CYCLOPOLYMERIZATION OF ALKYL α-(HYDROXYMETHYL)ACRYLATE (RHMA) ETHER DIMERS VIA ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

by

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to my lovely father, mother

and sisters

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ABSTRACT

CYCLOPOLYMERIZATION OF
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Thermal stability, high glass transition temperatures and limited shrinkage during polymerization as compared to non-cyclic linear polymers are considered to be advantageous properties of the polymers with high degrees of cyclization derived from cyclopolymerization of alkyl α-(hydroxymethyl)acrylate (RHMA) ether dimers. These cyclopolymers have been previously synthesized by conventional free radical polymerization. The conventional radical polymerization processes often yield polymers with ill-controlled molecular weights and high polydispersities because of irreversible termination reactions. However, alkyl α-(hydroxymethyl)acrylate (RHMA) ether dimers have never been cyclopolymerized by controlled radical polymerization techniques.

The purpose of this investigation is to get highly cyclized living aliphatic polymers with controlled molecular weights and low polydispersities. In order to attain this goal, ATRP was applied to alkyl α-(hydroxymethyl)acrylate (RHMA) ether dimers as monomer. CuBr/PMDETA catalyst system was employed and polymerizations were carried out in xylene. The results indicate that the desired cyclopolymers can be obtained by ATRP technique.

ÖZET

ATOM TRANSFER RADİKAL POLİMERİZASYONU (ATRP) YÖNTEMİ İLE ALKİL α-(HİDROKSİMETİL)AKRİLAT (RHMA) ETER DİMERLERİNİN HALKALI POLİMERİZASYONU

Yüksek derecede halkalı yapı gösteren alkil α-(hidroksimetil)akrilat eter dimerleri ısısal dayanıklılığa, yüksek camsı geçiş sıcaklıklarına ve polimerizasyon esnasında sınırlı miktarda çekilme payına sahip olma özelliklerinden dolayı halkalı olmayan lineer polimerlerden daha avantajlıdır. Bu halkalı polimerler, klasik serbest radikal polimerizasyon yöntemi ile sentezlenmişti. Serbest radikal polimerizasyonu ile genellikle kontrolsüz molekül ağırlıklı ve yüksek polidispersiyonlu polimerler elde edilir. Bunun sebebi tersinmez sonlanma reaksiyonlarıdır. Oysa, alkil α-(hidroksimetil)akrilat eter dimerleri şimdiye kadar kontrollü polimerizasyon yöntemleri ile polimerleştirilmedi.

Bu araştırmanın amacı, kontrollü molekül ağırlığına ve düşük polidispersiyona sahip aktif alifatik polimerler elde edebilmektir. Bu amaçla, atom transfer radikal polimerizasyon yöntemi, alkil α-(hidroksimetil)akrilat eter dimerlerinin siklopolimerleştirilmesi için uygulandı. CuBr/PMDETA katalizör sistemi kullanıldı ve reaksiyonlar ksilende yürütüldü. Elde edilen sonuçlar, arzu edilen halkalı polimerlerin ATRP yöntemi ile elde edilebileceğini gösterdi.

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LIST OF ABBREVIATIONS

CRP	Controlled Radical Polymerization
ATRP	Atom Transfer Radical Polymerization
RHMA	Alkyl α-(Hydroxymethyl)acrylate
EHMA	Ethyl α-(Hydroxymethyl)acrylate
BHMA	n-Butyl α-(Hydroxymethyl)acrylate
TBHMA	*tert*-Butyl α-(Hydroxymethyl)acrylate
PMDETA	*N,N,N,N',N'*-pentamethyldiethylenetriamine
DABCO	1,4-diazabicyclo[2.2.2] octane
EB*i*B	Ethyl 2-bromoisobutyrate
GPC	Gel Permation Chromatography
UV	Ultra Violet
NMR	Nuclear Magnetic Resonans Spectroscopy
T_g	Glass Transition Temperature
TLC	Thin Layer Chromatography
PCCD	Poly(1,4-cyclohexane-dimethanol 1,4-dicarboxylate)

1. INTRODUCTION

1.1. Material Requirements for Powder Coatings

Powder coating is by far the youngest of the surface finishing techniques in common use today. It was first used in Australia in aboout 1967. Over the past years powder coatings have increasingly gained popularity as a result of their ecological, economical and performance benefits [1].

There are two main types of powder available to the surface finisher [1]:

- Thermoplastic powders that will remelt when heated, and
- Thermosetting powders that will not remelt upon reheating. During the curing process (in the oven) a chemical cross-linking reaction is triggered at the curing temperature and it is this chemical reaction which gives the powder coating many of its desirable properties.

Desired properties of synthetic base-resin polymers can be summarized as follows:

- They should have active crosslinkable end groups.
- They should have weathering stability for outdoor applications.
- They should have high glass transition temperature (T_g) (55-60 ^oC). As a result of the relatively high curing temperatures, typically in the range of 150-200 ^oC, powder coatings are limited to substrates that can tolerate high temperatures.
- They should have controlled molecular weights. If their molecular weights can be controlled, such polymers can give tuneable crosslinked networks.

Among current materials, aromatic polyesters and aliphatic polyesters can partially satisfy the material requirements for powder coatings [2].

Figure 1.1 shows a typical aromatic polyester. Aromatic polyesters have high T_g's [2]. However, their weathering stabilities are low. They are sensitive to UV light because they are choromophores due to the aromatic units in the backbone, which makes them less suitable for outdoor applications. In addition, compared to their aliphatic counterparts their chemical stabilities are somewhat low, which comes from the poorer hydrolytic resistance.

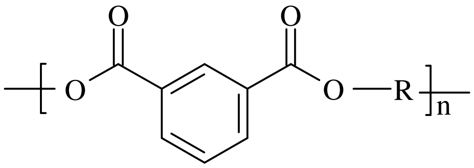


Figure 1.1. An example of aromatic polyester

Figure 1.2 shows a typical aliphatic polyester. Aliphatic polyesters are weathering stable. They are more UV transparent because they are not good chromophores. Their hydrolitic stabilities make them more resistant to water absorption in aqueous acidic and alkaline environments [3]. On the other hand, their T_g's are low. To increase their T_g's, it is necessary to increase their molecular weights, which leads to lower crosslink densities when used in thermosetting chemistry. This, with aliphatic systems, results in poor mechanical properties and low chemical resistance to nonpolar environments, detergents, oils, gasoline, etc.

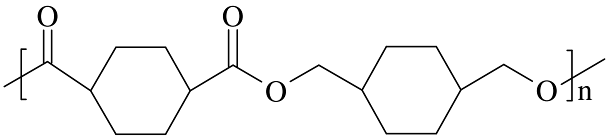


Figure 1.2. An example of aliphatic polyester (PCCD)

Thus, neither aromatic nor aliphatic systems can satisfy the desired resin properties. Therefore, there is a need for new polymers that can satisfy these requirements and can be used in powder coating.

All things considered, we believe that aliphatic cyclopolymers with reactive end groups may be good candidates for such a application.

1.1.1. Aliphatic Cyclopolymers

Aliphatic cyclopolymers are known to possess many advantageous properties such as high glass transition temperatures, excellent thermal stabilities and less shrinkage during polymerization than non-cyclic linear polymers [4,5,6].

Aliphatic cyclopolymers have been synthesized by conventional free radical polymerization [4]. Conventional free radical polymerization does not provide active crosslinkable end gropus. However, when controlled polymerization techniques can be applied for the synthesis of aliphatic cyclopolymers, active crosslinkable end groups can be generated. In addition, It may be possible to reach high T_g's (55-60 ^{o}C) at low molecular weigts (5-10K) because of low polydispersities and controlled molecular weights. Such polymers can give highly crosslinked polymer networks with different, improved (unknown) physical properties.

1.1.2. Controlled Polymerization

In controlled polymerizations techniques, the average molecular weight is controlled by the ratio of consumed monomer and initiator concentration, $[M]/[I]_o$ [7]. The main role of the initiator is to determine the number of growing polymer chains. Polydispersities are generally low ($1.0<M_w/M_n<1.5$). Molecular weights are typically in the range of 1000-150000.

Molecular weights increase with conversion linearly and polydispersities decrease with conversion (Figure 1.3). Livingness is also achieved with controlled polymerization techniques [7].

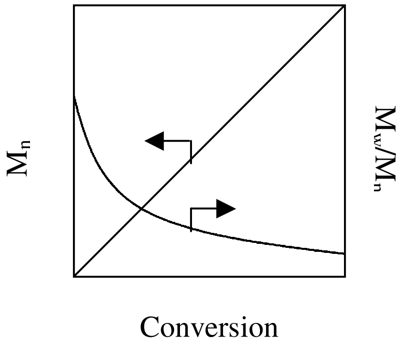


Figure 1.3. Shematic representation of the evolution of the molecular weights and polydispersities with conversion for a controlled/living polymerization

Most of the living polymerization systems were reported for anionic, cationic or group transfer polymerizations. However, the industrial applications of these techniques have been limited due to the need for high purity monomers and solvents, reactive initiators for active end groups, and anhydrous conditions. In contrast, free radical polymerization is probably the most important commercial process leading to high molecular weight polymers. A large variety of monomers can be polymerized radically under relatively simple experimental conditions which require the absence of oxygen but can be carried out in the presence of water [8]. However, free radical polymerization processes often yield polymers with ill-conrolled molecular weights and high polydispersities. The idea of combining the advantages of both living polymerization and radical polymerization has attracted much attention. Several controlled radical polymerization (CPR) processes have been extensively developed in the past decade, including nitroxide-mediated polymerization (NMP), reversible addition-fragmentation chain transfer polymerization (RAFT), and atom transfer radical polymerization (ATRP) [9].

1.2. Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is one of the most efficient controlled/living radical polymerization (CRP) method [10]. Well-defined polymers with low polydispersities and complex architectures can be achived by ATRP [11].

1.2.1. The mechanism of ATRP

A typical ATRP requires an activated halide (RX) as initiator, a transition metal in its lower oxidation state (M_t^n), a ligand that complexes with the metal and finally a monomer (M) (Figure 1.4) [10].

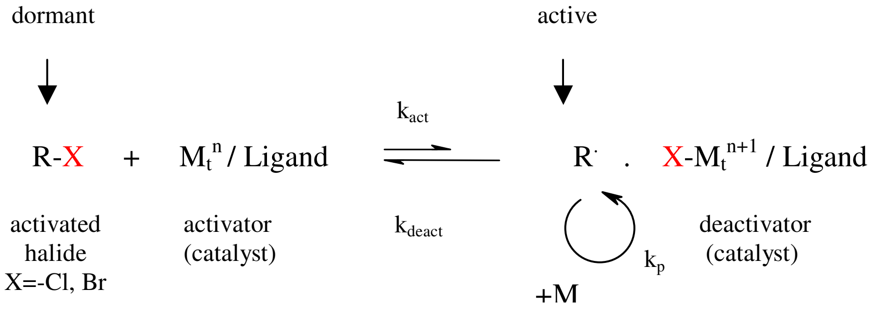


Figure 1.4. The mechanism of ATRP

In ATRP process, a rapid dynamic equilibrium is established between growing active radicals and dormant species where the rate constant of activation is expressed as k_{act}, and deactivation k_{deact}. Dormant species are reversibly activated by a halogen atom transfer to transition metal complex. Transition metal is oxidized by accepting the halogen atom to its inner coordination shpere. Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation k_p. The oxidized transition metal should rapidly deactivate the growing polymer chains to form the dormant species. Another words, the equilibrium is strongly shifted toward the dormant species. Therefore, the concentration of active radicals is kept low. Termination reactions between free radicals are reduced and monomer addition is controlled. 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.

Precise control over the chemistry and the structure of the initiator and active end group (X) allows the synthesis of end-functionalized polymers and block copolymers.

1.2.2. Typical Phenomenology in ATRP

1.2.2.1. Kinetics

Figure 1.5 shows a typical linear variation of conversion with time in semilogarithmic coordinates. Such a behavior indicates that there is a constant concentration of active species in the polymerization, and first-order kinetics with respect to monomer is followed. However, since residual termination reactions occur during the polymerization, the concentration of the deactivator species increases and deviation from linearity may be observed at high conversions.

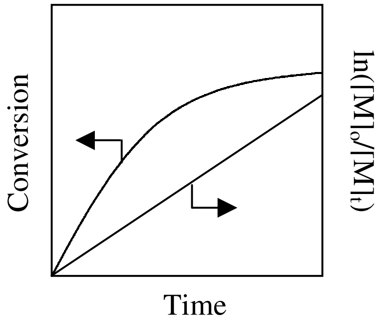


Figure 1.5. Schematic representation of the dependence of the conversion on time in linear and semilogarithmic coordinates

Results from kinetic studies of ATRP for styrene, methyl acrylate (MA), and methyl methacrylate (MMA) under homogeneous conditions indicate that the rate of polymerization is first order with respect to monomer, initiator and Cu(I) complex concentrations. The kinetically optimum ratio of 4,4’-dialkyl substituted 2,2’-bipyridine ligand to copper(I) halide in the homogeneous ATRP of both styrene and MA was detemined to be 2:1, which tentatively indicates that the coordination sphere of the active copper(I) center contains two bipyridine ligands [12]. Below this ratio the polymerization rate was usually slower, and above this ratio the polymerization rate remained constant. It should be noted that the optimum ratio can vary with regard to changes in the monomer, counterion, ligand, temperature, and other factors.

