ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ATOM TRANSFER GRAFT COPOLYMERIZATION BY USING POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

M.Sc. Thesis by

Mine BARLAN

Department : Polymer Science and Technology

Programme: Polymer Science and Technology

JANUARY 2003

ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ATOM TRANSFER GRAFT COPOLYMERIZATION BY USING POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

M.Sc. Thesis by
Mine BARLAN
(515011023)

Date of submission : 24 December 2002

Date of defence examination: 15 January 2003

Supervisor (Chairman): Prof.Dr. Ümit TUNCA

Members of the Examining Committee : Prof.Dr. Ayşen ÖNEN

Assoc.Prof.Dr. Seniha GÜNER

JANUARY 2003

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLY(2,6-DİMETİL-1,4-FENİLEN OKSİT) KULLANIMI İLE ATOM TRANSFER GRAFT KOPOLİMERİZASYONU

YÜKSEK LİSANS TEZİ

Mine BARLAN
(515011023)

Tezin Enstitüye Verildiği Tarih : 24 Aralık 2002

Tezin Savunulduğu Tarih : 15 Ocak 2003

Tez Danışmanı : Prof.Dr. Ümit TUNCA

Diğer Jüri Üyeleri : Prof.Dr. Ayşen ÖNEN

Doç.Dr. Seniha GÜNER

OCAK 2003

ACKNOWLEDGEMENT

I would like to express my gratitude to my thesis supervisor, Prof.Dr. Ümit TUNCA and co-supervisor Prof.Dr. Gürkan HIZAL for their invaluable help and also for their continous interest, tolerance and encouragement throughout this research.

I would like to thank to Prof.Dr. Metin H. ACAR who encouraged me starting my master study and offered moral support during all stages of this study.

I give special thanks to Şebnem İNCEOĞLU, Recep UÇAN, Fatmanur KASAPOĞLU, Selçuk YILMAZ, Okan ULAŞ, Eşref AYLAN and V.Barış GÖKÇE for their support in all possible ways.

I also thank to my colleagues Dalida HAYRABETYAN, Tuba ERDOĞAN, Berkant BEDRİ, Dolunay ŞAKAR, Murat PEHLİVAN, Sermin ARAS, Mustafa ÇIKILMAZKAYA, Çiğdem ÇELİK, Tuba ALOĞLU, Hümeyra MERT and Alper ÜSTÜN for their helpful attitude during my laboratory works.

I also would like to appreciate my parents Asuman and Ersin BARLAN, Saime DEMİRSEL, Emine KÖKALP, Didem and Uğur BARLAN for their moral support and patience during this work and my life.

Finally, I would like to dedicate this thesis to my uncle Ahmet KÖKALP who was impatient to see the final of my master study and left us. I thank to him for his support in all ways during my life and hope to see this final wherever he is.

January 2003 Mine BARLAN

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

ATRP	: Atom Transfer Radical Polymerization
DMP	: 2,6-dimethylphenol
PPO–OH	: Monofunctional poly(phenylene oxide)
PPO–2OH	: Bifunctional poly(phenylene oxide)
PPOBr	: Brominated poly(phenylene oxide)
MMA	: Methyl methacrylate
PMMA	: Poly(methyl methacrylate)

LIST OF TABLES

Page No :

LIST OF FIGURES

Page No:

LIST OF SYMBOLS

M_n	:	Number average molecular weight
M_w	:	Weight average molecular weight
M_n/M_w	:	Polydispersity
M_0/I_0	:	Initial ratio of monomer and initiator

ATOM TRANSFER GRAFT COPOLYMERIZATION BY USING POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

SUMMARY

The control of macromolecular structure has recently become an important facet of polymer science from an academic and industrial viewpoint. This interest is governed by the realization that control of macromolecular architecture can lead to the development of new polymeric materials with improved and/ or new mechanical and physical properties. With the exception of linear polymers, architectural diffirences lie in branched structures with regard to the number of branches and their relative placement in the macromolecule.

The field of radical polymerization has exploded with the advent of controlled radical polymerization processes. Radical polymerization is a very important commercial process used to prepare high molecular weight polymers. The only disadvantage of conventional radical polymerization is the poor control of macromolecular structures including end functionalities and polydispersities due to the chain transfer and termination process. Controlled architecture possesses some characteristics, which are molecular weight control, end group control, ability to form block copolymers and a living nature. Recently, the controlled/ 'living' radical polymerizations have been utilized for the synthesis of well-defined narrow polydispersity polymers. Of these methods, atom transfer radical polymerization (ATRP) appears to be a versatile method for the controlled radical polymerization of various monomers. Well-defined polymers with predictable molecular weights and with low polydispersities can be syntesized by ATRP. The control over molecular weight and functionality in ATRP has also allowed for the synthesis of numerous materials with many novel functionalities, compositions, and architectures. However, since ATRP is a complex multicomponent system, it is important to understand and consider all of its components to make full use of this methodology and find optimum polymerization conditions for the preparation of specific materials for particular applications.

In this study, a macroinitiator, brominated poly(2,6-dimethyl-1,4-phenylene oxide)s was synthesized according to a known procedure and was used for the preparation of styrene and methyl methacrylate grafted poly(2,6-dimethyl-1,4-phenylene oxide)s via ATRP. High radical stability of the macroinitiator lead to crosslinking and gelation in copper-catalyzed ATRP of monomers. GPC (Gel Permeation Chromatography) studies of the obtained polymers show that graft polymers were formed with uncontrolled molecular weights. Some additives and various grafting methods were also studied in this work in order to prevent the gelation of the macroinitiator and uncontrolled molecular weight of the resulting polymers.

POLİ(2,6-DİMETİL-1,4-FENİLEN OKSİT) KULLANIMI İLE ATOM TRANSFER GRAFT KOPOLİMERİZASYONU

ÖZET

Makromolekül yapılarının kontrolü son zamanlarda polimer biliminin akademik ve endüstriyel yönden önemli bir hedefi haline gelmiştir. Bu ilgiye makromolekül mimarisi kontrolünün iyileştirilmiş ve/ veya yeni mekanik ve fiziksel özelliklere sahip yeni polimerik maddelerin geliştirilmesine varabileceği gerçeği hakimdir. Mimari farklılıklar, lineer polimerler bir yana, dal sayısına ve dalların makromolekül üzerindeki bağıl yerleşimlerine bağlı olarak dallanmış yapılarda yatmaktadır.

Radikal polimerizasyonu alanı kontrollü radikal polimerizasyon yöntemlerinin keşfiyle büyük bir patlama yapmıştır. Radikal polimerizasyonu yüksek molekül ağırlıklı polimerlerin eldesinde kullanılan çok önemli bir ticari yöntemdir. Klasik radikal polimerizasyonunun tek dezavantajı zincir transfer ve sonlanma reaksiyonlarından dolayı makromolekülün yapısıyla birlikte fonksiyonalitesi ve polidispersitesi üzerinde düşük bir kontrole sahip olmasıdır. Kontrollü mimari denilince molekül ağırlık kontrolü, uç grup kontrolü, blok kopolimer oluşturabilme ve yaşayan karakter akla gelmektedir. Son yıllarda, iyi tanımlanmış düşük polidispersiteye sahip polimerlerin sentezinde kontrollü/ 'yaşayan' polimerizasyon yöntemleri kullanılmaktadır. Bu metodlardan atom trasfer radikal polimerizasyonu (ATRP) çeşitli monomerlerin kontrollü radikal polimerizasyonu için etkili bir yöntemdir. ATRP ile ayarlanabilir molekül ağırlıklarına ve düşük polidispersitelere sahip iyi tanımlanmış polimerler sentezlenebilir. ATRP yöntemindeki moleküler ağırlık ve işlevsellik kontrolü, yeni işlevlere, düzenlemelere ve mimarilere sahip çok sayıda maddenin sentezine olanak sağlar. Ancak, ATRP yönteminin çok bileşenli karmaşık bir sistem olması dalayısıyla, bu metodun tam olarak kullanılması ve özel maddelerin hazırlanmasında en iyi koşulların bulunması için yöntemin tüm bileşenlerinin anlaşılması ve göz önünde tutulması önemlidir.

Bu çalışmada, makrobaşlatıcı olan bromlanmış poli(2,6-dimetil-1,4-fenil oksit)ler bilinen bir yöntemle sentezlenmiş ve ATRP ile graft poli(2,6-dimetil-1,4-fenil oksit) hazırlanmasında kullanılmıştır. Makrobaşlatıcının yüksek radikal kararlılığı, bakır katalizli ATRP yönteminde çapraz bağlanma ve jel oluşumu sonucunu yaratmıştır. Oluşan polimerlerin GPC (Jel Geçirgenlik Kromatografisi) çalışmaları graft polimerlerin kontrolsüz molekül ağırlıklarında oluştuğunu göstermiştir. Makrobaşlatıcının jelleşmesinin engellenmesi ve sonuç polimerlerin molekül ağırlıklarının kontrolünün sağlanması için çeşitli ilave maddeler ve graft polimerizasyon metodları üzerine de çalışılmıştır.

1. INTRODUCTION

The synthesis of polymers with well-defined compositions, architectures, and functionalities, has long been great interest in polymer chemistry.

Controlled/'living' polymerizations developed in the past forty years, including cationic, anionic, and group transfer polymerizations, provide the opportunity to prepare controlled molecular weight and well-defined architecture. Living polymerization techniques are employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination. Free radical polymerization is an important industrial process to prepare high molecular weight polymers. One of the prime advantages of 'living' free radical procedures over traditional free radical systems is that the concentration of propagating radicals is reduced. This leads to a dramatic lowering in the occurence of unwanted termination reactions, such as radical-radical chain coupling, since the rate of these bimolecular processes is proportional to $[R\cdot]^2$. This feature opens up a wide range of possibilities in the synthesis of complex macromolecular architectures by 'living' free radical procedures.

The past few years have witnessed the rapid growth in the development and understanding or new controlled/ 'living' radical polymerization (CRP) methods including nitroxide-mediated polymerization, atom transfer radical polymerization (ATRP), and radical addition-fragmentation chain-transfer. ATRP was developed by designing an appropriate catalyst (transition metal compound and ligands), using an initiator with the suitable structure, and adjusting the polymerization conditions such that the molecular weights increased linearly with conversion and polydispersities were typical of a living process. This allowed for an unprecedented control over the chain topology (stars, combs, branched), the composition (block, gradient, alternating, statistical), and the end functionality for a large range of radically polymerizable monomers. However, since ATRP is a complex multicomponent system, it is important to understand and consider all of its components to make full

use of this methodology and find optimum polymerization conditions for the preparation of specific materials for particular applications.

Polymers with suitable pendant functional groups are of great interest as macroinitiators for the synthesis of graft copolymers with controlled architectures and properties. The use of polyfunctional initiators under normal free radical conditions would lead to chain-chain coupling and eventually to a crosslinked network. However, the application of the same concept to 'living' free radical system may be excepted to result in the desired architecture, with few unwanted coupling products. Any compounds, including macromolecular species, can be potentially be used to initiate ATRP as long as they contain activated halogen atom.

In this study, the atom transfer radical polymerization technique has been applied to the preparation of styrene-*g*-poly(2,6-dimethyl-1,4-phenylene)oxide and methyl methacrylate-*g*-poly(2,6-dimethyl-1,4-phenylene) oxide copolymers.

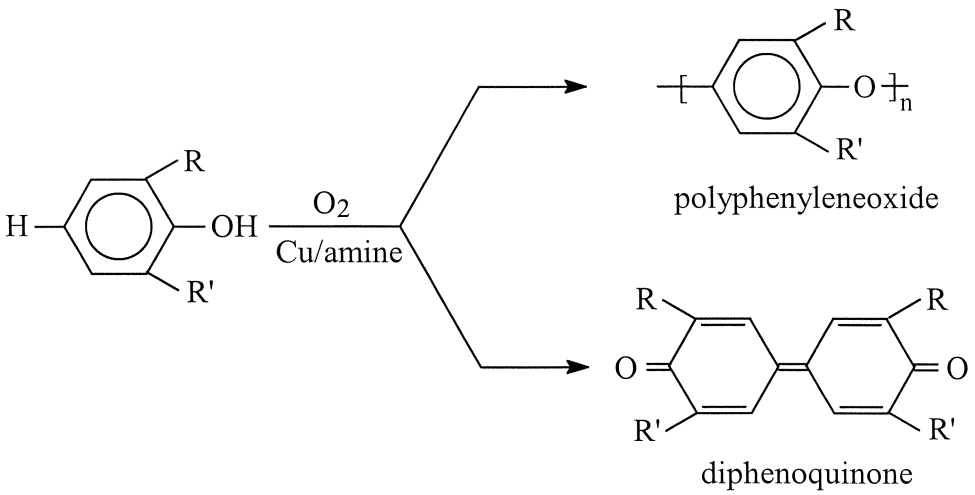
2. THEORETICAL PART

2.1. Poly(phenylene oxide)

Poly(phenylene oxide)s are useful materials for engineering thermoplastic applications because of their thermal, oxidative and chemical stability. However, raw PPO is expensive and difficult to process but ready blending with polymers such as polystyrene gave an acceptable balance of properties. Poly(2,6-dimethyl-1,4-phenylene oxide), PPO® resin, is the most commercial poly(phenylene oxide) and is sold as a blend with polystyrene and other additives as Noryl® resin by the General Electric Co.

2.1.1. Syntheses

Poly(phenylene oxide)s are synthesized from phenols in good yields by a variety of oxidative coupling procedures and other types of step-growth polymerization reactions [1].

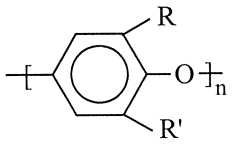
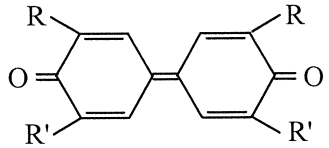


(2.1)

The copper-catalyzed oxidation of 2,6-dimethylphenol in the presence of oxygen in order to obtain PPO was first reported by Hay in 1959 (2.1) [2]. Many phenols can be used in oxidative coupling polymerization reactions [3, 4]. These phenols usually have substituents in the two ortho positions (Table 2.1.). Phenols with only one ortho substituent and an open para position can be oxidatively coupled but the polymer is

usually highly branched and colored. Oxidative coupling polymerization of 2,6-diphenylphenol gives poly(phenylene oxide) in high yield [5, 6]. However, when the substituents are large and bulky the polymer cannot form because of steric hindrance and the diphenoquinone forms in high yield [4]. No oxidation occurred when both substituents were chloro and nitro because of the high oxidation potential of these phenols. When one substituent was chloro and the other methyl, a branched polymer was formed because of a chloro displacement reaction [4].

Table 2.1. Product yields of the oxidative coupling of 2,6-disubstitued phenols

			
R	R'	Polymer (%)	Diphenoquinone (%)
Methyl	Methyl	85	3
Methyl	Ethyl	82	-
Ethyl	Ethyl	81	-
Methyl	i-propyl	62	-
i-propyl	i-propyl	-	53
Methyl	Phenyl	93	5
Phenyl	Phenyl	96	3
Methyl	t-butyl	-	45
t-butyl	t-butyl	-	97
Methyl	Methoxy	60	-
Methoxy	Methoxy	-	74
Methyl	Chloro	83	-
Chloro	Chloro	-	-
Methyl	Bromo	18	-
Nitro	Nitro	-	-

Catalysts for oxidative coupling polymerizations are usually composed of a transition metal salt and a base and molecular oxygen is normally the oxidizing agent. Copper-catalyzed systems often contain a copper halide and either an aliphatic or heterocyclic amine used as ligand for copper. A wide variety of amines has been used and they show a wide variation in activity [7, 8, 9]. Table 2.2.

illustrates this variation in catalyst activity [10]. When diamines such as N,N,N',N'- tetramethylethylene diamine (TMEDA) are used they often combined with an aliphatic monoamine [7]. N,N'-di-*t*-buthylethylenediamine forms a very active catalyst that is not easily hydrolyzed during polymerization [9]. Di-*n*-butylamine also forms a catalyst with copper that is not sufficiently affected by water to require addition of a drying agent [11]. The types of heterocyclic amines that are used include pyridine [1], morpholine, 4-N,N-(dimethylamino)pyridine [12], and diazobicyclononene [13]. Many polymeric amines are also reported to function as ligands, including poly(vinylpyridine) [14, 15], imidazole polymers [16], poly(N,N-dialkylaminostyrene)s [17], poly(iminotrimethylene)s [18] and oligomeric amines [15]. It was also demonstrated that with monodentate amines the catalytic activity varied with the ligand to copper ratio. With pyridine, the C–O coupling reaction was optimum at a ligand/Cu ratio of about 100/1 [19]. With bidentate amine, such as N,N,N',N'-tetramethylethylene diamine (TMEDA), the C–O coupling reaction maximized at one diamine per copper. It was found that when the polymerization reaction was carried out in a nonpolar solvent like toluene with an active catalyst like Cu/TMEDA, in the presence of anhydrous $MgSO_4$ to remove the water formed, that only low molecular weight polymer was formed. If more polar solvents, chlorobenzene or o-dichlorobenzene, were used somewhat higher molecular weight polymer was formed (Table 2.3.). When larger amount of TMEDA were added the molecular weight obtained was further increased. Instead of using excess of the diamine, tertiary amines such as trimethylamine, N,N-dimethylalkylamines or N-methylpyrrolidine could be used. In all cases the rate of polymerization, as measured by the rate of oxygen absorption, remained essentially constant indicating that the reaction was terminated in the very last stages. The assumption was made that initially the catalyst was soluble in the reaction mixture because of the presence of the polar phenol and in the latter stages of the reaction, when the phenol was no longer present, the catalyst became insoluable. The additional amine added presumably solubilized the catalyst by coordination of the copper complex in the trans positions. More bulky amines such as triethylamine were not effective and molecular models also confirm that this trans coordination cannot readily take place.

