. Hao and Fujimori [157] claimed that the presence of the *cis* linkage configuration of the maleimide unit in the styrene-phenylmaleimide copolymers can be considered as structural evidence for the participation of the CTC complex in the propagation step.

In addition, the number-average molecular weight (M_n), polydispersity (PD, M_w/M_n), and conversion for the homopolymer and copolymers are also listed in Table 4.1. The conversion was around 50% except for the first run in Table 4.1. The number-average molecular weight (M_n), and the polydispersity index (M_w/M_n) values almost linearly decreased with the increase of BaMI in monomer feed.

Table 4.1 Photoinduced Radical Polymerization of BaMI (M_2) with St (M_1) in Dimethylsulfoxide at Room Temperature^a

Run	Monomer Feed (mol%)		Copolymer Composition ^b (mol%)		Conversion (%)	<i>cis/trans</i> ^b	M_n^c	M_w/M_n^c
	F_1	F_2	f_1	f_2				
1	90	10	69,2	30,2	22,3	2,1	3752	1,91
2	70	30	56,8	43,2	42,1	2,5	3136	1,75
3	50	50	50,0	50,0	56,0	3,0	3203	1,60
4	30	70	44,5	55,5	48,1	2,8	1982	1,21
5	10	90	18,9	88,1	49,3	1,1	1810	1,14
6	--	100	--	100	49,0	--	1881	1,23

^a Photoinitiator: DMPA ($c = 0.008$ M), [BaMI] + [St] = 0.091 M, and irradiation time: 92 h.

^b Determined by ¹H-NMR data.

^c Determined by GPC measurements.

In the IR spectra of the copolymers, our main aim was to observe characteristic absorptions of benzoxazine ring for further polymerization of BaMI-St copolymers to obtain cured polymers. After photoinitiated radical polymerization of BaMI (M_2) with St (M_1) at room temperature by using DMPA as an initiator, polymerization reaction was observed with the appearance of succinimide C–N–C vibrations at 1180 cm^{-1} instead of the equivalent maleimide bands at 1145 cm^{-1} . The characteristic absorption bands of benzoxazine ring of BaMI-St copolymers was observed with in FT-IR spectrum (Fig. 4.2) at 1234 cm^{-1} (asymmetric stretching of C–O–C), at 1019 cm^{-1} (symmetric stretching of C–O–C), at 1386 cm^{-1} (asymmetric stretching of C–N–C), at 1112 cm^{-1} (symmetric stretching of C–N–C), at 950 and 1499 cm^{-1} (trisubstituted benzene ring), at 1332 and 1299 cm^{-1} (CH_2 wagging mode). [158–159].

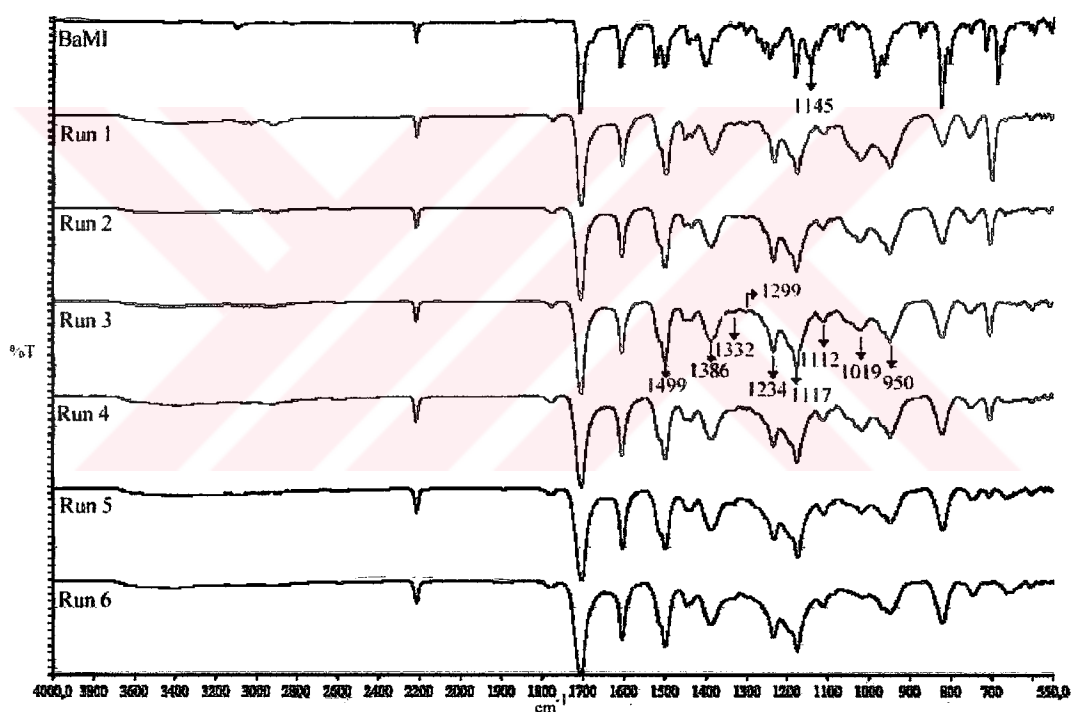


Figure 4.2 FT-IR spectra of BaMI monomer, BaMI-St copolymers (Table 4.1, Run 1, Run 2, Run 3, Run 4, Run 5) and BaMI homopolymer (Table 4.1, Run 6).

The $^1\text{H-NMR}$ spectrum of BaMI gave further support to its chemical structure (Fig. 4.3). The oxazine ring was characterized with the absorption peaks at 4.82 ($-\text{Ph-CH}_2\text{-N-}$) and 5.60 ppm ($-\text{O-CH}_2\text{-N-}$) [160,161]. After photo induced radical polymerization of BaMI with St, the characteristic absorption peaks belong to oxazine ring was observed with in $^1\text{H NMR}$ of BaMI-St copolymer at 4.73 ($-\text{Ph-CH}_2\text{-N-}$) and 5.56 ppm ($-\text{O-CH}_2\text{-N-}$) (Fig. 4.4).

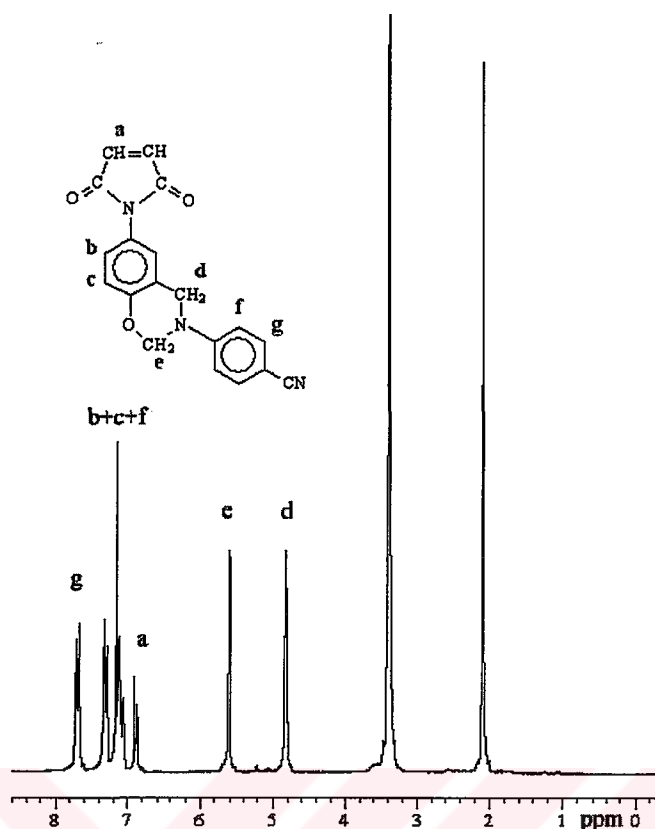


Figure 4.3 ^1H NMR spectrum of BaMI monomer in DMSO.

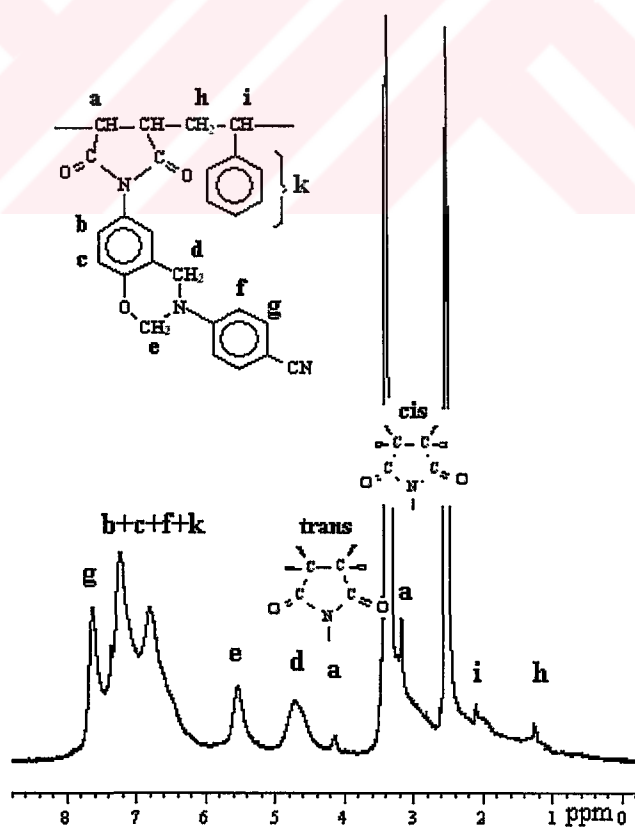


Figure 4.4 ^1H NMR spectrum of BaMI-St copolymer (Table 4.1, Run 4) in DMSO.

4.1.2 Copolymerization Behavior

A number of studies concerning the mechanism of the alternating radical copolymerization between electron-donor and electron-acceptor monomers have been performed, and some kinetic treatment models (terminal model, the penultimate unit effect model, the EDA complex participation model) [163] were proposed. By analyzing their data, Ito and Yamashita [164] concluded that the penultimate unit effect model gave a better fit to the composition data than did the terminal model, but the terminal model gave the best fit to the triad fraction data. In more recent articles, Hao and coworkers [162,163] showed that although the complex participation model may appear to be better than other models, any difference among copolymerization models disappears when the monomer unit sequence in the copolymers is rigidly alternating. In this case, the copolymerization models merge together [163].

For the BaMI-St system, we calculated terminal-model reactivity ratios by the well-known extended Kelen-Tüdös (Ex. K-T) method from the composition of the monomer feed and that of the instantaneously formed copolymer [165].