1.2.3. ATRP Components

As a multicomponent system, ATRP is composed of the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Sometimes an additive is used. For a successful ATRP, other factors, such as solvent and temperature, must also be taken into consideration.

1.2.3.1. Initiators

The main role of the initiator is to determine the number of growing polymer chains. In ATRP, activated alkyl halides (RX) are typically used as the initiator and the rate of the polymerization is first order with respect to the concentration of RX. Initiation is accomplished with homolytic cleavage of activated halides and addition of generated radicals to monomer (Figure 1.6). 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. When X is either bromide or chloride, the molecular weight is well controlled [13,14].

Initiation:

$$\text{R-X} + \text{M}_t^{n} / \text{Ligand} \rightleftharpoons \text{R}^{\cdot} \;\; . \;\; \text{X-M}_t^{n+1} / \text{Ligand}$$

$$\text{R}^{\cdot} + \text{M} \longrightarrow \text{RM}^{\cdot}$$

Figure 1.6. The mechanism of initiation

Two parameters are important for a successful ATRP initiating system. First, the probability of side reactions should be minimized. R-X bonds can be cleaved not only homolytically but also heterolytically, which depends mostly on the initiator structure and the choice of the transition metal catalyst. For example, side reactions are observed for Cu-mediated ATRP of p-methoxystyrene, likely due to the heterolytic cleavage of C-X bond or oxidation of the radical to the corresponding carbocation [10]. Second, initiation should be fast in comparison with propagation, which leads to narrow molecular weight distributions. Fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously.

Tertiary activated alkyl halides are better initiators than secondary ones, which are better than primary alkyl halides. Bromides give faster initiation than chlorides.

In general, any alkyl halide with radical stabilizing group on the α-carbon, such as aryl, carbonyl, or nitrile can be used as ATRP initiators. Polyhalogenated compounds (e.g., CCl_4 and $CHCl_3$) and compounds with a weak R-X bond, such as N-X, S-X, can also be used as ATRP initiators (Figure 1.7).

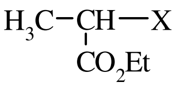
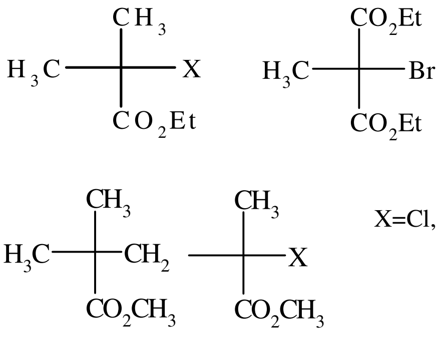
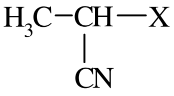
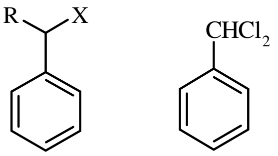
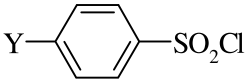
Haloalkanes CCl_4 (X=Cl, Br) CCl_3Br	Haloesters $CCl_3CO_2CH_3$ $CHCl_2CO_2CH_3$  $H_3C-CH(CO_2Et)-X$  X=Cl, Br
Haloketones CCl_3COCH_3 $CHCl_2COPh$	
Halonitriles  $H_3C-CH(CN)-X$	
Haloalkylbenzenes  R=H, CH_3 X=Cl, Br	Sulfonyl Chlorides  CH_3SO_2Cl (Y=H, OMe, Cl, etc.) CCl_3SO_2Cl

Figure 1.7. The examples of initiators used in ATRP

1.2.3.2. Transition Metals

To generate growing radicals, the metal center should undergo an electron transfer reaction with the abstraction of a (pseudo) halogen. There are several prerequisites that a transition metal has to satisfy to result in a succesfull ATRP process:

- The metal center must have at least two readily accessible oxidation states separated by one electron.
- The metal center should have reasonable affinity toward a halogen.
- The coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo) halogen.
- The ligand should complex the metal relatively strongly.
- Position and dynamics of the ATRP equilibrium should be appropriate for the particular system.

A variety of transition metals have been employed in ATRP (Figure 1.8) [15,16,17]. (They are shown in bold and underlined). Among them copper catalyst is superior in terms of versatility and cost. Styrenes, (meth)acrylates esters and amides, and acrylonitrile have been successfully polymerized using copper-mediated ATRP [18].

Group :	6	7	8	9	10	11
	Cr	Mn	**Fe**	Co	**Ni**	**Cu**
	Mo	Tc	**Ru**	**Rh**	**Pd**	Ag
	W	**Re**	Os	Ir	Pt	Au

Figure 1.8. The transition metals used in ATRP

1.2.3.3. Ligands

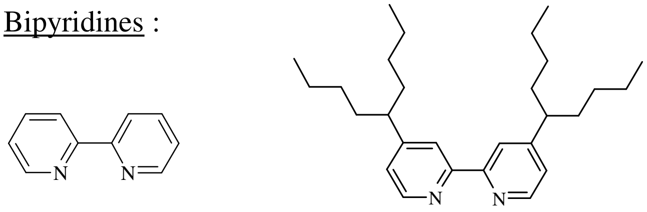
There are two main roles of ligands in ATRP. One is to solubilize the metal salt in the organic media. They control solubilities and ensure stability of the complex in different monomers, solvents and temperatures. Polymers with lower polydispersities are usually obtained with a homogenous catalyst due to fine-tuning of the equilibrium. The second role is to adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer. Another words, the ligand playes a crucial role in tuning the activity of the related catalyst in the activation and deactivation steps of the ATRP mechanism. Fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate, leading to a narrow molecular weight distribution. Relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate [12].

Atom transfer equilibrium is affected by the elecronic and steric effects of the ligand [19]. For example, good π-acceptor or electron donating ligands efficiently stabilize the lower oxidation state of the metal center. This shifts the atom transfer equilibrium toward the dormant species (P_nX) because more electron donating ligands facilitate the migration of the halide to active polymer chain, which leads to fast deactivation. When the ligands with electron-withdrawing substituents are used, reduced catalytic activity is observed. On the other hands, less sterically hindered complexes increase the rate of activation, as the metal center is easy to access for the halogen atom. Bulky ligands reduce the rate of activation [20].

For copper-mediated ATRP, nitrogen-based polydentate ligands work particularly well (Figure 1.9), including pyridine derivatives [21], linear, branched, or cyclic aliphatic polyamines [22], imine derivatives [23], picolylamine derivatives [24], phenanthroline derivatives, and terpyridine derivatives. In contrast, sulfur, oxygen, or phosphorus ligands are less effective due to inappropriate electronic effects or unfavorable binding constants.

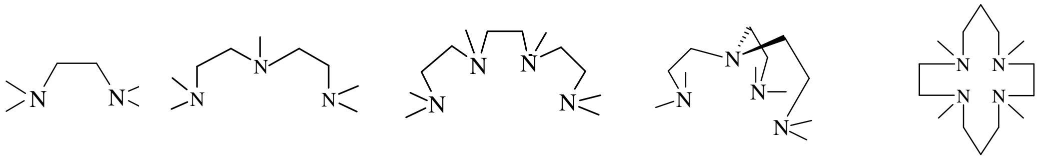
Initially, cuprous halides complexed by byridines were used as catalyst. Better solubility of the transition metal complex in nonpolar reaction media was achieved by adding long alkyl substituents to the ligand. The same strategy was also used in picolylamine and imine derivatives. Ligands with long alkyl substituents have more solubilizing effect. Alkylamines are also used. They can be bidentate, tridentate or tetradentate and they can be linear, branched or cyclic. Their efficiencies depend on their electronic and steric effects.

Bipyridines :



bpy dNbpy

Alkylamines :



TMEDA PMDETA HMTETA Me$_6$TREN

Picolylamine derivatives :

BPMOA TPMA

Imine derivatives :

Figure 1.9. The examples of nitrogen ligands used in Cu-mediated ATRP

Copper forms cationic complexes with tetradentate or two bidentate ligands and neutral complexes with tridentate ligands. Copper(I) prefers a tetrahedral or square planar configuration. Copper in its higher oxidation state, coordination spheres expand by accepting a halogen atom. Copper(II) prefers a trigonal bipyramidal configuration with tetradentate or two bidentate ligands and prefers a square pyramidal configuration with tridentate ligands (Figure 1.10)

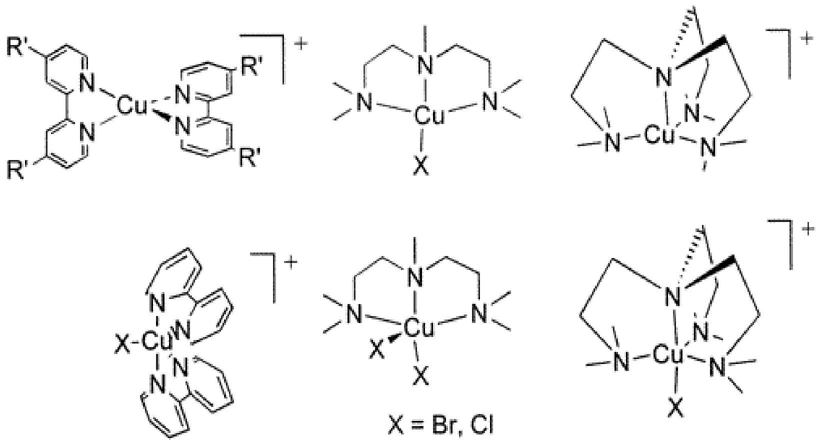


Figure 1.10. Copper complexes used as ATRP catalyst

Bipyridines have more rigid, planar structure in comparison with alkyl amines. Therefore, the expansion of coordination sphere is more difficult in the bipyridine complexes, which leads to difficult activation and decreases the polymerization rate. Thus, aliphatic amines are more suitable for activation because of their easily expandable coordination spheres. In summary, number of cordination, nature of the ligand and bulkiness affect the polymerization rate.

Apart from bipyridines, alkylamines were successfully used as ligands for copper mediated ATRP [25]. Particularly, a commercially available tridentate ligand, *N,N,N,N,N*-pentamethyldiethylenetriamine (PMDETA), showed high activity and solubility in less polar media [26].

1.2.3.4. Monomers

Various monomers have been successfully polymerized using ATRP: styrenes, (meth)acrylates, (meth)acrylamides, dienes, acrylonitrile, vinylpyridine, and other monomers which contain substituents that can stabilize the propagating radicals [27, 28, 29, 30]. Ring-opening polymerization is also possible.

Even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. The product of k_p and the equilibrium constant ($K_{eq}=k_{act}/k_{deact}$) essentially determines the polymerization rate. ATRP will occur very slowly if the equilibrium constant is too small. This is plausibly the main reason why polymerization of less reactive monomers such as olefins, halogenated alkenes, and vinyl acetate has not yet been successful. Because each monomer has a specific equilibrium constant, optimal conditions for polymerization, which include concentration and type of the catalyst, temperature, solvent, may be quite different. In contrast, too large of an equilibrium constant will lead to a large amount of termination because of 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

Because each monomer has a specific equilibrium constant, optimal conditions for polymerization which include concentration and type of the catalyst, temperature, solvent, and aaditin of some additives have to be investigated for each monomer system.

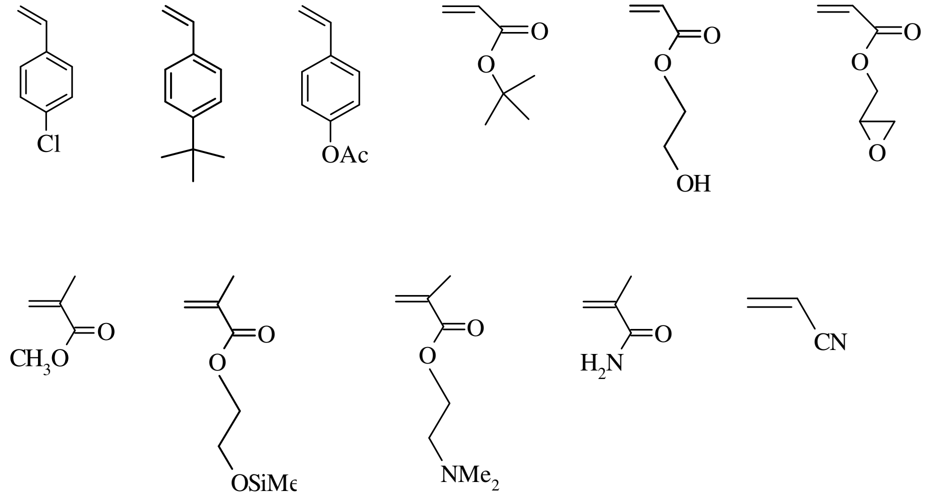


Figure 1.11. Examples of monomers polymerized by ATRP

1.2.3.5. Solvents

ATRP can be carried out in bulk, in solution or in heterogeneous systems (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used for different monomers. A solvent is sometimes necessary, especially when the obtained polymer is insoluble in its monomer (e.g., polyacrylonitrile).

Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP) and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent, should be minimized [31].

1.2.3.6. Temperature and Reaction Time

The rate of polymerization in ATRP increases with increasing temperature due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. As a result of higher the rate of radical propagation than the rate of radical termination, higher k_p/k_t ratios and better control ("livingness") may be observed at higher temperatures. However, chain transfer and other side reactions become more pronounced at elevated temperatures. In general, the solubility of the catalyst increases at higher temperatures; however, catalyst decomposition may also occur with the temperature increase. The optimal temperature depends mostly on the monomer, the catalyst and the targeted molecular weight.

