

STRUCTURE-REACTIVITY RELATIONSHIP OF ACRYLIC ACID ESTER ETHER  
DIMERS IN ATRP

by

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B.S. in Chem., Boğaziçi University, 2005

Submitted to the Institute for Graduate Studies in  
Science and Engineering in partial fulfillment of  
the requirements for the degree of  
Master of Science

Graduate Program in Chemistry

Boğaziçi University

2007

**to my lovely family**

## ACKNOWLEDGEMENT

I would like to express my deepest gratitude to my thesis supervisor, Assistant Prof. Dr. A. Ersin Acar for his invaluable guidance, support, encouragement and help in every stage of this project. It was a great pleasure for me to work with him.

I also would like to thank to Prof. Dr. Selim Küsefođlu and Prof. D.r Ümit Tunca for their advices and comments on the final manuscripts.

I would like to extend my thanks to Burcu Selen Çađlayan and Ayla Türkekul for their great patience and help running a large number of NMR experiments supporting my laboratory works. I am also thankful to Gökhan Çaylı and Sinan Şen because of their helps for TGA and DSC analysis.

I would like to thank my labmates Selda Erkoç, Engin Dođan, Aydın Can, Erhan Özkal and Berçem Dutađacı for being helpful and their frinedship. I also would like to express my thanks to Ceren Yılmaz who helped me in the early stage of the experiments.

I also thank to Hanife Tunç and Özge Yılmaz for their endless support and friendship.

I am greatful to the all the members of the chemsitry department. I wish to thank especially to Hülya Metiner, always willing to help and share the problems.

Finally, I owe great thanks to my family for their encouragement, support and endless love throught my life.

## ABSTRACT

### STRUCTURE-REACTIVITY RELATIONSHIP OF ACRYLIC ACID ESTER ETHER DIMERS IN ATRP

Aliphatic cyclopolymers synthesized by the cyclopolymerization of alkyl  $\alpha$ -(hydroxymethyl)acrylate ether dimers have high thermal stabilities, high glass transition temperatures and show limited shrinkage during polymerization. Cyclopolymerizations of RHMA ether dimers by ATRP have been previously investigated in the literature for three different alkyl groups: ethyl, n-butyl and *tert*-butyl groups. It was found that as the bulkiness of the substituent group increased cyclization efficiency also increased. However, ATRP cyclopolymerization has not been investigated with dimers that contain bulkier substituents. It is known that cyclization efficiency in conventional free radical polymerization is higher for adamantyl  $\alpha$ -(hydroxymethyl)acrylate ether dimer than the ones containing smaller alkyl groups such as ethyl, t-butyl. However, the effect of such bulky groups on the ATRP process was unknown. Therefore, ATRP's of more bulky RHMA ether dimers such as adamantyl and cyclohexyl  $\alpha$ -(hydroxymethyl)acrylate ether dimers were investigated. CuBr/PMDETA was employed as the catalyst complex and polymerizations were carried out in xylene. The results showed that, highly cyclized soluble aliphatic cyclopolymers could be obtained by the ATRP process with both monomers. However, the polydispersities of the cyclopolymers obtained were higher than the cyclopolymers obtained with the t-butyl derivative, indicating that the ATRP process was less controlled with bulkier groups. The livingness of the cyclopolymers was checked by the copolymerization studies with n-butyl and t-butyl acrylate comonomers where the cyclopolymers obtained were used as macroinitiators. Results suggest that cyclopolymers were living, however, copolymers obtained had high polydispersities most probably due to the slow initiation from the cyclic backbone. Preliminary studies on the physical properties of the cyclopolymers were also carried out.

## ÖZET

### ATRP HALKALI POLİMERLEŞTİRİLMESİNDE YAPI-ÖZELLİK İLİŞKİLERİ

Alkil  $\alpha$ -(hidroksimetil) eter dimerlerinin (RHMA) halkalı polimerleştirilmesiyle sentezlenen alifatik halkalı polimerler yüksek ısıl dayanıklılığa, yüksek camsı geçiş sıcaklığına sahiptirler ve polimerleşme sırasında sınırlı çekme gösterirler. RHMA eter dimerlerinin ATRP ile halkalı polimerleştirilmesi literatürde üç farklı alkil grup için araştırılmıştır: etil, n-bütil ve *tert*-bütil. Alkil grupların hacminin artmasıyla halkalaşma etkinliğinin arttığı bulunmuştur. Fakat, ATRP halkalı polimerleştirilmesi daha hacimli alkil grup içeren dimerlerle araştırılmamıştır. Serbest radikal polimerleşmesinde halkalaşma etkinliği adamantil  $\alpha$ -(hidroksimetil) eter dimerinde etil, t-butyl gibi daha küçük alkil gruplar içeren dimerlere oranla daha yüksektir. Fakat, bu büyük hacimli grupların ATRP üzerinde etkisi bilinmemektedir. Bu yüzden, daha hacimli RHMA eter dimerlerinin, mesela adamantil ve sikloheksil  $\alpha$ -(hidroksimetil) eter dimerleri, ATRP'leri araştırılmıştır. CuBr/PMDETA katalizör olarak kullanılmıştır ve polimerleşme ksilende gerçekleştirilmiştir. Sonuçlar gösterdi ki, iki monomerle gerçekleştirilen ATRP yöntemi ile yüksek derecede halkalı çözüner alifatik polimerler elde edilebilmektedir. Fakat, elde edilen halkalı polimerlerin moleküler ağırlık dağılımları t-bütil türeviyle elde edilen halkalı polimerlerden daha yüksektir. Bu, ATRP yönteminin, daha hacimli gruplarla daha az kontrollü olduğunu gösterir. Halkalı polimerlerin yaşayan olma özellikleri, elde edilen polimerlerin makrobaşlatıcı olarak kullanılarak, n-bütil ve t-bütil komonomerleriyle kopolimerleşme çalışmalarıyla kontrol edildi. Sonuçlar gösterdi ki, halkalı polimerler yaşayanıdır, fakat elde edilen kopolimerler yüksek ihtimalle halkalı yapıdan yavaş başlamadan (tetiklenmeden) dolayı yüksek moleküler ağırlık dağılımına sahiptirler. Halkalı polimerlerin fiziksel özellikleri üzerinde ön çalışma gerçekleştirilmiştir. Elde edilen polimerlerin yüksek camsı geçiş sıcaklıklarına sahip oldukları ve yüksek sıcaklıklara dayanıklı oldukları gözlemlenmiştir.

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## LIST OF ABBREVIATIONS

ATRP	Atom Transfer Radical Polymerization
ATRA	Atom Transfer Radical Addition
RHMA	Alkyl $\alpha$ -(hydroxymethyl)acrylate
ADHMA	1-Adamantyl $\alpha$ -(hydroxymethyl)acrylate
CHMA	Cyclohexyl $\alpha$ -(hydroxymethyl)acrylate
PMDETA	<i>N,N,N,N',N'</i> -pentamethyldiethylenetriamine
DABCO	1,4-Diazabicyclo[2.2.2]octane
EB <i>i</i> B	Ethyl 2-bromoisobutyrate
n-BuLi	n-Butyllithium
GPC	Gel Permatation Chromatography
NMR	Nuclear Magnetic Resonans Spectroscopy
T <sub>g</sub>	Glass Transition Temperature
TLC	Thin Layer Chromatography
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
SEC	Size Exclusion Chromatography

# 1. INTRODUCTION

## 1.1. Powder Coating and Material Requirements

Since its first use in 1967 in Australia, powder coating has been used in a wide range of applications. In powder coatings, the coating particles are sprayed over a substrate, subsequently melted and cured at relatively high temperatures, 150°C to 220°C.

Powder coating uses coating materials in dry, powdered form. It works on the principle that opposite charges attract. The powder is pneumatically fed from a reservoir through a spray gun where the powder gains low amperage, high-voltage positive charge. Parts to be painted are electrically grounded so that the positively charged powder particles are strongly attracted to the parts' surfaces. The powder coated part is then passed through an oven where the powder melts and fuses into a smooth coating [1].

Powder coatings do not produce hazardous overspray wastes or wastewater sludges, and most importantly, do not release volatile organic compounds (VOC's) when cured. With powder coating, users can collect the powder overspray and reuse it, resulting in transfer efficiencies up to 99%. The continuing success of powder coatings is not only due to their economical and ecological advantages but also due to their improved performance and the variety of substrates on which they can be applied. The durability of certain powder coatings is at least equal to, if not higher than highly durable liquid paints and, today, they are applied not only on metallic substrates such as aluminum and steel, but also on cladding elements and other nonmetallic substrates [2,3].

The powder resin mixtures that are used in powder coatings can be divided into two, as thermoplastic and thermoset resin mixtures:

- Thermoplastic resins form a coating, but do not undergo a change in molecular structure. These resins can be re-melted after they have been applied.

Thermoplastic resins are mainly used in functional coatings, such as thick, protective coatings on dishwasher trays.

- Thermoset resins crosslink to form a permanent film that withstands heat and can not be re-melted. They are used for decorative and protective coatings for architectural structures, on appliances and furniture, and elsewhere. Thermosetting resins are characterized by their excellent adhesion to metal.

Among current materials, polyester systems have the leading share in the powder coating world market because of their advantages and good cost performance. Two types of polyester resins, aromatic and aliphatic, are being used. Aromatic polyesters have high glass transition temperatures ( $T_g$ ) but they are not weathering stable due to the aromatic uv-chromophores that they contain in their structure. Their chemical stabilities are also low compared to aliphatic polyesters. The aliphatic polyesters, on the other hand, although they are chemically more stable and have higher weathering stabilities, they suffer from low  $T_g$ 's. In order to achieve the  $T_g$  values that are required in powder coatings (55-70°C), the molecular weight of the aliphatic polymers have to be increased so much that the resulting coatings end up having low crosslink densities, and thus, poor mechanical properties and low chemical resistance.

As a consequence, there is a need for new aliphatic polymers with excellent chemical stability and high  $T_g$ .

## **1.2. Aliphatic Cyclopolymers with High Glass Transition Temperatures Derived from Alkyl $\alpha$ -(Hydroxymethyl)acrylate (RHMA) Ether Dimers**

Polymers with high degrees of cyclization derived from cyclopolymerizations of 1,6-dienes are advantageous in terms of their excellent thermal stability and high glass transition temperatures compared to conventional linear aliphatic polymers (Figure 1.1) [4]. In addition, with these monomers, shrinkage during polymerization is low with respect to non-cyclic linear analogues [5,6]. Taking all into consideration, aliphatic cyclopolymers may be good candidates as base resins for powder coatings.