Extended Kelen-Tüdös method considers possible drift in composition of the copolymer as a result of considerable monomer conversions. This method essentially uses the equation 4,1:

$$\eta = (r_1 + r_2/\alpha) \xi - r_2/\alpha \quad (\text{Eq. 4.1})$$

where η and ξ are functions of both feed and copolymer compositions defined as,

$$\eta = G / (H + \alpha) \quad (\text{Eq. 4.2})$$

$$\xi = H / (H + \alpha) \quad (\text{Eq. 4.3})$$

H and G are defined using a conversion-dependent constant Z, which is expressed as,

$$Z = \log(1 - \xi_1) / \log(1 - \xi_2) \quad (\text{Eq. 4.4})$$

ξ_1 and ξ_2 are respectively the partial molar conversions in monomers M_1 and M_2 and given as,

$$\xi_1 = \xi_2 \cdot (Y/X) \quad (\text{Eq. 4.5})$$

$$\xi_2 = [w(\mu + X)] / (\mu + Y) \quad (\text{Eq. 4.6})$$

where,

$$Y = f_1 / f_2 \quad (\text{Eq. 4.7})$$

$$X = F_1 / F_2 \quad (\text{Eq. 4.8})$$

$$\mu = \mu_2 / \mu_1 \quad (\text{Eq. 4.9})$$

μ_2 and μ_1 represent the molecular weights of monomer 1 and 2, respectively, and w is the total fractional conversion. Thus, the H and G values are defined,

$$H = Y / Z^2 \quad (\text{Eq. 4.10})$$

$$G = (Y-1) / Z \quad (\text{Eq. 4.11})$$

and α is an arbitrary parameter, usually taken as,

$$\alpha = (H_{\max} \cdot H_{\min})^{1/2} \quad (\text{Eq. 4.12})$$

The experimental data were treated by extended Kelen-Tüdös method to find r_1 and r_2 . Monomer reactivity ratios (r_2 and r_1) were obtained using experimental data, presented Table 4.2, from Ex. K-T plots of ξ versus η (Figure 4.5).

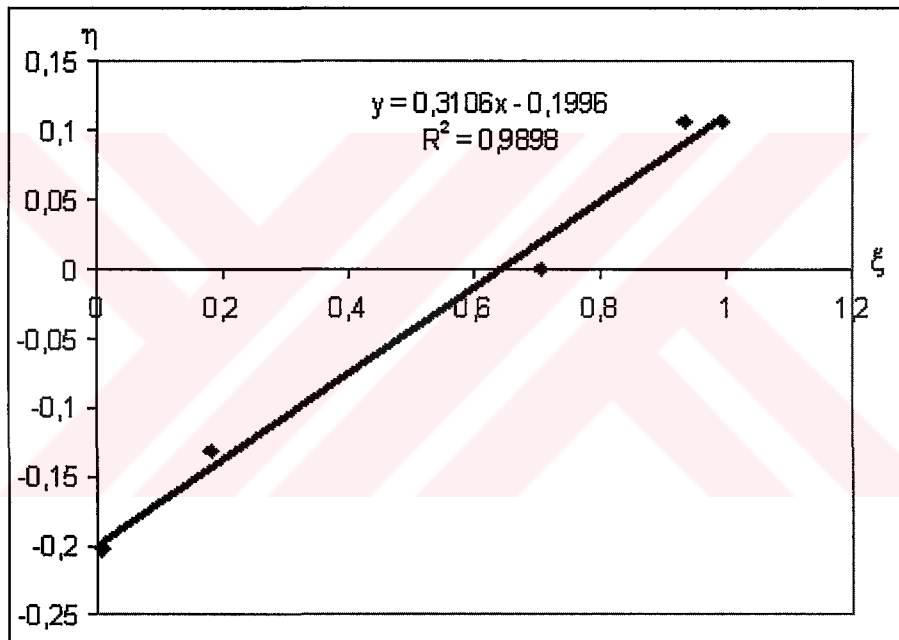


Figure 4.5 Extended Kelen-Tüdös plots of ξ versus η for the photoinduced radical copolymerization of BaMI (M_2) with St (M_1). $Tg \alpha = (r_1 + r_2/\alpha)$, intercept r_2/α and $\alpha = 0,4178$.

The reactivity ratios were found to be $r_1 = 0,111$ and $r_2 = 0,083$. The values r_1 and r_2 are low and the $r_1 \cdot r_2$ are quite low ($r_1 \cdot r_2 \ll 1$) showing that the studied system has a high tendency to form alternating copolymers. The cross-propagation to homopropagation rate constants determined are listed Table 4.3. From the results, it was found that the rate constant of cross-propagation was much higher than that of homopropagation.

Table 4.2. E-K-T Parameters for Monomer BaMI and St Using ^1H NMR Spectroscopic Data^a

Run	Monomer Feed (mol %)		Copolymer Composition ^b (mol%)		Conversion (%)	H	Parameters of Ex. K-T Equation		
	F ₁	F ₂	f ₁	f ₂			G	ξ	η
1	90	10	69,2	30,8	22,3	60,764	6,485	9,932x10 ⁻¹	1,060 x10 ⁻¹
2	70	30	56,8	43,2	42,1	5,8630	6,651 x10 ⁻¹	9,335 x10 ⁻¹	1,059 x10 ⁻¹
3	50	50	50,0	50,0	56,0	1	0	7,053 x10 ⁻¹	0
4	30	70	44,5	55,5	48,1	9,200 x10 ⁻²	-6,714 x10 ⁻²	1,805 x10 ⁻¹	-1,317 x10 ⁻¹
5	10	90	18,9	81,1	49,3	2,873 x10 ⁻³	-8,517x10 ⁻²	6,830 x10 ⁻³	-2,025x10 ⁻¹

^a Photoinduced radical polymerization of BaMI (M₂) with St (M₁) in DMSO at room temperature, photoinitiator: DMPA (c = 0.008 M), [BaMI] + [St] = 0.091 M, and irradiation time: 92 h.

^b Determined by ^1H -NMR data.

Table 4.3 Monomer Reactivity Ratios (r_1, r_2)

M_1	M_2	$r_1 = \frac{k_{11}}{k_{12}}$	$r_2 = \frac{k_{22}}{k_{21}}$	$r_1 \cdot r_2$	$\frac{1}{r_1} = \frac{k_{12}}{k_{11}}$	$\frac{1}{r_2} = \frac{k_{21}}{k_{22}}$
St	BaMI	0,111	0,083	0,0092	9,009	12,048

The 1: 1 alternating structure was formed especially in the feed ratio range of 50: 50 to 30: 70 (F_1/F_2). BaMI rich monomer feed has more alternating tendency than St rich monomer feed. This is in agreement with values of cross-propagation reported in Table 4,3. Additionally, we found that when the amount of BaMI excessive in the feed ratio (10:90= F_1/F_2), the composition of copolymer deviated from the 1: 1 ratio.

4.1.3. Feed-Copolymer Composition Profile

The theoretical composition curve was generated using equation 4.13 that shows the relationship between the feed and copolymer composition in the terminal model.

$$f_1 = \frac{F_1^2 (r_1 - 1) + F_1}{F_1^2 (r_1 + r_2 - 2) + 2F_1(1 - r_2) + r_2} \quad (\text{Eq. 4.13})$$

The composition of the copolymer as a function of that of the feed is depicted in Figure 4.6. The experimental points follow this curve showing a copolymerization with high tendency to alternation for the studied system where f_i stands for molar fractions of the monomers (M_1 or M_2) in the copolymer, and F_i represents those in the feed.

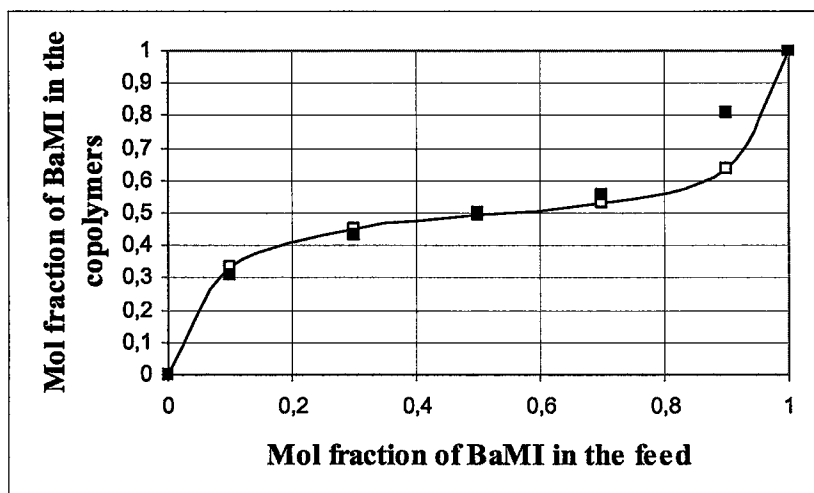


Figure 4.6 Copolymer composition curves: (□) prediction by terminal model, using $r_1=0,111, r_2=0,083$; (■) experimental points.

4.1.4 Structural Data for the Copolymers of St (1) and BaMI (2)

The statistical distributions of the diad monomer sequences, 1-1, 2-2, and 1-2 were calculated by using the method proposed by Igarashi [166]:

$$X' = \Phi_1 - [2\Phi_1\Phi_2] / [1 + ((2\Phi_1 - 1)^2 + 4r_1r_2\Phi_1\Phi_2)^{1/2}], \quad (\text{Eq.4.12})$$

$$Y' = \Phi_2 - [2\Phi_1\Phi_2] / [1 + ((2\Phi_1 - 1)^2 + 4r_1r_2\Phi_1\Phi_2)^{1/2}], \quad (\text{Eq.4.13})$$

$$Z' = 4\Phi_1(1 - \Phi_1) / [1 + ((2\Phi_1 - 1)^2 + 4r_1r_2\Phi_1\Phi_2)^{1/2}], \quad (\text{Eq.4.14})$$

where r_1 and r_2 are the reactivity ratios of St and BaMI, respectively. Φ_1 and Φ_2 are the mole fractions of St and BaMI in the copolymer, obtained from ^1H NMR spectra. The mol fractions of the 1-1, 2-2 and 1-2 sequences, that is blockiness, are designated by X' , Y' , and Z' , respectively (Table 4.4). The mean sequence lengths μ_1 and μ_2 were calculated utilizing the reactions [167].

$$\mu'_1 = 1 + r_1(\Phi_1 \setminus \Phi_2) \quad (\text{Eq.4.15})$$

$$\mu'_2 = 1 + r_2(\Phi_2 \setminus \Phi_1) \quad (\text{Eq.4.16})$$

where the r_1 and r_2 values used from Table 4.3 (E-KT method).