At high monomer conversions, the rate of propagation slows down considerably; however, the rate of any side reaction does not change significantly, as most of them are monomer concentration independent. Prolonged reaction times leading to nearly complete monomer conversion may not increase the polydispersity of the final polymer but will induce loss of end groups. Thus, to obtain polymers with high end-group functionality or to subsequently synthesize block copolymers, conversion must not exceed 95% to avoid end-group loss [30].

As mentioned previously, the material requirements for powder coatings can be satisfy with controlled polymerization and aliphatic cyclopolymers. In this work ATRP was applied to the synthesis of aliphatic cyclopolymers. The cyclomonomers that were used are RHMA ether dimers with different alkyl substituents.

1.3. Cyclopolymers of RHMA Ether Dimers

The aliphatic cyclopolymers obtained from RHMA ether dimers (Figure 1.12) are known to possess many advantageous properties such as high glass transition temperatures, excellent thermal stabilities and less shrinkage during polymerization than non-cyclic linear polymers. These cyclopolymers have been synthesized by conventional free radical polymerization [32].

For the successful synthesis of cyclopolymers, it is important to understand and control the factors that affect cyclization efficiency.

1.3.3. The Factors Affecting Cyclization in Conventional Free Radical Polymerization

During the cyclopolymerization of RHMA ether dimers via conventional free radical polymerization, the desired intramolecular cyclization leads to ring structures and gives linear, soluble, high molecular weight polymers. Major problems arise from imperfect cyclization. Intermolecular reaction with another difunctional monomer gives uncyclized pendent groups that lead to crosslinking in most cases (Figure 1.13) [33, 34].

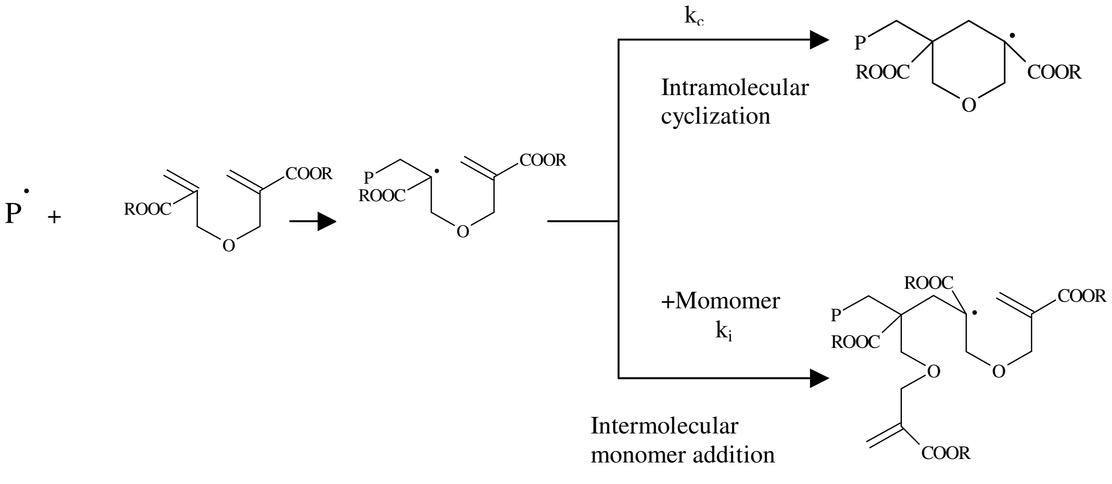


Figure 1.12. Intramolecular cyclization and intermolecular monomer addition

Cyclization is affected by the bulkiness of alkyl (R) groups and temperature. Bulky R groups greatly incease cyclization efficiency. They can inhibit intermolecular monomer addition and/or promote intramolecular cyclization despite a disadvantage in activation energry for cyclization. Higher temperatures also facilitate cyclization. The monomers can overcome their activation energies for cyclization at high temperatures. In conclusion, thermally stable and sterically large terminal alkyl groups provide better cyclization efficiency [33].

2. OBJECTIVES

RHMA ether dimers have been polymerized using conventional free radical polymerization. Radical polymerization processes often yield polymers with ill-controlled molecular weights and high polydispersities because of irreversible termination reactions. In addition, polymers obtained by conventional free radical polymerization contain dead end groups.

The purpose of this investigation is to get highly cyclized living aliphatic polymers with controlled molecular weights and low polydispersities. In order to attain this goal, we decided to apply ATRP to alkyl α-(hydroxymethyl)acrylate (RHMA) ether dimers as monomer. Polymerizations were carried out in xylene. Cu(I)Br/PMDETA was chosen as the active catalyst complex and ethyl 2-bromoisobutyrate (EB*i*B) was employed as the initiator.

As mentioned previously, in the polymerization of RHMA ether dimer monomers by conventional free radical polymerization, cyclization is affected by the bulkiness of alkyl (R) group and temperature. Bulky terminal alkyl groups greatly incease cyclization efficiency. High temperatures also favor cyclization. However, the effects of these factors were not known in the ATRP cyclopolymerization system. Therefore, we investigated the steric effect of alkyl group and temperature effect in ATRP cyclopolymerization system.

3. EXPERIMENTAL

3.1. Monomer Synthesis

3.1.1. Materials

Ethyl acrylate, *n*-butyl acrylate, *tert*-butyl acrylate, paraformaldehyde, 1,4diazabicyclo[2.2.2]octane (DABCO), t-butyl alcohol, hydrochloric acid (HCl), copper (I) chloride (CuCl), potassium permagnate ($KMnO_4$) were used as received without purification. The solvents; methylene chloride, hexane, methanol were all obtained from Merck and used as received.

3.1.2. Apparatus

^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Varian Gemini 400 MHz spectrometer.

3.1.3. Synthesis of Ethyl α-(Hydroxymethyl)acrylate Ether Dimer

Ethyl acrylate (25 g, 0.25 mol), paraformaldehyde (7.5 g, 0.25 mol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (2 g, 4.8 wt%) were added into a 50 mL three-necked round-bottom flask fitted with a condenser and a magnetic stirrer. The mixture was stirred at 95 ^oC for 4 days. The reaction progress was monitored by thin layer chromatography (TLC) using silica gel plates and CH_2Cl_2 as the eluting and diluting solvent. TLC plates were visualized using potassium permagnate solution. At the end of the fourth day, the mixture was diluted with 100 mL hexane, washed three times with 50 mL of 3% HCl, and then with 50 mL of distilled water. The organic layer was separated and evaporated under reduced pressure to give crude monomer. The solution that remained over was diluted with methylene chloride : hexane mixture with the 4:3 ratio and passed through silica column prepared with the same solvent mixture. Evaporation of the solvent gave the pure monomer as a clear liquid in 42 per cent yield.

^{13}C-NMR ($CDCl_3$): δ= 14.34 (CH_3), 60.88 (CH_2-$\mathit{C}H_3$), 69.07 (CH_2-O), 125.75 (C=CH_2), 137.41 ($\mathit{C}H_2$=C), 165.92 (C=O) ppm.

^{1}H-NMR ($CDCl_3$): δ= 1.25 (t, 3H, CH_3), 4.16 (m, 2H, CH_2) , 4.20 (s, 2H, OCH_2), 5.85 (s, 1H, CH=C), 6.26 (s, 1H, CH=C) ppm.

3.1.4. Synthesis of *n*-Butyl α-(Hydroxymethyl)acrylate Ether Dimer

n-Butyl acrylate (32 g, 0.25 mol), paraformaldehyde (7.5 g, 0.25 mol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (2.5 g, 6 wt%) and were added into a 50 mL three-necked round-bottom flask fitted with a condenser and a magnetic stirrer. The mixture was stirred at 95 °C for 4 days. The reaction progress was monitored by thin layer chromatography (TLC) using silica gel plates and CH_2Cl_2 as the eluting and diluting solvent. TLC plates were visualized using potassium permagnate solution. At the end of the fourth day, the mixture was diluted with 100 mL methylene chloride, washed three times with 50 mL of 3% HCl, and then with 50 mL of distilled water. The organic layer was separated and evaporated under reduced pressure to give crude monomer. Vacuum distillation in the presence of a free-radical inhibitor, CuCl, gave the pure monomer as a clear liquid in 47 per cent yield.

^{13}C-NMR ($CDCl_3$): δ= 13.88 (CH_3), 19.37 (CH_2-$\mathit{C}H_3$), 30.80 ($\mathit{C}H_2$-CH_2-$\mathit{C}H_2$), 64.79 (O-CH_2-$\mathit{C}H_2$), 69.09 (CH_2-O), 125.72 (C=CH_2), 137.42 ($\mathit{C}H_2$=C), 165.99 (C=O) ppm.

^{1}H-NMR ($CDCl_3$): δ= 0.90 (t, 3H, CH_3), 1.36 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 4.12 (t, 2H, CH_2), 4.21 (s, 2H, OCH_2), 5.85 (s, 1H, CH=C), 6.26 (s, 1H, CH=C) ppm.

3.1.5. Synthesis of *tert*-Butyl α-(Hydroxymethyl)acrylate Ether Dimer

t-Butyl acrylate (64 g, 0.5 mol), paraformaldehyde (15 g, 0.5 mol), 1,4-diazabicyclo[2.2.2]octane (DABCO) (2.5 g, 2.9 wt%) and t-butyl alcohol (4 g, 4.7wt%) were added into a 250 mL three-necked round-bottom flask fitted with a condenser and a magnetic stirrer. The mixture was stirred at 95 °C for 4 days. The reaction progress was monitored by thin layer chromatography (TLC) using silica gel plates and CH_2Cl_2 as the eluting and diluting solvent. TLC plates were visualized using potassium permagnate solution. At the end of the fourth day, the mixture was diluted with 150 ml of methylene chloride, washed three times with mL of 3% HCl, and then with 100 mL of distilled water. The organic layer was separated and evaporated under reduced pressure to give crude monomer. Vacuum distillation in the presence of a free-radical inhibitor, CuCl, gave the pure monomer as a clear liquid in 30-40 per cent yield.

^{13}C-NMR ($CDCl_3$); δ= 28.26 (CH_3), 69.19 (CH_2-O), 81.13 [C-($\mathit{C}H_3$)$_3$], 124.69 (C=CH_2), 138.83 ($\mathit{C}H_2$=C), 165.26 (C=O) ppm.

^{1}H-NMR ($CDCl_3$): δ= 1.46 (s, 9H, CH_3), 4.17 (s, 2H, OCH_2), 5.78 (s, 1H, CH=C), 6.17 (s, 1H, CH=C) ppm.

3.2. Polymer Synthesis

3.2.1. Materials

Ethyl-2-bromoisobutyrate, copper(I)bromide (CuBr) (Aldrich, 99.999%), and pentamethyldiethylene triamine (PMDETA) (Aldrich, 99%) were used as received without purification. The solvents; methylene chloride and methanol were obtained from Merck and used as received. Xylene (mixture of isomers) was purified by distillation over Na metal and benzophenone.

3.2.2. Apparatus

^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Varian Gemini 400 MHz spectrometer. GPC analysis were done using a Agilent 1100 Series GPC-SEC Analysis System. PL Gel 5 µm MIXED-C Column was calibrated against polystyrene standarts.

3.2.3. The Procedure for the Solution ATRP of RHMA Ether Dimers

All glassware, needles and stirring bars were dried overnight in an oven at 150 ^{o}C and purged with nitrogen gas before use. All liquid chemicals were purged with nitrogen for at least 20 minutes prior to use. The polymerization of RHMA ether dimers was conducted in a three-necked round bottom flask using xylene as the solvent. The reaction flask fitted with a stirring bar was sealed with rubber septa and purged with nitrogen for 15 minute. Then the monomer was dissolved in xylene and transferred into the reaction flask by syringe. The solution was stirred and purged with nitrogen for 30 min. Then, the solution was immersed into a preheated oil bath. 2 mL of this solution was taken via syringe and added onto CuBr which was sealed with rubber septa in a vial and purged with nitrogen for 15 minute. PMDETA was added to this solution containing the CuBr. The resulting solution was stirred and heated until homogenous. This solution was then transferred into the reaction flask by syringe. Ethyl-α-bromoisobutyrate (EB*i*B) was introduced into the reaction flask by syringe. Polymerizations were carried out under nitrogen at the proper temperature. The final polymers were dissolved in methylene chloride and precipitated into methanol/water and dried in a vacuum oven overnight.

Monomer conversion was determined by gravimetric methods. The determination of the molar masses and molecular weight distributions has been carried out by size exclusion chromatography (SEC) with a refractometer detector with poly(styrene) (PS) standards. Characterization of the polymer samples has been performed by proton and carbon NMR spectroscopy.

3.2.4. The Procedure for the Purification of the Resulting Polymers

To remove the catalyst, all polymers were dissolved in methylene chloride and passed through a basic aluminum oxide column prepared with the same solvent, collecting the only fraction that eluted. Polymers were reprecipitated into methanol/water and dried in a vacuum oven overnight. The pure polymers were dissolved in chloroform and analyzed by GPC and NMR.