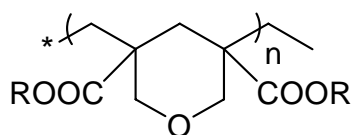


Figure 1.1. An example of aliphatic cyclopolymer obtained by cyclopolymerization of 1,6-dienes.

Cyclopolymerization can be performed by free radical polymerization of 2,6-disubstituted 1,6-dienes through sequential intramolecular-intermolecular propagation to give soluble cyclopolymer under appropriate conditions. For example alkyl  $\alpha$ -(hydroxymethyl)acrylate ether dimers with different R-groups have been successfully cyclopolymerized via conventional free radical polymerization (Figure 1.2) [7,8]. The polymers obtained contain six-membered tetrahydropyran repeat units in their backbones.

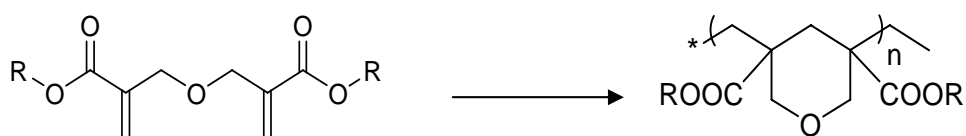


Figure 1.2. Cyclopolymerization of alkyl  $\alpha$ -(hydroxymethyl)acrylate ether dimers

### 1.2.1. Factors Affecting the Cyclopolymerization of Alkyl $\alpha$ -(Hydroxymethyl)acrylate Ether Dimers

Factors which generally affect the cyclopolymerization include monomer concentration, steric interaction of the ester functionality, and polymerization temperature[9].

#### 1.2.1.1. Steric Interaction of the Ester Functionality

In the cyclopolymerization of  $\alpha$ -(hydroxymethyl)acrylates ether dimers, substituent effects on cyclization efficiency have been attributed qualitatively to steric effects, which either inhibit intermolecular monomer addition or promote intramolecular cyclization as shown in the Figure 1.3. Monomers with bulky ester groups appeared to polymerize through the available intramolecular cyclization pathway with greater efficiency than the

monomers without significant steric constraints [10]. The fraction of cyclized units in cyclopolymers for different ether dimers of  $\alpha$ -(hydroxymethyl)acrylates was in the order of adamantyl>t-butyl>isobornyl>ethyl>methyl [11].

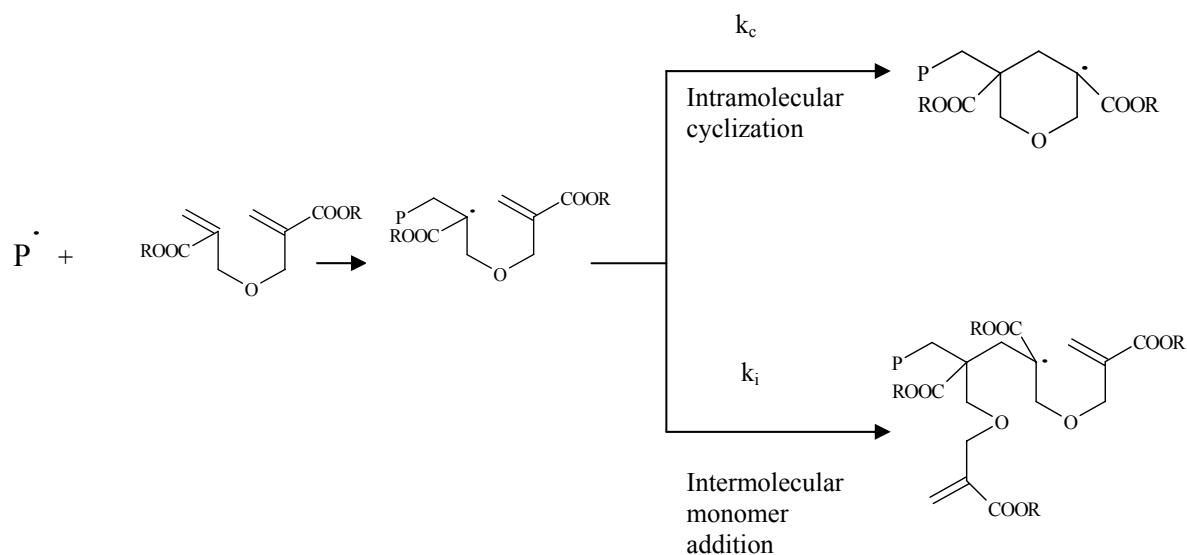


Figure 1.3. Intra- and intermolecular cyclization pathways of RHMA ether dimers.

### 1.2.1.2. Polymerization Temperature

While the enthalpy term (in the free-energy expression for the cyclization process) is temperature independent, the entropy term has a temperature factor and that, since the entropy change is less favored for cyclization than for the intermolecular addition, increasing temperature disfavors the latter more than cyclization; that is, cyclization is favored [4].

### **1.2.2. Comments on the Limitations of the Current Available Cyclopolymers**

All the cyclopolymers that were discussed previously have been synthesized by conventional free radical polymerization technique. Therefore, the cyclopolymers obtained contained dead-end groups that could not be functionalized further. Since the majority of the powder coating base resins require end group functionalities such as alcohol or acid, the conventional radical polymerization can not be used for the synthesis of end-functional cyclopolymers. Therefore, we became interested in ‘living’ controlled radical

polymerization techniques which are known to give rise to living polymers that can be end-functionalized further. In addition, these techniques give polymers with predictable molecular weights and low polydispersities.

### **1.3. Controlled/Living Radical Polymerization**

The basic theory and comprehension of radical polymerization was established by the 1950s [12]. There are lots of publications about conventional radical polymerization and it is still one of the most common used method to synthesize polymers. The conventional radical polymerization can be applied to the polymerization of large numbers of monomers under mild conditions. Second advantage is facile copolymerization between various monomers [13]. In addition, free radical polymerization requires only absence of oxygen and polymerization can be done in the presence of large amounts of water and at temperatures ranging from 0°C to 100°C. However, as mentioned before, there are some limitations in the conventional free radical polymerization such as poor control over molecular weight, high polydispersity, dead-end functionality, chain architecture and composition [12].

Living polymerizations such as anionic, cationic, coordination, ring opening polymerizations are almost free from side reactions such as termination and chain transfer reactions, and thus, can generate polymers with well defined architectures, controlled molecular weights and living end groups [14]. Also living polymerizations provide synthesis of polymers with low polydispersities. However, monomers, polymerization conditions may be limited for the type of the living polymerization technique chosen. In some cases functional groups on the monomers may result in side reactions, and thus, for some processes control over the polymerization can be difficult.

To overcome the limitations, controlled radical polymerization has been developed and there is a sharp increase in the number of the publications on the controlled radical processes from 1990s up to now. In controlled radical polymerization, synthesized polymers have narrow molecular weight distributions ( $1.1 < M_w/M_n < 1.5$ ). During polymerization a linear growth of molecular weight with monomer conversion is observed (Figure 1.4). The polymers obtained have living end groups. Different polymer

architectures (linear, star, comb and branched) as well as polymer compositions (random, block, graft and gradient copolymers) can be achieved [15].

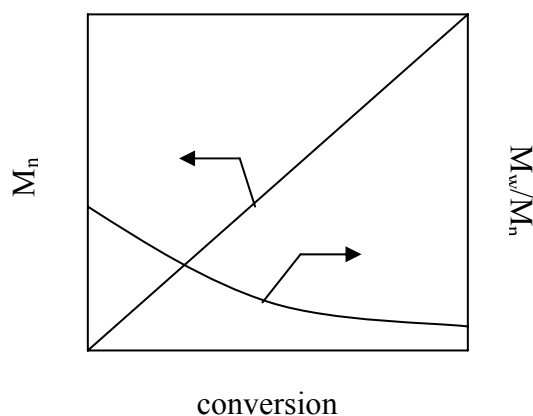


Figure 1.4. Schematic representation of the evolution of the molecular weight and polydispersity with conversion

The types of controlled/living radical polymerizations are namely atom transfer radical polymerization (ATRP), nitroxide mediated polymerization-NMP, and various degenerate transfer processes such as reversible addition fragmentation transfer (RAFT) and catalytic chain transfer polymerizations. Among them, one of the most successful and the most studied technique is the atom transfer radical polymerization (ATRP).

### 1.3.1. Atom Transfer Radical Polymerization

ATRP was developed independently by Matyjaszewski and Sawamoto in 1995 [16,17,18]. This method was used successfully to polymerize styrenes, (meth)acrylates and variety of other monomers in a controlled fashion, yielding polymers with molecular weights predetermined by the ratio of the concentrations of the consumed monomer to the initiator introduced. Polymers obtained by the ATRP technique have low polydispersities as well. Because of its radical nature, ATRP is tolerant to many functional groups; therefore, polymers with various functionalities can be easily obtained.

### 1.3.1.1. Origin of ATRP

ATRP is a transition metal catalyzed radical polymerization. This method is originated from the atom transfer radical addition (ATRA) reaction, which is also catalyzed by a transition metal complex. ATRA is an extension of Kharasch Addition Reaction [13]. Figure 1.5 shows the steps of ATRA. Alkyl halide **1**, by the help of the transition metal complex **6**, generates radical **2**. In the presence of large amounts of alkene **3** an addition occurs that produces radical **4**, which is then trapped by the transition metal halide **7** in its higher oxidation state to produce the alkyl halide **5** and the transition metal halide in the lower oxidation state **6**.

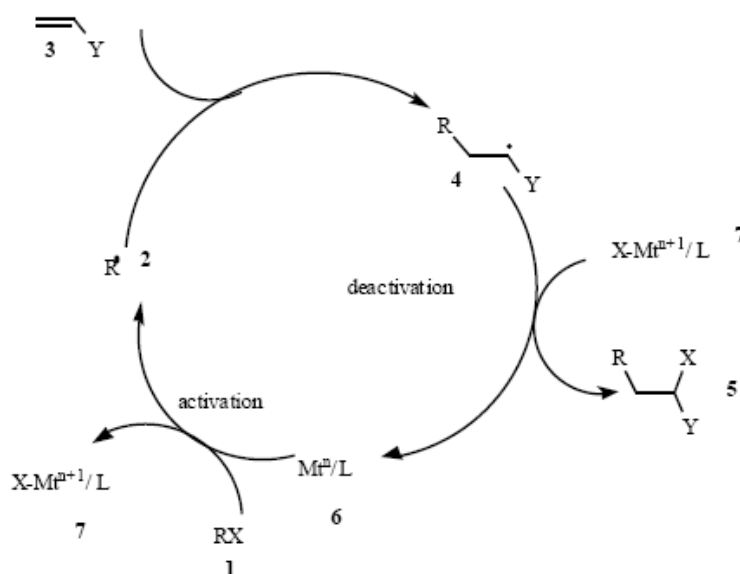


Figure 1.5. The mechanism of ATRA.