The intermonomer linkages and mean sequence length distributions for the (St-BaMI) copolymers are listed in Table 4.4, for the series of (St-BaMI) copolymers, μ'_2 varied from 1,0369 to 1.3562 slightly as the mole ratio of $\Phi_2 \setminus \Phi_1$ increased. The calculated mole fraction of 1-2 linkages obtained in each copolymer was relatively high (Figure 4.7), indicating an alternating tendency of the copolymer formation, which was also calculated from the reasonably low values ($\sim 0,0092$) of $r_1 r_2$.

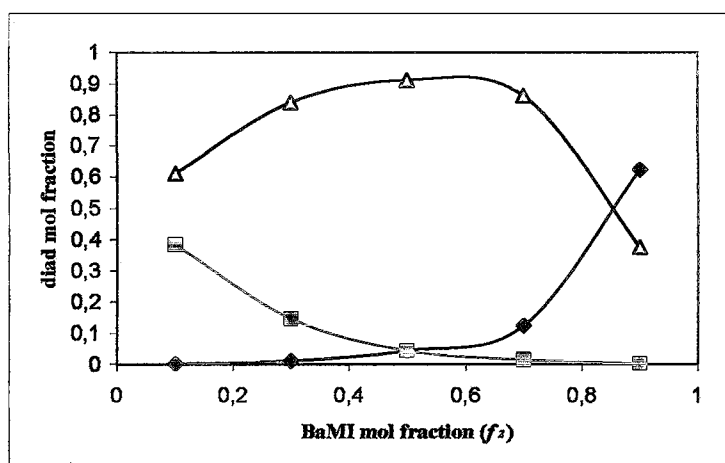


Figure 4.7 Diad monomer sequence fractions vs the BaMI mol fraction for the BaMI-St copolymers: 1-1, 2-2 and 1-2 diads.

Table 4.4 Structural Data for the Copolymers of St (1) with BaMI (2)

Run	Composition ^a (Mol Fraction)		Blockiness ^b (Mol Fraction)		Alternation ^b (Mol Fraction)		Mean Sequence Length	
	Φ_1	Φ_2	1-1 (X')	2-2(Y')	1-2 (Z')	μ'_1	μ'_2	$\frac{\mu'_1}{\mu'_2}$
1	69,2	30,8	0,3862	0,0022	0,6115	1,2494	1,0369	1,2049
2	56,8	43,2	0,1471	0,0111	0,8418	1,1459	1,0631	1,0779
3	50,0	50,0	0,0438	0,0438	0,9124	1,1110	1,0830	1,0259
4	44,5	55,5	0,0138	0,1238	0,8623	1,0890	1,1035	0,9869
5	18,9	81,1	0,0006	0,6226	0,3769	1,0259	1,3562	0,7565

^a Determined from ¹H NMR spectra.

^b Statistically calculated using reactivity ratios ($r_1 = 0.111$ and $r_2 = 0.083$).

4.1.5 The Influence of the Reaction Conditions on the Characteristics of the Copolymers

Different copolymerization conditions were examined to estimate the influence of the solvents with different polarities (dimethylsulfoxide and dichloromethane) and the influence of the comonomers' total molar concentration (C_t) on the number-average molecular weight (M_n), *cis/trans* ratio and polydispersity index (M_w/M_n) of the resulting polymers. The initial ratio of the comonomers was chosen as 1:1 for which the EDA concentration is greatest and also the overall rate of polymerization (R_p) is maximum [168].

The effect of the C_t was examined by considering that an increase in the total monomer concentration should shift the equilibrium (4.3) to the right and thereby increase the concentration of the charge transfer complex. This will lead to an increase in copolymer stereoregularity [168]. From this point of view, the influence of the C_t on the copolymers' characteristics, the copolymerization in DMSO was conducted by using three different values of the above-mentioned C_t parameter. For the series of (BaMI-St) copolymers performed in DMSO (Run 3, 7 and 8 in Table 4.5), the number-average molecular weights (M_n) decrease dramatically with the diminution of C_t . In addition *cis/trans* ratios of the copolymers synthesized in DMSO (Table 4.5) correlate well with the C_t . Highest *cis/trans* ratio (3,8) was founded for the Run 8 which has the highest C_t (0,167 M).

The effect of the solvent was examined by considering that the equilibrium constant for CTC formation (K) is generally solvent dependent [170] and that the equilibrium can be perturbed if one or both of the complex participants is strongly solvated [169]. Dissociation of the excited complex to the solvated free ions is known to be favored in polar solvents. From this point of view, the influence of the solvent on the properties of the copolymers was examined by copolymerization performed in dichloromethane. Although, the comonomers' total molar concentrations (C_t) are higher in the case of DMSO, the *cis/trans* ratio of the copolymer that was produced in dichloromethane was noticeably higher. This result agrees with the assumption that lower polarity of the solvent promotes the CTC formation in high concentration.

The PD values for BaMI-St copolymers in Table 4.5 approximately have the same value (1,60 (Run 3); 1.58 (Run 7); 1.48 (Run 9)) except the PD value (6,52) of Run 8 which has the highest M_n and C_t value.

Table 4.5 Preparation of Copolymer of BaMI with Styrene^a via Photoinitiated Polymerization.

Run	Reaction Conditions ^a		Monomer Feed		Copolymer Composition ^b		Conversion (%)	<i>cis/trans</i> ^b	M_n^c ($\times 10^3$)	M_w/M_n^c
	Solvent	C_i (M)	F_2 (%)	F_1 (%)	f_1 (%)	f_2 (%)				
3	DMSO	0,091	50	50	50	50	56	3,0	3,2	1,60
7	DMSO	0,100	50	50	50	50	53,25	3,1	5,9	1,58
8	DMSO	0,167	50	50	50	50	55,16	3,8	66	6,52
9	CH ₂ Cl ₂	0,040	50	50	50	50	45,16	3,3	1,7	1,48

^a The concentration of photoinitiator DMPA was 0.008 mol/L and irradiation time: 92 h.

^b Calculated from ¹H-NMR data

^c Obtained by GPC measurements

4.1.6 Thermal Behavior

The thermal behavior of the synthesized polymers was investigated by DSC. In general, glass transitions of polymaleimides are difficult to observe because they exhibit low changes in heat capacity and are very broad. When heated for the first time, all the polymers showed broad, very shallow and scarcely noticeable glass transitions. Therefore, more material than usual and the scan rate at 10 °C/min were used. The observed T_g 's are summarized in (Table 4.6).

Table 4.6 Thermal Properties of Synthesized Polymers

Run	Monomer Feed	Copolymer composition ^b	M_n^c	T_g^d	T_{exo}^d
	F_2 (%)	f_2 (%)			
1 ^e	10	30,8	3752	190	280
2 ^e	30	43,2	3136	217	280
3 ^e	50	50,0	3203	230	280
4 ^e	70	55,5	1982	209	280
5 ^e	90	81,1	1810	202	>300
6 ^f	100	100	1881	200	>300
8 ^g	50	50	65639	231	290
9 ^h	50	50	1698	220	280

^a Photoinitiator: DMPA ($c = 0.008$ M), irradiation time: 92 h.

^b Determined by ¹H-NMR data.

^c Determined by GPC measurements.

^d Determined by DSC measurements (10° C / min).

^e [BaMI] + [St] = 0.091 M

^f [BaMI] = 0,084

^g [BaMI] + [St] = 0.167 M

^h [BaMI] + [St] = 0.040 M

The T_g values for the copolymers range between 190 and 231 °C. The highest T_g values (230 °C (Run 3), 231 °C (Run 8), 220 °C (Run 9)) were obtained when the ratio for BaMI/St in the feed was 1:1 (Figure 8, 9, 10). This result shows that the heat resistance properties, such as glass transition temperature will be largely dependent not only on the copolymer composition but also on the sequence distribution in the copolymer. Moreover, in the DSC experiments of BaMI homopolymer and BaMI-St copolymers an exothermic peaks centred at 280°C or >300 °C. This exothermic peak was assigned to be from the ring-opening polymerization of benzoxazine moieties of BaMI-St copolymer.

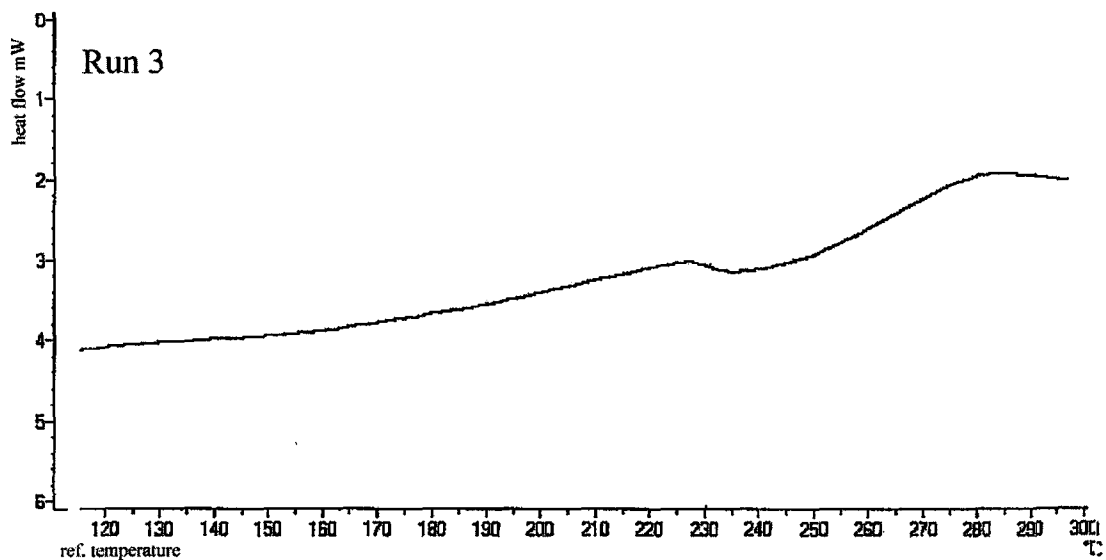


Figure 4.8 DSC scan of Run 3 (scan rate 10 °C/min).