Table 2.2. Activity of various amine as ligands

Ligand	[2,6-dimethylphenol]/[Cu]
Pyridine	40
Diethylamine	200
Di-*n*-butylamine	200
N,N,N',N'-tetramethylethylene diamine	750
N,N'-di-*t*-buthylethylene diamine	900

Table 2.3. Oxidative polymerization of 2,6-dimethylphenol with TMEDA

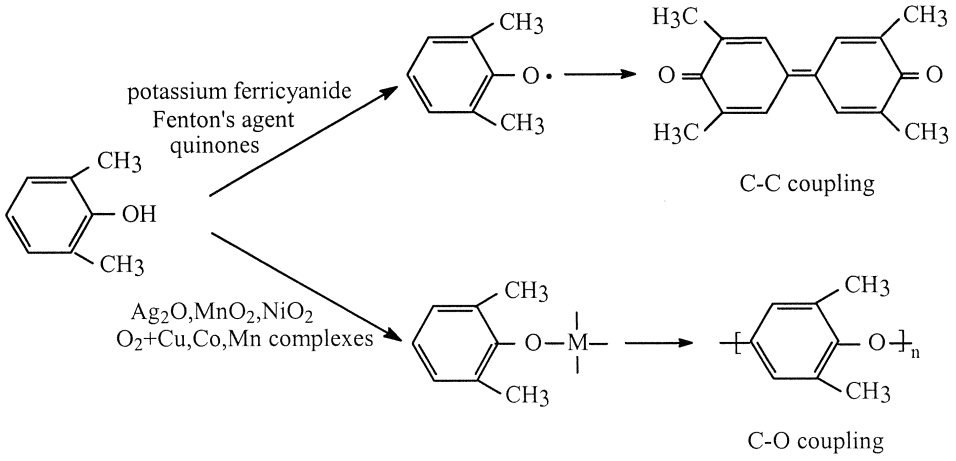
Solvent	[CuCl] (M/1000)	[TMEDA] (M/1000)	[η] dec./g.
Toluene	15	15	0.30
Chlorobenzene	15	15	0.37
o-Dichlorobenzene	15	15	0.48
Chlorobenzene	7.7	7.7	0.28
Chlorobenzene	7.7	15.4	0.33
Chlorobenzene	7.7	23.1	0.92

In addition to copper-catalyst systems, a variety of manganese-catalyst systems are described in the literature. Many are similar to the copper systems since they require a ligand and a base. Some of catalysts are effective at very low manganese concentrations. A combination of manganese chloride, benzoin oxime and sodium hydroxide in toluene and methanol is described by Olander [20]. High molecular weight polymer is formed with a manganese to monomer ratio of 1:2000. Other systems use ligands such as triethanolamine [21] and o-hydroxyazo compounds [22]. Thiols have also been used in manganese-catalyzed systems [23].

Cobalt amine complexes have also been used as catalysts in oxidative polymerization [24]. A large number of patents were issued describing various complexes of manganese and cobalt salts as catalysts. However, oxidation of 2,6-dimethylphenol with reagents such as $K_3Fe(CN)_6$ gave principally the diphenoquinone (50% plus a low molecular weight yellow resin) (2.2) [25]. These reactions presumably proceed through a phenoxy radical intermediate. Small amounts of the diphenoquinone are always produced in the reaction. When the oxidative

polymerization of 2,6-dimethylphenol is carried out at 100°C, the major product is diphenoquinone [7]. The diphenoquinone at this temperature, in the presence of the amine, was shown to undergo an oxidation-reduction reaction with two moles of phenol to give biphenol [26]. The bisphenol would then be preferentially oxidized to the diphenoquinone and cycle would continue. When the ligands are aliphatic amines the diphenoquinone also reacts with the amine [27]. When the nitriles are used as ligands [28] instead of amines the oxidation of 2,6-dimethylphenol gives a high yield of the diphenoquinone at room temperature [26]. Nitriles coordinate preferentially with copper(I) in the tetrahedral configuration and an intermediate complex with the phenoxide ion and copper(II) is not formed.

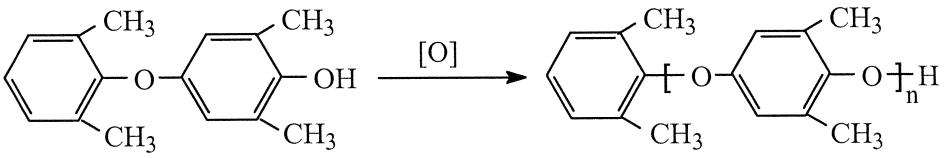
Poly(phenylene oxide)s are also prepared with non-catalytic systems by using metal oxides and other inorganic compounds as the oxidizing agent instead of molecular oxygen (2.2). Manganese dioxide [29], lead dioxide [30], silver oxide [31] and sodium bismuthate [32] produce high molecular weight polymer from many 2,6-disubstituted phenols including 2,6-diphenylphenol, 2-benzyl-6-methylphenol and 2-benzyl-6-methylphenol [33].



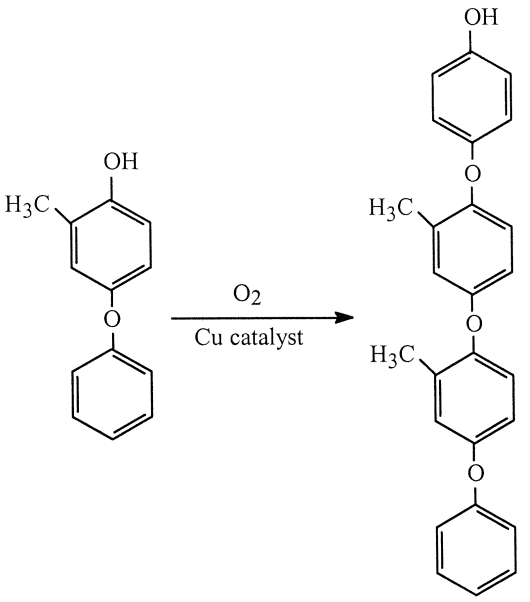
(2.2)

The mechanism of oxidative polymerization reaction was studied and discussed in several reviews [34-36]. Endres and Kwiatek first showed that the reaction behaved like a step-growth polymerization [37]. They also showed that oxidation of dimer, 4-(2,6-dimethyloxyl)-2,6-dimethylphenol gave high molecular weight polymer (2.3). Copper demonstrated that in the initial stages of the oxidation of the dimer an equilibration occurred and monomer, dimer, trimer, and tetramer could be detected by gas phase chromatography [38]. Mijs demonstrated that in the initial stages of the oxidation of a series of dimers, only one product was formed, which was not the

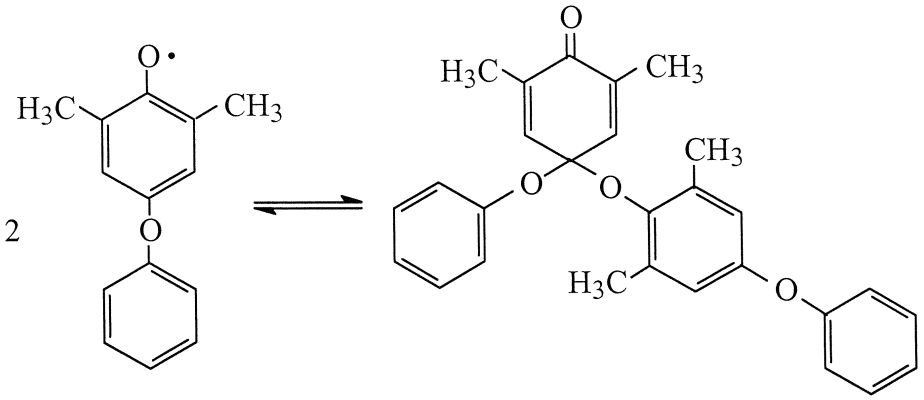
product that would have been formed by a head to tail coupling reaction of the dimer (2.4) [39]. With this and other information it was postulated that the polymerization reaction proceeded through a quinone ketol intermediate (2.5) followed by a benzidine-like rearrangement to give the linear structure [40]. It is also accepted that redistribution of phenoxy macroradicals makes an important contribution during the polymerization process. Especially in tha absence of 2,6-dimethylphenol in the reaction mixture (at the end of the polymerization), the redistribution reaction is responsible for the molecular weight and polydispersity of the obtained polymer [41, 42].



(2.3)

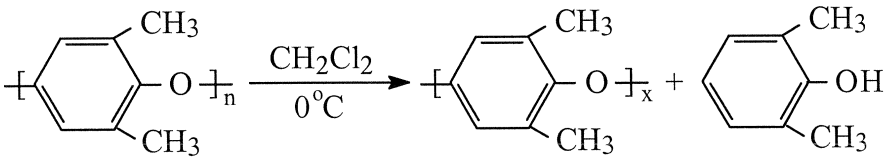


(2.4)



(2.5)

Several methods are avaible for the preparation of poly(phenylene oxide) with a well-defined molecular weight by utilizing the redustribution reaction. Low molecular weight PPO with a very narrow molecular weight distribution can be made by redistributing low molecular weight oligomers in methylene chloride at 0°C (2.6) [43]. Either the dimer, the trimer or a mixture of these and other low oligomers redistribute in the presence of a small amount of an initiator such as the diphenoquinone to produce 2,6-dimethylphenol and higher molecular weight oligomers. The higher molecular weight oligomers form a complex with methylene chloride and precipitate from the solution. The isolated polymer has a molecular weight of approximately 1800 and a dispersity (M_w/M_n) of 1.08.



(2.6)

Precipitation polymerization in the oxidative coupling polymerization of 2,6-dimethylphenol also gives well-defined monofunctional polymers in high yields [44, 45]. A poor solvent or a solvent-nonsolvent mixture is used as the polymerization medium. PPO with a certain molecular weight percipitates out of the reaction mixture, giving rise to polymers with a well-defined molecular weight. Van Aert adjust the polarity of the reaction mixture with a solvent mixture of toluene (solvent for PPO) and 2-propanol (nonsolvent for PPO) [45]. Molecular weights can easily be adjusted by using particular solvent composition and independent of the ligand system used. The results of precipitation polymerization of DMP using two different Cu(I)Cl-amine catalyst systems are presented in the Table 2.4. Cu(I)Cl with a combination N,N'-di-*t*-butylethylene amine (DBEDA) and di-*n*-butylamine (DBA), being secondary amines, and N,N,N',N'-tetraethylene diamine (TEED) as an example of tertiary amine.

Table 2.4. The results of precipitation polymerization of DMP

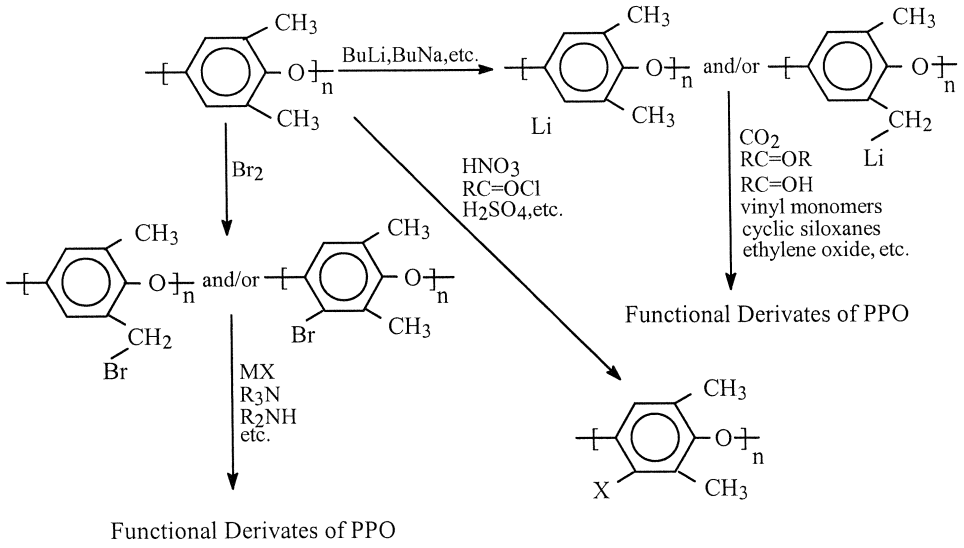
Toluene/2-propanol % v/v	Amine	M_n (gr/mol) H-NMR	M_n (gr/mol) GPC	M_n/M_w
0	DBA/DBEDA	2750	2800	1.66
	TEED	2700	3300	1.95
5	DBA/DBEDA	3300	3000	1.75
	TEED	3400	3400	2.05
10	DBA/DBEDA	4500	4500	1.71
	TEED	4550	4500	1.96
15	DBA/DBEDA	5500	6000	2.04
	TEED	5750	5100	2.09
20	DBA/DBEDA	7500	6900	2.22
	TEED	7400	6500	2.22

There are also several methods for oxidative coupling applied to the synthesis of bifunctional PPO. The first one is based on the reaction between a perfectly stoichiometric ratio of narrow molecular weight distribution PPO–OH and 3,3',5,5'-tetramethyl-4,4'-diphenoquinone [46]. Since PPO–OH with narrow molecular weight distribution can be prepared only for a certain range of molecular weights [46, 43] the molecular weight of the PPO–2OH prepared by this procedure is limited. Second one is based on the condensation of two PPO–OH via their phenyl end groups using formaldehyde and a Lewis acid [47-48]. The third one is based on the oxidative copolymerization of 2,6-dimethylphenol (DMP) with 2,2'-di(4-hydroxy-3,5-dimethylphenyl) propane (TMBPA) and gives perfectly bifunctional α,ω-bis(2,6-dimethylphenol)-poly(2,6-dimethyl-1,4-phenylene oxide) [47-48]. The oxidation potential of the TMBPA is lower than that of DMP, and therefore, for a low ratio between the DMP and TMBPA and certain reaction conditions and time, perfectly bifunctional PPO–2OH with number-average molecular weights in the range of 500-600 can be obtained. Since the reaction is performed in solution, and molecular weight of the polymer is controlled by the ratio between the TMBPA and DMP, it is essential to stop the polymerization after a certain reaction time. Before this reaction time, the PPO–2OH oligomer has poor functionality. At longer reaction times the redistribution of the PPO–2OH can

provide polymers with an uncontrollable molecular weight. The modification of this method achieved by Percec consisting of the oxidative copolymerization of a low ratio of DMP and TMBPA in a mixture of solvents which precipitates a certain molecular weight of PPO–2OH [49].

2.1.2. Reactions

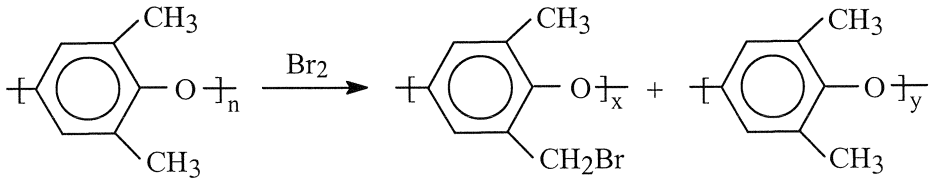
PPO was also found to be easily functionalized (2.7). Halogenation [50, 51] alkylation [52], carboxylation [53], sulfonation [54, 55] and nitration [56] produce the corresponding derivated polymers (2.7). Halogenation can take place on the nucleus or the methyl group depending on the conditions and many derivates of these bromo-substituted polymers have been synthesized [57, 58]. Metallation with butyl lithium yields first the ring metallated product which at longer times converts to the side chain metallated product [52, 53, 59]. Graft copolymers have been synthesized from the metallated polymers [60].



(2.7)

Hay brominated PPO with molecular bromine under diffirent temperatures by using chlorinated solvents with different boiling temperatures (2.8) [50]. The degrees of the bromination on the nucleus or the methyl group depend on the conditions and Table 2.5. summarizes the structures of the brominated as analyzed by NMR spectroscopy. These results suggested that to get over 90% methyl bromination (vs. ring bromination), the bromination must be carried out at temperatures no less than 135°C in either chlorobenzene or 1,1,2,2,-tetrachloroetan. Thus, brominations were then carried out at high temperature to different degrees (from 0,5 to 100% per

PPO unit). White achieved the electrophilic aromatic bromination of the aromatic ring of PPO at room temperature [51] .

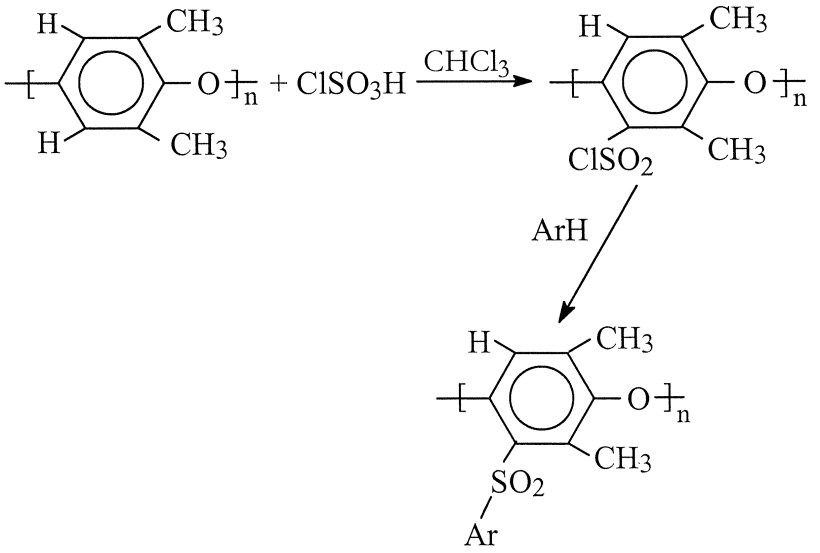


(2.8)

Table 2.5. Bromination of PPO in chlorinated solvent

Solvent	Reaction Temperature (°C)	Brominated PPO % $-CH_2Br$	% Br
$CHCl_3$	65	none	100
$ClCH_2CH_2Cl$	85	immeasurable	100
Cl_2CHCH_2Cl	110	29	71
C_6H_5Cl	135	89	11
$Cl_2CHCHCl_2$	148	93	7

The sulfonation reaction was achieved in a two-step process (2.9). The first step involved the reaction of PPO with chlorosulfonic acid [61]. The sulfonated PPO was hygroscopic and unstable. Sulfonated groups were converted into stable sulfone groups by reacting with aromatic compounds at elevated temperatures (120°C) [62].