### 1.3.1.2. Kinetics and Mechanism of ATRP

The general mechanism of ATRP is shown in Figure 1.6. The mechanism is similar to ATRA. In the case of ATRP, more than one addition occurs. Also, two new concepts appear; dormant species and the active species. The dormant species are the activated alkyl halides, and the active species are the propagating radical chains. Since the halide and the radical species before and after the addition of the monomers possess comparable reactivities, the activation-addition-deactivation cycle repeats itself until all of the monomer present is consumed. This process results in a chain-growth polymerization [13].

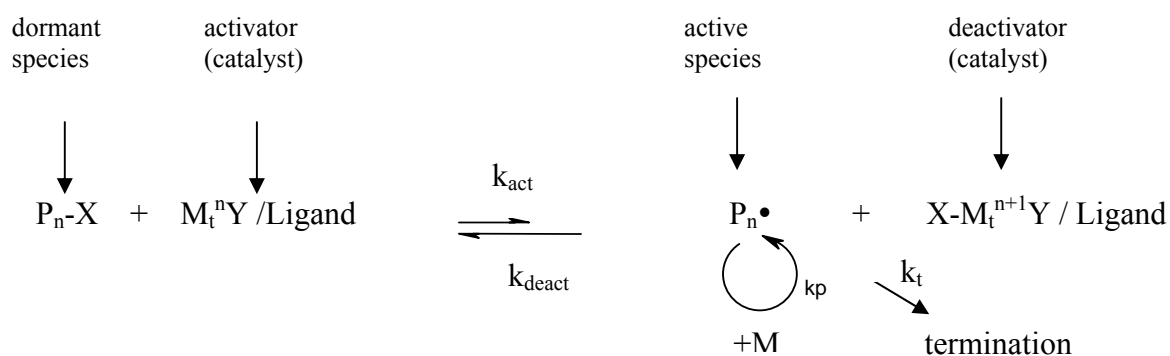


Figure 1.6. The mechanism of ATRP

In ATRP, since only activated halides initiate the polymerization by interacting with the transition metal catalyst, one polymer chain is formed per initiator. The halide that has been used in the initiator is transferred to the next monomer added and thus when a monofunctional initiator is used, the polymer end groups contain the initiator structure in one end and the halide at the other end.

The rate of ATRP shows first-order kinetic with respect to the monomer, initiator and transition metal complexes. The degree of control in ATRP is strongly affected by the position of the equilibrium ( $K_{ATRP} = k_{act}/k_{deact}$ ) and by all rate constants.  $K_{ATRP}$  depends on the solvent, temperature, monomer (i.e. structures  $PX$  and  $P\bullet$ ), and structure of  $Cu/\text{Ligand}$  complexes [19].

In a successful ATRP, the number of added monomer molecules at one activation step is small so that polymers with low polydispersities can be obtained. This means  $k_{act} < k_{deact}$ . This also reduces the probability of side reactions such as termination reactions. Actually, termination as a side reaction in any radical polymerization is unavoidable; however, the activation-deactivation cycle in ATRP minimizes termination by creating a steady, low concentration of short-lived, active radical chain ends [20]. This provides the livingness of most of the polymer end groups and low polydispersity. In addition, since the initiator is consumed at early stages of the ATRP process, the molecular weight distribution of the resulting polymers are low.

### 1.3.1.3. Components of ATRP

ATRP is a multicomponent system and the proper control depends on a delicate balance between them. Generally, ATRP technique requires four main components; monomer, initiator, transition metal and ligand. Solvent and sometimes additives may be used. For successful ATRP, temperature and reaction time should also be taken into account [21].

#### 1.3.1.3.1. Monomers

A variety of monomers, such as styrene and its derivatives, (meth)acrylates, (meth)acrylamides, acrylonitriles, have been successfully polymerized using ATRP. On the other hand, controlled homopolymerizations of some monomers such as vinyl acetates, halogenated alkenes and  $\alpha$ -olefins are difficult. These monomers lack conjugation and, thus, their radicals are highly reactive, less stable and more prone to termination and chain transfer [22]. Figure 1.7 shows structures of some monomers polymerized by ATRP.

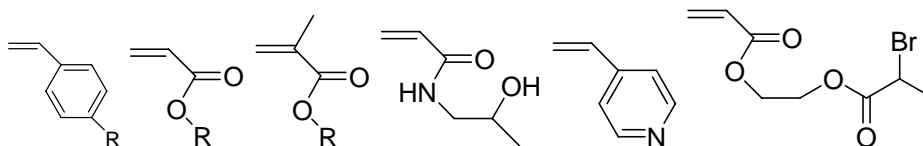


Figure 1.7. Some of the monomers used in ATRP.

Each monomer has its own unique atom transfer equilibrium constant for its active and dormant species under a given reaction condition. In the absence of any side reaction, other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant determines the polymerization rate [21]. ATRP will occur very slowly if the equilibrium constant is too small. In contrast, too large equilibrium constant will lead to large amount of termination reactions due to high radical concentration. Thus, for a specific monomer, concentration of propagating radicals and the rate of radical deactivation need to be adjusted to maintain the control. Because each monomer has a specific equilibrium constant, optimal condition for polymerization, i.e. concentration, type

of the catalyst, temperature and solvent may be different. Therefore each monomer should be considered by taking into account the optimum conditions.

### 1.3.1.3.2. Initiators

The number of growing chains is determined by the relative proportion of the initiator concentration. The initiator forms an initiating radical species via homolytic cleavage of its labile bond such as C-halogen by the metal catalyst. In most cases, the dissociated halogen or its equivalent is subsequently reattached to the propagating radical chain end to give a dormant species. Figure 1.8 shows some of the initiators used in ATRP.

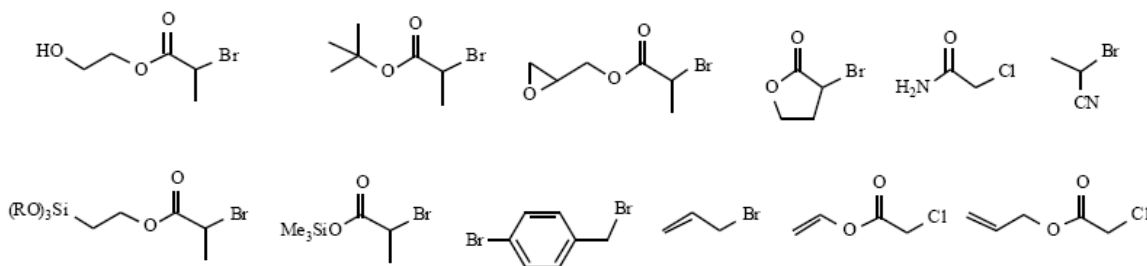


Figure 1.8. Some of the ATRP initiators

The initiator is thus chosen so that the initiation occurs fast and is quantitative. The theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of the initiator as shown in the below:

$$DP = [M]_0 / [\text{initiator}]_0 \times \text{conversion}$$

Generally, potential ATRP initiators are any alkyl halide with activating substituents on the  $\alpha$ -carbon, such as aryl, carbonyl or allyl groups. Polyhalogenated compounds (e.g.  $\text{CCl}_4$  and  $\text{CHCl}_3$ ) and compounds with a weak R-X bond, such as N-X, S-X and O-X, can be used as ATRP initiators. In addition to low molar mass initiators, various macroinitiators and multifunctional initiators have been successfully used for ATRP [13,21]. Often, the structure of the initiator is analogous to the structure of the polymer end group.

Halogens in the initiators (R-X) include iodine, chlorine and bromine, where the reactivity of the C-X bond increases in the following order  $\text{Cl} < \text{Br} < \text{I}$ , but the stability of the C-X bond decreases vice versa. Therefore, chlorines and bromines are used widely. The stabilizing groups in the initiator are  $\text{CN} > \text{C(O)R} > \text{C(O)OR} > \text{Ph} > \text{Cl} > \text{Me}$ . Multiple functional groups may increase the activity of the alkyl halide, e.g. carbon tetrachloride, benzhydryl derivatives, and malonates. Tertiary alkyl halides are better initiators than secondary ones, which are better than primary alkyl halides.

R-X bond in the initiator can not only be cleaved homolytically, it can be cleaved heterolytically also, and that may cause side reactions. This depends mostly on the initiator structure and the choice of the metal catalyst. For example, in the atom transfer radical polymerization of *p*-methoxystyrene, side reactions were observed. This is most likely due to the heterolytic cleavage of R-X bond or oxidation the radical to the corresponding carbocation [23].

#### 1.3.1.3.3. Transition Metals

Transition metals are one of the most important components of ATRP. Their role, with the help of the ligand, is to catalyze the polymerization reaction. As a catalyst, the complex induces reversible activation (homolytic cleavage) of the dormant C-halogen bond via a one-electron redox reaction at the metal center. In this process, the metal center attacks the halogen and is oxidized via a single electron transfer followed by halogen abstraction, and thus generates a growing radical on the polymer end group. Sooner or later, the oxidized metal center donates the halogen back to the growing radical where reduction of the metal center occurs.

The requirements for the catalyst efficiency are [24] :

- The metal complex must have an accessible one-electron redox couple to promote atom transfer.
- Upon one-electron oxidation, the coordination number of the metal center must increase by one in order to accommodate a new ligand. For example, in most

systems with the copper-based ATRP, the lower oxidation state of the metal is presumed to be tetra-coordinate and the higher oxidation state is presumed to be pentacoordinate.

- The catalyst must show selectivity for atom transfer and therefore possess a low affinity for alkyl radicals and the hydrogen atoms on alkyl groups. If not, then the transfer reactions, such as  $\beta$ -H elimination and the formation of organometallic derivatives, may be observed.
- The metal center must not be a strong Lewis acid, otherwise the ionization of certain initiators/end groups to carbocations may occur.