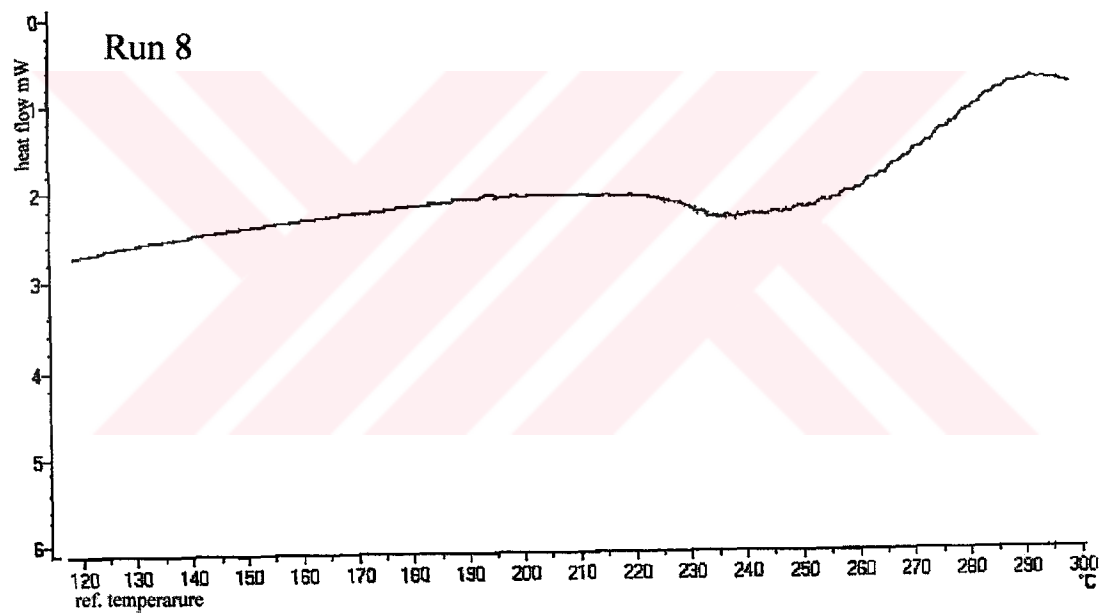


Figure 4.9 DSC scan of Run 8 (scan rate 10 °C/min).

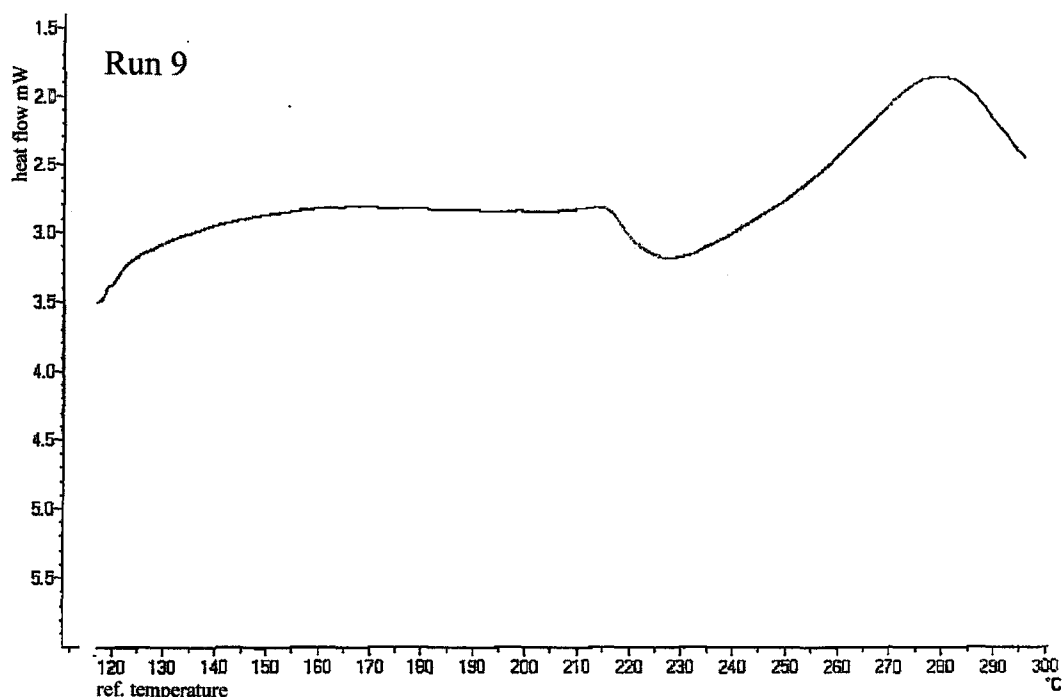
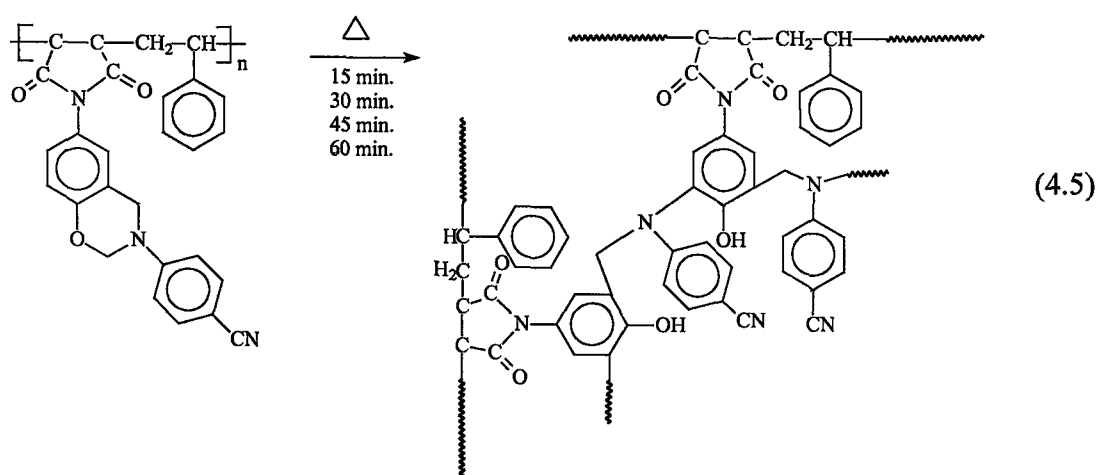


Figure 4.10 DSC scans of Run 9(scan rate 10 °C/min).

4.1.7 Thermal Ring-Opening Polymerization of Benzoxazine Moieties of BaMI-St Copolymer

The thermal polymerization behavior of BaMI-St was monitored with a DSC. BaMI-St copolymer showed a glass transition temperature at 230 °C and an exothermic peak centered at 280 °C in its DSC heating scan. This exothermic peak was assigned to be from the ring-opening polymerization of benzoxazine moieties of BaMI-St copolymer (Run 3).



From the DSC result, ring-opening polymerization of pendant benzoxazine groups of BaMI-St were performed at a certain temperature determined IR measurements. The same amount of BaMI-St copolymer (Run 3) samples was further polymerized at 280 °C for 15 min., 30 min., 45 min.,60 min. to give a cured polymer and reddish brown, phenolic-resin like product was obtained (4.5). Obtained product did not exhibit any exothermic behavior in DSC scanning analysis. In this stage of curing, polymerization of benzoxazine groups occurred to significantly increase the crosslinking density of the cured resin concomitantly with increasing the reaction time.

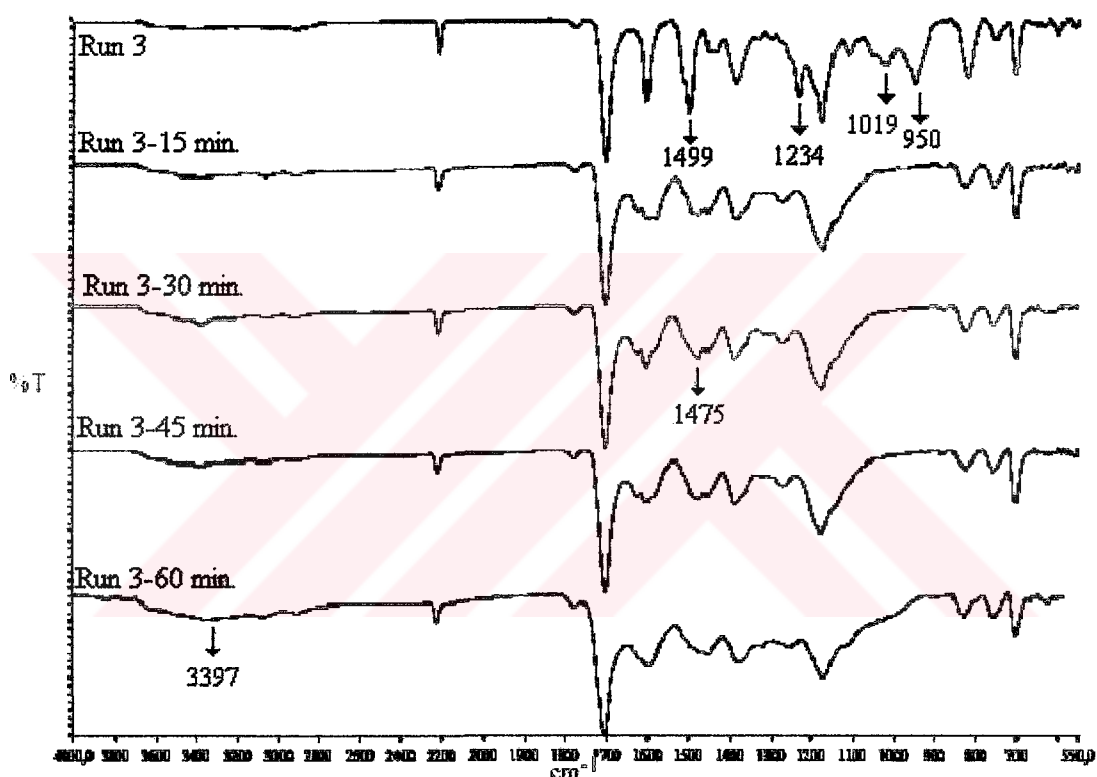


Figure 4.11 IR spectra of copolymer (Table1, Run 3) and crosslinked polymers obtained from thermal curing of Run 3 (Table 1).

The further polymerization mechanism of BaMI was also monitored with an IR (Fig. 4.11). While the samples were further polymerized at 280 °C for 15 min, 30 min., 45 min.,60 min, the occurrence of the ring-opening reaction of benzoxazine ring was observed with the decrease of intensity of absorption bands at 1233 cm^{-1} (C–O–C asymmetric stretching mode), sharply decrease of intensity of absorption bands at 1029 cm^{-1} (C–O–C symmetric stretching mode) and with the appearance of absorption bands at 1475 cm^{-1} (tetra-substituted benzene ring) and 3377 cm^{-1} (-OH of phenol).The intensity of absorption peaks of trisubstituted benzene (1499 and 934

cm^{-1}) decreased, also to indicate the performance of the ring opening reaction of the benzoxazine ring. Although increasing reaction time caused slightly differences in the intensity of absorption bands of phenol, C–O–C asymmetric stretching mode, C–O–C symmetric stretching mode and tetra-substituted benzene ring, the ring-opening polymerization was not completely performed since the absorption peak of trisubstituted benzene was still observed.