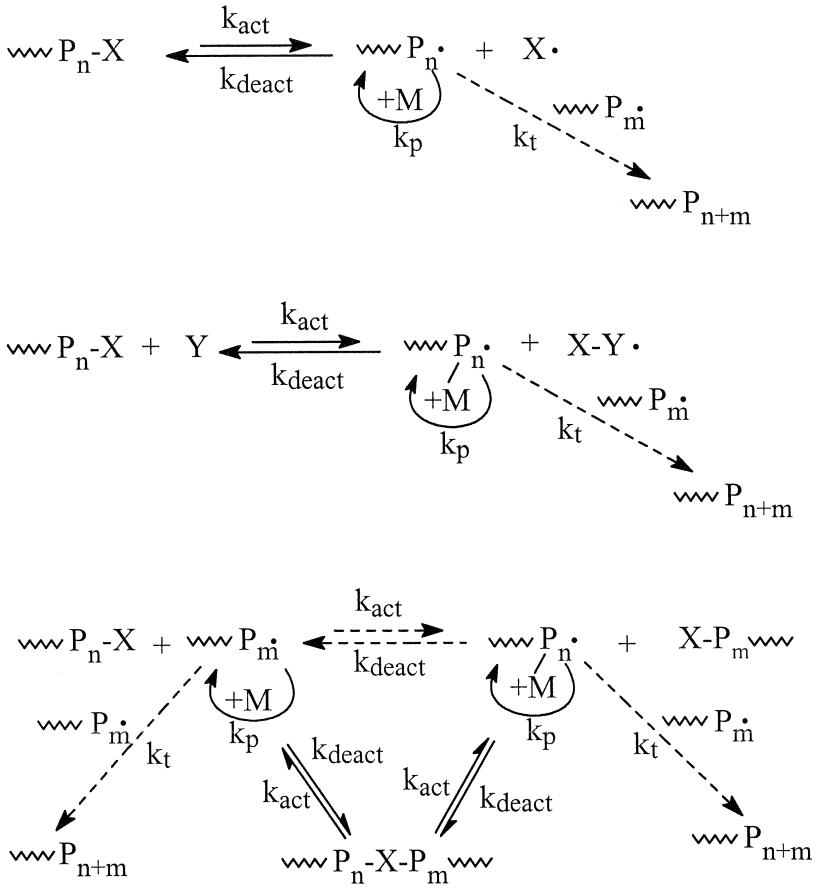
(2.9)

Friedel-Crafts substitution reactions can be carried out through two hydrogen atoms on the aromatic ring of PPO [63]. The first avaible position from the aromatic ring

occurs easily by the treatment of the PPO with the sulfonyl chloride or acid chlorides in the presence of a Friedel-Crafts catalyst. The presence of one carbonyl or sulfonyl group attached to a PPO phenyl ring, drastically decreases the nucleophilicity of the remaining unsubstituted position and, therefore, no disubstittution of phenylenic units was realized. This is due to the strong electron withdrawing character of the carbonyl and sulfonyl groups. When bulky substituents are attached to the PPO backbone, steric hinderance also decreases the accessability of nearby unsubstituted positions [64]. Consequently, electronic factors retard the second electrophilic substitution on the same PPO phenyl ring while steric factors also contribute to limit the degree of monosubstitution to about 80%.

2.2. Controlled/Living Radical Polymerization

The development of controlled/living radical polymerization (CRP) methods has been a long-standing goal in polymer chemistry, as a radical process is more tolerant of functional groups and impurities and is leading industrial method to produce polymers [65]. Despite its tremendous industrial utility, CRP has not been realized until recently, largely due to the inevitable, near diffusion-controlled bimolecular radical coupling and disproportionation reactions. However, the rapid growth in the development and understanding of new CRP methods have witnessed the past few years [66, 67]. All of these methods are based on establishing a rapid dynamic equilibration between a minute amount of the dormant species. The dormant chains may be alkyl halides, as in atom transfer radical polymerization (ATRP) or degenerative transfer (DT), thioesters, as in reversible addition fragmentation chain transfer process (RAFT), alkoxyamines, as in nitroxide mediated polymerization (NMP) or stable free radical polymerization (SFRP), and potentially even organometallic species. Free radicals may be generated by the spontaneous thermal process (NMP, SFRP) via a catalyzed reaction (ATRP) or reversibly via degenerative exchange process with dormant species (DT, RAFT).

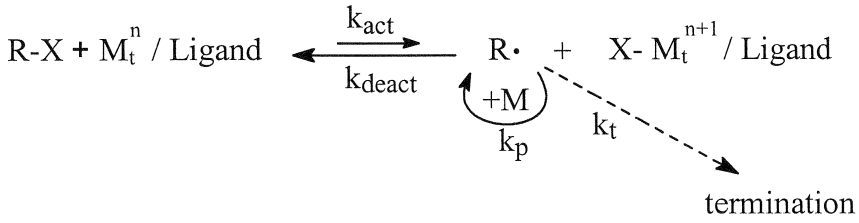


(2.10)

All of the CRP methods, shown in Scheme 2.10, include activation and deactivation steps (with rate constants k_{act} and k_{deact}), although in RAFT and DT the scheme may be formally simplified to just the exchange process with the apparent rate constant k_{exch}. Generated free radicals propagate and terminate (with rate constants k_p and k_t), as in a conventional free-radical polymerization. Thus, although termination occurs, under appropriate conditions its contribution will be small (less than a few percent of total number of chains) and these radical polymerizations behave as nearly living or controlled systems.

2.2.1. Atom transfer radical polymerization

Atom transfer radical polymerization (ATRP) is one of the most widely used living free radical polymerization and seems to be the most versatile one. This technique has been successfully applied to prepare poly(methyl methacrylate) [68-71], as well as acrylates [72] and styrene(s) [73-75] with well-controlled molecular weights and well-defined structures. A typical ATRP system consists of a alkyl halide as initiator, a transition metal complex as halogen atom transfer agent between the active and dormant chains, and monomer.



(2.11)

The schematic representation of the mechanism of ATRP is given in 2.11. ATRP establishes an equilibrium between active and dormant radicals by using a reversible redox reaction between a low oxidation state metal and an organic halide. The halogen atom is homolytically transferred from the alkyl halide (R–X), with the rate constant k_{act}, yielding a carbon-centered radical (R·) and a metal whose oxidation state has increased by one ($X–M_t^{n+1}$). This radical can than initiate the polymerization of monomers (M). The propagating radical reacts reversibly, with the rate constant k_d, with the metal halide to re-form the lower oxidation state transition metal and an oligomer with a halogen end group. This process can then repeat itself, resulting in the formation of well-defined polymer. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of polymerization. This process generates oxidized metal complexes, $X–M_t^{n+1}$/ Ligand, as persistent radicals to reduce the stationary concentration of the growing radicals and thereby minimize the contribution of termination [76]. A successful ATRP will have not only a small contribution of terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation.

The rate of polymerization is defined by (2.12), where R_p is the rate of polymerization, k_p is the rate constant of polymerization, $K_{eq}= k_{act}/k_{deact}$ is the equilibrium constant, [M] is the concentration of monomer, $[R–X]_o$ is the initial concentration of initiator, $[M_t^n]$ is the concentration of the lower state metal, and $[X–M_t^{n+1}]$ is the concentration of the higher state metal.

$$R_p = k_p K_{eq} [M] [R\text{-}X]_0 \frac{[M_t^n]}{[X\text{-}M_t^{n+1}]} \quad (2.12)$$

2.2.1.1. Monomers

A variety of monomers have been successfully polymerized using ATRP. Typical monomers include styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile, which contain substituents that can stabilize the propagating radicals [77,78]. Ring-opening polymerization has been also successful [79,80]. However, even using the same catalyst under the same conditions, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling and disproportionation, the magnitude of the equilibrium constant ($K_{eq}= k_{act}/k_{deact}$) determines the polymerization rate. ATRP will not occur or occur very slowly if the equilibrium constant is too small. In contrast, too large equilibrium constant will lead to a large amount of termination because of a high radical concentration. This will be accompanied by a large amount of deactivating higher oxidation state metal complex; which will shift the equilibrium toward dormant species and may result in the apparently slower polymerization [81]. Each monomer possesses its own intrinsic radical propagation rate. Thus, for a specific monomer, the concentration of propagating radicals and the rate of deactivation need to be adjusted to maintain polymerization control. However, since ATRP is a catalytic process, the overall position of the equilibrium not only depends on the radical (monomer) and the dormant species, but also can be adjusted by the amount and reactivity of the transition-metal catalyst added.

Styrene

ATRP of styrene and its derivates has been reported for copper [82-84, 73], iron [85], ruthenium [86] and rhenium [87]. A variety of compounds such as allylic halides and functional α-haloesters [88], polyhalogenated alkanes [83, 89], and arenesulfonyl chlorides [90] have been used successfully as the initiators for the copper-mediated styrene ATRP. Higher reaction temperatures and nonpolar solvents [91] are recommended for styrene ATRP. Polystyrenes with molecular weights ranging from 1000 to 100000 with low polydispersities have been prepared.

Methyl methacrylate

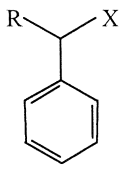
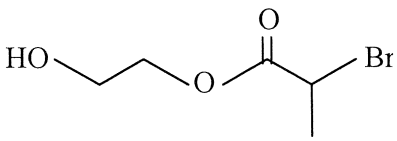
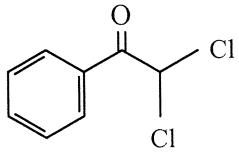
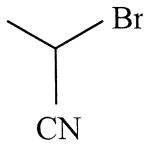
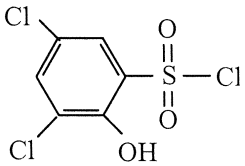
ATRP of methyl methacrylate has been reported for ruthenium [92, 93], copper [68, 94], nickel [95-97], iron [85, 98, 99], palladium [100] and rhodium [101] catalytic systems. Initiation plays an important role in ATRP of MMA. The best initiators

include sulfonyl chlorides [68] and halopropionitrile [85] because these initiators have sufficiently large apparent rate constants of initiation. Most polymerizations of MMA were carried out in solution at temperatures ranging from 70 to 90°C. Well-defined PMMA can be prepared within the molecular weight range from 1000 to 180000.

2.2.1.2. Initiators

Alkyl halides (R–X) are typically used as ATRP initiator such as halogenated alkanes, benzylic halides, α-haloesters, α-haloketones and α-halonitrils (Table 2.6.). When the initiating moiety is attached to macromolecular species, macroninitiators are formed and can be used to synthesize block/graft copolymers [102].

Table 2.6. Types of initiators used in ATRP systems

Halogenated Alkanes	$RCCl_3$ R= H, Cl, Br, Ph, CF_3, CO_2CH_3, C_nH_{2n+1}
Benzylic Halides	 R= H, CH_3 X= Br, Cl
α- Haloesters	
α- Haloketones	
α- Halonitrils	
Sulfonyl Halides	

The main role of initiator in ATRP is to determine the number of growing polymer chains. If the initiation is fast and transfer and termination negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator at full monomer conversion (2.13).

$$DP = [M]_0 / [Initiator]_0 \times conversion \qquad (2.13)$$

There are also several considerations for the initiator choice;

(1) Molecular Structure

Halogenated initiators and macro initiators can be activated by various types of aryl, sulfonyl, and carbonyl groups are also used in ATRP systems. The stabilizing group order in the initiator is roughly CN > C(O)R > C(O)OR > Ph > Cl > Me. Tertirary alkyl halides are better initiators than secondary ones, which are better than primary alkyl halides. These have been partially confirmed by recent measurements of activation rate constants [103-105]. Sulfonyl chlorides also provide faster initiation than propagation.

(2) Bond strenght in the alkyl halides

To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition-metal complex. The general order of bond strenght in the alkyl halides is R–Cl > R–Br > R–I. Thus, alkyl chlorides should be the least efficient initiators. Fluorine is not used because the C–F bond is too strong to undergo homolytic cleavage. The use of alkyl iodides requires special precautions due to their light sensitivity, the low affinity of iodine toward most metals, and the possibility of heterolytic cleavage of the R–I bond.

(3) Catalyst

Successful initiation in ATRP can depend strongly on the choice of catalyst. For example, 2-bromoisobutyrophenone initiates the controlled polymerization of MMA catalyzed by ruthenium or nickel complexes but has not been successfully used in copper-mediated ATRP. This is ascribed to the reduction the resulting electrophilic radical by copper(I) species as the copper catalysts have lower redox potentials.

(4) Addition

The method or the order of reagent addition can be crucial. For example, slow addition of the benzhydryl chloride initiator to the $CuCl(dNbpy)_2$-catalyzed ATRP of MMA generates a lower concentration of benzhydryl radicals thus reduces the rate of termination between the radicals.

2.2.1.3. Transition metal complexes

Transition metal complexes are perhaps the most important components of ATRP. It is the key of ATRP since it determines the position of the atom transfer equilibrium and dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient ATRP catalyst. First, fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously. Second, the equilibrium between the alkyl halide and the transition metal is strongly shifted toward the dormant species side. This equilibrium position will render most of the growing polymer chains dormant and produce a low radical concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized. Third, fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing approximately the same rate, leading to a narrow molecular weight distribution. Fourth, relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate. Fifth, there should be no side reactions such as β–H abstraction or reduction/oxidation of the radicals.

(a) Transition metal

The catalyst should be high selective for atom transfer process and should have high lability of the resulting $X–M_t^{n+1}$ species (higher oxidation state of metal). It should participate in a one-electron process, which should result in oxidative addition/reductive elimination but not in atom transfers process. Additionally, the metal should have a high affinity for halogen atom (X), but a low affinity for hydrogens and alkyl radicals. Otherwise, transfer reactions (β–hydrogen elimination) and the formation of organometallic derivatives may be observed reducing selectivity of propagation and control of the process. Ligand should complex the metal relatively strongly. Eventually, the position and dynamics of the ATRP equilibrium should be appropiate for the particular system. It must also be remembered that

ATRP is an atom transfer process. Thus, the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a halogen.

$Fe(II)Br_2$, Cu(I)Cl, Cu(I)Br, $Ru(II)Cl_2$ are the most important catalysts used in ATRP.

Iron

Several iron-based ATRP catalytic systems are used for the controlled polymerization of styrene and MMA [85]. Ferrous halide complexed by $N(n\text{Bu})_3$, $P(n\text{Bu})_3$, and dNbpy ligands promote controlled polymerizations with high initiator efficiencies and leading to polymers with low polydispersities. The choice of initiator was also important in the polymerization and fast initiation was essential to obtain well-defined PMMA. Ethyl-2-bromoisobutyrate, 2-bromopropionitrile, and *p*-toluenesulfonyl chloride yielded polymers with predictable molecular weights and low polydispersities.

Copper

Copper catalysts are superior in ATRP in terms of versatility and cost. Styrenes, (meth)acrylate esters and amides, and acrylonitrile have been successfully polymerized using copper mediated ATRP [77, 78, 106]. Various polydentate ligands such as phenanthroline and its derivates [107-109], substituted 2,2':6,2"-terpyridine [110], and pyridineimines [94, 111] have been used to complex cuprous halides. Counterions other than halides have also been used [112-115].

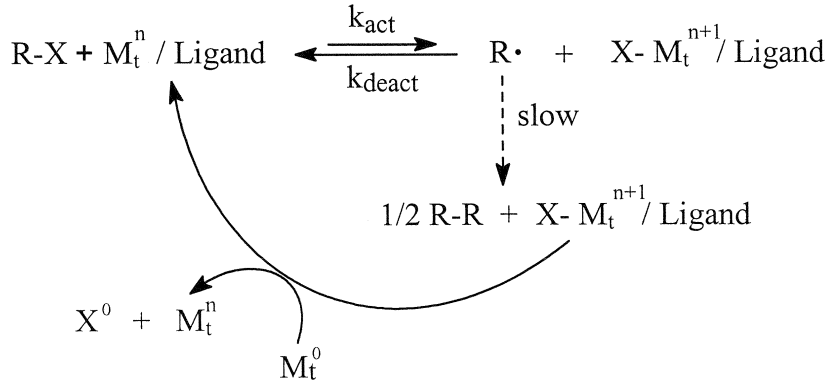
(b) Ligand

The main role of the ligand in ATRP is to solubilize the transition-metal salt in the organic media and to adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer [116]. Ligands may be even more important than metal centers, since they can fine-tune selectivities and force the complex to participate in a one electron transfer process needed for ATRP in comprasion with the preferred two-electron-transfer process, such as oxidative addition and reductive elemination for Ni and Pd complexes. In addition to primary roles of tuning atom transfer equilibrium constants and dynamics as well as selectivities, they control solubilities in the reaction mixture and ensure stability of the complexes in different monomers, solvents, and temperatures.

Nitrogen based ligands have been attracting interest in ATRP. Since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper bipyridine complexes, the employment of the simple amines in ATRP may lead to faster polymerization rates [85, 116]. Activity of N-based ligands in ATRP decreases with the number of coordinating sites N4 > N3 > N2 >> N1 and with the number of linking C-atoms C2 > C3 >> C4. It also decreases in the order R_2N- ~ PyrEnDash– > R–N= > Ph–N= > Ph–NR–. The most widely used amine ligands for ATRP systems are tris[2-(dimethylamino)ethyl]amine (Me-TREN), N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA), and tetramethylethylenediamine (TMEDA).

2.2.1.4. Additives

In some cases, additives can accelarate ATRP. When a small amount of copper(0) was added to the styrene and (meth)acrylates ATRP systems, a significant rate increase was observed [117, 118]. For example, the ATRP of methyl acrylate with a 1:0.2:0.4 ratio of methyl-2-bromopropionate, CuBr and dNbpy in the presence of Cu(0) was 10 times faster than without Cu(0), with comparable control over the molecular weights and polydispersities in both cases. A plausible explanation for the significant rate increase by adding copper metal is as follows. The copper(II) that is generated in the equilibrium reaction between copper(I) and the activated alkyl halide is necessary for the controlled polymerization (2.14). Copper(I), the deactivator, altough allowing for greater control of polymerization the system may produce more deactivator than is necessary for the control of the polymerization, resulting in slower polymerizations.The addition of the zerovalent metal, copper powder, slowly removed excess deactivator by a simple electron transfer process and simultaneously increased the concentration of copper(I) (2.14). Removal of small amounts of copper(II) enhanced the rate, yet there was still a sufficient concentration of copper(II) to maintain control of polymerization.