3.2.5. ATRP of Ethyl α-(Hydroxymethyl)acrylate Ether Dimer

Experiment 1. EHMA ether dimer (1.01 g, 4.2 mmol) was polymerized in 4 mL xylene (1.04 M) by using CuBr (6.03 mg, 0.042 mmol) and PMDETA (9 μL, 0.043 mmol) catalyst system and ethyl-α-bromoisobutyrate (7 μL, 0.047 mmol) initiator according to the given procedure. The polymerization was carried out at 70 ^{o}C for 5 hours. The reaction mixture was initially green-yellow and clear and turned green-brown with time. Polymer was not

3.2.6. ATRP of *n*-Butyl α-(Hydroxymethyl)acrylate Ether Dimer

Experiment 1. BHMA ether dimer (2.0 g, 6.7 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (9.7 mg, 0.067 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 70 ^{o}C for 6 hours. The reaction mixture was initially blue and clear and turned green, deep green and deep green-brown with time. The reaction mixture was initially homogeneous and it became heterogeneous with time. The resulting polymer was dissolved with 5 ml methylene chloride and precipitated into 40 mL methanol and 5 mL water and dried in a vacuum oven overnight. The obtained polymer was as a glasslike, soluble, 0.26 g, in a 13 per cent yield.

Experiment 2. BHMA ether dimer (2.01 g, 6.7 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (9.6 mg, 0.067 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 70 ^{o}C for 6 hours. The reaction mixture was initially blue and clear and turned green, deep green and deep green-brown with time. The reaction mixture was initially homogeneous and it became heterogeneous with time. The resulting polymer was dissolved with 5 ml methylene chloride and precipitated into 40 mL methanol and 5 mL water and dried in a vacuum oven overnight. The obtained polymer was as a glasslike, soluble, 0.73 g, in a 37 per cent yield.

Experiment 3. BHMA ether dimer (1.02 g, 3.4 mmol) was polymerized in 4 mL xylene (0.85 M) by using CuBr (9.7 mg, 0.068 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and ethyl-α-bromoisobutyrate (6 μL, 0.04 mmol) initiator according to the given procedure. The polymerization was carried out at 70 ^{o}C for 5 hours. The reaction mixture was initially yellow and clear and turned yellow-green, deep yellow with time. The resulting polymer was dissolved with 5 ml methylene chloride and precipitated into 40 mL methanol and 5 mL water and dried in a vacuum oven overnight. The obtained polymer was as a glasslike, soluble, 0.27 g, in a 27 per cent yield.

Experiment 4. BHMA ether dimer (2.02 g, 6.8 mmol) was polymerized in 7 mL xylene (0.97 M) by using CuBr (9.8 mg, 0.068 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 100 ^{o}C for 8 hours. The reaction mixture was initially blue-yellow and clear and turned light green-yellow, deep green-yellow and deep green-brown with time. The reaction mixture was initially homogeneous and it became heterogeneous with time. The resulting polymer was dissolved with 6 ml methylene chloride and precipitated into 40 mL methanol and 6 mL water and dried in a vacuum oven overnight. The obtained polymer was as a glasslike, soluble, 0.83 g, in a 41 per cent yield.

Experiment 5. BHMA ether dimer (2.04 g, 6.8 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (9.7 mg, 0.068 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 100 ^{o}C for 18 hours. The reaction mixture was initially blue-yellow and clear and turned light green-yellow, deep green-yellow and deep green-brown with time. The reaction mixture was initially homogeneous and it became heterogeneous with time. The resulting polymer was as a jello and dissolved with 7 ml methylene chloride and precipitated into 40 mL methanol and 7 mL water and dried in a vacuum oven overnight. The obtained polymer was as a glasslike, soluble, 1.26 g, in a 62 per cent yield.

3.2.7. ATRP of *tert*-Butyl α-(Hydroxymethyl)acrylate Ether Dimer

Experiment 1. TBHMA ether dimer (2.01 g, 6.7 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (9.6 mg, 0.067 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 70 ^{o}C for 2 hour. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially colorless and clear and turned yellow-green, dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 6 ml methylene chloride and precipitated into 40 mL methanol and 8 mL water and dried in a vacuum oven overnight. The obtained polymer was powder, soluble, 0.58 g, in a 29 per cent yield.

Experiment 2. TBHMA ether dimer (2.02 g, 6.8 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (9.7 mg, 0.068 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 70 ^{o}C for 8 hours. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially yellow and clear and turned yellow-green, dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 6 ml methylene chloride and precipitated into 40 mL methanol and 8 mL water and dried in a vacuum oven overnight. The obtained polymer was powder, soluble, 0.72 g, in a 36 per cent yield.

Experiment 3. TBHMA ether dimer (2.01 g, 6.7 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (9.6 mg, 0.067 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 70 ^{o}C for 18 hours. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially yellow and clear and turned yellow-green, dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 6 ml methylene chloride and precipitated into 40 mL methanol and 8 mL water and dried in a vacuum oven overnight. The obtained polymer was powder, soluble, 1.52 g, in a 76 per cent yield.

Experiment 4. TBHMA ether dimer (1.02 g, 3.4 mmol) was polymerized in 4 mL xylene (0.85 M) by using CuBr (4.9 mg, 0.034 mmol) and PMDETA (8 μL, 0.038 mmol) catalyst system and ethyl-α-bromoisobutyrate (5 μL, 0.034 mmol) initiator according to the given procedure. The polymerization was carried out at 100 ^{o}C for 2 hours. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially yellow and clear and turned yellow-green, dirty green and deep green-brown with time.

The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 40 mL methanol and 8 mL water and dried in a vacuum oven overnight. The obtained polymer was powder, soluble, 0.63 g, in a 62 per cent yield.

Experiment 5. TBHMA ether dimer (2.04 g, 6.8 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (9.8 mg, 0.068 mmol) and PMDETA (16 µL, 0.076 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 µL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 100 ^oC for 8 hours. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially yellow and clear and turned yellow-green, dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 4 ml methylene chloride and precipitated into 40 mL methanol and 8 mL water and dried in a vacuum oven overnight. The obtained polymer was powder, soluble, 1.2 g, in a 60 per cent yield.

Experiment 6. TBHMA ether dimer (1.01 g, 3.4 mmol) was polymerized in 4 mL xylene (0.85 M) by using CuBr (4.9 mg, 0.034 mmol) and PMDETA (8 µL, 0.038 mmol) catalyst system and ethyl-α-bromoisobutyrate (5 µL, 0.034 mmol) initiator according to the given procedure. The polymerization was carried out at 100 ^oC for 18 hours. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially yellow and clear and turned yellow-green, dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 4 ml methylene chloride and precipitated into 40 mL methanol and 8 mL water and dried in a vacuum oven overnight. The obtained polymer was powder, soluble, 0.71 g, in a 71 per cent yield.

Experiment 7. TBHMA ether dimer (2.04 g, 6.8 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (4.9 mg, 0.034 mmol) and PMDETA (8 µL, 0.038 mmol) catalyst system and ethyl-α-bromoisobutyrate (5 µL, 0.034 mmol) initiator according to the given procedure. The polymerization was carried out at 70 ^oC for 18 hours. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially yellow and clear and turned yellow-green, dirty green and deep green-brown with time.

The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 40 mL methanol and 8 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.86 g, in a 43 per cent yield.

Experiment 8. TBHMA ether dimer (1.04 g, 3.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (9.8 mg, 0.068 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 70 °C for 6 hours. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially yellow and clear and turned yellow-green, dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 4 ml methylene chloride and precipitated into 40 mL methanol and 8 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.63 g, in a 63 per cent yield.

Experiment 9. TBHMA ether dimer (2.02 g, 6.8 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (19.4 mg, 0.135 mmol) and PMDETA (30 μL, 0.143 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 100 °C for 12 minutes. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially yellow and clear and turned yellow-green, dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 40 mL methanol and 8 mL water and dried in a vacuum oven overnight. The obtained polymer was powder, soluble, 1.53 g, in a 77 per cent yield.

Experiment 10. TBHMA ether dimer (2 g, 6.7 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (19.2 mg, 0.134 mmol) and PMDETA (30 μL, 0.143 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 70 °C for 3.75 hours. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially yellow and clear and turned yellow-green, dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 40 mL methanol and 8 mL water and dried in a vacuum oven overnight. The obtained polymer was powder, soluble, 1.96 g, in a 98 per cent yield.

Experiment 11 (Blank experiment). All glassware, needles and stirring bars were dried overnight in an oven at 150 °C and purged with nitrogen gas before use. The vial fitted with a stirring bar was sealed with rubber septa and purged with nitrogen for 15 minute. Then TBHMA ether dimer (0.51 g, 1.7 mmol) was dissolved in 2 mL xylene and transferred into the vial by syringe. The solution was stirred and purged with nitrogen . Then, the solution was immersed into a preheated oil bath at 70 °C. After 24 hours, the solution was still colorless and clear. No precipitation was observed in hexane.

Experiment 12 (Kinetic study). All glassware, needles and stirring bars were dried overnight in an oven at 150 °C and purged with nitrogen gas before use. Xylene and PMDETA were purged with nitrogen prior to use. TBHMA ether dimer (2.0 g, 6.7 mmol) was added to a three-necked round bottom flask. The reaction flask fitted with a stirring bar was sealed with rubber septa and purged with nitrogen for 30 minute. 7 mL xylene was transferred into the reaction flask by syringe. 2 mL xylene and PMDETA (16 µL, 0.076 mmol) were added onto CuBr (9,6 mg, 0.067 mmol) which was sealed with rubber septa in a vial and purged with nitrogen for 15 minute.. The resulting solution was stirred and heated until homogenous. This solution was then transferred into the reaction flask by syringe. Then, the reaction flask was immersed into a preheated oil bath at 70 °C. Ethyl-α-bromoisobutyrate (EBiB) was introduced into the reaction flask by syringe. The reaction mixture was green-brown. The color did not change during polymerization. 2 mL samples were taken at regular intervals using a syringe purged with nitrogen. The resulting polymers were precipitated into 30 mL methanol and 6 mL water and dried in a vacuum oven overnight.

4. RESULTS AND DISCUSSION

The purpose of the project is to get highly cyclized reactive aliphatic polymers with controlled molecular weights and low polydispersities.

In this section, we are reporting the results on the cyclopolmerization of RHMA ether dimers by ATRP (R=ethyl, *n*-butyl and *tert*-butyl), which has not been reported up to now in the literature. First, the synthesis and characterization of the monomers will be discussed. Then, results and discussion on the cyclopolymerization of these monomers by ATRP will be presented.

4.1. DABCO-catalyzed Synthesis of RHMA Ether Dimers

The mechanism of formation of RHMA monomers shown in Figure 4.1 is called Baylis-Hillman reaction. The reaction of formaldehyde with acrylate esters is catalyzed by 1,4-diazabicyclo[2.2.2] octane (DABCO) [32]. The mechanism of the Baylis-Hillman reaction consists of three steps:

1. Nucleophilic Michael addition of the base DABCO to alkyl acrylate, forming the zwitterionic intermediate

2. An aldol type reaction with the aldehyde, forming a second zwitterionic intermediate

3. The subsequent release of the base via β-elimination, leading to the formation of RHMA product

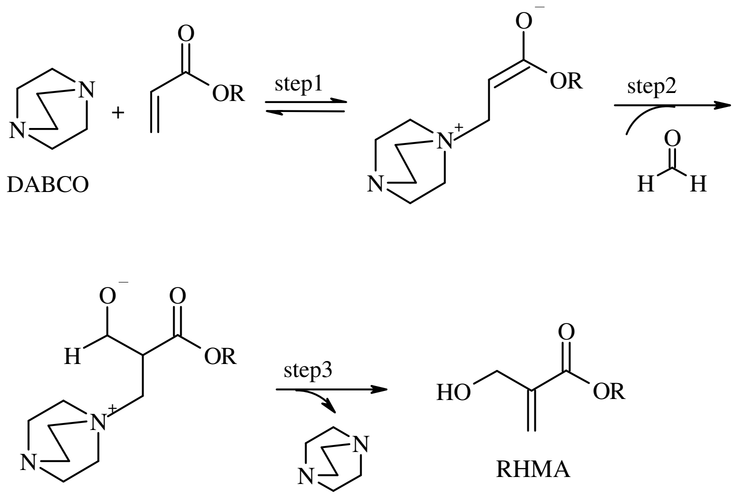


Figure 4.1. DABCO-catalyzed synthesis of RHMA monomers

Step 3, at high temperatures, combines with base-catalyzed ether formation, which generates RHMA ether dimers (Figure 4.2).

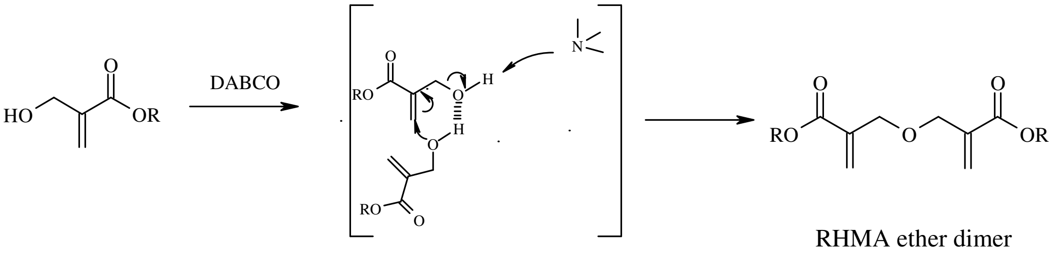


Figure 4.2. DABCO-catalyzed formation of RHMA ether dimers

Conversion of RHMA ether dimers is thermodynamically favorable and merely requires continued heating of the reaction mixture in the presence of DABCO. The presence of water liberated during ether formation can actually cleave the ether back to the RHMA. It would probably facilitate the reaction and improve the overall yield of ether dimer if water were removed during the later stages of the synthesis of RHMA ethers. Similarly, the formation of acetal derivatives of RHMA is also reversible and is gradually driven back to the alcohol and then to the ether as the reaction is forced to completion or final equilibrium [34].