5. CONCLUSIONS

In this thesis, photoinduced radical homopolymerization of BaMI and its copolymerization with styrene were performed at room temperature to give linear polymers containing benzoxazine moieties using ω , ω -dimethoxy- ω -phenylacetophenone (DMPA) as photoinitiator. The participation of this CTC complex in the propagation step could be sustained by the presence of less thermodynamically stable cis succinimide units in BaMI-St copolymers evidenced by ^1H NMR spectroscopy. Monomer reactivity ratios for the studied monomer pairs were determined using extended Kelen-Tüdös method because of non-negligible conversions. The reactivity ratios were found to be $r_1 = 0,111$ and $r_2 = 0,088$. The values r_1 and r_2 are low and the $r_1 \cdot r_2$ are quite low ($r_1 \cdot r_2 \ll 1$) showing that the studied system has a high tendency to form alternating copolymers. The precise 1 : 1 alternating structure was formed especially in the feed ratio range of 50 : 50 to 30 : 70 (F_1/F_2). Additionally, we found that when the amount of BaMI excessive in the feed ratio ($10/90 = F_1/F_2$), the composition of copolymer deviated from the 1 : 1 ratio. This results confirmed by the calculation of the monomer diad sequences fractions. The thermal behavior of the new synthesized polymers was investigated by differential scanning calorimetry. The copolymers showed a good thermal stability having the glass transition temperature around 200 $^{\circ}\text{C}$. The highest Tg values were obtained when the ratio for St /BaMI in the feed was 1:1. This result shows that glass transition temperature will be largely dependent not only on the copolymer composition but also on the sequence distribution in the copolymer. Different copolymerization conditions were examined to estimate the influence of the used solvents and comonomers' total molar concentration on the number-average molecular weight (M_n), polydispersity index (M_w/M_n) and cis/trans ratio of the resulting polymers. The thermal polymerization behavior of BaMI-St was monitored with a DSC. The ring-opening polymerization of pendant benzoxazine groups of BaMI-St were performed at a certain temperature and determined IR measurements. The resulting polymer are expected to have higher thermal properties.

This work clearly demonstrates thermally polymerizable benzoxazine groups can successively be incorporated into polymer chains in alternating manner by taking advantage of CTC polymerization. Obvious advantage of this macromolecular design would allow thermal crosslinking of polymers either themselves or in the presence of bifunctional low molar mass benzoxazine derivatives.



REFERENCES

- [1] **Block, H., Lord, P.W. and Walker, S.M.** 1975. Structure And Molecular Relaxation of Alternating Copolymers of Styrene And N-Substituted Maleimides, *Polymer*, **16** (10), 739-744.
- [2] **Romero Colomer, F., Meseguer Duenas, J.M., Gomez Ribelles, J.L., Barrales-Rienda, J.M. and Bautista de Ojeda, J. M.,**1993. Side-Chain Liquid Crystalline Poly(N-Maleimides). 5. Dielectric Relaxation Behavior of Liquid Crystalline Side-Chain And Amorphous Poly(N-Maleimides). A Comparative Structural Study, *Macromolecules*, **26** (1), 155-166.
- [3] **Oishi, T., Onimura, K., Isobe, Y., Yanagihara, H. and Tsutsumi, H.,** 2000. Asymmetric Anionic Polymerization Of Maleimides Bearing Bulky Substituents, *J. Polym. Sci. Part A Polym. Chem.*, **38** (2), 310-320.
- [4] **Tebbe, H., Van Ackern, F. and Tieke, B.,** 1995. New Amphiphilic Copolymers of N-Phenylmaleimides And Vinyl Ethers - Thermal-Properties, Langmuir And Langmuir-Blodgett-Films, Gas Permeation, *Macromol. Chem. Phys.*, **196**(5), 1475-1486.
- [5] **Chiang, W.Y. and Lu, J.Y.,** 1994. Preparation And Properties of New Photo-Functional Polymers .1. N-Substituted Maleimide Styrene Copolymers Containing Pendant Para-Nitrobenzyl Groups, *Macromol. Chem. Phys.*, **195** (2), 591-600.
- [6] (a) **Noordegraaf, M.A., Kuiper, G.J., Marcelis, A.T.M. and Sudholter, E.J.R.,** 1997. Rigid Maleimide-Alt-Vinylpyridine Copolymers With Pendant Chromophores. Synthesis, Characterization and Monolayer Formation, *Macromol. Chem. Phys.*, **198** (11), 3681-3697,
(b) **Serhatli, I.E., Yagci, Y., Haltmer, E., Zentel, R., Schmalzlin, E., Hohenadl, S., Brauchle, C. and Meerholz, K.,** 2001. Crosslinkable Maleimide Copolymers for Stable NLO Properties, *J. Polym. Sci. Part A Polym. Chem.*, **39** (10), 1589-1595.
- [7] **Ning X, Ishida H.,** 1994. Phenolic Materials Via Ring-Opening Polymerization: Synthesis And Characterization of Bisphenol-A Based Benzoxazines And Their Polymers, *J. Polym. Sci. Chem. Ed.*, **32**,1121.

- [8] **Ishida H, Low HY.**, 1997. A Study On The Volumetric Expansion of Benzoxazine-Based Phenolic Resin, *Macromolecules*, **30**, 1099.
- [9] **Kim, H. J, Brunovska, Z. and Ishida, H.**, 1999. Synthesis And Thermal Characterization of Polybenzoxazines Based On Acetylene-Functional Monomers, *Polymer*, **40**, 6565.
- [10] **Blomquist, A.T. and Ferris, A.F.**, 1951. The Kinetics of The Thermal Decomposition of Peresters. I. the Effect of Perbenzoate Concentration On the Decomposition of T-Butyl Perbenzoate, *J. Am. Chem. Soc.*, **73**, 3408.
- [11] **Blomquist, A. T. and Berstein, I.A.**, 1951. The Kinetics of The Thermal Decomposition of Peresters. III. The Effect of P-Substituents On The Unimolecular Decomposition of T-Butyl Perbenzoates, *J. Am. Chem. Soc.*, **73**, 5546.
- [12] **Bartlett, P.D. and Rūhardt, C.**, 1959. Peresters. IV. Substituent Effects Upon The Concerted Decomposition of T-Butyl Phenylperacetates, *J. Am. Chem. Soc.*, **82**, 1756.
- [13] **Bartlett, P.D., Benzing, E.P. and Pincock, R.E.**, 1960. Peresters. V. Di-T-Butylperoxyoxalate, *J. Am. Chem. Soc.*, **82**, 1762.
- [14] **Bartlett, P.D. and Pincock, R.E.**, 1960. Peresters. VI. Ethyl, benzyl, p-Nitrobenzyl and p-Methoxybenzyl t-Butyl-peroxyoxalates, *J. Am. Chem. Soc.*, **82**, 1769.
- [15] **Cohen, S.G. and Sparrow, D.B.**, 1950. Some Reactions of Diisopropyl Peroxydicarbonate, *J. Am. Chem. Soc.*, **72**, 611.
- [16] **Odian, G.**, 1992. *Principles of polymerization*, Third Edition, John Wiley & Sons, Inc., N.Y., 198-267.
- [17] **Flory, P. J.**, 1953. Principles of polymer chemistry, Cornell University Press, Ithaca.
- [18] **Bamford, C. H., Barb, W. G., Jenkins, A. D. and Onyon, P. F.**, 1958. The kinetics of vinyl polymerization by radical mechanisms, Butterworths, London.
- [19] **Blyth, J. and Hoffmann, A.W.**, 1845. *Ann.*, **53**, 292.
- [20] **Dietliker, K.**, 1991. Chemistry and technology of UV and EB formulations for coatings, inks and paints, Sita Technology Ltd., London.

- [21] **Walling, C.**, 1957. Free radicals in solution, Wiley, New York, 273.
- [22] **Turro, N.J.**, 1978. Modern molecular photochemistry, The Benjamin/Cummerings Publishing Co., Inc. Menlo Park Ca, 368.
- [23] **Murov, S.L.**, 1973. *Handbook of photochemistry*, Marcel Dekker, Inc., New York.
- [24] **Folkes, M. J., Hope, P. S., Eds.**; 1993. Polymer Blends and Alloys Chapman & Hall: London, England
- [25] **Olabisi, O., Robeson, L. M. and Shaw, M. T.**, 1979. *Polymer*, in *Polymer Miscibility*; Academic Press: New York, N. Y.
- [26] **Gao, J. and Penlidid, A. J.**, 1998. *Macromol. Sci., Rev. Macromol. Chem. Phys. C38(4)*, 651-780.
- [27] **Kuchanov, S. I.** *Adv. Polym. Sci.* 1992, 103, 1. Tirrell, D. A. In *Comprehensive Polymer Science and Engineering*, 2nd ed.; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., 1989. Eds.; Pergamon: London, , 3, 195.
- [28] **Odian, G.**, 1991. *Principles of Polymerization*, 3rd ed., Wiley & Sons: New York,; Chapter 6.
- [29] **Rempp, P. F., Lutz, P. J.**, 1989. In *Comprehensive Polymer Science*; Eastmond, G. C, Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon: London, Vol. 4
- [30] **Dostal, H.**, 1936. *Monatsh. Chem.* 69, 424.
- [31] **Mayo, F. R. and Lewis, F. M.**, *J. Am. Chem. Soc.* 1944. Copolymerization. I. A Basis for Comparing the Behavior of Monomers in Copolymerization; The Copolymerization of Styrene and Methyl Methacrylate, 66, 1594. Alfrey, T., Jr.; Goldfinger, G. *J. Chem. Phys.* 1944, 12, 115. Wall, F. T. *J. Am. Chem. Soc.* 1944. The Structure of Copolymers. II1, 66, 2050.
- [32] **Morris, L. M., Davis, T. P. and Chaplin, R. P.**, 2000. Radical Copolymerization Propagation Kinetics of Methyl Ethacrylate and Styrene, *Polymer*, 42, 941.
- [33] **Brandrup, J. and Immergut, E. H.**, 1989. Eds.; *Polymer Handbook*, 3rd ed., Wiley & Sons: New York, Chapter 2, 153.