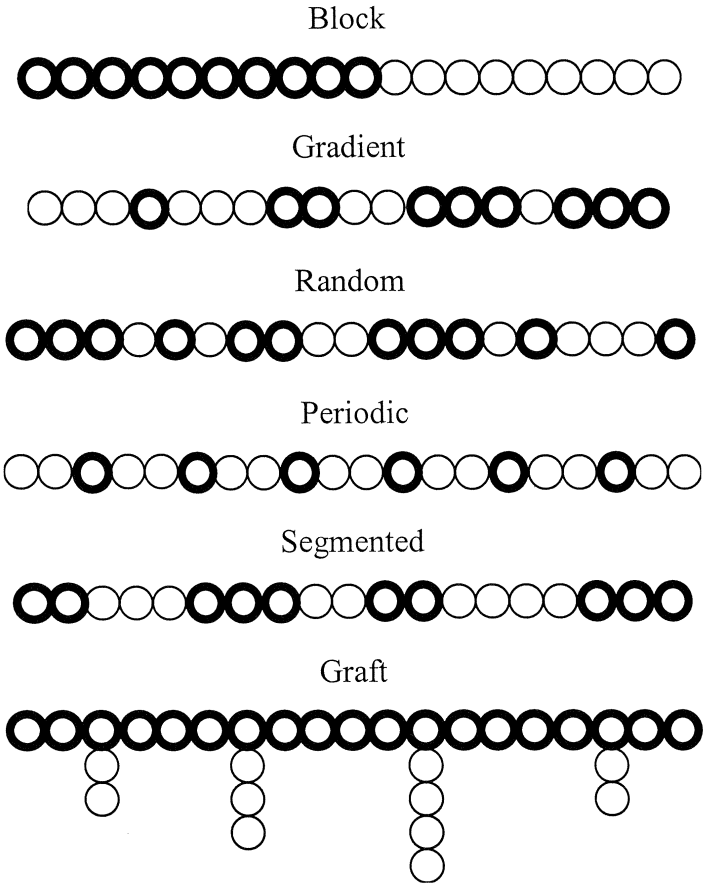


(2.14)

(e.g., CuX_2 + Cu^0 ⟷ 2 CuX)

2.3. Copolymers

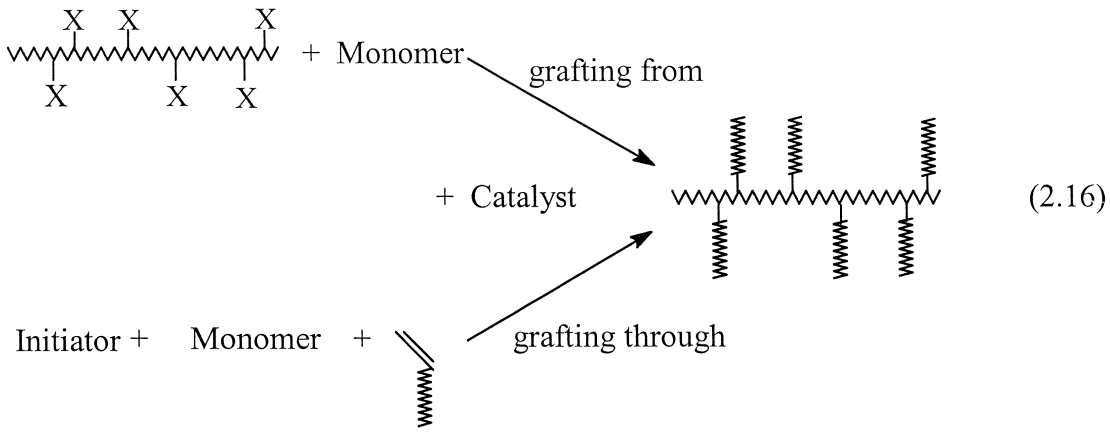
Homopolymers are derived from one species of monomer whereas copolymers are composed of two or more monomer units. Copolymers form two, three, four species of monomers are called bipolymers, terpolymers, quarter polymers etc. Copolymers are subdivided into block, gradient, random, periodic, segmented and graft copolymers (2.15).



(2.15)

Block copolymers are polymers which consist of two or more monomers that are segregated into separate regions of the polymer chain, but covalently bound to each other. Gradient copolymers exhibit a compositional gradient along the chain : one end of a bipolymer is enriched in first monomer unit and the other end in second monomer unit. Random copolymershave no continuous change in instantaneous composition. In periodic copolymers, monomeric units are arranged in periodic sequences. Multiblock copolymers with short block lengths are known as segmented copolymers. In graft copolymers, the blocks are connected to the main chain as side-chains.

The synthesis of graft copolymers can be accomplished through one of three routes: "grafting from" reactions (utilizing polymerization of grafts from a macroinitiator with pendant functionality), "grafting through" processes (operating by homo- or copolymerization of a macromonomer) and "grafting onto" (occuring when the growing chain is attached to a polymer backbone). The first two methods have been used in conjuction with ATRP in the design of graft copolymers and underscore the versatility of this controlled radical polymerization technique to synthesize a variety of (co)polymers (2.16).



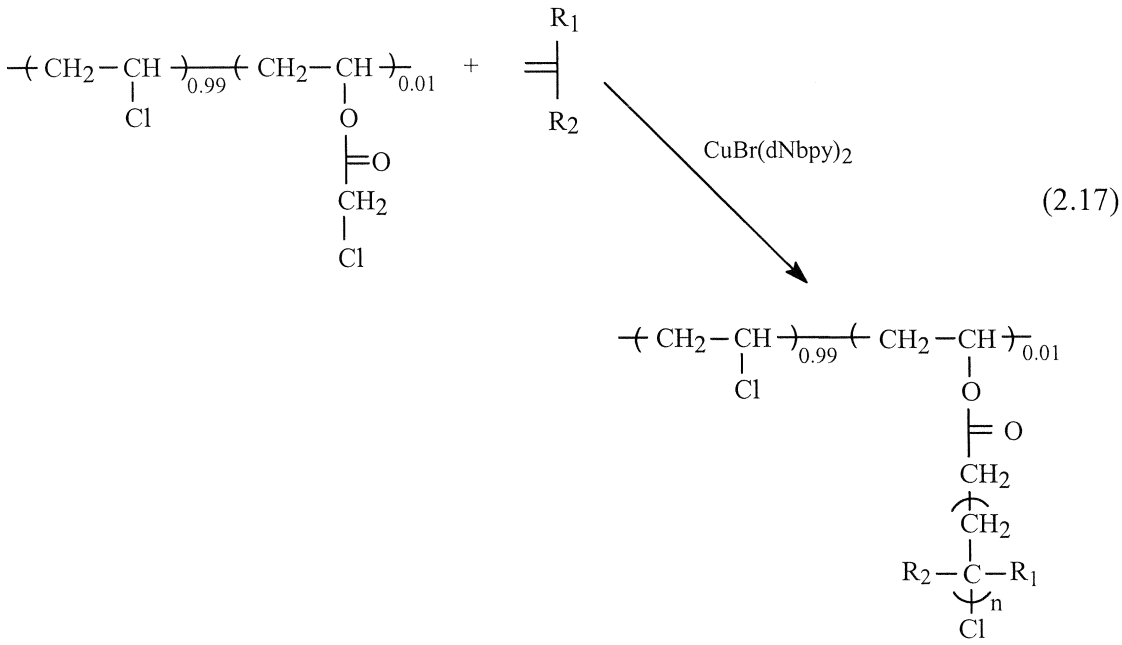
(2.16)

2.3.1. Grafting from

The polymerization of a monomer initiated by a polymer chain that have initiating sites attached to the backbone to yield grafts is referred as grafing from process (2.16). There are several examples of grafting from method using ATRP in order to prepare graft copolymers. Poly(vinyl) chloride [119], EXXPRO (poly(isobutylene-

co-p-methylstyrene-*co-p*-bromomethylstyrene) [120-122], polyethylene [123], polyisobutylene [124] are used to initiate ATRP of various monomers.

ATRP of vinyl monomers from pendant-functionalized poly(vinyl) chloride macroinitiators is given in (2.17). PVC containing 1% mol chloroacetate groups was used to ATRP of styrene, MA, nBA, and MMA. Table 2.7. demostrate that in each case the molecular weight of the copolymer increased above that of the macroinitiator yet polydispersity remained essentially the same. The polydispersity didn't decrease because of the variable quantity of initiating sites per chain. The large increase in molecular weight distribution for the MMA polymerization may originate from slow ATRP initiation of MMA from the primary alkyl halide sites.



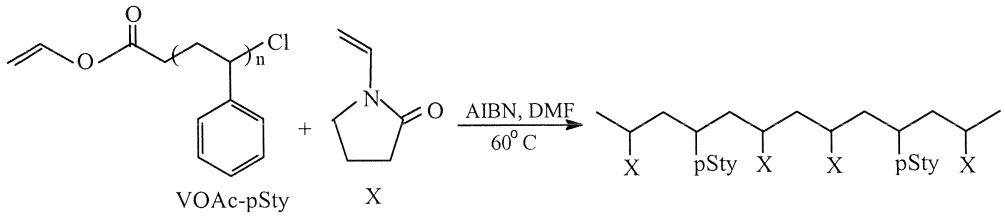
(2.17)

Table 2.7. The results of ATRP of vinyl monomers from PVC macroinitiators

second monomer	M_n (SEC)	M_w/M_n	mole % second monomer	Tg (°C)
	47400	2.66	0	83
Styrene	99500	3.72	80	80
MA	57700	2.40	50	21
MMA	83600	4.94	60	111
BA	81400	2.44	65	-19

2.3.2. Grafting through

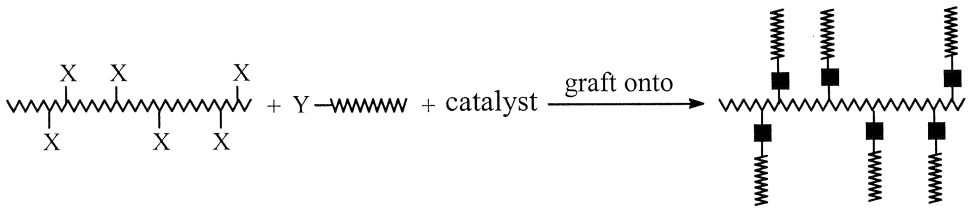
The polymerization of a monomer that in the presence of a polymer carrying pendant unsaturations results in grafting (2.16). The growing chain incorporates to the pendant unsaturation belonging the polymer chain. Copolymerization of vinyl ester terminal polystyrene macromonomers with N-vinyl pyrrolidinone using ATRP is an application of grafting through method [125]. Graft polymerization was performed using an AIBN–initiated polymerization in DMF at 60°C. As the macromonomer molecular weight increased, the graft density decreases. Polymerizations attempted with a higher molecular weight macromonomer (M_n= 15900) showed no intercorporation of polystyrene grafts.



(2.18)

2.3.3. Grafting onto

Grafting may also result from the reaction between a polymer molecule carrying one reactive site at a chain end, and another polymer with attached antagonist functions distributed at random along chain (2.19).



(2.19)

3. EXPERIMENTAL PART

3.1. Chemicals Used

3.1.1. Monomers

Methyl methacrylate (MMA, 99% Acros) was dried and distilled over CaH_2. Styrene (St, 99% Acros) was dried over CaH_2 and distilled under vacuum. 2,6-dimethylphenol (DMP, 98% Fluka) was recrystallized two times from hexane.

3.1.2. Solvents

Toluen was distilled over sodium. Tetrahydrofuran (THF) was dried and distilled over CaH_2. Chloroform, diphenyl ether and 1,2-dichlorobenzen were used as received.

3.1.3. Ligands

N,N,N',N',N''- Pentamethyldiethylenetriamine (PMDETA, 99% Aldrich) was dried and distilled over sodiumhydroxide. N,N'-Di-*t*-butylethylene diamine (DBEDA, 98% Aldrich) and di-*n*-butylamine (DBA, 99% Aldrich) were used as received.

3.1.4. Other chemicals

High molecular weight PPOs with were purchased from Aldrich. Br_2 (99% Merck), CuCl, CuBr, $CuBr_2$, Cu(0), ethyl-2-bromoisobutyrate (98% Aldrich), methanol, 1-phenyl-1-bromoetan, 2-propanol.

3.2. Synthesis of Initiator

3.2.1. Synthesis of poly(2,6-dimethyl-1,4-phenylene oxide)

Low molecular weight poly(2,6-dimethyl-1,4-phenylene oxide)s were synthesized according to the procedure of Van Aert [45]. A 1-L jacketed flask was thermostated at 40°C. O_2 was let through to the reactor flask. 0.5 grams of (0.004 mol) DMP, 0.35 g (0.002 mol) DBEDA, 2.61 g (0.02 mol) DBA were solved in 104 mL

solvent/nonsolvent mixture of 2-propanol with 5% v/v toluene. When the reaction mixture was heated to 35°C, the reaction was started by addition of 0.1 g (0.001 mol) CuCl to the reaction mixture. 12 g (0.097 mol) DMP in 62.5 mL solvent/nonsolvent mixture was added slowly in 1 hour. After a reaction time of 5 hours, precipitated polymer was filtered, washed with methanol, and dried in vacuum at 60°C to yield 11.25 g (90%). The polymer was reprecipitated twice from 60 mL chloroform in 750 L methanol: M_n= 6013, M_n/M_w= 1.56. ^{1}H-NMR ($CDCl_3$) δ 2.04 (6H, CH_3), 2.08 (6 H, CH_3), 2.17 (6H, CH_3), 6.36 (2H, Ar-H), 6.46 (2H, Ar-H), 7.09 (3H, Ar-H).

3.2.2. Bromination of poly(2,6-dimethyl-1,4-phenylene oxide)

Brominated poly(2,6-dimethyl-1,4-phenylene oxide) (PPOBr) was synthesized according to the procedure of Hay [58]. To a 2-L round- bottom flask equipped with a reflux condenser, PPO (2 g, 0.016 mol) was solved in 1,2-dichlorobenzen (30 mL). The system was brought to reflux at 150°C. 1,2-dichlorobenzen (18.5 mL, 0.18 mol) with 10% w/w bromine (0.86 mL, 0.017 mol) depending on the 50% bromination was added into the solution over a period 5-10 minutes. The system was kept reflux for an additional hour. The resulting polymer was recovered by precipitating into methanol. The precipitated polymer was filtered and dried in oven at 60°C for overnight to yield 2.76 g, purified by reprecipitation into metanol from chloroform solution: M_n= 7535, M_n/M_w= 1.7. The degree of bromination on the methyl groups determined by ^{1}H-NMR spectrum was 36%. ^{1}H-NMR ($CDCl_3$) δ 2.1 (CH_3 groups, 6H), 2.3 (Br, CH_3 groups, 3 H), 4.33 (CH_2Br,), 6.0-6.3 (Br, Ar-H), 6.47-6.9 (Ar-H).

Other polymers were prepared in the same way with varying amount of bromine depending on the desired bromination degree.

3.3. Syntheses of MMA and Styrene Grafted Poly(2,6-dimethyl-1,4-phenylene oxide) via ATRP

3.3.1. Grafting from

3.3.1.1. Typical atom transfer radical polymerization process

Styrene grafted PPO was prepared by ATRP of styrene using CuBr/PMDETA as catalyst and PPOBr as initiator at 110°C. The general procedure was carried out in bulk or in solvent as follows;

To a Schlenk tube equipped with magnetic stirring bar, monomer, ligand and catalyst were added in the order mentioned. In another Schlenk tube equipped with magnetic stirring bar, initiator was solved in monomer or in solvent. The tubes were subjected to freeze-pump-thaw cycles three times to remove the dissolved gas and purged with nitrogen gas flow for a few minutes. The tubes were then placed in termostated oil bath at given polymerization temperature. After some minutes, initiator solution was dropped slowly into monomer, ligand and catalyst system under nitrogen gas. After the polymerization, the reaction mixture was diluted with THF and was passed through a column of neutral alumina to remove the metal salts. In the cases of that gel formation was observed, gel was left in the column together with the metal salt. The excess THF was evaporated under reduced pressure. The sample was precipitated in methanol, added HCl (3-4 drops), filtered and dried in vacuum oven at 25°C for overnight. The conversions were determined gravimetrically.

3.3.1.2. Typical atom transfer radical polymerization process in the presence of $CuBr_2$

The general ATRP procedure of styrene in bulk using CuBr/PMDETA as catalyst and PPOBr as initiator at 110°C was carried out in the presence of $CuBr_2$ as follows;

To a Schlenk tube equipped with magnetic stirring bar, monomer, ligand, catalyst and $CuBr_2$ were added in the order mentioned. The solution of initiator in monomer was prepared in another Schlenk tube equipped with magnetic stirring bar. The tubes were degassed by three freeze-pump-thaw cycles. Nitrogen gas was given to the tubes for a few minutes. The tubes were placed in thermostated oil bath at given polymerization temperature. After some minutes, initiator solution was added dropwise to monomer, ligand, catalyst and $CuBr_2$ system under nitrogen. After the polymerization, the reaction mixture was dissolved in THF and was passed through a column of neutral alumina to remove the metal salt. In the cases of that gel formation was observed, gel was left in the column. The solution was concentrated under vacuum and precipitated in methanol containing 3-4 drops of HCl. The resulting polymer was filtered and dried in vacuum oven at 25°C for overnight. The conversions were determined gravimetrically.

3.3.1.3. Atom transfer radical polymerization by dropping catalyst system on initiator

PPOBr initiated ATRP of styrene was carried out by adding the catalyst system to the initiator instead of general procedure. The polymerization was catalyzed by CuBr/PMDETA in bulk or in solvent at 110°C. The procedure was as follows;

The initiator was dissolved in a Schlenk tube equipped with magnetic stirring bar in toluene or in monomer. Another Schlenk tube was equipped with magnetic stirring bar and charged with monomer, ligand and catalyst in the order mentioned. Two tubes were then degassed by three freeze-pump-thaw cycles and purging with nitrogen. The tubes were immersed in an oil bath with a preset temperature of 110°C. After some minutes, the monomer, ligand and catalyst system was added dropwise to the initiator solution under nitrogen over varying periods. After a given time, the reaction mixture was diluted with THF and passed through a column of neutral alumina. The gel phase of the reaction mixture was also removed while passing through the column. The solution was concentrated by evaporating the excess THF under reduced pressure, precipitated by addition of methanol with 3-4 drops of HCl. The resulting polymer was filtered and dried in vacuum oven at 25°C for overnight. The conversions were determined gravimetrically.