There are a number of transition metal complexes including complexes based on early, middle and late transition metals (e.g. Ru, Fe, Ni, Pd, Rh, Re) [25,26] that have been investigated and developed as efficient ATRP catalyst [27]. Of all the transition metals investigated, copper appears to be the most promising in terms of price and versatility. A variety of monomers including styrene and its derivatives, (meth)acrylic esters and acrylonitrile can be polymerized in controlled fashion [28].

#### 1.3.1.3.4. Ligands

In ATRP, the ligands act in two ways. First, it influences the concentration of the catalyst in solution and ensures the stability of the complexes in different monomers, solvents and temperatures. This is especially important in the polymerization of acidic monomers and monomers which contain functional groups such as pyridine and amines that can complex with the transition metal. Second, the ligand tunes the steric and the electronic properties of the metal/ligand complex. This aspect is very important as it affects the equilibrium between the dormant and active species [15]. Therefore the choice of the ligand is one of the key factors influencing the reactivity of the catalyst [29].

The electronic and steric effects of the ligands are important. Reduced catalytic activity or efficiency is observed when there is an excessive steric hindrance around the metal center or the ligand has strong electron-withdrawing substituents. Generally

electron-donating ligands stabilize better the higher oxidation state of the metal and accelerate the polymerization [30].

There are three main types of ligands used in ATRP:

- Nitrogen Ligands: These have been applied to the copper and iron-based ATRP catalyst complexes. Such examples are bipyridine, some tri-, tetra-, penta- and hexa-amines, etc.
- Phosphorus Ligands: They are used to complex rhenium, ruthenium, iron, rhodium, nickel and palladium, but not copper. The most used ligand is  $\text{PPh}_3$ .
- Miscellaneous Ligands: Cyclopentadienyl, indenyl and also oxygen-centered ligands, such as phenol or carboxylic acids are some examples and they have been applied to nickel and iron-based ATRP catalysts.

Among various ATRP catalyst complexes, copper complexes with amines remain perhaps the most promising ones due to their availability, versatility and low cost. So far, a range of multidentate nitrogen ligands were developed for copper-mediated ATRP, which includes pyridine derivatives, linear, branched or cyclic aliphatic polyamines, imine derivatives, phenanthroline derivatives, and terpyridine derivatives (Figure 1.9).

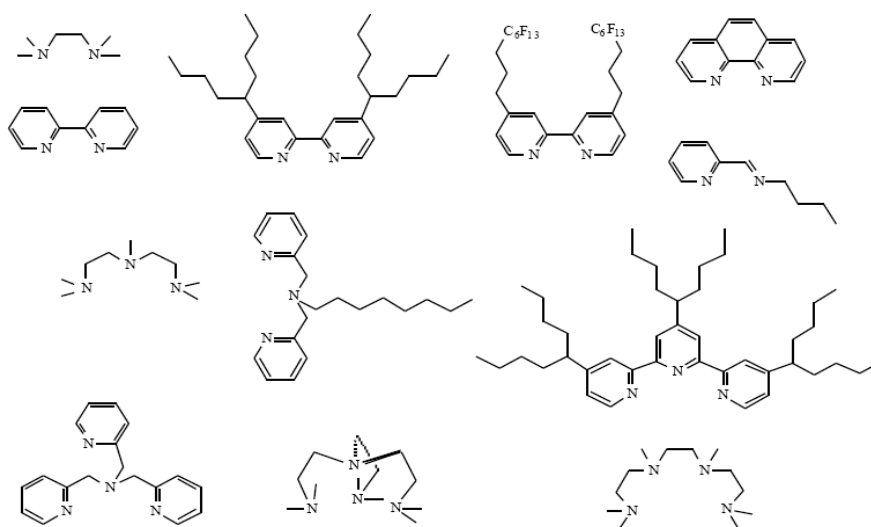


Figure 1.9. Examples of ligands used in ATRP

In copper-based ATRP, the activity of N-based ligands in ATRP decreases with the number of coordinating sites  $N_4 > N_3 > N_2 \gg N_1$  and with the number of linking C-atoms  $C_2 > C_3 \gg C_4$ . It also decreases in the order  $R_2N- \approx \text{PyrEnDash-} > R-N= > \text{Ph-N=} > \text{Ph-NR-}$ . Activity is usually higher for bridged and cyclic systems than linear analogues.

#### 1.3.1.3.5. Solvents

The radical polymerization is much less sensitive to solvent effects than ionic reactions. However, the structure and reactivity of the ATRP catalyst is strongly affected by the solvent. Polymerization can be carried out either in bulk or in solution, and both non-polar solvents (toluene, xylene, etc.) or polar solvents (ethylene, carbonate, DMF, water, etc) can be used [31]. Solution polymerizations are slower relative to bulk polymerizations but solvent sometimes becomes necessary, especially when the obtained polymer is insoluble in its monomers.

Solvent choice is dictated by several factors:

- With some solvents, there is the potential for chain transfer, depending upon the corresponding transfer constant,  $C_s$ .
- Solvent interactions with the catalyst system should be considered. Specific interactions with the catalyst, such as solvolysis of the halogen ligand or displacement of spectator ligands, should be avoided.
- Certain polymer end-groups, such as polystyryl halides, can undergo solvolysis or elimination of HX at 110°C to 130°C in many polar solvents.

#### 1.3.1.3.6. Additives

Metal catalyzed living or controlled radical polymerizations can generally be achieved with initiating systems consisting of an organic halide as an initiator and the metal complex as a catalyst. However these polymerizations are slow in some cases due to the low concentration of the active radical species [14]. In those cases, employing an additive may help to increase the rate of polymerization. For example, small increase in

rate of polymerization in ATRP of methyl methacrylate was observed by addition of phenol derivatives [24]. Some additives also provide better control on polymerization. These additives most probably can effectively reduce the metal species in higher oxidation states or form more efficient catalysts via coordination [14].

However, sometimes additives may decrease the polymerization rate. For example, addition of pyridine or  $\text{PPh}_3$  to the copper-mediated ATRP, leads to large decrease in the polymerization rate [21].

#### 1.3.1.3.7. Temperature and Reaction Time

Like in the case of conventional free radical polymerization, higher temperatures result in higher polymerization rate in ATRP since both the radical propagation rate constant and the atom transfer equilibrium constant increases with increasing temperatures. The energy of activation for radical propagation is appreciably higher than that for termination by radical combination and disproportionation. Therefore, higher  $k_p/k_t$  ratio and better control are obtained at higher temperatures. On the other hand, chain transfer and other side reactions may be more pronounced at higher temperatures [21]. Therefore, for successful ATRP, optimum temperature should be found depending on the monomer, catalyst and the other components of ATRP.

At higher 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 [21].

All information about ATRP and conventional free radical polymerization shows that, ATRP is superior to conventional free radical polymerization. By tuning the ATRP components such as catalyst complex, initiator, reaction temperature, time and solvent polymers with controlled molecular weights and low polydispersities can be obtained.

### 1.3.2. Cyclopolymerization of Alkyl $\alpha$ -(Hydroxymethyl)acrylate Ether Dimers via ATRP

As mentioned before, aliphatic cyclopolymers may satisfy the material requirements that are needed for the powder coating base resins. ATRP was chosen as the living/controlled polymerization technique in order to obtain cyclopolymers with living end groups, tunable molecular weights and low polydispersities. One of the main focuses in the present study was to tune the ATRP components for a successful ATRP process.

In this perspective, ATRP cyclopolymerization of three different alkyl  $\alpha$ -(hydroxymethyl)acrylate ether dimers have been previously studied in our research group. These alkyl groups were ethyl, n-butyl and t-butyl groups. In these studies, the polymerization parameters were adjusted to obtain well-defined polymers in a controlled manner. The alkyl substituents were chosen to see the effect of bulkiness on the cyclopolymerization. Also the temperature effect on the cyclization efficiency and properties of polymers were investigated.

The results showed that as the bulkiness increases, cyclization efficiency increases [32]. For example, the polymerization of ethyl  $\alpha$ -(hydroxymethyl)acrylate ether dimer gave crosslinked polymers while the monomer with t-butyl group gave cyclopolymer with six-membered tetrahydropyran units. These results are consistent with the results obtained on the cyclization efficiency in conventional radical polymerization [11,13].

## OBJECTIVE

ATRP of RHMA ether dimers with ethyl, n-butyl and *tert*-butyl as alkyl groups has been previously reported. Cyclization efficiency was found to increase with bulkiness of substituent group in RHMA ether dimers. However, cyclopolymerizations of more bulky adamantyl and cyclohexyl  $\alpha$ -(hydroxymethyl)acrylate ether dimers by ATRP were not studied. Such bulky groups, although they may be favorable for the cyclization, they may alter the ATRP process.

In this study, the aim is to get living cyclic polymers with reasonable polydispersities and predictable molecular weights. Bulkier adamantyl and cyclohexyl groups were selected as R groups in RHMA ether dimer and cyclopolymerizations were carried out in xylene by using CuBr/PMDETA as catalyst and ethyl 2-bromoisobutyrate (EBr/B) as initiator. In addition, temperature effect was also investigated. Copolymerization studies were performed to prove the livingness of the cyclopolymers obtained. Thermal properties of the cyclopolymers were also investigated.

### 3. EXPERIMENTAL

#### 3.1. Materials

1-Adamantanol (Fluka, >99%), cyclohexanol (Fluka, >99%), n-Butyllithium (n-BuLi) (2.5 M solution in hexane), acryloyl chloride (Fluka, >96%), triethylamine (TEA) (Merck, >99%), 1,4-Diazabicyclo[2.2.2]octane (Fluka, >95%), t-butyl alcohol (Merck, >99%), ethyl-2-bromoisobutyrate (Fluka, >97%), copper(I)bromide (CuBr) (Aldrich, 99.999%), and pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%) were used as received without purification. Tetrahydrofuran (extra pure) and xylene (mixture of isomers) were purified by distillation over Na metal and benzophenone. Dichloromethane, hexane, methanol and acetone (Merck) were used as received without purification.

#### 3.2. Instrumentation

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded using a Varian Gemini 400 MHz spectrometer (Varian Associates, Palo Alto, CA). SEC analyses were done using a Viscotek GPCmax VE-2001 Analysis System with a PL Gel 5  $\mu\text{m}$  MIXED-C Column that was calibrated against polystyrene standards.  $T_g$  values were determined with a Rheometric Scientific Differential Scanning Calorimeter DSC. TGA scans were performed under nitrogen flow using a TA Q50 at a heating rate of  $10^\circ\text{C}/\text{min}$ . All polymer samples were purified by passing through basic aluminum oxide columns to remove the copper catalyst followed by two reprecipitations before NMR, SEC, DSC and TGA analyses.