- [34] **Alfrey, T., Jr. and Price, C. C.**, 1947. Relative Reactivities in Vinyl Copolymerisation, *J. Polym. Sci.*, **2**, 101.
- [35] **Mayo, F. R. and Lewis, F. M.**, 1944. Copolymerization. I. A Basis for Comparing the Behavior of Monomers in Copolymerization; The Copolymerization of Styrene and Methyl Methacrylate, *J. Am. Chem. Soc.*, **66**, 1594.
- [36] **Coote, M. L., Davis, T. P.**, 2000. *Prog. Polym. Sci.*, **24**, 1217. **Cywar, D. W., Tirrell, D. A.** 1989. Determination of The Relative Rates of Addition of Styrene and Acrylonitrile to the 1-(1,3-Diphenyl)Propyl and 1-(3-Cyano-1-Phenyl)Propyl Radicals. Evidence For A Penultimate Effect In Radical Copolymerization, *J. Am. Chem. Soc.*, **111**, 7544. **Tanaka, H., Sasai, K., Sato, T., Ota, T.**, 1988. Fluorescence Evidence for Shear Flow-Induced Miscibility In A Blend of Polystyrene and Poly(Vinyl Methyl Ether), *Macromolecules*, **21**, 3534. **Hill, D. J. T.; Lang, A. P., O'Donnell, J. H., O'Sullivan, P. W.**, 1989. Determination of Reactivity Ratios From Analysis of Triad Fractions—Analysis of The Copolymerization of Styrene And Acrylonitrile As Evidence For The Penultimate Model, *Eur. Polym. J.*, **25**, 911.
- [37] **Jones, S. A., Prementine, G. S. and Tirrell, D. A.**, 1985. Model Copolymerization Reactions. Direct Observation of A "Penultimate Effect" In A Model Styrene-Acrylonitrile Copolymerization, *J. Am. Chem. Soc.*, **107**, 5275.
- [38] **Merz, E., Alfrey, T. and Goldfinger, G.**, 1946. Intramolecular Reactions In Vinyl Polymers As A Means of Investigation of The Propagation Step, *J. Polym. Sci.*, **1**, 75.
- [39] **Ham, G. E.**, 1954. Reactivity of Polar Monomers In Copolymerization, *J. Polym. Sci.*, **14**, 87.
- [40] **Barb, W. G.**, 1953. Effect of Nonterminal Monomer Units On The Reactivity of Polymeric Free Radicals, *J. Polym. Sci.*, **11**, 117.
- [41] **Hill, D. J. T., Lang, A. P., O'Donnell, H. H. and O'Sullivan, P. W.**, 1989. Determination of Reactivity Ratios From Analysis of Triad Fractions—Analysis of The Copolymerization Of Styrene And Acrylonitrile As Evidence For The Penultimate Model, *Eur. Polym. J.*, **25**, 911.
- [42] **Van Der Meer, R., Alberti, J. M., German, A. L. and Linssen, H. N.**, 1979. Evaluation of Monomer Reactivity Ratios of More Complex Copolymerization Schemes, With Application To The Penultimate Unit Effect

- In Methyl Acrylate-Butadiene Copolymerization, *J. Polym. Sci., Part A: Polym. Chem.*, **17**, 3349.
- [43] **Hill, D. J. T., O'Donnell, J. H. and O'Sullivan, P. W.**, 1985. Analysis of The Mechanism of Copolymerization of Styrene And Maleic Anhydride, *Macromolecules*, **18**, 9.
- [44] **Guillot, J., Vialle, J. and Guyot, A.**, 1971. Vinyl Chloride Copolymerization-Penultimate Effects With Conjugated Comonomer, *Macromol. Sci. Chem.*, **A5**, 735.
- [45] **Cowie, J. M. G.**, 1985. *In Alternating Copolymers*, Ed., Plenum, New York, Ch.1.
- [46] **Ellinger, L. P.**, 1968. *Advances in Macromolecular Chemistry*; Academic Pres, New York, **Vol.1**, 169.
- [47] **Cais, R. E., Farmer, R. G., Hill, D. J. T. and O'Donnell, J. H.**; 1979. An Analysis of the Complex Participation Model for Free-Radical Copolymerization, *Macromolecules*, **12**, 835.
- [48] **Vosburgh, W. C., Cooper, G. R.**, 1941. Complex Ions. I. The Identification of Complex Ions in Solution by Spectrophotometric Measurements *J. Am. Chem. Soc.*, **63**, 437. **Butler, G.B., Badgett, T. and Sharabash, M.**, 1970. Characterization of Charge Transfer Complex from Furan and Maleic Anhydride and Alternating Copolymer, *J. Macromol. Sci., Chem.*, **A4**, 51.
- [49] **Hanna, M. W. and Ashbaugh, A. L.**, 1964. Nuclear Magnetic Resonance Study of Molecular Complexes of 7,7,8,8-Tetracyanoquinodimethane and Aromatic Donors, *J. Phys. Chem.*, **68**, 811. **Sandoval, A. A.; Hanna, M. W.**, 1966. Nuclear Magnetic Resonance Study of Molecular Complexes of Dimethylformamide with Aromatic Donors, *J. Phys. Chem.*, **70**, 1203.
- [50] "Charge transfer" polymerization - and the absence thereof! **Hall, H. K., Padias, A. B.**, *J. Polym. Sci., Part A: Polym. Chem.* 2001, **39**, 2069. **Jones, S. A.; Tirrell, D. A.**, 1987. Model Copolymerization Reactions-Evidence Against Participation of Donor-Acceptor Complex in Reactions of the L-Butyl Radical with N-Phenylmaleimide and Styrene *J. Polym. Sci., Part A: Polym. Chem.*, **25**, 3177.
- [51] **Cowie, J. M. G.**, 1985. *In Alternating Copolymers*; Cowie, J. M. G., Ed., Plenum, New York, , Ch.2.
- [52] **Cais, R. E., Farmer, R. G., Hill, D. J. T. and O'Donnell, J. H.**, 1979. Analysis of the Complex Participation Model for Free-Radical

- Copolymerization, *Macromolecules*, **12**, 835. **Seiner, J. A. and Litt, M.**, 1971. Role of Monomer Charge-Transfer Complexes in Free Radical Copolymerization. 1. Derivation of Terminal Complex Model Equations, *Macromolecules*, **4**, 308. **Pittman, C. U. and Rounsefell, T. D.**, 1975. Computer-Programs to Study Charge-Transfer Polymerization Model, *Macromolecules*, **8**, 46.
- [53] **Hill, D. J. T., O'Donnell, J. H. and O'Sullivan, P. W.**, 1983. Analysis of the Complex-Dissociation Model for Free-Radical Copolymerization *Macromolecules*, **16**, 1295.
- [54] **Hill, D. J. T., O'Donnell, J. H. and O'Sullivan, P. W.**, 1985. Analysis of The Mechanism of Copolymerization of Styrene And Maleic-Anhydride, *Macromolecules*, **18**, 9.
- [55] **Hall, H. K. and Padias, A. B.**, 1990. Zwitterion and Diradical Tetramethylenes as Initiators of Charge Transfer Polymerization, *Acc. Chem. Res.*, **23**, 3.
- [56] **Staudinger, H.; Schneiders**, 1939. *J. Ann. Chim.*, **541**, 151.
- [57] **Odian, G.**, 1991. Principles of Polymerization, 3rd ed., Wiley & Sons: New York, Chapter 6.
- [58] **Cowie, J. M. G.**, In Comprehensive Polymer Science; **Allen, G., Bevington, J. C., Eastmond, G.C., Ledwith, A., Russo, S., Sigwalt, P.**, Eds.; Pergamon: Oxford, England, 1989; **Vol. 4**, Chapter 22.
- [59] **Hyde, P.; Ledwith, A.**, In Molecular Complexes; **Foster, R.**, Ed.; Paul Elek: London, 1974; **Vol. 2**.
- [60] **Butler, G. B.** In Anionic Polymeric Drugs, **Gonaruma, G., Ottenbrite, R. M., Vogl, O.**, 1980. Eds.; Wiley: New York, [61] **Walling, C.; Briggs, E.; Wolfstirn, K.; Mayo, F. R.**, 1948. Copolymerization. X. The Effect of meta- and para-Substitution on the Reactivity of the Styrene Double Bond, *J. Am. Chem. Soc.*, **70**, 1537.
- [62] **Barlett P. D. and Nozaki K.**, 1946. The Bucherer Reaction on 5-Hydroxybenzo (f) quinoline¹, *J. Am. Chem. Soc.*, **68**, 1595.
- [63] **Butler, G. B. and Campus, A. F.**, 1970. Studies In Cyclocopolymerization. V. Further Evidence For Charge-Transfer Complexes In Cyclocopolymerization, *J. Polym. Sci., Part A: Polym. Chem.*, **8**, 545.

- [64] **Butler, G. B. and Joyce, K. C.**, 1968. *J. Polym. Sci., Part C.*,**22**, 45.
- [65] **Butler, G. B. and Fujimori, K.**, 1972. Studies in Cyclo-copolymerization & Solvent Effects in Cyclo-copolymerization of Maleic Anhydride with Divinylether, *J. Macromol. Sci., Chem.*, **6**, 1533.
- [66] **Ragab, Y. A. and Butler, G. B.**, 1981. Structure Study of The Furan-Maleic Anhydride Copolymer, *J. Polym. Sci., Polym. Chem. Ed.*,**19**, 1175.
- [67] **Yamashita, Y., Iwatsuki, S. and Kokubo, T.**, *J. Polym. Sci., Part C.* 1968, **23**, 753.
- [68] **Andrews LJ, Keefer RM.**, 1964. Molecular Complexes in Organic Chemistry, San Francisco, CA, Holden-Day,.
- [69] **Briegleb G.**, 1961. Elektronen-Donator–Acceptor Komplexe. Berlin: Springer,.
- [70] **Milliken RS.**, 1952. Molecular Compounds and their Spectra. II, *J Am. Chem. Soc.*,**74**,811.
- [71] **Rzaev ZM.**, 1984. Polymers and copolymers of maleic anhydride. Baku, Elm, (in Russian).
- [72] **Donhebel, D. C., Tedder, J. M. and Walton, J. C.**, 1979. *Radicals*", Cambridge University Press, London.
- [73] **Mulliken, R. S.; Person, W. B.**, 1969. Molecular Complexes, A Lecture and Reprint Volume; Wiley-Interscience, New York.
- [74] **Matsuo, T. Bull.**, 1965. *Chem. SOC. Jpn.*, **38**, 557.
- [75] **Butler, G. B. and Do, C. H.**, 1989. The Effect of Donor-Acceptor Complexes on the Stereochemistry of Alternating Copolymers of Alkyl Vinyl Ethers with Maleonitrile and Fumaronitrile, *Makromol. Chem. Suppl.*, **15**, 93.
- [76] **Gosau, J. M. And Schluter, A. D.**, 1990. Propellane and Maleic-Anhydride-Face-Specific Copolymerization with Formation of an Alternating 1-1 Copolymer, *Chem. Ber.*,**123**, 2449.
- [77] **Arcus, C. L. and Bose**, 1959. *Chem. Ind. (London)*, 456.
- [78] **Arcus, C. L.** , 1955. *J. Chem.Soc.*, 2801.