3.3.2. Grafting onto

Grafting of PMMA onto PPOBr by ATRP was accomplished with two different experimental procedures.

The first procedure was based on grafting of PMMA onto PPOBr using ATRP in bulk. PMMA was prepared by ATRP of MMA using CuCl/PMDETA as catalyst system and ethyl-2-bromoisobutyrate as initiator with M_0/I_0= 100 and I_0/CuCl/PMDETA= 1/1/1 in bulk at 90°C. PPOBr with 58% bromination degree, M_n= 6680 and M_w/M_n= 1.3 was used. The procedure was as follows;

In a Schlenk tube equipped with magnetic stirring bar, methylmethacrylate (1.12 mL, 0.0105 mol), PMDETA (0.0219 mL, 0.000105 mol), CuCl (0.0103 gr, 0.000105 mol) and ethyl-2-bromoisobutyrate (0.0154 mL, 0.000105 mol) were added in the order mentioned. The tube was degassed by three freeze-pump-thaw cycles and placed in termostated oil bath at given polymerization temperature. In another Schlenk tube, PPOBr (0.05 gr, 0.000302 mol containing 0.000175 mol CH_2Br) was

dissolved in monomer (2.62 mL, 0.024 mol). The tube was subjected to freeze-pump-thaw cycles three times and purged with nitrogen. When MMA polymerization reached high conversions, Cu(0) (0.0103 gr, 0.000021 mol) and ligand (0.0087 mL, 0.000042 mol) were added in order to get optimum conditions for graft onto. The reaction mixture was purged with nitrogen flow over a 5 min. period to deplete oxygen. The initiator solution was dropped into the PMMA system. Thus, M_0/ CH_2Br= 200 and $CH_2Br/[CuCl]_0/[PMDETA]_0$ = 0.6/0.6/0.6 ratios were obtained where M_0 refers total monomer concentration. Other polymers were prepared changing Cu(0) values.

The second procedure was based on grafting of PMMA onto PPOBr via ATRP in solvent. PMMA was prepared by ATRP of MMA using CuCl/PMDETA as catalyst system and ethyl-2-bromoisobutyrate as initiator with M_0/I_0= 100 and I_0/CuCl/PMDETA= 1/1/1 in solvent at 90°C. PPOBr with 36% bromination degree, M_n= 7535 and M_w/M_n= 1.7 was used. The procedure was as follows;

In a Schlenk tube equipped with magnetic stirring bar, methyl methacrylate (1.28 mL, 0.012 mol), toluene (1.28 mL), PMDETA (0.025 mL, 0.00012 mol), CuCl (0.0118 gr, 0.00012 mol) and ethyl-2-bromoisobutyrate (0.0177 mL, 0.00012 mol) were added in the order mentioned. The tube was degassed by three freeze-pump-thaw cycles and placed in termostated oil bath at given polymerization temperature. In another Schlenk tube, PPOBr (0.05 gr, 0.000337 mol containing 0.00012 mol $-CH_2Br$) was solved in toluene (2 mL). The tube was subjected to freeze-pump-thaw cycles three times and purged with nitrogen. When MMA polymerization reached high conversions, Cu(0) (0.00152 gr, 0.000024 mol) and ligand (0.01 mL, 0.000048 mol) were added in order to get optimum conditions for graft onto. The reaction mixture was purged with nitrogen flow over a 5 min. period to deplete oxygen. The initiator solution was dropped into the PMMA system. Thus, $M_0/-CH_2Br$= 100 and $-CH_2Br/[CuCl]_0/[PMDETA]_0$= 1/1/1 ratios were obtained where M_0 refers total monomer concentration. Other polymers were prepared changing M_0/ CH_2Br, $CH_2Br/[CuCl]_0/[PMDETA]_0$ = 1/1/1, and Cu(0) values.

After a given time, the reaction mixtures were diluted with THF. The solutions were passed through a column of neutral alumina to remove the metal salts. The excess of THF was evaporated under reduced pressure. The samples were precipitated in

methanol, added HCl (3-4 drops), filtered and dried in vacuum oven at 25°C for overnight. The conversions were determined gravimetrically.

3.4. Characterization

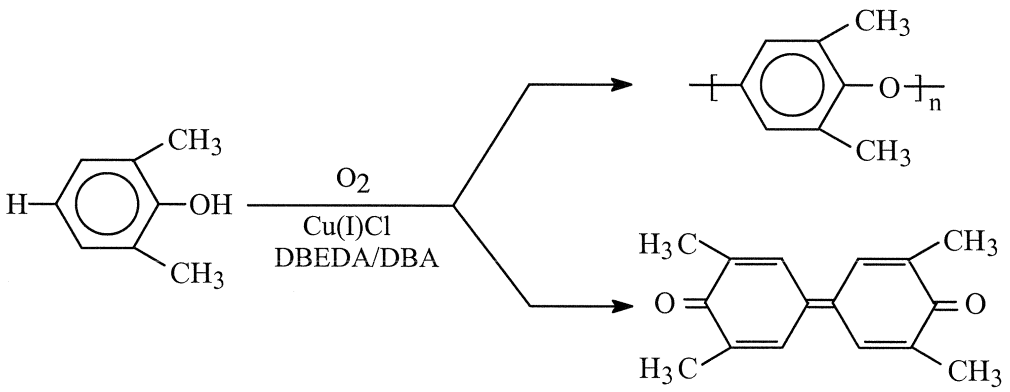
Molecular weights of the obtained polymers were measured by gel permeation chromatography. GPC analyses were performed with an Agilent Model 1100 instrument consist of pump and RI detector and four Water Styragel columns. THF was used as eluent at a rate of 0.3 mL/ min. at 30°C.

Molecular structures were determined by nuclear magnetic resonance. The ^{1}H-NMR spectra were recorded on a Bruker spectrometer in $CDCl_3$.

4. RESULTS AND DISCUSSIONS

4.1. Synthesis of Initiator

4.1.1. Synthesis of poly(2,6-dimethyl-1,4-phenylene oxide)



(4.1)

High molecular weight PPOs were supplied from Aldrich. Low molecular weight PPOs were synthesized according to a known procedure based on the precipitation polymerization in the oxidative coupling polymerization of DMP under the action of Cu/DBA-DBEDA catalyst and O_2 [45] (4.1). The polymers prepared possess a rather well-defined molecular weight that are not attainable by conventional methods due to the redistrubition reactions. Redistrubition of phenoxy macroradicals makes an important contribution during the polymerization process. Especially, in the absence of 2,6-dimethylphenol in the reaction mixture (i.e., at the end of the polymerization), the redistribution reaction is responsible for the molecular weight and polydispersity of the obtained polymer. In precipitation method, PPO with a certain molecular weight precipitates out of the reaction mixture, giving rise to polymers with a well-defined molecular weight. A typical ^{1}H-NMR spectrum of low molecular weight PPO is given in Figure 4.1.

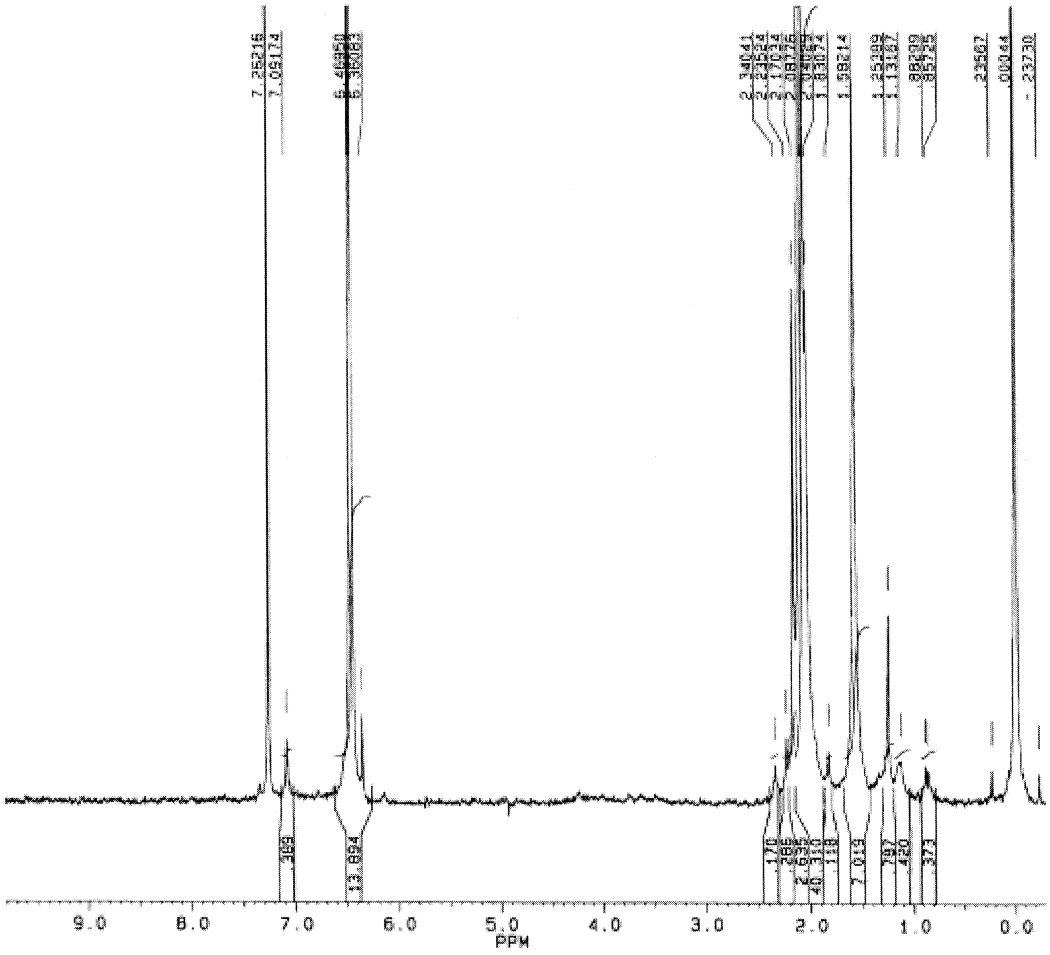
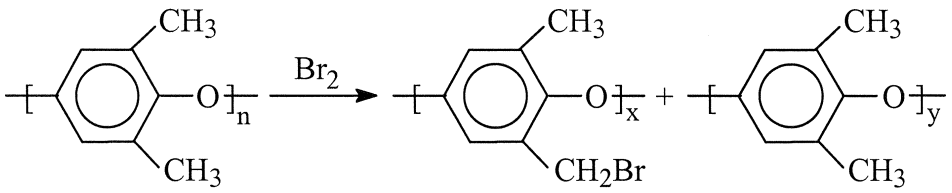


Figure 4.1 ^{1}H-NMR spectra of low molecular weight PPO

4.1.2. Bromination of poly(2,6-dimethyl-1,4-phenylene oxide)

Brominated poly(2,6-dimethyl-1,4-phenylene oxide) was synthesized as reported earlier [58]. Bromination was carried out with molecular bromine under 150°C using 1,2-dichlorobenzene as solvent (4.2).



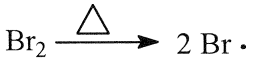
(4.2)

The bromination of methyl groups on poly(2,6-dimethyl-1,4-phenylene oxide) backbone is a chain reaction occur by a radical mechanism. The reaction is initiated with fragmentation of molecular bromine into two bromine radicals by heat. Hydrogen atom is abstracted from methyl group by a bromine radical resulting with hydrogen bromine and a methyl radical on the chain. The methyl radical reacts with a

bromine molecule resulting a brominated methyl on the PPO segment and a bromine atom (4.3).

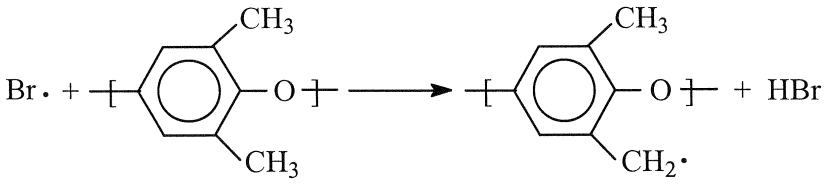
Chain Initiation

STEP 1



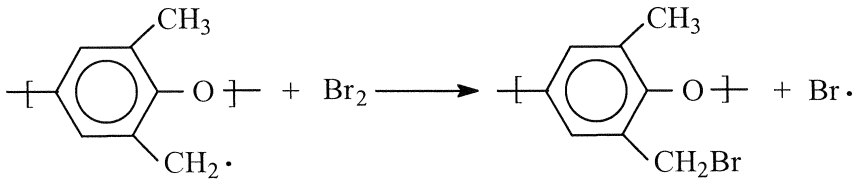
Chain Propagation

STEP 2



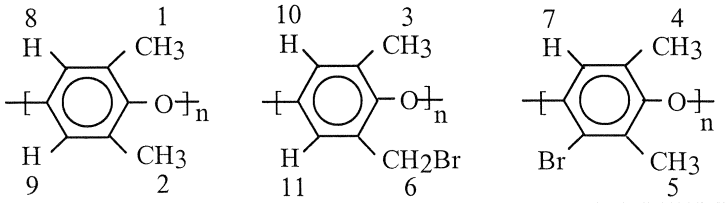
(4.3)

STEP 3



The degrees of bromination on methyl groups and aromatic ring were determined from NMR spectrums. Assignments of NMR peaks of brominated PPO are presented in Table 4.1. and ^{1}H-NMR spectrum of PPOBr with 36% bromination on methyl groups is given in Figure 4.2.

Table 4.1. Assignments of NMR peaks of brominated PPO



H	Peak (ppm)
1, 2, 3	2.1
4	2
5	2.3
6	4.35
7	6.0 - 6.3
8 ,9 ,10 ,11	6.3 - 6.8

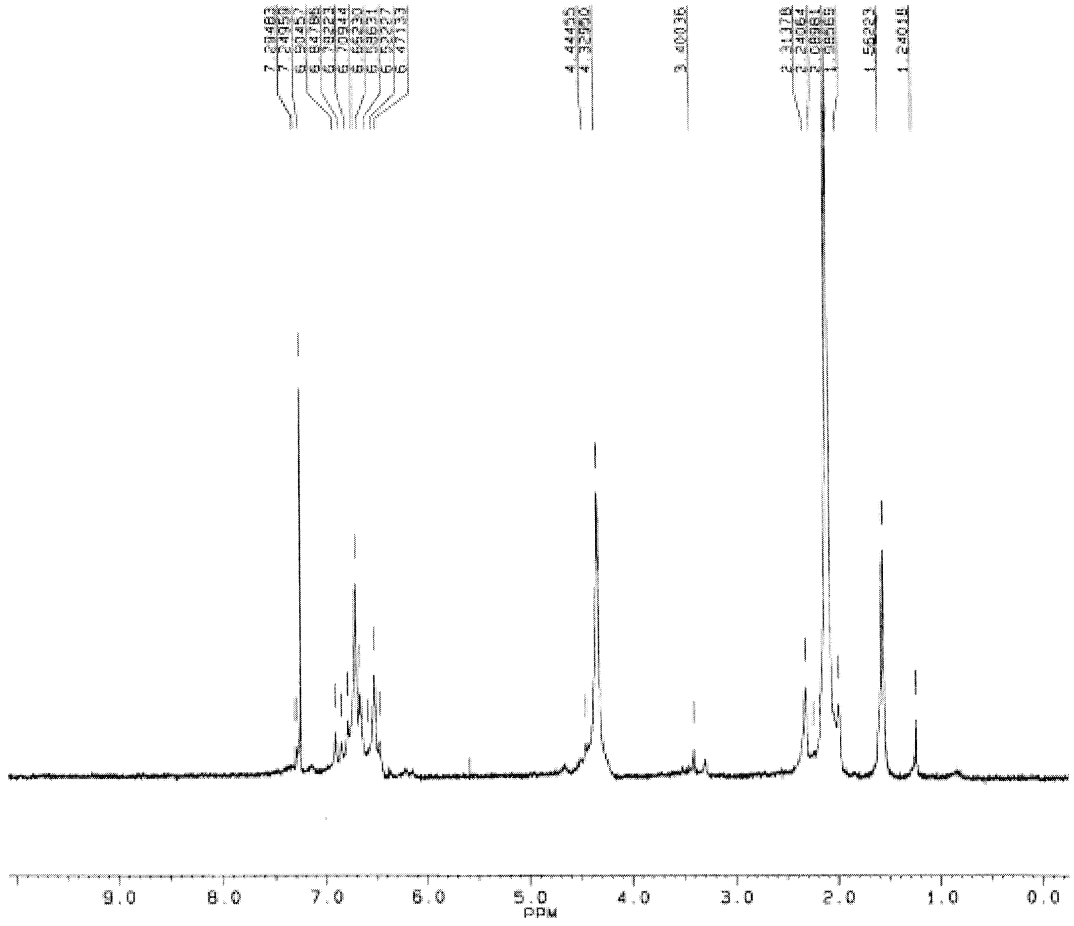


Figure 4.2 ^{1}H-NMR spectra of 36% brominated PPOBr

The results of bromination of different molecular weight PPOs are shown in Table 4.2. M_n and polydispersity were determined by GPC with polystyrene standarts.