Ethyl, *n*-butyl and *tert*-butyl acrylate ether dimers were successfully synthesized. *Tert*-butyl alcohol was added for the synthesis of *tert*-butyl ester ether dimer in order to improve homogeneity of the reaction mixture and facilitate conversion.

4.1.2. Characterization of RHMA ether dimers

Thin layer chromatography (TLC) is among the most useful tools for following the progress of organic chemical reactions and assaying the purity of organic compunds. The reaction progresses were monitored by thin layer chromatography (TLC) using silica gel (SiO_2) plates and CH_2Cl_2 as the elution and dilution solvent. TLC monitoring of the reaction mixtures showed the appearance and disappearance of what appeared to be an intermediate during the course of the reaction. When reactants disappeared during the reactions, RHMA and its ether dimer appeared. RHMA acetal derivative were also observed as byproduct (Figure 4.3).

In the synthesis of BHMA and TBHMA ether dimer monomers, excellent purity was obtained when acid extraction of the crude reaction mixture dissolved in CH_2Cl_2 was followed by vacuum distillation. The purity of the monomers was confirmed by ^{1}H-NMR and ^{13}C-NMR spectroscopy as listed in the experimental section.

Figure 4.3 shows the ^{13}C solution NMR spectra of TBHMA ether dimer before vacuum distillation. DABCO was competely eliminated with acid extraction. There is no peak around 47.1 ppm. There are peaks corresponding to TBHMA and its ether dimer. TBHMA acetal derivative was also observed as byproduct. Typical chemical shifts are observed for the *tert*-butyl carbons and the two vinylidene carbons as listed in the experimental section. The α-methylene carbon connected to the oxygen atom of the alcohol shows a characteristic downfield shift on going to the ether, i.e., from 63.15 to 69.19 ppm. Peaks around 66.3 ppm and 94.8 ppm belongs to acetal derivative of TBHMA ether dimer.

The ^{13}C-NMR and ^{1}H-NMR specta of TBHMA ether dimer after vacuum distillation are shown in Figure 4.4 and Figure 4.5. The peaks corressponding characteristic carbons and protons are listed in the experimental section. In the ^{13}C-NMR, there is no peak corressponding to α-methylene carbon connected to the oxygen atom of the alcohol of TBHMA. The amount of acetal derivative of TBHMA ether dimer is also negligible.

In the purification of the ethyl monomer, vacuum distillation was not applied. After acid extraction, the organic layer was diluted with methylene chloride : hexane mixture (4:3 ratio) and passed through silica column prepared with the same solvent mixture. Evaporation of the solvent gave the pure monomer, which was also confirmed by ^{1}H-NMR and ^{13}C-NMR as listed in the experimental section