- [79] **Arcus, C. L.** 1957. *J. Chem.Soc.*, **1189**, F1595
- [80] **Olson, K. G. and Butler, G. B.**, 1983., Stereochemical Evidence For The Participation of A Comonomer Charge-Transfer Complex In Alternating Copolymerization, *Macromolecules*, **16**, 707.
- [81] **Butler, G. B., Olson, K. G. and Tu, C. L.**, 1984. Monomer Orientation Control by Donor-Acceptor Complex Participation In Alternating Copolymerization, *Macromolecules*, **17**, 1884.
- [82] **Benesi, H. A.; Hildebrand, J. H.**, 1949. A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons, *J. Am. Chem. Soc.*, **71**, 2703.
- [83] **Hanna, M. W.; Ashbough, A. L.**, 1964. Nuclear Magnetic Resonance Study of Molecular Complexes of 7,7,8,8-Tetracyanoquinodimethane and Aromatic Donors^{1,2}, *J Phys Chem*, **68**, 811.
- [84] **H. M. McConnell**, 1958. Reaction Rates by Nuclear Magnetic Resonance, *J. Chem. Phys.*, **28**, 430.
- [85] **Mormann, W.; Schmaltz, K.** 1994. Polymers from Multifunctional Isocyanates. 9. Alternating Copolymers from 2-Propenyl Isocyanate and Maleic Anhydride, *Macromolecules*, **27**, 7115.
- [86] **Yang, C. P. and Wang, S. S.**, 1989., Studies On The Imidization of N-Substituted Polymaleamic Acids, *J. Polym. Sci., Polym. Chem. Ed.*, **A27**, 15.
- [87] **Sandreczki, T. C. and Brown, I. M.**, 1990., Characterization of The Free-Radical Homopolymerization of N-Methylmaleimide, *Macromolecules*, **23**, 1979.
- [88] **Nakayama, Y., and Smets, G.**, 1967. Radical And Anionic Homopolymerization of Maleimide And N-N-Butylmaleimide, *J. Polym. Sci.*, **A4(5)**, 1619.
- [89] **Elsabee, M. Z., and Mokhtar, S.**, 1983. Polymerization of N-aryl maleimides, *Eur. Polym. J.*, **19**, 451.
- [90] **Takeishi, M., Arimori, S., Iwasaki, N., Sekiya, K. and Sato, R.**, 1992. Polymerization of N-Substituted Maleimides Initiated by Thiophenol, *Polym. J.*, **24**, 365.

- [91] **Matsumoto, A., Oki, Y., Horie, A. and Otsu, T.**, 1991. Synthesis and Characterization of Poly(N-Trialkylsilylmaleimide)s Through Radical and Anionic Polymerizations, *Chem. Lett.*, **7**, 1141.
- [92] **Ratzsch, M., Steinert, V., Giese, B. and Farshchi, H.**, 1989. Investigations on the Reactivity of Para-Substituted N-Phenylmaleimides, *Makromol. Chem., Rapid Commun.*, **10**, 195.
- [93] **Abayasekara, D. R. and Ottenbrite, R. M.**, 1986. A Study of N-Substituent Effects on the Polymerization Properties of Maleimide, *Polym. Prepr.*, **27(1)**, 462.
- [94] **Mohamed, A. A., Jebrael, F. H. and Elsabee, M. Z.**, 1986., Copolymerization of styrene with N-arylmaleimides, *Macromolecules*, **19**, 32.
- [95] **Rittel, A. and Kucharski, M.**, 1989. Determination of Reactivity Ratios of Styrene and Some Alkyl Acrylates with N-Tolylmaleimide at High Conversion Steps *Acta Polym.*, **40**, 62.
- [96] **Rittel, A.**, 1989. *Acta Polym.*, **40**, 268.
- [97] **Konsulov, V. B. and Kirilov, V.**, 1991. *Chemia and Industria*, **62(2)**, 22
- [98] **Younes, U. E.**, 1985. *U.S. Patent*, No: 4 508 883.
- [99] **Oishi, T., Moriwaki, M., Momoi, M. and Fujimoto, M.**, 1989. Reactivities of N-(4-Substituted Phenyl)-Alpha-Chloromaleimide in Radical Copolymerization with Styrene or Methyl-Methacrylate *J. Macromol. Sci., Chem.*, **A26(6)**, 861.
- [100] **Oishi, T., Saeki, K. and Fujimoto, M.**, 1989. Reactivities of N-Alkyl- α -Chloromaleimide In Radical Copolymerizations With Styrene or Methyl Methacrylate, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 1429.
- [101] **Turner, S. R., Anderson, C. C. and Kolterman, K. M.**, 1989. Alternating Copolymerization as a Route for Synthesis of Novel Reactive Copolymers, *J. Polym. Sci., Polym. Lett. Ed.*, **27**, 253.

- [102] **Florjanczyk, Z. and Krawiec, W.**, 1989. Analysis of Composition Data for Copolymers of N-Phenylmaleimide with Styrene in Terms of Various Copolymerization Models, *Makromol. Chem.*, **190**, 2144.
- [103] **Florjanczyk, Z., Krawiec, W. and Such, K.**, 1990., A Study of The Relative Reactivity of Maleic Anhydride And Some Maleimides In Free Radical Copolymerization and Terpolymerization, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 795.
- [104] **Semchikov, J. D., Scherbakov, V. I., Hvatova, N. L., Stolyarova, N. E., Dyachkovskaya, O. S. and Razuvaev, G. A.**, 1982. New Organotin Imide-Containing Polymers, *Vysokomol. Soedin.*, **B24**, 516.
- [105] **Mamedova, S. G., Rzaev, R. M., Medyakova, L. V., Rustamov, F. B. and Askerova, N. M.**, 1987. *Vysokomol. Soedin.* 1987, **A29**.
- [106] **Fles, D. D., Vucovic, R., Ranogajec, F., Zuanic, M. and Fles, D.**, 1989. Copolymerization of Alpha-Methylstyrene and N-phenylmaleimide, *Polymeri*, **10**, 143.
- [107] **Fles, D. D., Vucovic, R. and Ranogajec, F.**, 1989., Copolymerization of α -Methylstyrene and N-Phenylmaleimide, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 3227.
- [108] **Konsulov, V. B. and Grozeva, Z. S.**, 1991. *Chemia and Industrya*, **62(6)**, 23.
- [109] **Borbely, J., Kelen, T., Consulov, V. and Grozeva, Z.**, 1991. Synthesis and Characterization of Poly-(Methyl Methacrylate-Co-N-4-Bromophenylmaleimide) ,*Polym. Bull.*, **26**, 253.
- [110] **Finter, J., Widmer, E. and Zweifel, H.**, 1984. A New Class of Photopolymers with Pendent Dimethylmaleimide Groups .2. Photocrosslinking of Homopolymers and Copolymers of N-(5-Methyl-3-Oxa-4-Oxohexen-5-Yl)-Dimethylmaleimide *Angew. Makromol. Chem.*, **128**, 71.
- [111] **Pradny, M.**, 1989. Interaction Between The Amino And Carbonyl Groups In Copoly(2-Dimethylaminoethyl Methacrylate N-Phenylmaleimide, *Makromol. Chem.*, **190**, 2229.
- [112] **Gong, B.-M. and Chien, J. W.**, 1989., Copolymer of Trifluoroethylmethacrylate-N-P-Methoxyphenyl Citraconimide As High Tge-Beam Resist, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 1149.

- [113] **Elsabee, M. Z., Sabaa, M. W. and Mokhtar, S.**, 1983. Co-Polymerization of N-Arylmaleimides With Vinyl-Acetate, *Polym. J.*, **15**, 429.
- [114] **Elsabee, M. Z., Sabaa, M. W. and Mokhtar, S.**, 1985. Copolymerization Of N-Arylmaleimide With Vinyl-Acetate Effect Of The Total Monomer Concentration On The Reactivity Ratios Of The Copolymerization, *Polym. J.*, **17**, 737.
- [115] **Konsulov, V. B., Grozeva, Z. S., Kelen, T. and Borbelly,** 1992. Copolymerization Of N-Chlorophenylmaleimides With Vinyl-Acetate, *J. Makromol. Chem.*, **193**, 847.
- [116] **Wagener, K. B. and Smith, M. A.**, 1989. Imaging The Reaction Behavior Of Network Polymers Via Linear Bulk-Polymerization, *Polym. Prepr.*, **30(1)**, 285.
- [117] **Rasulov, N., Medyakova, L. V., Kulieva, E. U., Rzaev, Z. M. and Zubov, V. P.**, 1986. Alternating Copolymerization Of N-Phenyl Maleimide With Cyclohexylvinyl Ketone, *Vysokomol. Soedin.*, **A28**, 2595.
- [118] **Hagiwara, T., Takeda, M., Hamana, H. and Narita, T.**, 1989., Copolymerization of N-phenylmaleimide and propylene oxide initiated with organozinc compounds, *Macromolecules*, **22**, 2026.
- [119] **Otsuka, M., Matsuoka, K., Takemoto, K. and Imoto, M.**, 1970. Vinyl Polymerization .252. Copolymerization Of Vinyl Chloride With N-(4-Substituted Phenyl)Maleimide, *Kogyo Kagaku Zasshi*, **73**, 1062.
- [120] **Horing, S., Jakowlew, S. and Ulbricht,** 1982. On The Glass Temperature And The Thermal-Stability Of Vinyl-Chloride Maleimide Co-Polymers, *J. Plaste und Kautschuk*, **29**, 622.
- [121] **Horing, S., Jakowlew, S. and Ulbricht,** 1983. Medium Effects On The Radical Co-Polymerization Of Vinyl-Chloride With N-Substituted Maleimides, *J. Plaste und Kautschuk*, **30**, 305.
- [122] **Otsu, T., Matsumoto, A. and Ito, H.**, 1990. *Chem. Express*, **5**, 901.
- [123] **Schmidt-Naake, C., Schmidt, H., Zitanski, B. and Berger, W.**, 1990. Modellselektion bei der Copolymerisation ternärer Donator-Acceptor systeme, *Makromol. Chem.*, **191**, 3033.