Molecular weights per a repeating unit were calculated as follows:

$$(M.W.)= (M.W.)_x* (x/n) + (M.W.)_y* (y/n)$$

n: initial PPO molecules

x: final brominated PPO molecules

y: final PPO molecules

(x/n)= ratio of final brominated PPO molecules to initial PPO molecules

(y/n)= ratio of final PPO molecules to initial PPO molecules

Number of CH_2Br groups on a PPOBr backbone was calculated as follows:

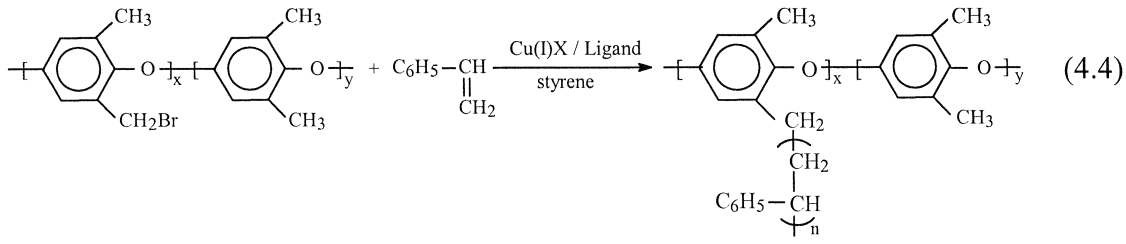
$$CH_2Br \text{ (unit/ mol)} = M_n (I_0)/ M_w (I_0) * -CH_2Br \% / 100$$

Table 4.2. Results of bromination of PPO

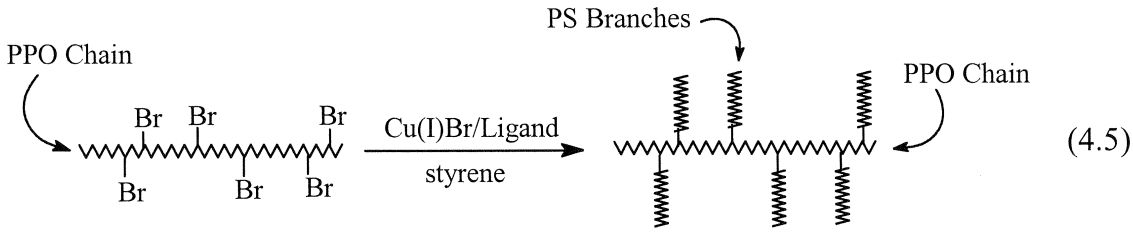
$-CH_2Br_{theo.}$ (%)	$-CH_2Br_{NMR}$ (%)	$-CH_2Br$ (unit/ mol)	$M_{n(GPC)}$	M_w/M_n	Molecular weight (gr/mol)
2	1.96	4.14	25700	1.80	121.55
10	8	23.56	37200	2.37	126.31
25	18.35	40.39	29600	1.88	134.48
50	39	72	27900	2.10	150.86
50	36	18.27	7535	1.70	148.40
90	58	23.37	6680	1.30	165.76

4.2. Synthesis of MMA and Styrene Grafted Poly(2,6-dimethyl-1,4-phenylene oxide) via ATRP

4.2.1. Grafting from



(4.4)



(4.5)

4.2.1.1. Typical atom transfer radical polymerization process

Brominated PPOs with various molecular weight, polydispersity and bromination degree were used to obtain styrene grafted PPO copolymers (4.4, 4.5). The styrene polymerization was catalyzed by the CuBr/PMDETA system at 110°C with M_0/I_0= 200. The other conditions and results are tabulated in Table 4.3. and 4.4. Table 4.3. and Table 4.4. show the results of low and high degree brominated PPO, respectively.

Table 4.3. ATRP of styrene initiated with low degree brominated PPOs

	Initiator											
Run	CH_2Br_{NMR} (%)	CH_2Br (unit/mol)	$Mn_{(GPC)}$	M_w/M_n	Time (min)	I_0/CuBr/PMDETA	Solvent	Conversion (%)	$Mn_{(theo)}$	$Mn_{(GPC)}$	M_w/M_n	Gel formation
3	1.96	4.14	25700	1.80	1110	1/ 0.3 / 0.3	DPE	27.9	31500	-(1)	-	-
4	1.96	4.14	25700	1.80	420	1/ 0.2 / 0.2	Toluene	-(2)	-	-(1)	-	-
5	8	23.56	37200	2.37	-(3)	1/ 0.5 / 0.5	-	-	-	-	-	+
6	8	23.56	37200	2.37	20(4)	1/ 0.5 / 0.5	Toluene	-	-	-	-	+
7	18.35	40.39	29600	1.88	120	1/ 0.5 / 0.5	-	5	30650	-(1)	-	+
8	18.35	40.39	29600	1.88	70(4)	1 / 1 / 1	-	-	-	-	-	+

(1) not measured, because of it was not soluble in THF
(2) not calculated, because of less precipitation
(3) gel formation in the beginning of polymerization
(4) gel formation after this time

Table 4.4. ATRP of styrene initiated with high degree brominated PPOs

	Initiator											
Run	CH_2Br_{NMR} (%)	CH_2Br (unit/mol)	$Mn_{(GPC)}$	M_w/M_n	Time (min)	I_0/CuBr/PMDETA	Solvent	Conversion (%)	$Mn_{(theo)}$	$Mn_{(GPC)}$	M_w/M_n	Gel formation
9	39	72	27900	2.1	240	1/ 0.08 / 0.08	-	17.46	31537	192400	1.86	-
10	39	72	27900	2.1	180	1/ 0.2 / 0.2	-	14.70	30960	203405	2.34	+(1)
11	39	72	27900	2.1	180	1/ 0.4 / 0.4	-	5.98	29145	233000	1.77	+(1)
12	39	72	27900	2.1	180	1/ 0.6 / 0.6	-	-	-	-	-	+(2)
13	58	23.4	6680	1.3	180	1/ 0.1 / 0.1	-	14.00	9600	181500	1.97	-
14	58	23.4	6680	1.3	180	1/ 0.2 / 0.2	-	9.52	8660	181000	1.96	+(1)
15	58	23.4	6680	1.3	180	1/ 0.4 / 0.4	-	12.80	9350	221900	1.96	+(1)
16	58	23.4	6680	1.3	180	1/ 0.6 / 0.6	-	-	-	-	-	+(2)

(1) conversion $Mn_{(theo)}$, $Mn_{(GPC)}$ and M_w/M_n were calculated from the soluble part of reaction mixture
(2) no precipitation was observed

Conversions and theoretical molecular weights were calculated as follows:

$$\% \text{ Conversion} = [(W_p)_f - (W_p)_i / M] * 100$$

Where $(W_p)_f$ represents the weight of final polymer, $(W_p)_i$ represents the weight of initiator and M represents the mass of the monomer initially taken.

$$M_{n\,(theo)} = M_n\,(I_0) + ([M_0]/ [I_0] * \text{conversion } (\%) * M_w\,(St))$$

As high molecular weight PPOBr with 1.96% bromination ratio is not dissolved in monomer, DPE or toluene was used as solvent in the reactions. When low catalyst/ligand ratios were used, no gel formation was observed. However, final products were not soluble in THF or chloroform. The molecular structure of these products could not be determined both by GPC and NMR .

However high molecuar weight PPOBr with 8% bromination ratio had a better solubility in monomer, the solution was rather viscous. The experiments both in bulk and solvent were resulted in gel formation of the reaction mixture. Gel formation in bulk polymerization was observed while dropping the initiator on the monomer/catalyst/ligand system. With the use of toluen, gel formation was delayed and occured after a short polymerization time. The gels were insoluble in THF or chloroform.

High molecular weight PPOBr with 18.35% bromination has no solubility problem in monomer. The polymerizations were carried out in bulk with varying catalyst/ ligand ratios. With low catalyst/ligand ratios, gel particules were formed while dropping initiator. After the polymerization time, some polymer precipated from the solved part with very low yield. However, the precipate was not soluble in THF or chloroform. When the catalyst/ligand ratio was increased the reaction mixture got gel after a short polymerization time.

High molecular weight PPOBr with 39% and low molecular weight PPOBr with 58% bromination can easily be solved in monomer. The reactions were carried out with increasing catalyst/ligand ratios. With very low catalyst/ligand ratios, no gel formation was observed. Increasing catalyst/ligand ratio cause increase in gel formation and decrease in the conversions. No precipitation was observed after a certain catalyst/ligand ratio. M_n results were determined from the resulting polymer by GPC after the gel phases were removed. GPC results were highly different comparing with theoretical values. Strong styrene peaks observed in NMR spectrum overlapped the molecular structure of the resulting polymer (Figure 4.3).

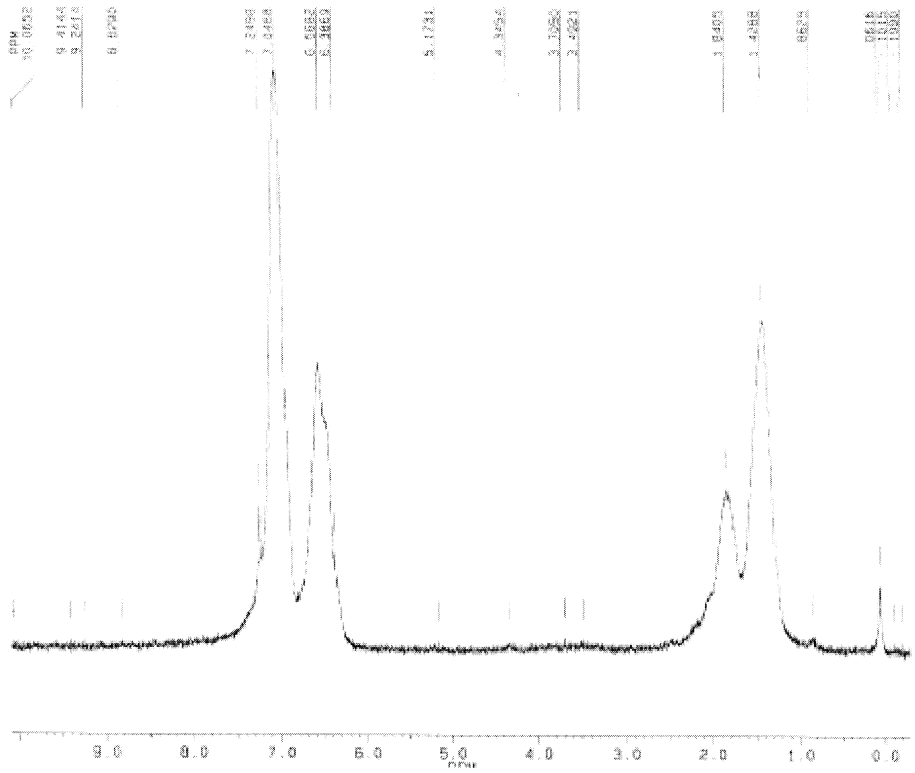
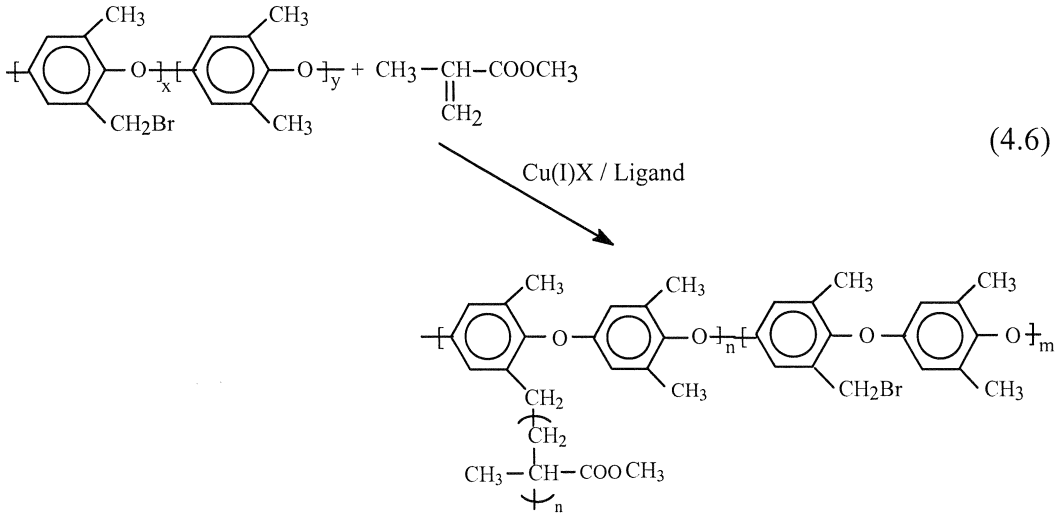


Figure 4.3 ^{1}H-NMR spectra of PS grafted PPOBr

ATRP of MMA initiated by low molecular weight PPOBr with 36% bromination degree was carried out with I_0/CuCl/PMDETA= 1/0.08/0.08 at 90°C to determine the structure of resulting polymer (4.6). The results are as follows:

Conversion= 9.5%, $M_{n(theo)}$= 9435, $M_{n(GPC)}$= 12997, $M_{n(NMR)}$= 36000. ^{1}H-NMR spectrum of the resulting polymer is given in Figure 4.4. ^{1}H-NMR spectrum of the resulting polymer implies that MMA grafted PPO was prepared with long PMMA branches and there are still –CH_2Br units on the backbone.



(4.6)

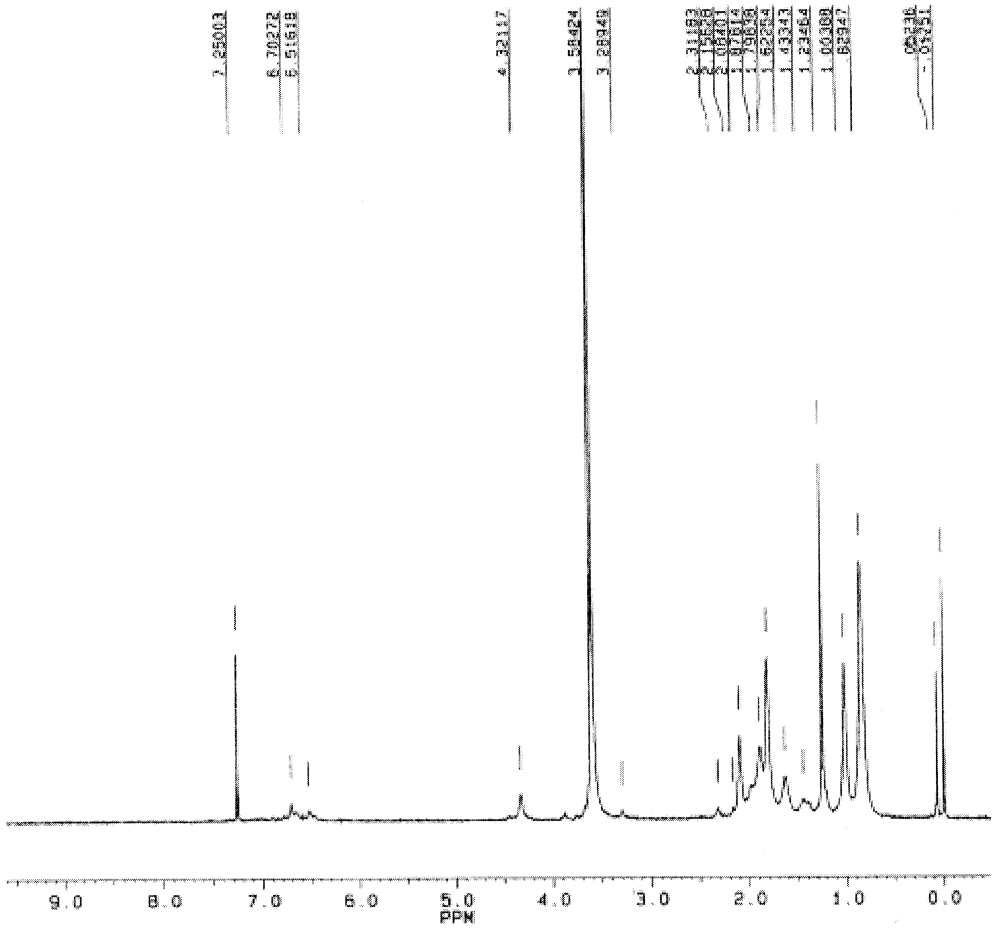
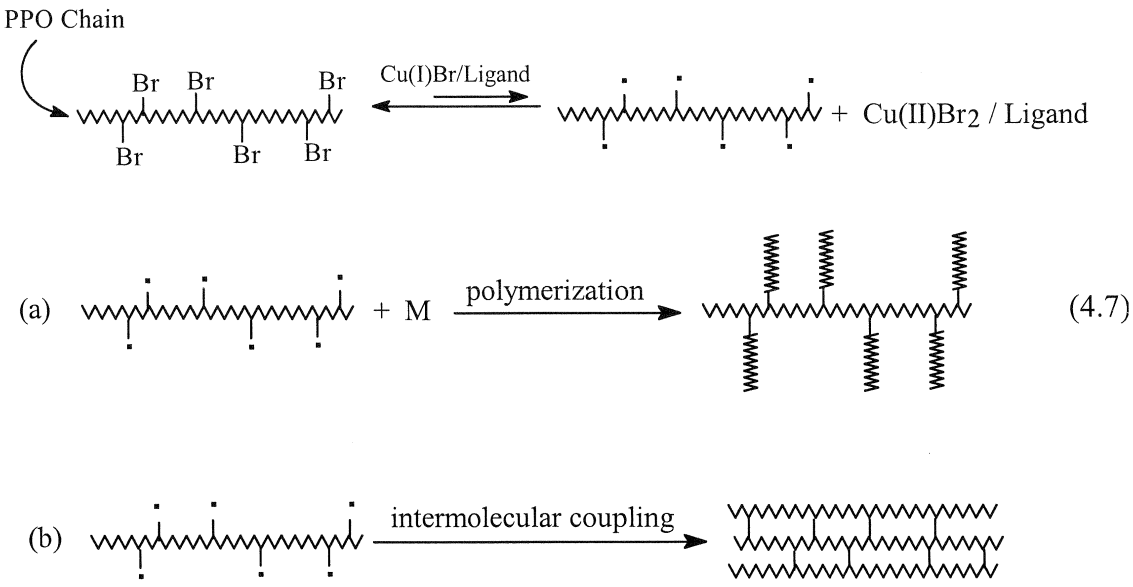


Figure 4.4 ^{1}H-NMR spectra of MMA grafted PPOBr

The bromomethyl groups on the polymer act as graft-initiating sites for the ATRP-based polymerizations of styrene and MMA (4.4, 4.6). The use of polyfunctional initiators with ATRP result in the desired graft polymers in general. Living free radical character of ATRP reduces the concentration of propagating radicals which inhibits the unwanted termination reactions. However, PPOBr initiated ATRP resulted in intermolecular coupling of the macroinitiator due to the high radical stability. Linear structure of PPO also facilitated the intermolecular coupling. It may also be supported by the number of growing directions. Theoretically, macroinitiators used in this work could grow in number of directions between 4.14 and 72 base on the following equation:

$$\text{Growing direction} = M_n\,(I_0) / M_w\,(I_0) * -CH_2Br\ \% / 100$$

Thus, it has been reported that for the linear polymer chains growing in five directions will lead to 25% of chains linked together and in 20 directions may lead to the complete cross linking and gelation [126].