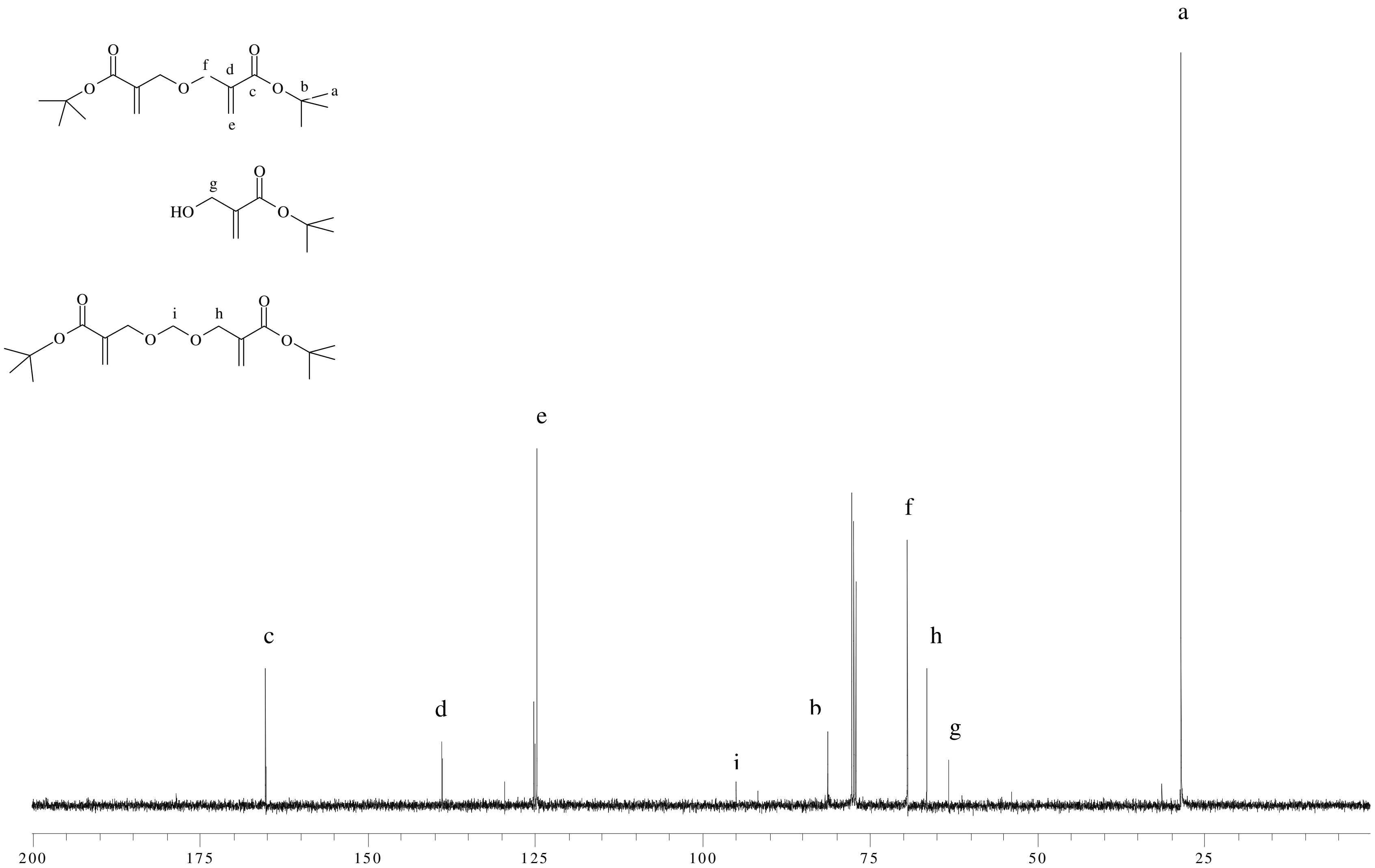


Figure 4.3. C-NMR spectrum of TBHMA before vacuum distillation

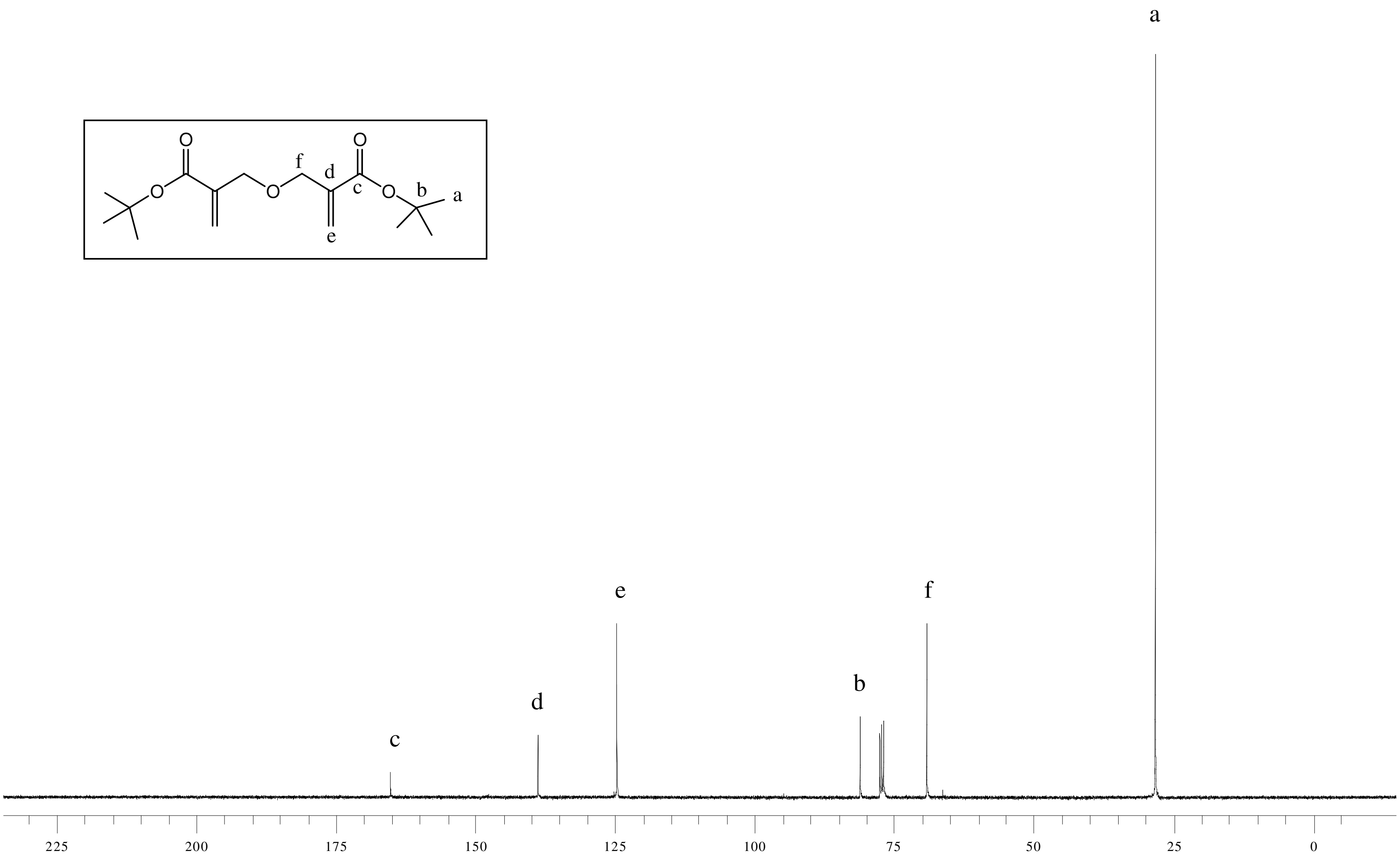


Figure 4.4. ^{13}C-NMR spectrum of TBHMA ether dimer

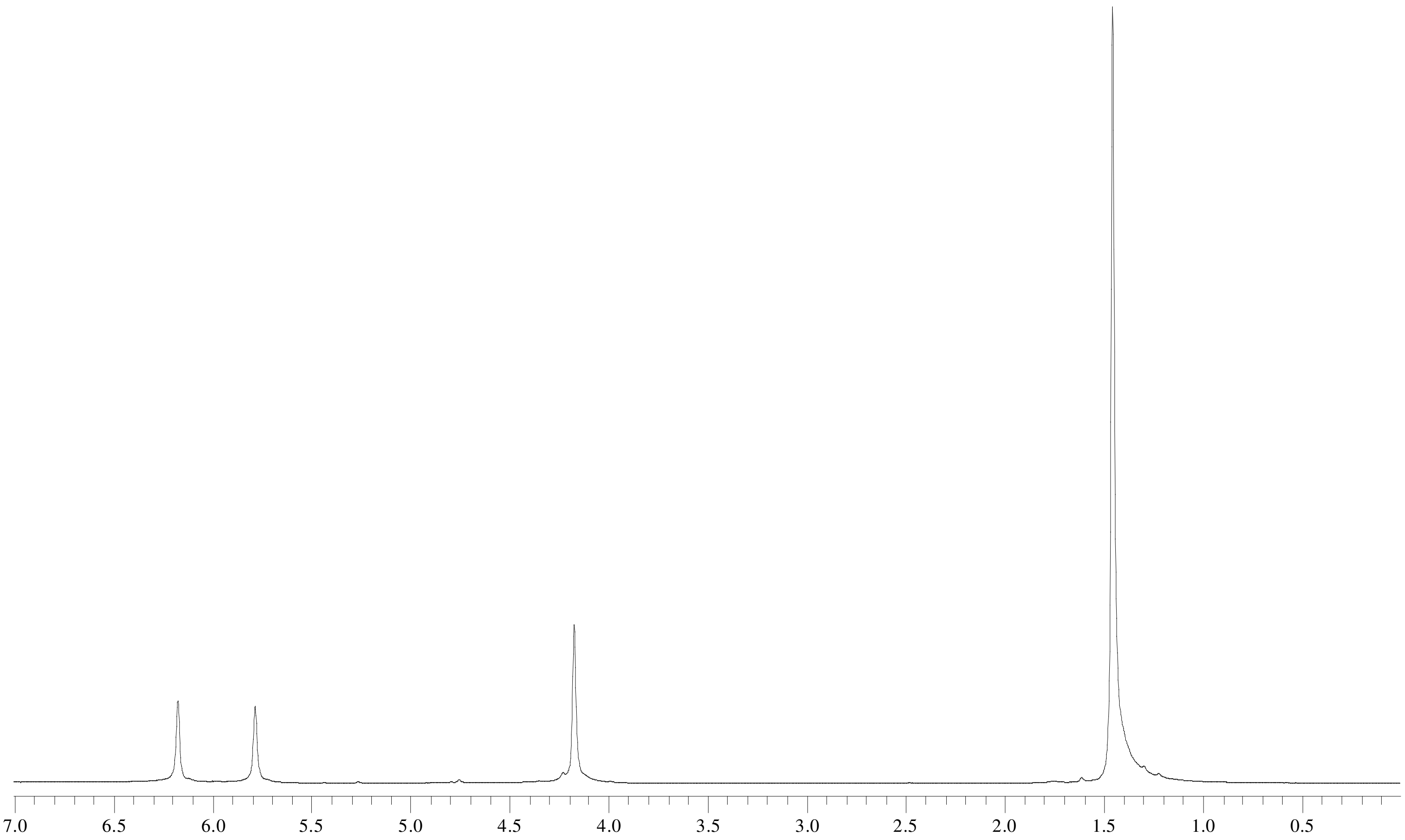


Figure 4.5. ^{1}H-NMR spectrum of TBHMA ether dimer

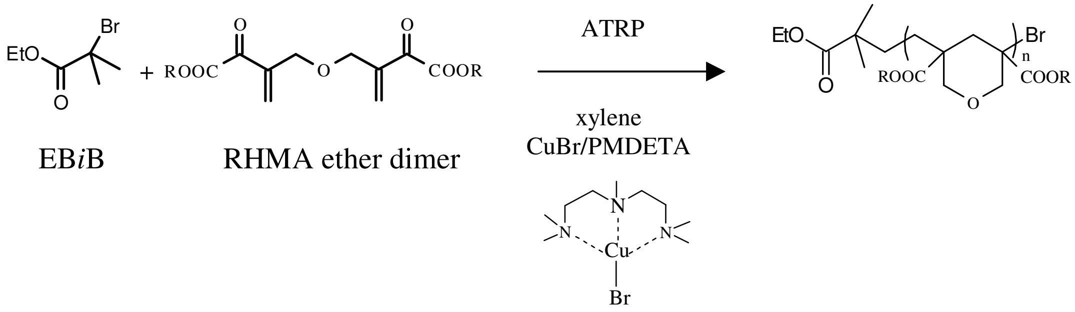
4.2. Cyclopolymerization of RHMA Ether Dimers via ATRP

When conditions are properly adjusted, ATRP allows well-controlled radical polymerization with predictable molecular weights and low polydispersities. The success of ATRP depends on the reversible activation of a dormant alkyl halide species (P_mX) through halojen abstraction by a transition metal complex, which is mostly copper based “Cu(I)X/ligand” (X=Cl, Br).

Selection of the proper combination of transition metal and ligand is critical for success of ATRP. Because the ligands provide solubility and adjust the redox potential of the metal center, offering appropriate reactivity and dynamics for the atom transfer. In the literature, a commercially available tridentate ligand, *N,N,N’,N’,N”*–pentamethyldiethylenetriamine (PMDETA), showed high activity [26]. In this study, the complex formed by Cu(I)Br/PMDETA was chosen as the active catalyst complex. We believed that this complex should lead to efficient ATRP of RHMA ether dimers.

Ethyl 2-bromoisobutyrate (EB*i*B) was employed as the initiator since tertiary activated alkyl bromides give fast initiation [13, 14]. C-Br bond is relatively weaker than C-Cl bond. Therefore, for higher polymerization rate, bromide based ATRP was employed. Polymerizations were carried out in xylene.

Figure 4.6 gives the general structure of the desired cyclopolymerization of RHMA ether dimers via ATRP with used initiator and active catalyst complex



R= $-CH_2CH_3$ (EHMA ether dimer)
R= $-CH_2CH_2CH_2CH_3$ (BHMA ether dimer)
R= $-C(CH_3)_3$ (TBHMA ether dimer)

Figure 4.6. Desired cyclopolymerization of RHMA ether dimers via ATRP

4.2.1. Intra- and Intermolecular Reactions

During the polymerization of RHMA ether dimers, the desired intramolecular reactions lead to cyclic structures and give linear, soluble polymers. Intermolecular reactions with another difunctional monomer give uncyclized pendent groups that can react with other propagating chains to give crosslinked or branched networks [32, 33]. The polymerization via ATRP is shown in Figure 4.7.

As mentioned previously, in the synthesis of cyclopolymers of RHMA ether dimers by conventional free radical polymerization, bulky R groups and high temperatures favor cyclization [32]. However, the effect of these factors were not known in ATRP of RHMA ether dimers. We believed that these factors will be important for us. Therefore, for the controlled synthesis of RHMA ether dimers by ATRP, the bulkiness of R group and temperature effect were investigated.

Other important factors such as solvent effects and ligand effects have not been investigated in this study. However, a more detailed study is currently ongoing.

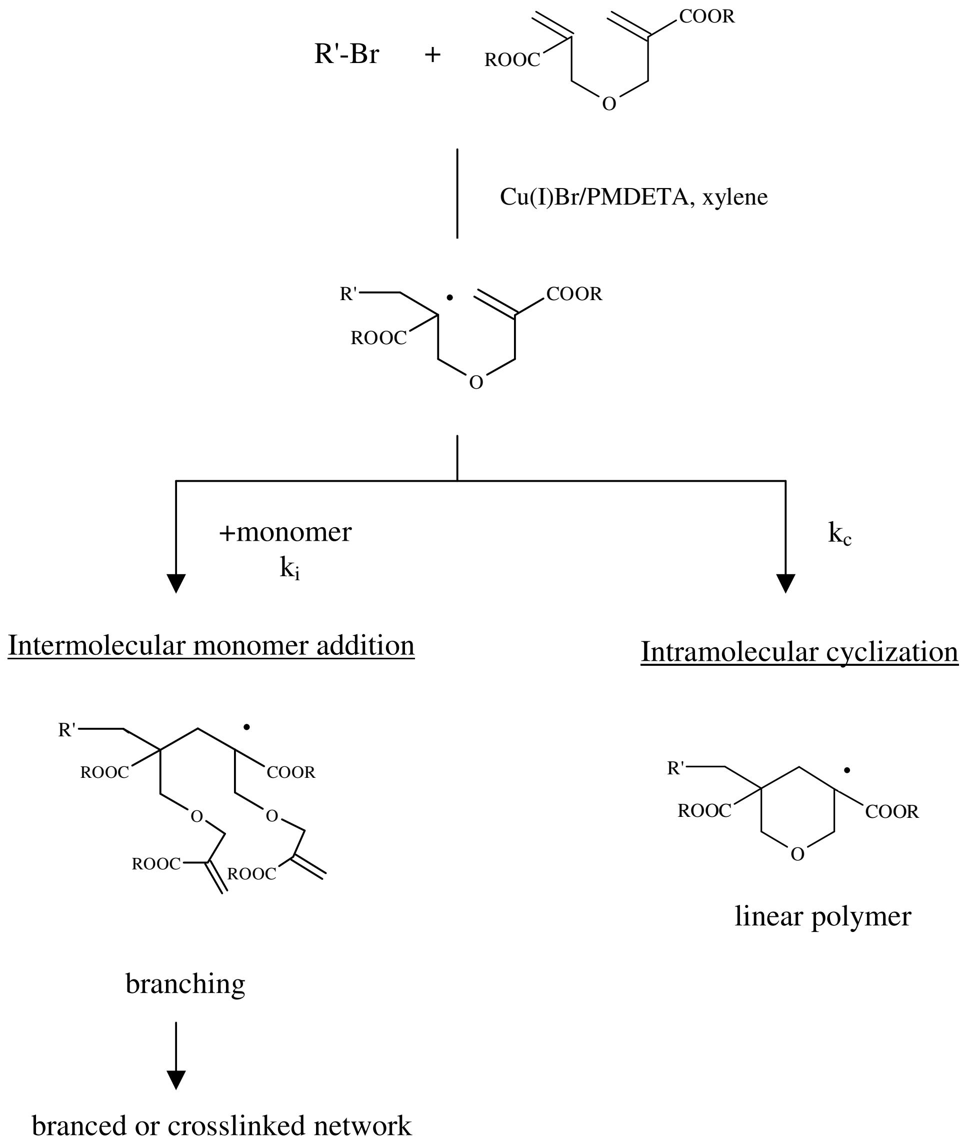
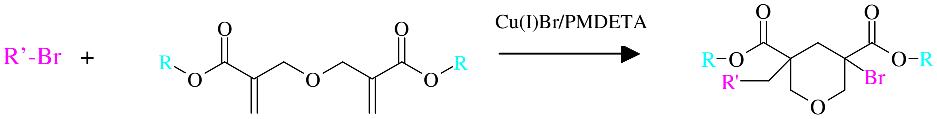


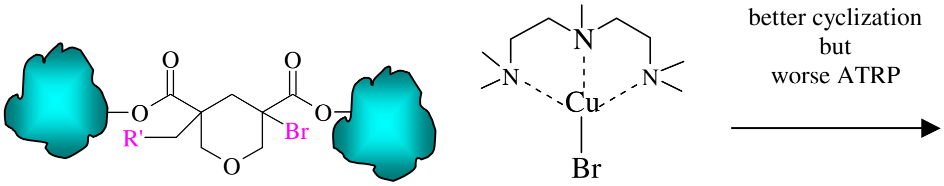
Figure 4.7. Polymerization of RHMA ether dimers via ATRP

4.2.1.1. Steric Effect of R Group

Bulky R groups may increase cyclization efficiency but they can reduce polymerization rate, because metal center is hard to access for halide, which may lead to worse ATRP or difficult activation and deactivation process. In contrast, small R groups may provide better ATRP, but may reduce cyclization efficiency (Figure 4.8). Therefore, the use of sterically different alkyl groups were planned (R=ethyl, *n*-butyl, *tert*-butyl).



Bulky R groups :



Small R groups :

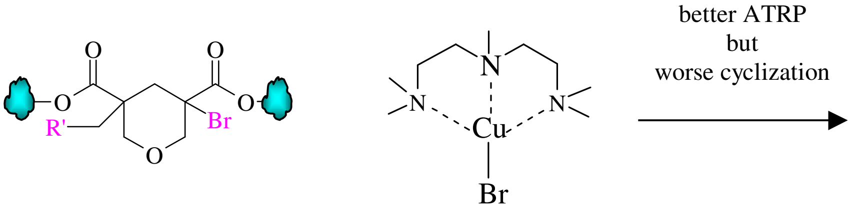


Figure 4.8. Steric factors on monomers

Polymerization of sterically different monomers at 70 °C

To see the effect of bulkiness of R group, RHMA ether dimers with sterically different substituents, ethyl, *n*-butyl, and *tert*-butyl, were polymerized under the same condition. The polymerizations were carried out with $[M]_o$:$[EB\textit{i}B]_o$:$[Cat]_o$=100:1:1 concentration ratios in xylene at 70 °C (Table 4.1).

Table 4.1. The results from ATRP of RHMA ether dimers at 70 °C [a,b]

Entry	Monomer	Time (h)	Conv [c] (%)	$M_{n,cal}$ (10^3 g/mol)	$M_{n,sec}$ (10^3 g/mol)	M_w/M_n
1	EHMA ether dimer	5	x-link	x-link	x-link	x-link
2	BHMA ether dimer	6	13	3.9	17.6	1.90
3	BHMA ether dimer	6	37	11.0	19.1	1.32 [d]
4	TBHMA ether dimer	2	29	8.6	8.6	1.05
5	TBHMA ether dimer	8	36	10.7	10.9	1.19
6	TBHMA ether dimer	18	76	22.6	24.2	1.30

[a] Conditions: solvent: xylene; [M]:[EB*i*B]:[Cat]=100:1:1 concentration ratio

[b] All polymers were soluble except entry 1

[c] Measured by gravimetric methods

[d] Bimodal polymer occurred

In the polymerization of ethyl α-(hydroxymethyl)acrylate (EHMA) ether dimer with $[M]_o$:$[EB\textit{i}B]_o$:$[Cat]_o$=100:1:1 concentration ratio at 70 °C, after 5 hours, insoluble polymer was formed. We believed that the reaction rate of intermolecular monomer addition is much higher than the rate of intramolecular cyclization. Ethyl group does not have enough bulkiness to inhibit intermolecular vinyl group addition reactions which gives highly uncyclized double bonds. These double bonds then most probably lead to highly crosslinked polymer network.

The polymerizations of *n*-butyl α-(hydroxymethyl)acrylate (BHMA) ether dimer were also carried out under the same condition (entries 2 and 3 in the Table 4.1). The resulting polymers were soluble, but they had high polydispersities, which may indicate branching or partial crosslinking of the growing chains. With respect to the ethyl derivative, the bulkier butyl group may have decreased the rate of intermolecular monomer addition and therefore prevented full crosslinking. However, *n*-butyl group may not be bulky enough to favor cyclization only. Uncyclized pendant groups, which could be detected by NMR (Figure 4.9) most probably increased the polydispersities. As an outcome the calculated molecular weights were different than the experimental ones.

^{13}C NMR characterization of the cyclopolymer obtained from BHMA ether dimer at 70 ^{o}C is shown in Figure 4.9 (entry 2 in Table 4.1). It clearly shows characteristic peaks of backbone carbons, cyclic ether groups, and cyclic ester carbonyls. The backbone quaternary carbon peak is at 45 ppm and ether methylenes of the cyclic structure are at 71 ppm. The peaks of ester alkyls are around at 14, 19, 30, and 65 ppm. The cyclic ester carbonyl is at 174 ppm. The spectrum also shows the presence of uncyclized pendant groups. Uncyclized ester carbonyl is around 165 ppm. Uncyclized double bonds are around 125 and 137 ppm.