- [124] **Rivas, B. L. and Pizarro, G. C.**, 1989. Copolymerization via Zwitterion—12. Copolymerization of 2-Ethyl-2-Oxazoline With *O*- and *P*-Methylphenylmaleimide, *Eur. Polym. J.*, **25(3)**, 231.
- [125] **Rivas, B. L. and Pizarro, G. C.**, 1989. Copolymerization via Zwitterions of *P*-Nitrophenyl Maleimide with Oxazoline Derivatives-15, *Eur. Polym. J.*, **25(12)**, 1227.
- [126] **Oishi, T., Fujimoto, T., Yoshimoto, M. and Kimura, T.**, 1989. Anionic Polymerizations of *N*-Substituted Isomaleimide, *Polym. J.*, **21**, 655.
- [127] **Culbertson, B. M., Post, L. K. and Aulabaugh, A. E.**, 1982. Copolymerization Of Allyl And Methallyl Substituted Phenols With Maleic-Anhydride And Maleimides, *Polym. Prepr.*, **23(1)**, 1.
- [128] **Varderbilt, D. P. and Butler, G. B.**, 1983. Bifunctional Synzymes Via Alternating Copolymerization, *Polym. Prepr.*, **24(2)**, 346.
- [129] **Aponte, M. A. and Butler, G. B.**, 1983. Synthesis And Study Of The Interactions Of Polymers Containing Nucleic-Acid Bases As Pendant Groups *Polym. Prepr.*, **24(2)**, 362.
- [130] **Ishida H. and Rodriguez Y.**, 1995. Catalyzing The Curing Reaction of A New Benzoxazine-Based Phenolic Resin, *J. Polym Sci Polym Chem Ed.*, **58**, 1751.
- [131] **Kim HJ.**, 1997. *PhD Dissertation*. Case Western Reserve University, Cleveland, OH.
- [132] **Ishida H.**, 1998. Versatile Phenolic stands up to the heat, in *Modern Plastics International*, 6, pp. 87–90., (Kaplan WA, Compiler).
- [133] **Ishida H. and Rodriguez Y.**, 1995., Curing Kinetics of A New Benzoxazine-Based Phenolic Resin By Differential Scanning Calorimetry, *Polymer*, **36**, 3151–3158.
- [134] **Ishida H. and Allen D.**, 1995. Rheological Characterization During Cure Of Near-Zero Shrinkage Polybenzoxazines *ACS Polym. Mater. Sci. Engng.*, **73**, 496–7.
- [135] **Ishida H. and Allen D.**, 1996., Physical and mechanical characterization of near-zero shrinkage polybenzoxazines, *J. Polym. Sci-B*, **34(6)**, 1019–30.

- [136] **Shen SB. and Ishida H.**, 1996., Development and characterization of high-performance polybenzoxazine composites *Polym. Comp.*, **17(5)**:710–719.
- [137] **Ishida H. and Low HY.**, 1997., A Study on the Volumetric Expansion of Benzoxazine-Based Phenolic Resin, *Macromolecules*, **30(4)**, 1099–106.
- [138] **Huang MT. and Ishida H.**, 1999., The Silane Interphase of Composites: Effects of Process Conditions On γ -Aminopropyltriethoxysilane, *Polym. Comp.*, **7(4)**, 233–47.
- [139] **Oishi, T. and Fujimoto, M.**, 1992. Synthesis and polymerization of n-[4-n'-(alpha-methylbenzyl)aminocarbonylphenyl]maleimide, *Polym. Chem*, **30 (9)**, 1821-1830.
- [140] **Oishi, T., Osubo, Y., Matsuaki, K. and Fujimoto, M.**, 1993., Synthesis And Polymerization of N-[4-(Cholesteroxycarbonyl)Phenyl]Maleimide, *Polymer*, **34 (7)**, 1504-1511.
- [141] **Cirpan, A., Alkan, S., Toppare, L., Hepuzer, Y. and Yagci, Y.**, 2002., Conducting Graft Copolymers of Poly(3-Methylthienyl Methacrylate) With Pyrrole And Thiophene, *J. Polym. Sci. Part A: Polym. Chem.*, **40**, 4131.
- [142] **Oishi, T., Sase, K. And Tsutsumi, H.**, 1998., Syntheses And Thermostabilities of N-[4-(N^r-Substituted Aminocarbonyl)Phenyl]Maleimide Polymers, *J. Poly. Sci. Part A: Polm. Chem.*, **36 (12)**, 2001-2012.
- [143] **Ahn, K.D. Kim, J.M., Lee, C.W. and Han, D.K.**, 2000., Synthesis and Radical Polymerization of Bifunctional Maleimides with Different Functional Reactivities, *J. Macromol. Sci. Pure. Appl. Chem.*, **37 (1-2)**, 117-131.
- [144] **Cianga, L. and Olaru, N.**, 2000. Synthesis and characterization of new optically active monomers based on 4-maleimidobenzoic acid, *Des. Monom. Polym.*, **3 (2)**, 209-230.
- [145] **Oishi, T., Kagawa, K. and Nagata, H.**, 1997., Synthesis and polymerization of maleimide containing an L-menthyl group, *Polymer*, **38 (6)**, 1461-1469.
- [146] **Hagiwara, T., Kawashima, N., Hamna, H. and Narita, T.**, 1997., Polymerization of N-(2,3,4,5,6-pentafluorophenyl)-maleimide, *Macromol. Rapid Commun.*, **18 (4)**, 303-311.
- [147] **Olson, K.G.; Butler, G.B.**, 1984., Stereochemical Evidence For Participation Of A Donor-Acceptor Complex In Alternating Copolymerization. 1. Model Compound Synthesis, *Macromolecules*, **17 (12)**, 2486-2501.

- [148] **Schmidt-Naake, G., Drache, M. and Leonhardt, K.**, 1998., The Influence of Charge-Transfer Complexes on The Copolymerization Behavior of Cyclic Maleic Acid Derivatives With Donor Monomers, *Macromol. Chem. Phys.*, **199** (3), 353-361.
- [149] **Yamada, M., Takase, I., Kouton N.**, 1971. *Kobunshi Kagaku*, **28**, 582.
- [150] **Zhang Xu, G., Hua Dong, J. and Yuan Qiu, K.**, 1997., Photopolymerization Of N-Substituted Phenyl Maleimide Initiated with N,N-Dimethyl-4-Toluidine, *J. Polym. Sci. Part A: Polym. Chem.*, **35**, 643.
- [151] **Kohli, P., Scranton, A. B. and Blanchard, G. J.**, 1998., Co-Polymerization of Maleimides and Vinyl Ethers: A Structural Study, *Macromolecules*, **31**, 5681.
- [152] **Kim, J. M., Lee, C. W., Han, D. K. and Ahn, K. D.**, 1999. Photopolymerization of Bifunctional Maleimides Based On Electron-Donor/Acceptor Systems, *J. Macromol. Sci. Pure Appl. Chem.*, **36**, 1387.
- [153] **Nakano, T., Tamada, D., Miyazakai, J., Kakiuchi, K. and Okamoto, Y.**, 2000., Synthesis of Novel π -Conjugated Polymer Having an Enyne Unit by Palladium-Catalyzed Three-Component Coupling Polymerization and Subsequent Retro-Diels-Alder Reaction, *Macromolecules*, **33**, 1487.
- [154] **Cubbon, R. C. B.**, 1965., The free radical and anionic polymerization of some N-substituted maleimides, *Polymer*, **6**, 419.
- [155] **Olson KG and Butler GB.** 1983., Stereochemical Evidence For The Participation of A Comonomer Charge-Transfer Complex In Alternating Copolymerization, *Macromolecules*, **16**,707.
- [156] **Oishi, T., Kagawa, K. and Nagata, H.**, 1997. Synthesis and polymerization of maleimide containing an L-menthyl group, *Polymer*, **38** (6), 1461-1469.
- [157] **Hao, X. and Fujimori, K.**, 1999. Alternating copolymerization of N-phenyl maleimide and styrene, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)*, **40**(2), 476.
- [158] **Dunkers, J. and Ishida, H.**, 1995. Vibrational Assignments of N,N-Bis(3,5-Dimethyl-2-Hydroxybenzyl)Methylamine In the Fingerprint Region, *Spectrochim Acta*, **51A**, 855.

- [159] **Dunkers, J. and Ishida, H.**, 1995. Vibrational assignments of 3-alkyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazines in the fingerprint region, *Spectrochim Acta*, **51A**, 1061.
- [160] **Agag, T. and Takeichi, T.**, 2001., Novel Benzoxazine Monomers Containing *p*-Phenyl Propargyl Ether: Polymerization of Monomers and Properties of Polybenzoxazines, *Macromolecules*, **34**,7257.
- [161] **Agag, T. and Takeichi, T.**, 2003., Synthesis and Characterization of Novel Benzoxazine Monomers Containing Allyl Groups and Their High Performance Thermosets, *Macromolecules*, **36**,6010.
- [162] **Hao, X. and Fujimori, K.**, 1999. Alternating Copolymerization Of N-Phenyl Maleimide And Styrene. *Polym. Prep.r (Am. Chem. So.Div. Polym. Chem.)*, **40(2)**, 476.
- [163] **Ha, N. T. H., Fujimori, K. and Craven, I. E.**, 1997., Relation Between The Alternating Monomer Unit Sequence And The Cis And Trans Linkage Configurations At The Cyclic Maleic Anhydride Units In The Copolymers Of Styrene And Maleic Anhydride Prepared In Carbon Tetrachloride, *Macromol. Chem. Phys.*, , **198**, 3507.
- [164] **Ito, K. and Yamashita, Y.**, 1966. Triad Distributions Of 1,1-Diphenylethylene-Methyl Acrylate Copolymer Determined From NMR Study, *J. Polym. Sci. Part A-1: Polym. Chem.*, **4**, 631.
- [165] **Kelen, T., Tüdös, F. and Turcsany, I.**, 1977. Analysis Of The Linear Methods For Determining Copolymerization Reactivity Ratios. IV. A Comprehensive And Critical Reexamination Of Carbocationic Copolymerization Data, *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 3047.
- [166] **Igarashi, S.**, 1963. Representation Of Composition And Blockiness Of The Copolymer By A Triangular Coordinate System ,*J Polym Sci Polym Lett Ed*, **1**, 359.
- [167] **Elias, H. G.**, 1971. *Macromolecules*, p. 761, vol.2., New York, Plenum Press.
- [168] **Gandini, A. and Belgacen, M.N.**, 1997. Furans in polymer chemistry, *Prog. Polym. Sci.* , **22 (6)**, 1203-1379.
- [169] **Andrews, L. J.; Keefer, R. M.** 1964. Molecular Complexes, in *Organic Chemistry*, Holden-Day: San Francisco.

- [170] **Olson, K. G. and Butler, G. B.,** 1984. Stereochemical Evidence For The Participation of A Donor-Acceptor Complex In Alternating Copolymerizations. 2. Copolymer Structure, *Macromolecules*, **17**, 2486.



AUTOBIOGRAPHY

Burçin Gacal was born in İstanbul on June 11, 1980. She was graduated from Bahçeşehir High School. She was admitted to Istanbul Technical University, Department of Chemistry in 1998. She was registered as M.Sc. student to the Polymer Science and Technology Program at Istanbul Technical University leading to a degree of Master of Science under the guidance of Professor. Dr. Yusuf Yagci, in 2004.

Scientific Activities

2004- 18th National Chemistry Symposia
(Kafkas University, Kars, Turkey)