(4.7)

4.2.1.2. Typical atom transfer radical polymerization process in the presence of $CuBr_2$

The styrene polymerization catalyzed by the CuBr/PMDETA and initiated by brominated PPO was carried out in the presence of $CuBr_2$ at 110°C with M_0/I_0= 200. Brominated PPO with high degrees were used as they gave better results with CuBr/PMDETA catalyst system. They also have higher solubility in styrene. The reaction times were increased as $CuBr_2$ will slow the polymerization. The results of this method are given in Table 4.5. The reactions that were carried out in the first method were repeated in the presence of $CuBr_2$ with changing CuBr/PMDETA ratios. Comprasion of the results of reactions with or without $CuBr_2$ are given in Table 4.6.

ATRP of styrene initiated by PPOBr was carried out in the presence of Cu(II)Br_2 with the aim of preventing gelation. Thus, the addition of Cu(II)Br_2 reduces the concentration of propagating radical [R·] (4.8), which may lead to decrease in radical-radical coupling since the rate of this bimolecular process is proportional to [R·]^2. However, gel formation was obsevered in all cases. As $CuBr_2$ slowed the reactions, the conversions decreased comparing with the same reaction conditions without $CuBr_2$. When the polymerization time was increased, the conversions increased. However, the M_n of the resulting polymer determined by GPC was again highly different from theoretical M_n values.

$$R\cdot + Cu(II)X_2 \rightleftharpoons R\text{-}X + Cu(I)X \qquad (4.8)$$

Table 4.5. ATRP of styrene initiated with high degree brominated PPOs via CuBr/$CuBr_2$/PMDETA system

	Initiator										
Run	CH_2Br_{NMR} (%)	CH_2Br (unit/mol)	$Mn_{(GPC)}$	M_w/M_n	Time (min)	I_0/CuBr/$CuBr_2$/PMDETA	Conversion (%)	$Mn_{(theo)}$	$Mn_{(GPC)}$	M_w/M_n	Gel formation
19	39	72	27900	2.1	300	1 / 0.5 / 0.05 / 0.5	2.9	28500	133700	2.64	+(1)
20	39	72	27900	2.1	200	1 / 0.2 / 0.1 / 0.35	-	-	-	-	+(2)
21	58	23.4	6680	1.3	180	1 / 0.2 / 0.1 / 0.35	-	-	-	-	+(2)
22	58	23.4	6680	1.3	300	1 / 0.6 / 0.2 / 0.6	3.26	7360	34100	1.85	+(1)
23	58	23.4	6680	1.3	300	1 / 0.6 / 0.4 / 0.6	-	-	-	-	+(2)
24	58	23.4	6680	1.3	300	1 / 0.6 / 0.2 / 0.9	-	-	-	-	+(2)

(1) conversion, $Mn_{(theo)}$, $Mn_{(GPC)}$ and M_w/M_n were calculated from the soluable part of reaction mixture
(2) no precipitation was observed

Table 4.6. Comparison of ATRP of styrene initiated with high degree brominated PPOs via CuBr/PMDETA system in the presence and absence of $CuBr_2$

	Initiator										
Run	CH_2Br_{NMR} (%)	CH_2Br (unit/mol)	$Mn_{(GPC)}$	M_w/M_n	Time (min)	I_0/CuBr/$CuBr_2$/PMDETA	Conversion (%)	$Mn_{(theo)}$	$Mn_{(GPC)}$	M_w/M_n	Gel formation
11	39	72	27900	2.1	180	1/ 0.2 / 0 / 0.2	14.7	30960	203405	2.34	+(1)
20	39	72	27900	2.1	200	1/ 0.2 / 0.1/ 0.35	-	-	-	-	+(2)
16	58	23.4	6680	1.3	180	1/ 0.2/ 0 / 0.2	9.52	8660	181000	1.96	+(1)
23	58	23.4	6680	1.3	180	1/ 0.2/ 0.1/ 0.35	-	-	-	-	+(2)
18	58	23.4	6680	1.3	180	1/ 0.6 / 0 / 0.6	-	-	-	-	+(2)
21	58	23.4	6680	1.3	300	1/ 0.6/ 0.2/ 0.6	3.26	7360	34100	1.85	+(1)
22	58	23.4	6680	1.3	300	1/ 0.6/ 0.4/ 0.6	-	-	-	-	+(2)
24	58	23.4	6680	1.3	300	1/ 0.6 / 0.2/ 0.9	-	-	-	-	+(2)

(1) conversion, $Mn_{(theo)}$, $Mn_{(GPC)}$ and M_w/M_n were calculated from the soluble part of reaction mixture
(2) no precipitation was observed

4.2.1.3. Atom transfer radical polymerization by dropping catalyst system on initiator

PPOBr initiated ATRP of styrene was experienced by adding catalyst system to initiator instead of general procedure. It was reported that the method or the order of reagent addition can be crucial [126]. It may also be suprising, but the heterogeneous catalytic systems may provide more efficient initiation than homogeneous ones when very reactive alkyl halide initiators are used, most likely due to slow dissolution of the catalyst and hence its lower instantaneous concentration.

PPOBr with 58% bromination degree on the methyl groups was used to initiate the polymerization. M_n and M_w/M_n values of the macroinitiator were 6680 and 1.3, respectively.The polymerization was catalyzed by CuBr/PMDETA in bulk or solvent at 110°C with M_0/I_0= 200. The other conditions and results of this procedure are summarized in Table 4.7. The results are compared with the results of ATRP of styrene initiated with the same PPOBr via general procedure in Table 4.8.

Gel formation was observed with the addition of the catalyst. The conversions were low and M_n values of the resulting polymers were again highly diffirent from the theoretical values similiar with earlier methods. However, the conversions increased comparing with the same experiments carried out via general ATRP procedure. This may be the result of catalyst loss during the addition of catalyst system on initiator solution. It must be remembered that conversions decreased with the increasing I_0/CuBr values. Thus, CuBr was solved in PMDETA and styrene at polymerization temperature, then added on initiator solution. An undefinite amount of catalyst may be left in the first tube due to its low solubility. So, the reactions were carried out with lower I_0/CuBr ratios comparing with theoretical values. The conversions were also increased with addition time of catalyst.

Table 4.7. ATRP of styrene initiated with high degree brominated PPO via CuBr/PMDETA system by dropping catalyst system on initiator

Run	Initiator				Dropping Time (min)	Reaction Time (min)	I_0/CuBr/PMDETA	Solvent	Conversion (%)	$Mn_{(theo)}$	$Mn_{(GPC)}$	M_w/M_n	Gel [1] formation
	CH_2Br_{NMR} (%)	CH_2Br (unit/mol)	$Mn_{(GPC)}$	M_w/M_n									
25	58	23.4	6680	1.3	10	180	1/ 0.2/ 0.2	Toluene	10	8760	249300	1.87	+
26	58	23.4	6680	1.3	30	180	1/ 0.2/ 0.2	Toluene	18	10430	204480	1.60	+
27	58	23.4	6680	1.3	30	180	1/ 0.6/ 0.6	Toluene	12.6	9300	183640	1.86	+
28	58	23.4	6680	1.3	30	180	1/ 0.6/ 0.6	-	11.14	9000	215875	2.05	+

(1) conversion, $Mn_{(theo)}$, $Mn_{(GPC)}$ and M_w/M_n were calculated from the soluable part of reaction mixture

Table 4.8. Comparison of conventional ATRP of styrene initiated with high degree brominated PPO to the dropping catalyst procedures

Run	Initiator				Dropping Time (min)	Reaction Time (min)	I_0/CuBr/PMDETA	Solvent	Conversion (%)	$Mn_{(theo)}$	$Mn_{(GPC)}$	M_w/M_n	Gel formation
	CH_2Br_{NMR} (%)	CH_2Br (unit/mol)	$Mn_{(GPC)}$	M_w/M_n									
16	58	23.4	6680	1.3	-	180	1/ 0.2 / 0.2	-	9.52	8660	181000	1.96	+(1)
25	58	23.4	6680	1.3	10	180	1/ 0.2 / 0.2	Toluene	10	8760	249300	1.87	+(1)
26	58	23.4	6680	1.3	30	180	1/ 0.2 / 0.2	Toluene	18	10430	204480	1.60	+(1)
18	58	23.4	6680	1.3	-	180	1/ 0.6 / 0.6	-	-	-	-	-	+(2)
27	58	23.4	6680	1.3	30	180	1/ 0.6/ 0.6	Toluene	12.6	9300	183640	1.86	+(1)
28	58	23.4	6680	1.3	30	180	1/ 0.6/ 0.6	-	11.14	9000	215875	2.05	+(1)

(1) conversion, $Mn_{(theo)}$, $Mn_{(GPC)}$ and M_w/M_n were calculated from the soluble part of reaction mixture
(2) no precipitation was observed

4.2.2. Grafting onto

Grafting of PMMA onto PPOBr by ATRP was accomplished to prevent the gel formation, low conversion and high M_n values observed in grafting from process. Thus, ATRP of styrene initiated with high degree brominated PPO by grafting from resulted in gel formation with high I_0/CuBr/PMDETA ratios. Gel formation increased and conversions were decreased with increasing high I_0/CuBr/PMDETA ratios. M_n values were also highly different from theoretical values. These observations suggest that grafting onto process may be more successful.

The CuCl and PMDETA amounts of the desired PPOBr initiated ATRP of MMA would be used to prepare ethyl-2-bromoisobutyrate initiated ATRP of MMA. A part of the catalyst would spend during this reaction. Then, with the addition of PPOBr the crosslinking would be prevented due to low catalyst amounts and PMMA would graft onto PPOBr by ATRP. However, gel formation could not be prevented and grafting onto prosess could not achieved.

Grafting of PMMA onto PPOBr was carried out under two different experimental procedures. PMMA was prepared by ATRP of methylmethacrylate using CuCl/PMDETA as catalyst system and ethyl-2-bromoisobutyrate as initiator with M_0/I_0= 100 and I_0/CuCl/PMDETA= 1/1/1 at 90°C. PPOBr with 58% -CH_2Br, M_n= 6680 and M_w/M_n= 1.3

The first procedure was based on grafting of PMMA onto PPOBr using ATRP with M_0/I_0= 200 in bulk. The CuCl and PMDETA amounts of the desired PPOBr initiated ATRP of MMA were used to prepare ethyl-2-bromoisobutyrate initiated ATRP of MMA. The amounts of initiator and monomer in ethyl-2-bromoisobutyrate initiated ATRP of MMA was determined according to these amounts using M_0/I_0=100 and I_0/CuCl/PMDETA= 1/1/1 equations. The required amount of monomer that must be added to the system to ensure M_0/I_0= 200 ratio of the PPOBr initiated ATRP was determined and used to solve PPOBr. Thus, the conditions used for PPOBr initiated ATRP with M_0/I_0= 200 in bulk were prepared by adding PPOBr solution in the system. The results of this procedure are summarized in Table 4.9.

The second procedure was based on grafting of PMMA onto PPOBr via ATRP with varying M_0/I_0 ratios in solvent. The CuCl and PMDETA amounts of the desired PPOBr initiated ATRP of MMA were used to prepare ethyl-2-bromoisobutyrate

initiated ATRP of MMA in toluene. The amounts of initiator and monomer in ethyl-2-bromoisobutyrate initiated ATRP of MMA was determined according to these amounts using M_0/I_0= 100 and I_0/CuCl/PMDETA= 1/1/1 equations. PPOBr was solved in toluene instead of solving in required amount of monomer to ensure M_0/I_0= 200 ratio. Thus, the conditions used for PPOBr initiated ATRP with varying M_0/I_0 ratios in bulk were prepared by adding PPOBr solution on the system. The results of this procedure are summarized in Table 4.10. ^{1}H-NMR spectrum of a resulting polymer is shown in Figure 4.5. The spectrum implies the presence of PPMA and also unachieved grafting reaction of PMMA onto PPOBr.

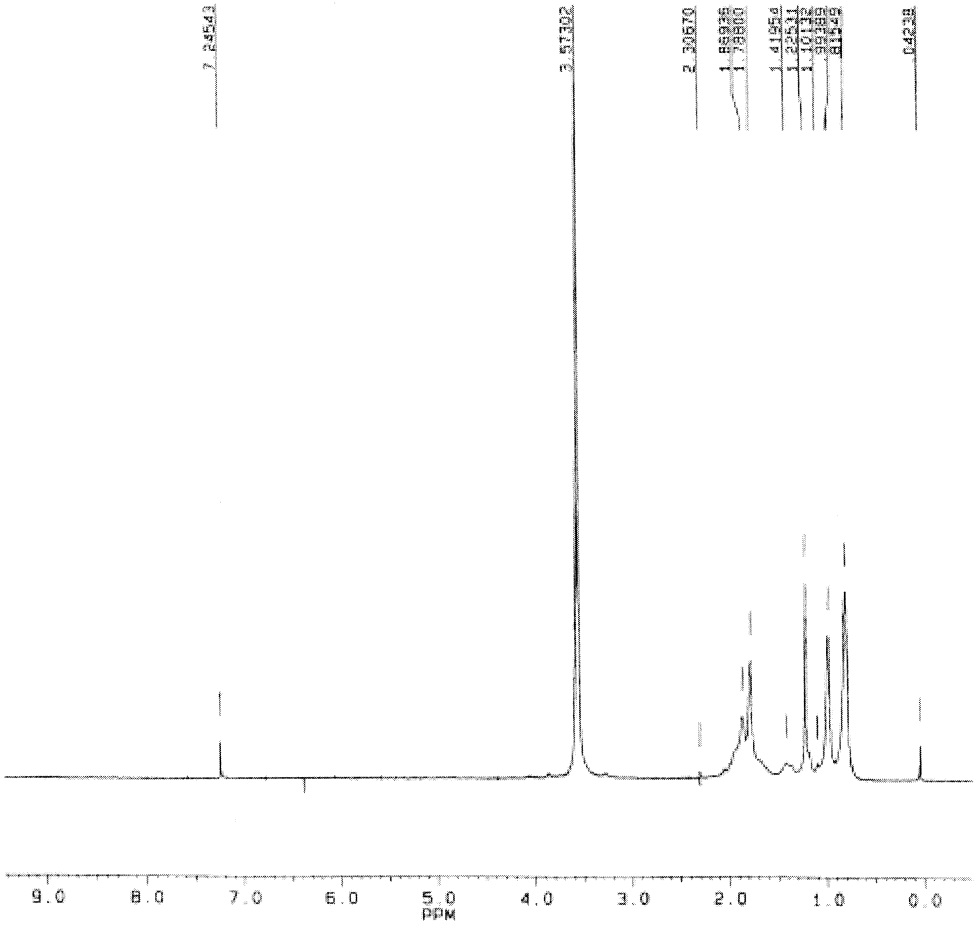


Figure 4.5 ^{1}H-NMR spectra of the resulting polymer of the grafting onto reaction of PMMA onto PPOBr

Table 4.9. Results of PMMA grafting on high degree brominated PPO by ATRP in bulk

Run	PMMA[2] M_n	PMMA[2] M_w/M_n	M_0/I_0[3]	Time (min)	I_0/CuCl/PMDETA	CuCl/Cu(0)/PMDETA	Conversion (%)	$Mn_{(theo)}$	$Mn_{(GPC)}$	M_w/M_n	Gel[1] formation
29	9750	1.11	200	180	1/ 0.6 / 0.6	1/ 0.2 / 0.4	14.4	9560	13490	1.08	+
30	9960	1.19	200	180	1/ 0.6 / 0.6	1/ 0.2 / 0.4	11.37	8960	21830	2.15	+
31	8320	1.25	200	180	1/ 0.6 / 0.6	1/ 0.4 / 0.8	3.38	7360	13390	1.11	+

(1) conversion, $Mn_{(theo)}$, $Mn_{(GPC)}$ and M_w/M_n were calculated from the solved part of reaction mixture
(2) ethyl-2-bromoisobutyrate initiated ATRP in bulk with M_0/I_0= 100
(3) PPOBr with 58% -CH_2Br, M_n= 6680 and M_w/M_n= 1.3

Table 4.10. Results of PMMA grafting on high degree brominated PPO by ATRP in bulk in toluen

Run	PMMA[2] M_n	PMMA[2] M_w/M_n	PMMA[2] M_0/I_0[3]	Time (min)	I_0/CuCl/PMDETA	CuCl/Cu(0)/PMDETA	Conversion (%)	$Mn_{(theo)}$	$Mn_{(GPC)}$	M_w/M_n	Gel[1] formation
32	7870	1.19	40	1200	1/ 0.2/ 0.2	1 / 0 / 1	30	8740	9890	1.1	+
33	7030	1.2	40	240	1/ 0.2/ 0.2	1/ 0.5 / 1	4	7690	11960	1.08	+
34	5940	1.19	40	1080	1/ 0.2/ 0.2	1/ 0.5 / 1	28	8640	10200	1.1	+
35	11930	1.15	40	1200	1/ 0.2/ 0.2	1/ 0.5 / 1	45	9340	14550	1.05	+
36	10370	1.19	80	240	1/ 0.4/ 0.4	1/ 0.5 / 1	51	11615	13080	1.09	+
37	12030	1.23	80	1080	1/ 0.4/ 0.4	1/ 0.5 / 1	74	13480	15190	1.01	+
38	9430	1.3	100	1200	1/ 1/ 1	1 / 0 / 1	44	11970	12190	1.1	+
39	11350	1.26	100	1200	1/ 1/ 1	1/ 0.2 / 0.4	56	13135	15320	1.1	+

(1) conversion, $Mn_{(theo)}$, $Mn_{(GPC)}$ and M_w/M_n were calculated from the soluble part of reaction mixture
(2) ethyl-2-bromoisobutyrate initiated ATRP in bulk with M_0/I_0= 100
(3) PPOBr with 36% -CH_2Br, M_n= 7535 and M_w/M_n= 1.7

5. CONCLUSIONS AND RECOMMENDATIONS

In conclusion, a multifunctional macroinitiator, brominated poly(2,6-dimethyl-1,4-phenylene oxide)s was used in the preparation of styrene and methyl methacrylate grafted poly(2,6-dimethyl-1,4-phenylene oxide)s via ATRP. Grafting through and grafting onto routes were accomplished in order to achieve the desired reaction with controlled molecular weights, and high conversions.