### 3.3. Synthesis of Monomers

#### 3.3.1. Synthesis of 1-Adamantyl Acrylate

The synthesis was carried out under inert atmosphere using nitrogen. 1-Adamantanol (10 g, 0.0657 mol) and THF (120 mL) were added to a 250 mL three necked round bottom flask fitted with a condenser, magnetic stirrer and addition funnel. The reaction temperature was adjusted to  $-20^{\circ}\text{C}$  using ice, salt and acetone. n-BuLi (26 mL, 0.0650 mol) was added dropwise to the reaction mixture. The solution was stirred for 30 min. Then, acryloyl chloride (7.1358 g, 0.0788 mol) was added dropwise to the mixture at room temperature. The reaction was allowed to stir for 30 hours. The reaction progress was monitored by thin layer chromatography (TLC) using silica gel plates and  $\text{CH}_2\text{Cl}_2$  as the eluting and diluting solvent. TLC plates were visualized using potassium permanganate solution. At the end of the 30 hours, the mixture was diluted with 50 mL dichloromethane and washed once with 50 mL of distilled water. The organic layer was separated and evaporated under reduced pressure to give crude product as an oil. The oily mixture was dissolved in minimum amount of dichloromethane : hexane mixture (2:10) (v/v) and passed through silica column prepared with the same solvent mixture. Evaporation of the solvent gave the pure product as a clear liquid in 80 per cent yield.

$^1\text{H}$  NMR:  $\delta$  1.60 (br, 6H), 2.08 (br, 9H), 5.68 (dd, 1H), 6.02 (dd, 1H), 6.26 (dd, 1H).

$^{13}\text{C}$  NMR:  $\delta$  31.18, 36.24, 41.36, 80.45, 129.28, 130.82, 165.35 ppm.

#### 3.3.2. Synthesis of Cyclohexyl Acrylate

The synthesis was carried out under inert atmosphere using nitrogen. Cyclohexanol (25.04 g, 0.25 mol), TEA (36.43 g, 0.36 mol) and dichloromethane (320 mL) were added to a 250 mL three necked round bottom flask fitted with a condenser, magnetic stirrer and addition funnel. The reaction bath temperature was adjusted to  $0^{\circ}\text{C}$  using ice. Acryloyl chloride (27.153 g, 0.3 mol) was added dropwise by addition funnel to the reaction flask. The mixture was stirred for 2 hours. The reaction progress was monitored by thin layer chromatography (TLC) using silica gel plates and  $\text{CH}_2\text{Cl}_2$  as the eluting and diluting

solvent. At the end of the 2 hours, the mixture was diluted with 50 mL dichloromethane and washed once with 50 mL of distilled water. The organic layer was separated and evaporated under reduced pressure to give crude product as an oil. The oily mixture was dissolved in minimum amount of dichloromethane : hexane mixture (5:7) (v/v) and passed through silica column prepared with the same solvent mixture. Evaporation of the solvent gave the pure product as a clear liquid in 91 per cent yield.

$^1\text{H}$  NMR:  $\delta$  1.40 (br, 6H), 1.72 (br, 2H), 1.85 (br, 2H), 4.81 (br, 1H), 4.79 (dd, 1H), 5.80 (dd, 1H), 6.22 (dd, 1H) ppm.

$^{13}\text{C}$  NMR:  $\delta$  23.95, 25.59, 31.81, 72.96, 129.37, 130.33, 165.91 ppm.

### **3.3.3. Synthesis of 1-Adamantyl $\alpha$ -(Hydroxymethyl)acrylate (ADHMA) Ether Dimer**

The synthesis was carried out under dry conditions using  $\text{CaCl}_2$  tube. 1-adamantyl acrylate (6.3334 g, 0.0303 mol), paraformaldehyde (0.9247 g, 0.0303 mol), DABCO (0.4619 g, 4.9 wt%) and t-butanol (1.8466 g, 19.2 wt%) were added to a 100 mL three necked round bottom flask fitted with a condenser and magnetic stirrer. The reaction bath temperature was adjusted to  $80^\circ\text{C}$ . The mixture was stirred for 6 days. The reaction progress was monitored by thin layer chromatography (TLC) using silica gel plates and  $\text{CH}_2\text{Cl}_2$  as the eluting and diluting solvent. At the end of the 6 days the mixture was dropped into acetone where 1-adamantyl  $\alpha$ -(hydroxymethyl)acrylate (ADHMA) ether dimer was precipitated as white solid in 67 per cent yield.

### **3.3.4. Synthesis of Cyclohexyl $\alpha$ -(Hydroxymethyl)acrylate (CHMA) Ether Dimer**

The synthesis was carried out under dry conditions using  $\text{CaCl}_2$  tube. Cyclohexyl acrylate (5 g, 0.0325 mol), paraformaldehyde (0.975 g, 0.0325 mol), DABCO (0.3379 g, 4.9 wt%) and t-butanol (1.5193 g, 19.2 wt%) were added to a 100 mL three necked round bottom flask fitted with a condenser and magnetic stirrer. The reaction bath temperature was adjusted to  $80^\circ\text{C}$ . The mixture was stirred for 2 days. The reaction progress was monitored by thin layer chromatography (TLC) using silica gel plates and  $\text{CH}_2\text{Cl}_2$  as the eluting and diluting solvent. At the end of the 2 days the mixture was diluted with 10 mL

dichloromethane and washed once with 10 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 dichloromethane : hexane with (7:4) (v/v) and passed through silica column prepared with the same solvent mixture. Evaporation of the solvent gave the pure monomer as a light orange solid in 38.8 per cent yield.

$^1\text{H}$  NMR:  $\delta$  1.33 (br, 12H), 1.65 (br, 4H), 1.77 (br, 4H), 4.19 (s, 4H), 4.79 (br, 2H), 5.80 (d, 2H), 6.22 (d, 2H) ppm.

$^{13}\text{C}$  NMR:  $\delta$  23.80, 25.63, 31.72, 69.22, 73.07, 125.40, 138.00, 165.41 ppm.

### 3.4. Polymer Synthesis

#### 3.4.1. The Procedure for the Solution ATRP of RHMA Ether Dimers

All glassware, needles and stirring bars were dried overnight in an oven at 150 °C and purged with nitrogen 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 10 mL one-necked round bottom flask using xylene as the solvent. The reaction flask fitted with a stirring bar and CuBr in it, was sealed with rubber septa and purged with nitrogen for 10 minutes. Then the monomer was dissolved in xylene and transferred into the reaction flask by syringe. The solution was stirred and purged with nitrogen for 20 minutes. Then the flask was immersed into a preheated oil bath. Then, PMDETA was added to the reaction flask. The resulting solution was stirred and heated until homogeneous. Ethyl  $\alpha$ -bromoisobutyrate (EBiB) was introduced into the reaction flask by syringe. The final polymers were precipitated into relevant twice and dried in a vacuum oven overnight.

Monomer conversion was determined by gravimetric methods. The determination of molar masses and molecular weight distributions has been carried out by size exclusion chromatography (SEC) with a refractive index detector against poly(styrene) (PS)

standards. Characterization of the polymer samples has been performed by proton and carbon NMR spectroscopy.

### **3.4.2. ATRP of 1-Adamantyl $\alpha$ -(Hydroxymethyl)acrylate Ether Dimer**

Experiment 1. ADHMA ether dimer (1.0037 g, 2.2 mmol) was polymerized in 2.3 mL xylene (0.96 M) by using CuBr (3.2 mg, 0.022 mmol) and PMDETA (4.6  $\mu$ L, 0.022 mmol) catalyst system and ethyl  $\alpha$ -bromoisobutyrate (3,3  $\mu$ L, 0.042 mmol) initiator according to the given procedure. The polymerization was carried out at 80°C for 3 hours. The reaction mixture was initially light green and clear but turned to green-brown and hazy with time indicating that the mixture became heterogeneous. The resulting polymer was precipitated into 50 mL acetone and dried in a vacuum overnight. The polymer was obtained as a white, soluble powder, 0.5960 g, in 60 per cent yield.

Experiment 2. ADHMA ether dimer (1.0080 g, 2.2 mmol) was polymerized in 2.3 mL xylene (0.96 M) by using CuBr (3.2 mg, 0.022 mmol) and PMDETA (4.6  $\mu$ L, 0.022 mmol) catalyst system and ethyl  $\alpha$ -bromoisobutyrate (3,3  $\mu$ L, 0.022 mmol) initiator according to the given procedure. The polymerization was carried out at 80°C for 4 hours. The reaction mixture was initially light green and clear but turned to green-brown and hazy with time indicating that the mixture became heterogeneous. The resulting polymer was precipitated into 50 mL acetone and dried in a vacuum overnight. The polymer was obtained as a white, soluble powder, 0.3825 g, in 38 per cent yield.

Experiment 3. ADHMA ether dimer (1.0076 g, 2.2 mmol) was polymerized in 2.3 mL xylene (0.96 M) by using CuBr (3.2 mg, 0.022 mmol) and PMDETA (4.6  $\mu$ L, 0.022 mmol) catalyst system and ethyl  $\alpha$ -bromoisobutyrate (3,3  $\mu$ L, 0.022 mmol) initiator according to the given procedure. The polymerization was carried out at 80°C for 4 hours. The reaction mixture was initially light green and clear but turned to green-brown and hazy with time indicating that the mixture became heterogeneous. The resulting polymer was precipitated into 50 mL acetone and dried in a vacuum overnight. The polymer was obtained as a white, soluble powder, 0.5240 g, in 52 per cent yield.

Experiment 4. ADHMA ether dimer (1.0035 g, 2.2 mmol) was polymerized in 2.4 mL xylene (0.92 M) by using CuBr (3.2 mg, 0.022 mmol) and PMDETA (4.6  $\mu$ L, 0.022 mmol) catalyst system and ethyl  $\alpha$ -bromoisobutyrate (3,3  $\mu$ L, 0.022 mmol) initiator according to the given procedure. The polymerization was carried out at 80°C for 5 hours. The reaction mixture was initially light green and clear but turned to green-brown and hazy with time indicating that the mixture became heterogeneous. The resulting polymer was precipitated into 50 mL acetone twice and dried in a vacuum overnight. The polymer was obtained as a white, soluble powder, 0.3055 g, in 30.4 per cent yield.