The results obtained by the polymerizations of the bulkier monomer tert-butyl α-(hydroxymethyl)acrylate (TBHMA) ether dimer were consistent with living and controlled nature of an ATRP system (entries 4, 5, and 6 in the Table 4.1). All resulting polymers were soluble. Polydispersities remained low even at high conversions. In addition, calculated molecular weigths were close to experimental ones. The success in controlling the ATRP of TBHMA ether dimer was likely due to the fact that the rate of intramolecular cyclization was much higher than the rate of intermolecular monomer addition. *Tert*-butyl group has sufficient bulkiness to inhibit intermolecular reactions and favor cyclization reactions.

^{13}C-NMR and ^{1}H-NMR characterization of the cyclopolymer obtained from TBHMA ether dimer at 70 ^{o}C (entry 5 in Table 4.1) is shown in Figure 4.10 and Figure 4.11.

In the ^{13}C-NMR characterization, the spectrum clearly shows peaks characteristic of backbone carbons, cyclic ether groups, ester carbonyls. The backbone quaternary carbon peak is at 45 ppm and ether methylenes of the cyclopolymer are at 71 ppm.The peaks of ester alkyls are at 28 and 82 ppm. The ester carbonyl also at 174 ppm.. There is no evidence about the presence of uncyclized double bonds.

In summary, a strong effect of ester substituent on cyclopolymerization via ATRP was observed. Cyclization efficiency at 70 ^{o}C increased in the following order: ethyl, *n*-butyl, *tert*-butyl esters.

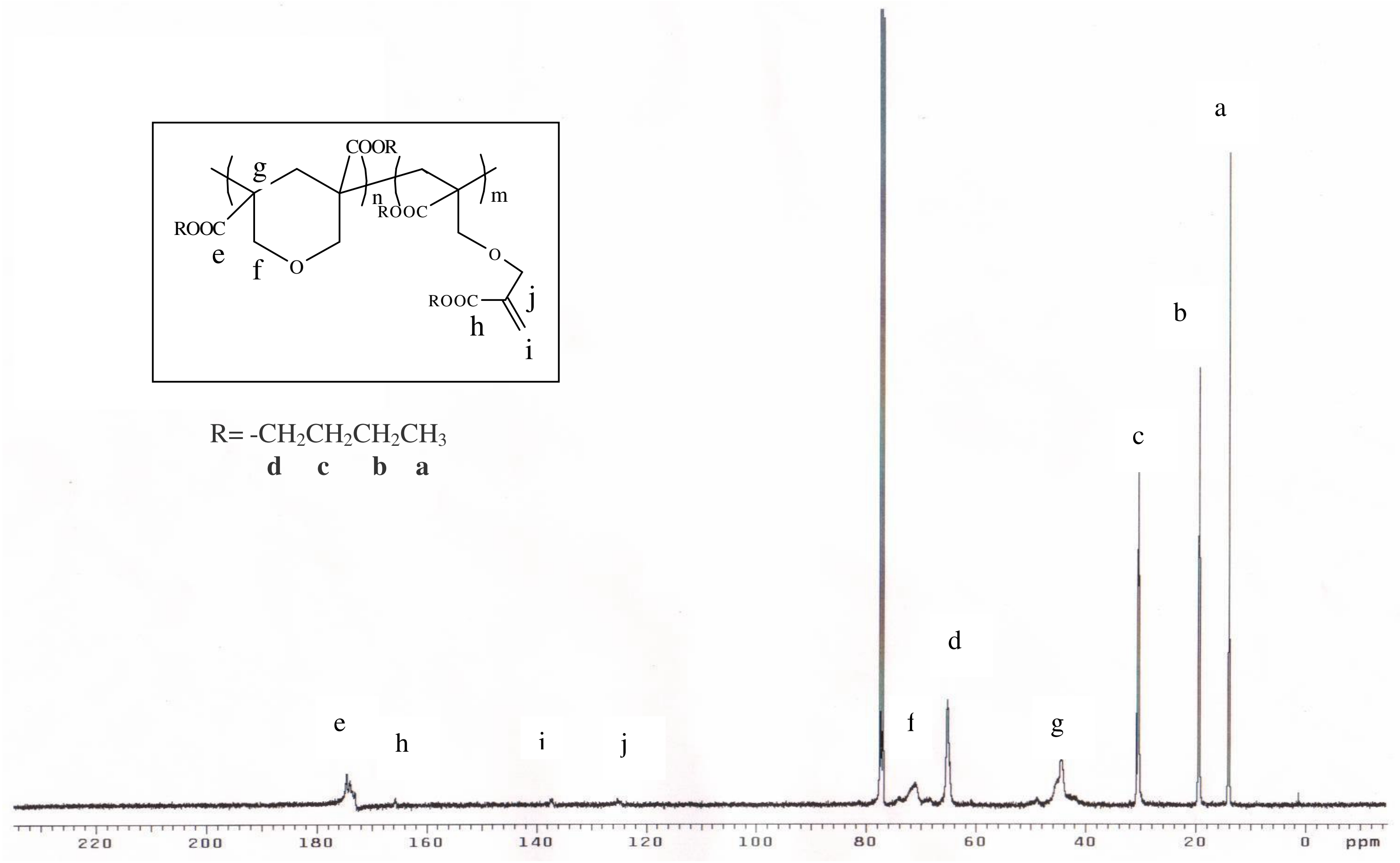


Figure 4.9. ^{13}C-NMR spectrum of poly(BHMA ether dimer)

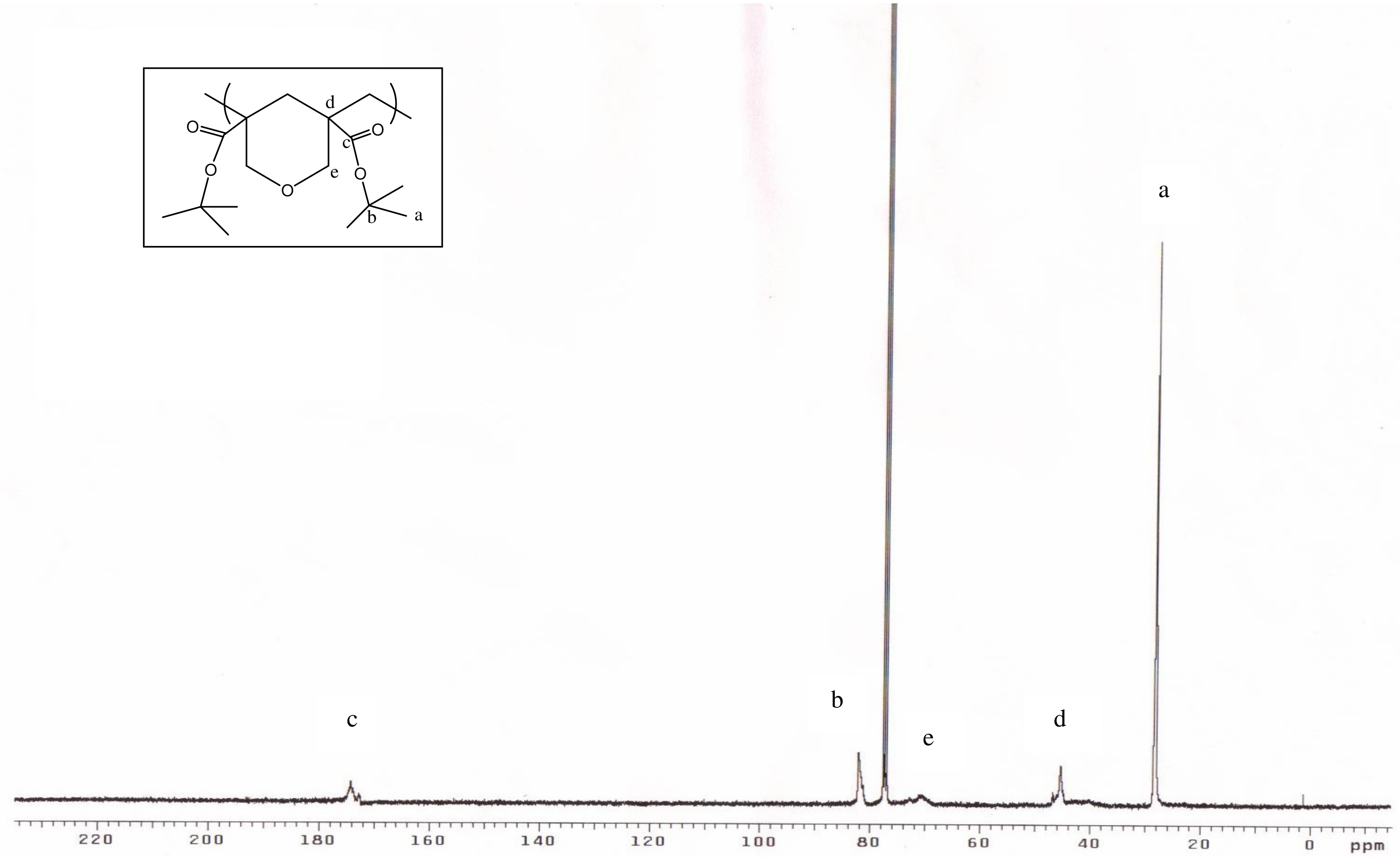


Figure 4.10. ^{13}C-NMR spectrum of poly(TBHMA ether dimer)

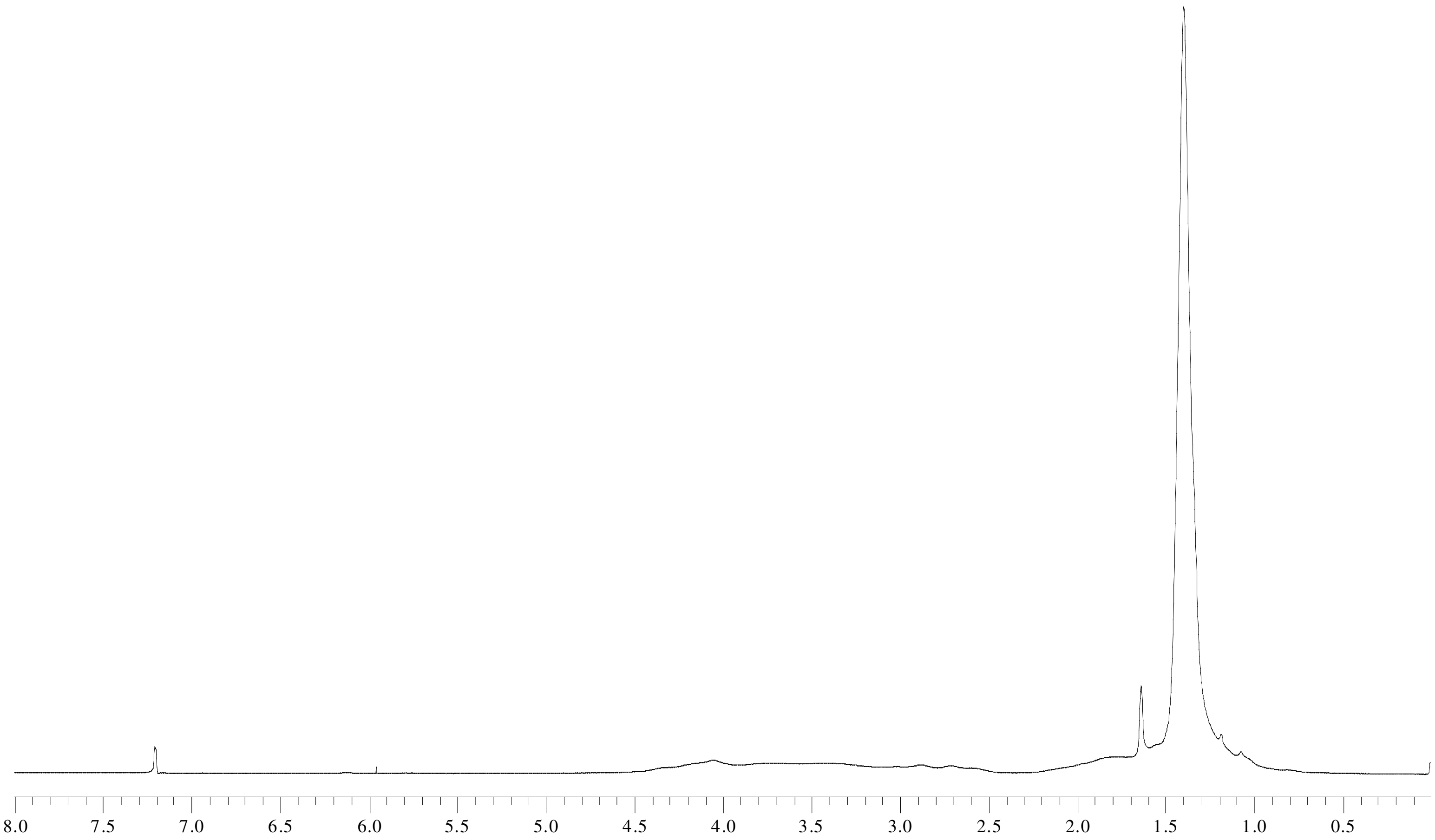


Figure 4.11. ^{1}H-NMR spectrum of poly(TBHMA ether dimer)

Increasing the ratio of monomer to initiator concentration $[M]_0:[I]_0=200:1$ at 70 ^{o}C in the TBHMA ether dimer polymerization resulted in increased molecular weights, whereas molecular weight distribution remained narrow (entry 1 in the Table 4.2) as expected. The polymerization of TBHMA ether dimer with a low $[M]_0:[I]_0=50:1$ ratio was carried out to obtain polymer with a low degree of polymerization (enrty 2 in the Table 4.2).