However, in grafting through route, the intermolecular crosslinking of the macroinitiator was observed instead of the desired ATRP due to the high radical stability, linear character and high number of initiating sites of the macroinitiator. Various macroinitiators with number of directions changing between 4.14 and 72 base were used in this work. Gelation could not be prevented also by deactivating or slowing the formation of macroinitiator. Grafting reaction of PMMA onto PPOBr could not be achieved with the conditions used in this work.

These studies did not give succesful results to contribute the development of atom transfer graft copolymerization. However, the results of this work can inspire other researches. To get the optimum polymerization conditions in graft onto process in order to get graft PPO is still possible.Using PPOBrs with very low initiating sites per a chain (low molecular weight and low % bromination) in ATRP would yield star like architecture. The resulting gels can be also examined.

REFERENCES

[1] **White, D.M.,** 1989. Poly(phenylene oxide)s, Comprehensive Polymer Science, **5,** 473-481. Pergamon Press.

[2] **Hay, A.S., Blanchard, H.S., Endres, G.F., Eustance, J.W.,** 1959. J.Am.Chem.Soc., **81,** 6335.

[3] **H.S., Endres, Hay, A.S., Eustance, J.W., and Kwiatek, J.,** 1965. Polym. Prep. Am. Chem. Soc. Div. Polym. Chem., **2(2),** 325.

[4] **Hay, A.S.,** 1962. J. Pol.Sci., **58,** 581.

[5] **White, D.M., Klopfer, H.J.,** 1970. J.Polm.Sci., Part A-1, **8,** 1427.

[6] **White, D.M., Klopfer, H.J.,** 1972. J.Polm.Sci., Part A-1, **10,** 1565.

[7] **Hay, A.S.,** 1967. U.S. Patent 3306875.

[8] **Hay, A.S.,** 1967. U.S. Patent 3306874.

[9] **Hay, A.S.,** 1977. U.S. Patent 4028341.

[10] **Hay, A.S.,** 1998. J. Polym. Sci.: Part A: Polym. Chem., **36,** 505-517.

[11] **Bennett, J.G., Cooper, G.D.,** 1978. U.S. Patent 4092294.

[12] **Verlaan., J.P.J., Alferink., P.J.T., G.Challa,** 1984. J. Mol. Catal., **24,** 235

[13] **Wieden, H., Bahr, U.,** 1969. Br. Patent, 1134613.

[14] **Tsuchida, E., Kaneko, M., Nishide, H.,** 1972. Macromol. Chem., **151,** 221.

[15] **Tsuchida, E., Nishikawa, H., Terada, E.,** 1976. J. Polym. Sci., Polym. Chem. Ed., **14,** 825.

[16] **Tsuchida, E.,** 1985. Chem. Abstr., **102,** 185554z.

[17] **Tsuchida, E., Nishide, H., Nishiyama,** 1974. Macromol. Chem., **175,** 3047.

[18] **Konin, C.E., Hiemstra, B.L., Challa, G., van de Velle, M., Goethals, E.J.,** 1985. J. Mol. Catal., **32,** 309.

[19] **Finkbeiner., H, Hay, A.S., Blanchard, H.S., Endres, G.F.,** 1966. J. Org. Chem., **31,** 549.

[20] **Olander, W.K.,** 1977. U.S. Patent 4054553.

[21] **Komoto, H., Ohmura, K.,** 1973. Makromol. Chem., **166,** 57.

[22] **Ueno, K., Maruyama, T., Inoue, H., Tatsukami, Y., Isobe, M.,** 1983. Eur. Pat. Appl. 0059958.

[23] **Kaneko, M., Yamada, A.,** 1981. Makromol. Chem., **182,** 101.

[24] **Bussink, J., Lohuizen, O.E., Vollbracht, L.,** 1967. U.S. Patent 3337501.

[25] **Haynes, C.G., Turner, A.H., Waters, W.A.,** 1956. J. Chem. Soc., 2824.

[26] **Hay, A.S.,** 1971.U.S. Patent 3631208.

[27] **Hay, A.S., White, D.M., Boulette, B.M., Nye, S.A, Chao, H.S.-I.,** 1988. J. Org. Chem., **53,** 5959.

[28] **Hay, A.S.,** 1965. U.S. Patent 3210384.

[29] **McNelis, E.J.,** 1966. J. Org. Chem., **31,** 1255.

[30] **Dort, H.M., Jonge, C.R.H., Mijs, W.J.,** 1968. J. Polym. Sci., Part C, **22,** 431.

[31] **Lindgren, B.O.,** 1960. Acta Chem. Scand., **14,** 1203.

[32] **Kon, E., McNelis, E.J.,** 1975. J. Org. Chem., **40,** 1515.

[33] **Sugie, T., Ishihara, K., Honda, K.,** 1976. Jpn. Pat. 5130899.

[34] **Hay, A.S.,** 1967. Advances in Polymer Science, **4,** 496.

[35] **Hay, A.S., Shenian, P., Gowan, A.C., Erhardt, P.F., Haaf, W.R., Theberge, J.E.,** 1969. Encyclopedia of Polymer Science and Technology, Interscience Publishers, New York, **10,** 92.

[36] **Finkbeiner, H.L., Hay, A.S., White, D.M.,** 1977. Polymerization Processes, Schildneck, C., Ed., Wiley- İnterscience, New York.

[37] **Endres, G.F., Kwiatek, J.,** 1962. J. Pol. Sci., **58,** 593.

[38] **Cooper, G.D., Blanchard, H.S., Endres, G.F., Finkbeiner, H.L.,** 1968. J. Am. Chem. Soc., **87,** 3996.

[39] **Mijs, J., Lohuizen, O.E., W.J., Bussink,Vollbracht, L.,** 1967. Tetrahedron, **23,** 2253.

[40] **Cooper, G.D.,** 1969. Annals of N. Y. Acad. of Sci., **159,** 278.

[41] **Hudec, P., Kotas, J., Vilimova, L.,** 1982. Makromol. Chem. Rapid Commun., **3,** 405.

[42] **Koch, W., Heitz, W.,** 1983. Makromol. Chem., **184,** 779.

[43] **White, D.M.,** 1979. Macromolecules, **12,** 1008.

[44] **Bialy, J., Penczek, St.,** 1967. Polym. (Warsaw), 214.

[45] **Aert, H.A.M., Venderbosch, R.W., Genderen, M.H.P., Lemstra, P.J., Meijer, E.W.,** 1995. J. M. S.- Pure Appl. Chem., **A(32),** 515.

[46] **White, D.M.,** 1981. J. Polym. Sci. Polym. Chem. Ed., **19,** 1367.

[47] **Heitz, W., Stix, W., Kress, H.J., Koch,W., Risse, W.,** 1984. Polym. Prep. Am. Chem. Soc. Div. Polym. Chem., **25,** 136.

[48] **Risse, W., Heitz, W.,** 1985. Preprints, Makromolekulares Kolloquium, Freiburg, West Germany, 50.

[49] **Nava, H., Percec, V.,** 1986. J. Polm. Sci. Polym. Chem., **24,** 965-990.

[50] **Hay, A.S.,** 1968. U.S. Patent 3 528 858.

[51] **White, D.M., Orlando, C.M.,** 1975. ACS Symp. Ser., **6,** 178.

[52] **Hay, A.S., Chalk, A.J.,** 1968. J. Polym. Sci., Polym. Lett. Ed., **6,** 105.

[53] **Hay, A.S., Chalk, A.J.,** 1969. J. Polym. Sci., Part A-1, **7,** 691.

[54] **Huang, Y., Cong, G., MacKnight, W.J.,** 1986. Macromolecules, **19,** 2267.

[55] **Hay, A.S.,** 1970. U.S. Patent 3 528 858.

[56] **Crivello, J.V.,** 1981. J. Org. Chem., **46,** 3056.

[57] **Hay, A.S.,** 1966. U.S. Patent 3 262 892.

[58] **Hay, A.S.,** 1968. U.S. Patent 3 378 505.

[59] **Hay, A.S.,** 1968. U.S. Patent 3 402 144.

[60] **Bostick, E.E, Hay, A.S., Chalk, A.J.,** 1970. U.S. Patent 3 522 326.

[61] **Ward III., W.J, Asalemne, R.M., Heller, J.,** 1973. U.S. Patent 3 780 496.

[62] **Li, G.,** 1985. U.S. Patent 4 521 224.

[63] **Percec, E.S., Li, G.,** 1986. U.S. Patent 4 596 860.

[64] **Olaf, G.A., Kobayashi, S., Nishimura, J.,** 1973. J. Am. Chem. Soc., **95,** 564.

[65] **Matyjaszewski, K., Gaynor, S.G.,** 2000. Applied Polymer Science, Craver, C.D., Carraher, C.E., Jr., Eds., Pergamon Press, Oxford, UK, 929.

[66] Controlled Radical Polymerization, **Matyjaszewski, K.,** 1998. Am. Chem. Soc., Washington, DC, **685.**

[67] Controlled / Living Radical Polymerization, Progress in ATRP, NMP and RAFT, **Matyjaszewski, K.,** 2000. Am. Chem. Soc., Washington, DC, **768.**

[68] **Grimaud, T., Matyjaszewski, K.,** 1997. Macromolecules, **30,** 2216.

[69] **Grubbs, R.B., Hawker, C.J., Dao, T., Frechet, J.M.J.,** 1997. Angew. Chem., Int. Ed., Engl., **36,** 270.

[70] **Percec, V., Barboiu, B.,** 1997. Polym. Prepr., **38,** 733.

[71] **Matyjaszewski, K., Wang, J.-S., Grimaud, T., Shipp, D.A.,** 1998. Macromolecules, **31,** 1527.

[72] **Coca, S., Davis, K., Miller, P., Matyjaszewski, K.,** 1997. Polym. Prepr., **38,** 639.

[73] **Matyjaszewski, K., Patten, T.E., Xia, J.,** 1997. J. Am. Chem. Soc., **119,** 674.

[74] **Percec, V., Barboiu, B., Neumann, A., Ronda, J.C., Zhao, M.,** 1996. Macromolecules, **29,** 3665.

[75] **Patten, T.E., Xia, J., Abernathy, T., Matyjaszewski, K.,** 1996. Science, **272,** 866.

[76] **Fischer, H.,** 1999. J. Polym. Sci., Part A: Polym. Chem., **37,** 1885.

[77] **Patten, T.E., Matyjaszewski, K.,** 1998. Adv. Mater., **10,** 901.

[78] **Matyjaszewski, K.,** 1999. Chem. Eur. J., **5,** 3095.

[79] **Pan, C.-Y., Lou, X.-D.,** 2000. Macromol. Chem. Phys., **201,** 1115.

[80] **Chen, X.-P, Padias, A.B., Hall, H.K,** 2001. Makromolecules, **34,** 3514.

[81] **Queffelec, J., Gaynor, .G., Matyjaszewski, K.,** 2000. Makromolecules, **33,** 8629.

[82] **Matyjaszewski, K., Wang, J.-S.,** WO Pat. 9718247, U.S. Patent 5 763 548

[83] **Wang, J.-S., Matyjaszewski, K.,** 1995. Makromolecules, **28,** 7901.

[84] **Percec, V., Barboiu, B.,** 1995. Makromolecules, **28,** 7970.

[85] **Matyjaszewski, K., Wei, M, Xia, J., McDermott, N.E.,** 1997. Makromolecules, **30,** 8161.

[86] **Kotani, Y., Kamigaito, M., Sawamoto, M.,** 2000. Macromolecules, **33,** 6746.

[87] **Kotani, Y., Kamigaito, M., Sawamoto, M.,** 1999. Macromolecules, **32,** 2420.

[88] **Matyjaszewski, K., Coessens, V., Nakagawa, Y., Xia, J., Qiu, J., Gaynor, S., Coca, S., Jasieczek, C.,** 1998. ACS Symp. Ser., **704,** 16.

[89] **Desrtarac, M., Bessiere, J.-M., Boutevin, B.,** 1998. J. Polym. Sci., Part A: Polym. Chem., **36,** 2933.

[90] **Percec, V., Barboiu, B., Kim, H.,** 1998. J. Am. Chem. Soc., **120,** 305

[91] **Matyjaszewski, K., Nakagawa, K., Jasieczek, C.G.,** 1998. Macromolecules, **31,** 1535.

[92] **Kato, M., Kamigaito, M., Sawamoto, M., Higashimura, T.,** 1995. Macromolecules, **28,** 1721.

[93] **Simal, F., Demonceau, A., Noels, A.F.,** 1999. Angew. Chem., Int. Ed., Engl., **38,** 538.

[94] **Haddleton, D.M., Jasieczek, C.B., Hannon, M.J., Shooter, A.J.,** 1997. Macromolecules, **30,** 2190.

[95] **Granel, C., Dubois, P., Jerome, R., Teyssie, P.,** 1996. Macromolecules, **29,** 8576.

[96] **Uegaki, H., Kotani, Y., Kamigaito, M., Sawamoto, M.,** 1998. Macromolecules, **31,** 6756.

[97] **Moineau, G., Minet, M., Dubois, P., Teyssie, P., Senninger, T., Jerome, R.,** 1999. Macromolecules, **32,** 27.

[98] **Ando, T., Kamigaito, M., Sawamoto, M.,** 1997, Macromolecules, **30,** 4507.

[99] **Louie, J., Grubbs, R.H.,** 2000. Chem. Commun., 1479.

[100] **Lecomte, P., Drapier, I, Dubois, P., Teyssie, P., Jerome, R.,** 1997. Macromolecules, **30,** 7631.

[101] **Moineau, G., Granel, C., Dubois, P., Jerome, R., Teyssie, P.,** 1998. Macromolecules, **31,** 542.

[102] **Matyjaszewski, K., Coca, S., Gaynor, S. G., Nakagawa, Y., Jo, S. M.,** WO Pat. 9801480, U.S. Patent 5 789 487

[103] **Goto, A., Fukuda, T.,** 1999. Makromol. Rapid. Commun., **20,** 633.

[104] **Matyjaszewski, K., Goebelt, B., Paik, H.-J., Horwitz, C.P.,** 2001. Macromolecules, **34,** 430.

[105] **Matyjaszewski, K., Paik, H.-J., Zhou, P., Diamanti, S.J.,** 2001. Macromolecules, **34,** 5125.

[106] **Patten, T. E., Matyjaszewski, K.,** 1990. Acc. Chem. Res., **32,** 895.

[107] **Destarac, M., Bessière, J. M., Boutevin, B.,** 1997. Makromol. Rapid Commun., **18,** 967.

[108] **Cheng, G. L., Hu, C. P., Ying, S. K.,** 1999. Makromol. Rapid Commun., **20,** 203.

[109] **Wang, G. L., Hu, C. P., Ying, S. K.,** 1999. Polymer, **40,** 2167.

[110] **Kickelbick, G., Matyjaszewski, K.,** 1999. Makromol. Rapid Commun., **20,** 341.

[111] **Amass, A. J., Wyres, C.A., Colclough, E., Hohn, I. M.,** 1999. Polymer, **41,** 1697.

[112] **Singha, N. K., Klumperman, B.,** 2000. Makromol. Rapid Commun., **21,** 1116.

[113] **Davis, K., Paik, H.-J., Matyjaszewski, K.,** 1999. Macromolecules, **32,** 1767.

[114] **Matyjaszewski, K., Wei, M., Xia, J., Gaynor, S. G.,** 1998. Makromol. Chem. Phys., **199,** 2289.

[115] **Woodworth, B. E., Metzner, Z., Matyjaszewski, K.,** 1998. Macromolecules, **31,** 7999.

[116] **Xia, J., Zhang, X.,** 2000. ACS Symp. Ser., **760,** 207.

[117] **Matyjaszewski, K., Coca, S., Gaynor, S. G., Wei, M., Woodworth, B. E.,** 1997. Macromolecules, **30,** 7348.

[118] **Cheng, G. L., Hu, C. P., Ying, S. K.,** 1999. J. Mol., Catal. A.: Chem., **144,** 357.

[119] **Paik, H.-J., Gaynor, S. G., Matyjaszewski, K.,** 1998. Makromol. Rapid Commun., **19,** 47.

[120] **Gaynor, S. G., Matyjaszewski, K.,** 1998. ACS Symp. Series, **685,** 396.

[121] **Fonagy, T., Ivan, B., Szesztay, M.,** 1998. Makromol. Rapid Commun., **19,** 479.

[122] **Hong, S. C., Pakula, T., Matyjaszewski, K.,** 2001. Polym. Met. Sci. Eng., **84,** 767.

[123] **Matyjaszewski, K., Teodorescu, M., Miller, P. J., Peterson, M. L.,** 2000. J. Polym. Sci. Part A: Polym. Chem, **38,** 2440.

[124] **Truelsen, J. H., Kops, J., Batsberg, W.,** 2000. Makromol. Rapid Commun., **21,** 98.

[125] **Matyjaszewski, K., Beers, K. L., Kern, A., Gaynor, S. G.,** 1998. J. Polym. Sci. Part A: Polym. Chem, **36,** 823.

[126] **Matyjaszewski, K., Xia, J.,** 2001. Chem. Rev., **101,** 2921-2990.

AUTOBIOGRAPHY

Mine BARLAN is born in Istanbul in 1977. She graduated from Kadıköy Girls High School in 1995. Then, she admitted Chemistry Department in Istanbul Technical University in 1995 and graduated in 1999. She has been studying master work at Polymer Science and Technology Programme in Istanbul Technical University since 2000.