Experiment 5. ADHMA ether dimer (1.0018 g, 2.2 mmol) was polymerized in 2.5 mL xylene (0.88 M) by using CuBr (3.2 mg, 0.022 mmol) and PMDETA (4.6  $\mu$ L, 0.022 mmol) catalyst system and ethyl  $\alpha$ -bromoisobutyrate (3,4  $\mu$ L, 0.023 mmol) initiator according to the given procedure. The polymerization was carried out at 100°C for 4 hours. The reaction mixture was initially light green and clear but turned to green-brown and hazy with time indicating that the mixture became heterogeneous. The resulting polymer was precipitated into 50 mL acetone and dried in a vacuum overnight. The polymer was obtained as a white, soluble powder, 0.3306 g, in 33 per cent yield.

Experiment 6. ADHMA ether dimer (1.0076 g, 2.2 mmol) was polymerized in 2.3 mL xylene (0.96 M) by using CuBr (3.2 mg, 0.022 mmol) and PMDETA (4.6  $\mu$ L, 0.022 mmol) catalyst system and ethyl  $\alpha$ -bromoisobutyrate (3,3  $\mu$ L, 0.022 mmol) initiator according to the given procedure. The polymerization was carried out at 100°C for 3 hours. The reaction mixture was initially light green and clear but turned to green-brown and hazy with time indicating that the mixture became heterogeneous. The resulting polymer was precipitated into 50 mL acetone and dried in a vacuum overnight. The polymer was obtained as a white, soluble powder, 0.2805 g, in 28 per cent yield.

### **3.4.3. ATRP of Cyclohexyl $\alpha$ -(Hydroxymethyl)acrylate Ether Dimer**

Experiment 1. CHMA ether dimer (0.9846 g, 2.8 mmol) was polymerized in 2.9 mL xylene (0.97 M) by using CuBr (4.0 mg, 0.028 mmol) and PMDETA (5.9  $\mu$ L, 0.028 mmol) catalyst system and ethyl  $\alpha$ -bromoisobutyrate (4.2  $\mu$ L, 0.028 mmol) initiator according to the given procedure. The polymerization was carried out at 80°C for 4 hours. The reaction

mixture was initially pink and clear. After about 10 minutes the color turned to green. The reaction mixture was initially homogeneous and it became heterogeneous with time. The resulting polymer was precipitated into 50 mL methanol twice and dried in a vacuum overnight. The polymer was obtained as a white, soluble powder, 0.3125 g, in 32 per cent yield.

Experiment 2. CHMA ether dimer (0.9976 g, 2.8 mmol) was polymerized in 3.0 mL xylene (0.95 M) by using CuBr (4.0 mg, 0.028 mmol) and PMDETA (5.9  $\mu$ L, 0.028 mmol) catalyst system and ethyl  $\alpha$ -bromoisobutyrate (4.2  $\mu$ L, 0.028 mmol) initiator according to the given procedure. The polymerization was carried out at 80°C for 5 hours. The reaction mixture was initially pink and clear. After about 10 minutes the color turned to green. The reaction mixture was initially homogeneous and it became heterogeneous with time. The resulting polymer was precipitated into 50 mL methanol twice and dried in a vacuum overnight. The polymer was obtained as a white, soluble powder, 0.4828 g, in 48 per cent yield.

Experiment 3. CHMA ether dimer (0.9883 g, 2.8 mmol) was polymerized in 3.0 mL xylene (0.95 M) by using CuBr (4.0 mg, 0.028 mmol) and PMDETA (5.9  $\mu$ L, 0.028 mmol) catalyst system and ethyl  $\alpha$ -bromoisobutyrate (4.2  $\mu$ L, 0.028 mmol) initiator according to the given procedure. The polymerization was carried out at 80°C for 5 hours. The reaction mixture was initially pink and clear. After about 10 minutes the color turned to green. The reaction mixture was initially homogeneous and it became heterogeneous with time. The resulting polymer was precipitated into 50 mL methanol twice and dried in a vacuum overnight. The polymer was obtained as a white, soluble powder, 0.6387 g, in 65 per cent yield.

Experiment 4. CHMA ether dimer (0.9942 g, 2.8 mmol) was polymerized in 3.0 mL xylene (0.95 M) by using CuBr (4.0 mg, 0.028 mmol) and PMDETA (5.9  $\mu$ L, 0.028 mmol) catalyst system and ethyl  $\alpha$ -bromoisobutyrate (4.2  $\mu$ L, 0.028 mmol) initiator according to the given procedure. The polymerization was carried out at 100°C for 5 hours. The reaction mixture was initially pink and clear. After about 10 minutes the color turned to green. The reaction mixture was initially homogeneous and it became heterogeneous with time. The resulting polymer was precipitated into 50 mL methanol twice and dried in a vacuum

overnight. The polymer was obtained as a white, soluble powder, 0.8066 g, in 81 per cent yield.

Experiment 5. CHMA ether dimer (1.0221 g, 2.9 mmol) was polymerized in 3.0 mL xylene (0.97 M) by using CuBr (4.2 mg, 0.029 mmol) and PMDETA (6.1  $\mu$ L, 0.029 mmol) catalyst system and ethyl  $\alpha$ -bromoisobutyrate (4.3  $\mu$ L, 0.029 mmol) initiator according to the given procedure. The polymerization was carried out at 100°C for 5 hours. The reaction mixture was initially pink and clear. After about 10 minutes, the color turned to green. The reaction mixture was initially homogeneous and it became heterogeneous with time. The resulting polymer was precipitated into 50 mL methanol twice and dried in a vacuum overnight. The polymer was obtained as a white, soluble powder, 0.8892 g, in 87 per cent yield.

Experiment 6 (Kinetic Study). CHMA ether dimer (1.9839 g, 5.6 mmol) was polymerized in 5.8 mL xylene (0.96 M) by using CuBr (8.1 mg, 0.056 mmol) and PMDETA (12  $\mu$ L, 0.056 mmol) catalyst system and ethyl  $\alpha$ -bromoisobutyrate (8.4  $\mu$ L, 0.056 mmol) initiator according to the given procedure. The polymerization was carried out at 80°C. 0.8 and 0.6 mL of samples were taken at regular time intervals using a syringe purged with nitrogen. The resulting polymers were precipitated into 50 mL methanol twice and dried in vacuum overnight.

#### **3.4.4. Bulk Copolymerization of Poly(ADHMA ether dimer) with n-Butyl Acrylate**

Experiment 1. All liquid chemicals were purged with nitrogen for at least 15 min prior to use. The copolymerization was conducted in a 10 mL one-necked round bottom flask. CuBr (4.8 mg, 0.036 mmol) was added to the pre-purged (nitrogen for 10 minutes) sealed reaction flask fitted with a stirring bar. The solid macroinitiator poly(ADHMA ether dimer) (0.2011 g, 0.018 mmol) was dissolved in 5 mL n-butyl acrylate in a vial. Then the solution was transferred to the reaction flask and degassed for 20 minutes. The reaction flask was immersed into a preheated oil bath at 80°C. PMDETA (7.44  $\mu$ L, 0.036 mmol) was added to the reaction flask. The polymerization was carried out under nitrogen at 80°C for 5 hours. The final polymer was precipitated into methanol:water (5:3) (v/v) and dried in a vacuum oven overnight. The polymer was obtained as a white, soluble powder, 0.3222 g.

Experiment 2. All liquid chemicals were purged with nitrogen for at least 15 min prior to use. The copolymerization was conducted in a 10 mL one-necked round bottom flask. CuCl (1.5 mg, 0.015 mmol) and was added to the pre-purged (nitrogen for 10 minutes) sealed reaction flask fitted with a stirring bar. The solid macroinitiator poly(ADHMA ether dimer) (0.087 g, 0.007 mmol) was dissolved in 4 mL n-butyl acrylate in a separate vial. Then the solution was transferred to the main reaction flask containing the copper and degassed for 20 minutes. The reaction flask was then immersed into a preheated oil bath at 80°C. PMDETA (3.24  $\mu$ L, 0.015 mmol) was added to the reaction flask. The polymerization was carried out under nitrogen at 80°C for 5.5 hours. The final polymer was precipitated into methanol:water (5:3) (v/v) and dried in a vacuum oven overnight. The polymer was obtained as a white, soluble powder, 0.103 g.

#### **3.4.5. Bulk Copolymerization of Poly(CHMA ether dimer) with t-Butyl Acrylate**

Experiment 1. All liquid chemicals were purged with nitrogen for at least 15 min prior to use. The copolymerization was conducted in a 10 mL one-necked flask. CuBr (3.7 mg, 0.027 mmol) and was added to the reaction flask fitted with a stirring bar and which had been sealed with a rubber septa and purged with nitrogen for 10 minutes. The solid macroinitiator poly(CHMA ether dimer) (0.1038 g, 0.014 mmol) was dissolved in 5 mL t-butyl acrylate in a vial. Then the solution was transferred to the reaction flask and degassed for 20 minutes. The reaction flask was immersed into a preheated oil bath at 80°C. PMDETA (5.73  $\mu$ L, 0.027 mmol) was added to the reaction flask. The polymerization was carried out under nitrogen at 80°C for 5 hours. The final polymer was precipitated into methanol:water (5:2) (v/v) and dried in a vacuum oven overnight. The polymer was obtained as a white, soluble powder, 0.1442 g.

Experiment 2. All liquid chemicals were purged with nitrogen for at least 15 min prior to use. The copolymerization was conducted in a 10 mL one-necked flask. CuCl (3.62 mg, 0.036 mmol) and was added to the reaction flask fitted with a stirring bar and which had been sealed with a rubber septa and purged with nitrogen for 10 minutes. The solid macroinitiator poly(CHMA ether dimer) (0.095 g, 0.018 mmol) was dissolved in 4 mL t-butyl acrylate in a vial. Then the solution was transferred to the reaction flask and degassed for 20 minutes. The reaction flask was immersed into a preheated oil bath at 80°C.

PMDETA (7.57  $\mu\text{L}$ , 0.036 mmol) was added to the reaction flask. The polymerization was carried out under nitrogen at 80°C for 6 hours. The final polymer was precipitated into methanol:water (5:3) (v/v) and dried in a vacuum oven overnight. The polymer was obtained as a white, soluble powder, 0.1256 g.

#### **3.4.6. The procedure for the Purification of the Resulting Polymers**

To remove the catalyst, all polymers were dissolved in dichloromethane and passed through a basic aluminum oxide column prepared with the same solvent. The polymers were precipitating into the corresponding non-solvent mixtures used. The pure polymers were dissolved in chloroform for NMR analysis and tetrahydrofuran (THF) for GPC analysis.