Table 4.2. The results from ATRP of TBHMA ether dimer at different ratios and 70 ^{o}C [a,b]

Entry	$[M]_o:[I]_o:[Cat]_o$	Time (h)	Conv[c] (%)	$M_{n,cal}$ (10^3 g/mol)	$M_{n,sec}$ (10^3 g/mol)	M_w/M_n
1	200:1:1	18	43	25.6	16.4	1.16
2	50:1:1	6	63	9.4	5.8	1.17
3	100:0:0	24	0	-	-	-

[a] Conditions:$[M]_o$ =0.96 M in xylene

[b] All polymers were soluble

[c] Measured by gravimetric methods

The low polydispersities obtained and the closeness of the theoretical molecular weights to the experimental ones directed us to a more detailed investigation. First, a blank experiment was done (entry 3 in Table 4.2) to show that polymerizations were mainly due to the ATRP process and not air or thermal polymerization. No polymerization was observed in the absence of the initiator at 70 ^{o}C.

Second, kinetics of ATRP of TBHMA ether dimer were investigated. The results of the kinetic study of TBHMA ether dimer at 70 ^{o}C are shown in Table 4.3. The data indicates that controlled polymerizations were achieved with $[M]_o:[I]_o:[Cu(I)/PMDETA]_o=100:1:1$ concentration ratio. The measured molecular weights were close to the calculated values. The molecular weight distributions remained quite low during the ATRP process.

Table 4.3. The results from the kinetic study of TBHMA ether dimer ATRP at 70 °C [a,b]

Entry	Time (h)	Conv[c] (%)	$M_{n,cal}$ (10^3 g/mol)	$M_{n,sec}$ (10^3 g/mol)	M_w/M_n
1	1.5	45.6	13.6	13.5	1.12
2	3	66.9	19.9	18.8	1.15
3	4.5	76.4	22.8	21.0	1.18
4	6	85.6	25.5	22.3	1.19

[a] Conditions: $[M]_o$=0.96 M in xylene; $[M]_o$:$[EB\textit{i}B]_o$:$[Cat]_o$=100:1:1

[b] All polymers were soluble

[c] Measured by gravimetric methods

A linear plot of ln ($[M]_0/[M]$) versus time was observed for the ATRP of TBHMA ether dimer, which indicates that the number of active species (k_p [$P^\cdot$]) remains essentially constant throughout the course of the reaction (Figure 4.12). This behavior, combined with the observation of linear evolution of molecular weight with conversion (Figure 4.13), show that the process is well controlled, and that initiation is fast.

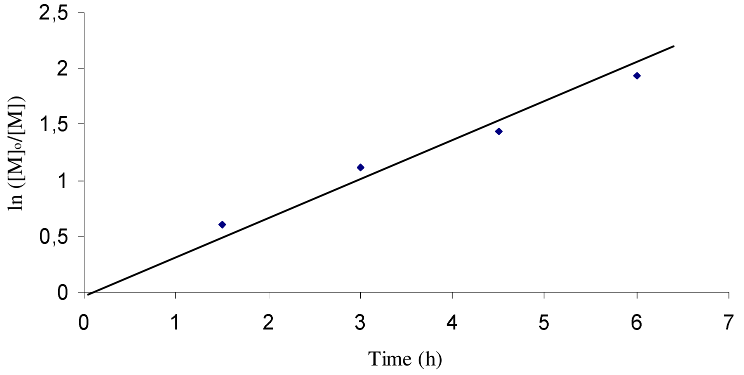


Figure 4.12. Plot of ln ($[M]_0/[M]$) *versus* time for TBHMA ether dimer polymerization by ATRP. Conditions: 70 °C; [M]=0.96 M; $[M]_o$:$[I]_o$:$[Cu]_o$:$[L]_o$=100:1:1:1

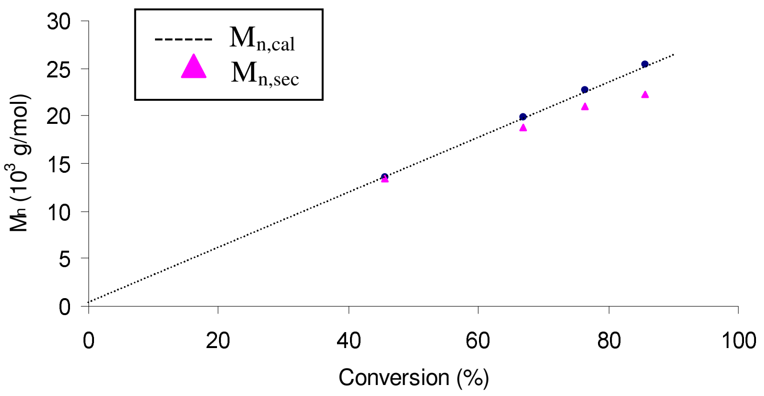


Figure 4.13. Plot of M_n *versus* conversion for TBHMA ether dimer polymerization by ATRP. Conditions: 70 ^{o}C; [M]=0.96 M; $[M]_o$:$[I]_o$:$[Cu]_o$:$[L]_o$=100:1:1:1

According to the literature in conventional free radical polymerization of TBHMA ether dimer, high temperatures favor the cyclization. Therefore the effect of temperature was also investigated.

4.2.1.2. Temperature Effect

Up to now, polymerizations were carried out 70 ^{o}C. To see the temperature effect on ATRP cyclopolymerization system, polymerizations were also caried out at 50 and 100 ^{o}C with $[M]_o$:$[EB\textit{i}B]_o$:$[Cat]_o$=100:1:1 concentration ratio.

Polymerization at 50 ^{o}C

The ATRP of TBHMA ether dimer gave insoluble polymer in 18 hours at 50 ^{o}C. We believed that the reaction rate of intermolecular monomer addition is much higher than the rate of intramolecular cyclization. 50 ^{o}C is not enough to promote cyclization and ATRP of the individual acrylate units at low temperature give rise to a crosslinked network.. The t-butyl ether dimer could not overcome its activation energy for cyclization at 50 ^{o}C.

Polymerization at 100 °C

The polymerizations of BHMA and TBHMA ether dimer at 100 °C (Table 4.4) resulted in the increase of the polydispersities when compared to 70 °C (Table 4.1). However, the polydispersities of poly(TBHMA ether dimer), in general, were lower than 1.5. All polymers were soluble.

Table 4.4. The results from ATRP of RHMA ether dimers at 100 °C [a,b]

Entry	Monomer	Time (h)	Conv[c] (%)	$M_{n,cal}$ (10^3 g/mol)	$M_{n,sec}$ (10^3 g/mol)	M_w/M_n
1	BHMA ether dimer	8	41	12.2	24.3	3.15
2	BHMA ether dimer	18	62	18.5	29.8	10.09
3	TBHMA ether dimer	2	62	18.5	17.6	1.13
4	TBHMA ether dimer	8	60	17.9	19.1	1.44
5	TBHMA ether dimer	18	71	21.2	18.5	1.48

[a] Conditions: $[M]_o$=0.96 M in xylene; $[M]_o:[EB\textit{i}B]_o:[Cat]_o$=100:1:1

[b] All polymers were soluble

[c] Measured by gravimetric methods

High temperatures may increase cyclization. However, at high temperatures, the events which may lead to high polydispersities can be summarized as follows:

- Uncontrolled Monomer Additions
- Catalyst Decomposition or Precipitation
- Side Reactions (termination reactions, reaction of residual oxygen, etc.)

Uncontrolled Monomer Additions

Increasing the temperature most probably increases both the rate of ATRP process and the conventional radical addition reactions which happens before the deactivation of the growing radical. The polydispersity may increase with increasing temperature due to the relative increase of the radical propagation rate constant with respect to the atom transfer equilibrium rate constants. As a result, conventional radical polymerization may become more pronounced. Another words, uncontrolled monomer addition reactions may be more possible before deactivation, which leads to higher polydispersities.

Catalyst Decomposition or Precipitation

In general, the solubility of the catalyst increases at higher temperatures. However, decomposition of catalyst complex may also occur with the increasing temperature, which leads to precipication of Cu(I/II)/Br and lower polymerization rate. As a result of the decrease of the concentration of activator and deactivator catalyst complex, the control of the polymerization may be disturbed or not since the Cu(I)/Cu(II) concentration ratio is the determining factor for the control of the polymerization. Cu(I) is activator and Cu(II) is deactivator. Higher activator concentration relative to deactivator concentration gives higher polymerization rate and higher polydispersity. Because uncontrolled monomer addition reactions may be more possible before deactivation. Another words, conventional radical polymerization may become more pronounced. However, higher deactivator concentration relative to activator concentration leads to controlled polymerization but slower polymerization rate. Therefore, decomposition of catalyst complex may be the reason of the variable conversions and somewhat higher polidispersities despite of same polymerization conditions and reaction times. Therefore, the reason of the lower conversion and higher polydispersity of entry 4 relative to entry 3 in the Table 4.4 may be catalyst precipitation.

Side Reactions

With the higher inrease of the activation rate relative to deactivation rate at elevated temperatures, the presence of high amount of active species may lead to early termination reactions, which suggests a poorer control of the polymerization. The reactions may be very fast at high temperature. However, chain transfer and other side reactions become more pronounced at elevated temperatures. Therefore, multimodal distribution of polymer chains may be observed in GPC analysis. At higher temperatures it is also known that residual oxygen may induce polymerization, which may result in higher polydisperisties as well [26]. The reason is the reaction of oxygen with copper and finally precipitation of the CuO. The precipitation of CuO results in the decrease of the amount of the deactivator, Cu(II), which also leads to uncontrolled monomer additions before deactivation and higher polydispersities.

In this study, we also investigated the effect of catalyst to initiator molar ratio. The reason is to increase the polymerization rate with increasing catalyst concentration.

4.2.2. Catalyst to Initiator Molar Ratio Effect

Although the rate of the reaction increased with increasing catalyst concentration, the higher polydispersities indicated poorer control over the polymerization.

The data in Table 4.1 indicates that controlled polymerizations were achieved with 1:1 catalyst-to-initiator ratios at 70 ^{o}C and that all the polymerizations showed high initiator efficiencies (initiator efficiency $f = M_{n,cal}/M_{n,sec}$) and low polydispersities. With a increase of the catalyst-to-initiator ratio, 2:1, the rate of polymerization increased and the initiator efficiency decreased. 98 per cent conversion was obtained in 3.75 hours (entry 2 in Table 4.5). The relatively lower initiator efficiency at higher catalyst-to-initiator ratio was likely due to the higher radical concentration at the beginning of the polymerization which resulted in the termination of some of the propagating chains by radical coupling reactions.Therefore, the polydispersity is rather high, indicating poor control.

When the amount of catalyst was increased at 100 ^{o}C, the reaction solution quickly became viscous, and the conversion reached 77 % within 12 minutes, which indicates that polymerization rate highly increased with increasing catalyst amount at 100 ^{o}C (entry 3 in Table 4.5). The reaction mixture was light green and homogeneous at the beginning, but turned heteregeneous at higher conversions. The heterogeneity was likely due to the low solubility of copper(II), generated by irreversible chain termination reactions, in the polymerization solution.

Table 4.5. The results from ATRP of RHMA ether dimers with $[M]_o$:$[EB\textit{i}B]_o$:$[Cat]_o$=100:1:2 concentration ratio [a,b]

Entry	Monomer	Temp	Time	Conv[c]	$M_{n,cal}$	$M_{n,sec}$	M_w/M_n
		(°C)	(h)	(%)	(10^3 g/mol)		
1	BHMA ether dimer	70	6	27	8.0	17.6	2.12
2	TBHMA ether dimer	70	3.75	98	29.2	27.6	1.97
3	TBHMA ether dimer	100	0.2	77	22.9	35.1	2.05

[a] Conditions: $[M]_o$=0.96 M in xylene

[b] All polymers were soluble

[c] Measured by gravimetric methods

4. CONCLUSIONS

In summary, a strong effect of ester substituent on cyclopolymerization via ATRP was observed. For the ethyl, and *n*-butyl ester ethers , it is much more difficult to form controlled high molecular weight, linear polymer with no pendent (uncyclized) acrylate units. Cyclization efficiency at 70 ^{o}C increased in the following order: ethyl, *n*-butyl, *tert*-butyl esters.

Temperature also affected the control of the polymerizations. 50 ^{o}C is not enough to activate TBHMA ether dimer for cyclization. Insoluble polymer occurred. Although high temperatures favor cyclization, the polymerizations of BHMA and TBHMA ether dimer at 100 ^{o}C resulted in the increase of the polydispersities when compared to 70 ^{o}C. However, the polydispersities of poly(TBHMA ether dimer), in general, were lower than 1.5. The increase in the poldispersity is likely due to the fact that uncontrolled monomer additions, catalyst decomposition and other side reactions become more pronounced at elevated temperatures.

The results indicate that the cyclopolymerizations of TBHMA ether dimer by ATRP were consistent with living and controlled nature of the polymerization under suitable conditions. Clearly, presence of the bulky tert-butyl ester facilitated cyclopolymerization. According to the results of kinetic study at 70 ^{o}C with the [M]:[EBiB]:[Cat]=100:1:1 concentration ratio, high conversions and low molecular weight distributions were obtained as well as linear evolutions of molecular weight with conversion.

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