## 4. RESULTS AND DISCUSSION

In the project, the aim was to get cyclic aliphatic polymers from acrylic acid ester ether dimers via atom transfer radical polymerization. The monomers that were chosen possessed bulky substituents in their structures to observe the effect of bulkiness on the ATRP polymerization. In addition, a number of ATRP cyclopolymerizations were carried out at higher temperatures (100 °C) to observe the effect of temperature on both cyclization and ATRP. The physical properties of the corresponding polymers were also investigated.

We are reporting the results of the cyclopolymerization of cyclohexyl and adamantyl derivatives of the RHMA ethers dimers by ATRP which have not been reported up to now. First, the synthesis and characterization of the monomers will be discussed and then, the results and discussion of the cyclopolymerization studies will be presented. Finally, preliminary results of the copolymerization studies will be presented.

### 4.1. Synthesis of the Monomers

#### 4.1.1. Synthesis of 1-Adamantyl and Cyclohexyl Acrylates

**Synthesis of 1-Adamantyl Acrylate:** In order to synthesize bulky adamantyl esters, 1-adamantanol was converted *in situ* to the corresponding lithium alkoxide using n-BuLi prior to the reaction with acryloyl chloride. The reaction scheme is shown in Figure 4.1. Since adamantyl group is very bulky, the nucleophilic character of the tertiary alcohol is limited. Deprotonation of 1-adamantanol by n-BuLi increased the nucleophilicity. Several attempts were made to synthesize adamantyl esters by reacting 1-adamantanol with acryloyl chloride in the presence of pyridine but the yields did not exceed 32 per cent. Similar experiments were also carried out in the presence of triethylamine as a base, however, by-product formation was observed after 2 hours.

**Synthesis of Cyclohexyl Acrylate:** Since cyclohexyl group is less bulky than adamantyl group, corresponding ester synthesis could be achieved in the presence of triethylamine as shown in Figure 4.1.

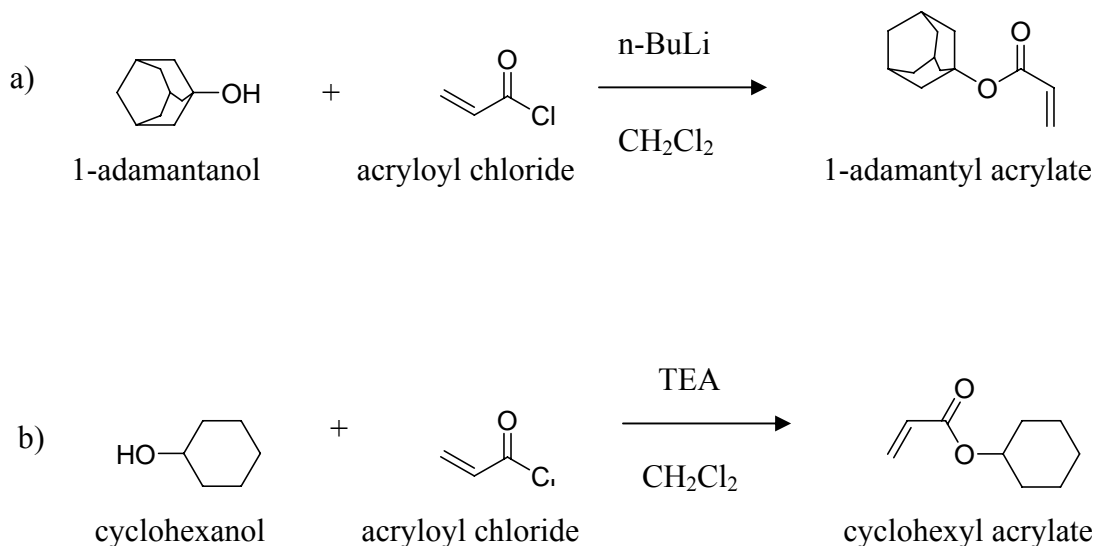


Figure 4.1. Synthesis of a) 1-adamantyl acrylate and b) cyclohexyl acrylate

#### 4.1.2. Characterization of Acrylates

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of the pure acrylates are presented in Figures 4.2-4.5. The spectra showed that, there were no peaks corresponding to the starting materials or other impurities. Typical chemical shifts were observed that are characteristic to 1-adamantyl ester and cyclohexyl ester.

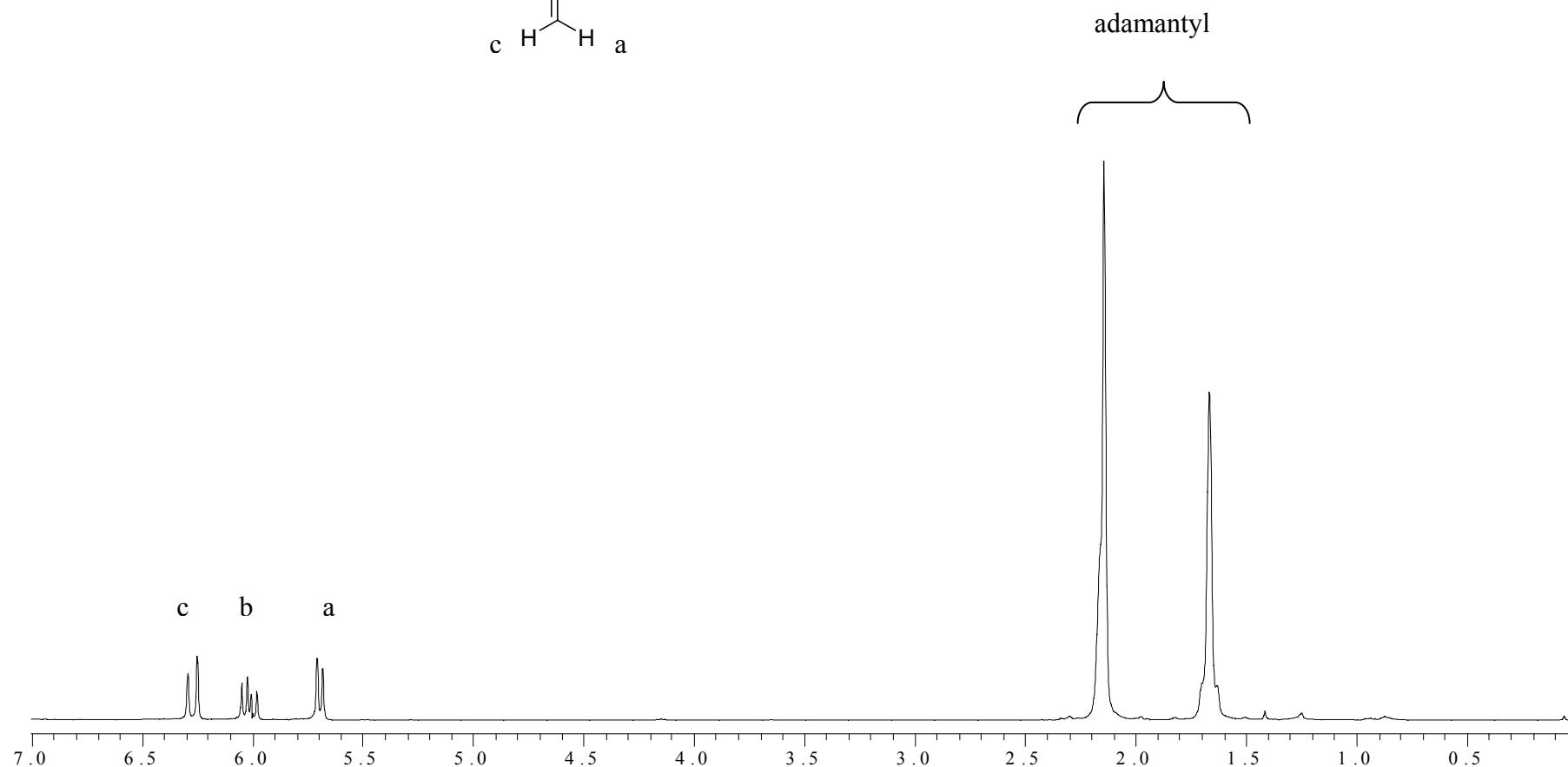
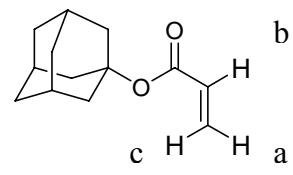


Figure 4.2. <sup>1</sup>H-NMR of 1-adamantyl acrylate

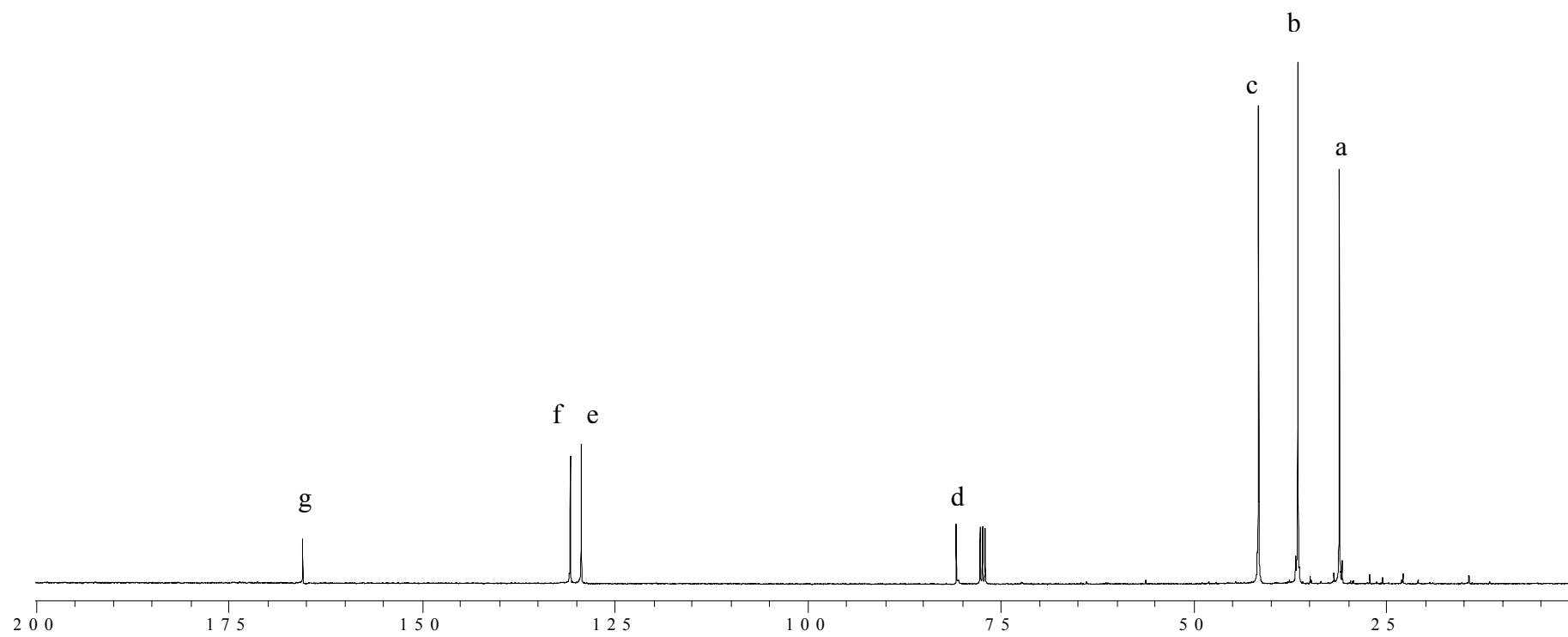
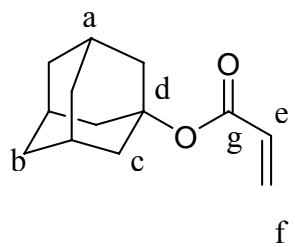


Figure 4.3. <sup>13</sup>C-NMR spectrum of 1-adamantyl acrylate

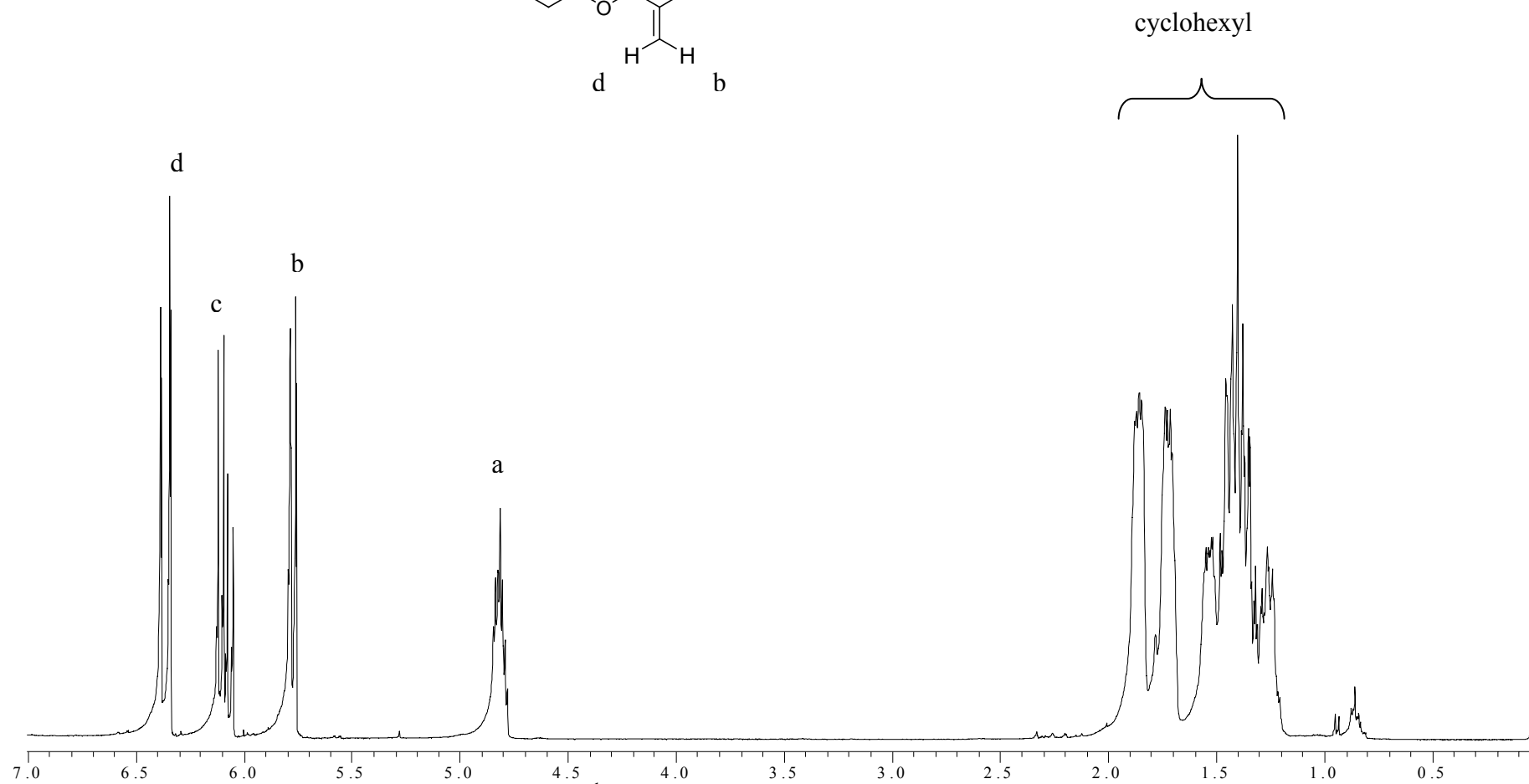
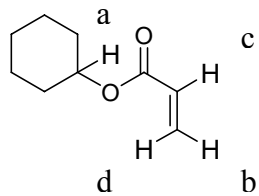


Figure 4.4. <sup>1</sup>H-NMR spectrum of cyclohexyl acrylate

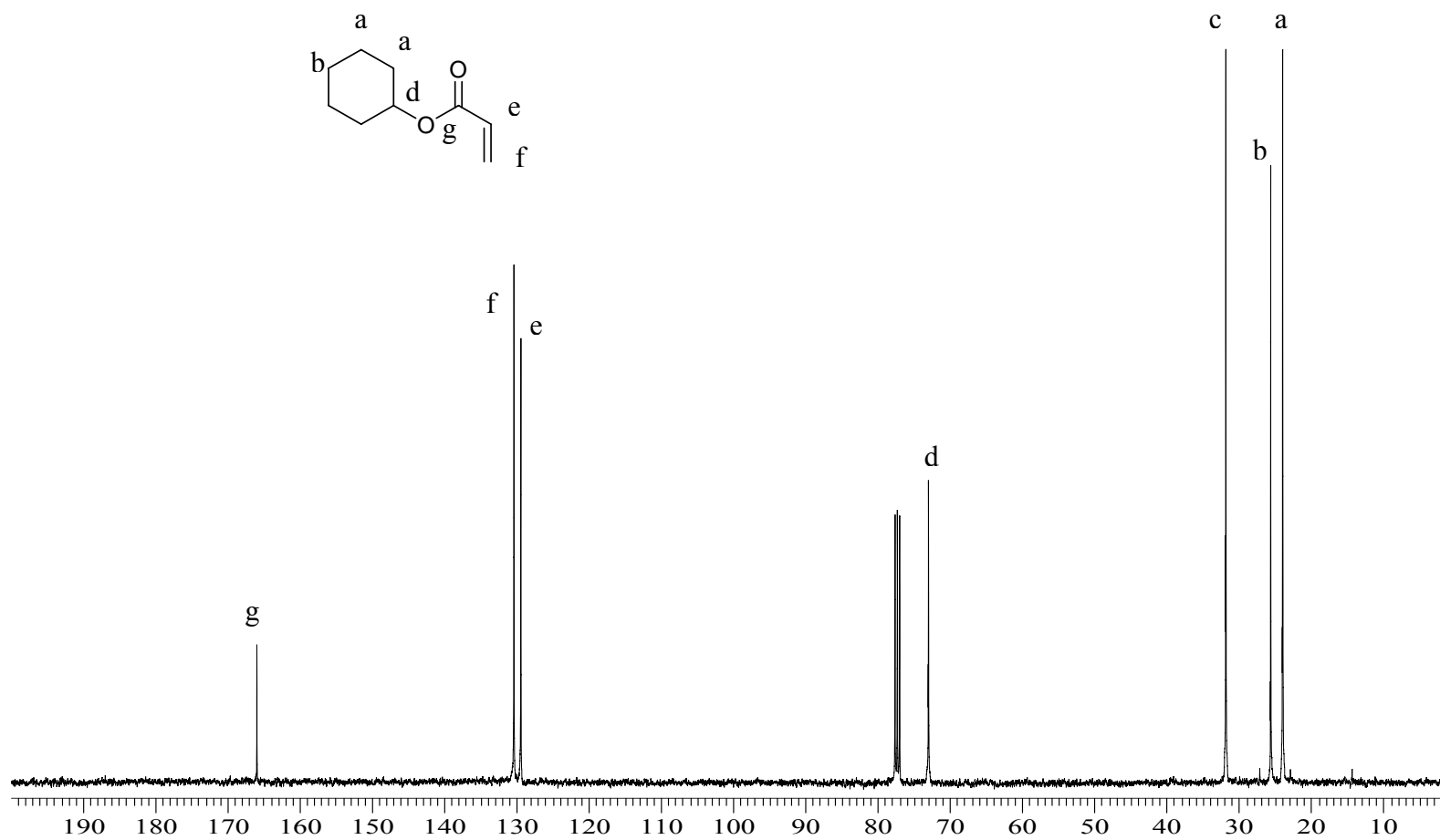


Figure 4.5.  $^{13}\text{C}$ -NMR spectrum of cyclohexyl acrylate.

### 4.1.3. Synthesis of RHMA Ether Dimers

RHMA ether dimers were synthesized by the extended Baylis-Hillman reaction from the corresponding acrylates. The Baylis-Hillman reaction, which is a tertiary amine-catalyzed coupling of an  $\alpha,\beta$ -unsaturated carbonyl compound with an aldehyde, is among the most useful C-C bond forming reactions in organic synthesis [34]. Acrylates are one of the compounds which can undergo the Baylis-Hillman reaction. The reaction pathway that produces the RHMA ether dimer is shown in Figure 4.6. The addition of formaldehyde to acrylate ester is catalyzed by 1,4-Diazabicyclo[2.2.2]octane (DABCO). Key step is the addition of the amine catalyst, DABCO, to  $\alpha,\beta$ -unsaturated ester to form a stabilized nucleophilic anion. This *in situ* generated nucleophile then adds to the aldehyde and RHMA product is obtained by the subsequent elimination of the amine. At higher temperatures, conversion of RHMA to ether dimer which is shown in the Figure 4.6 is thermodynamically favorable.

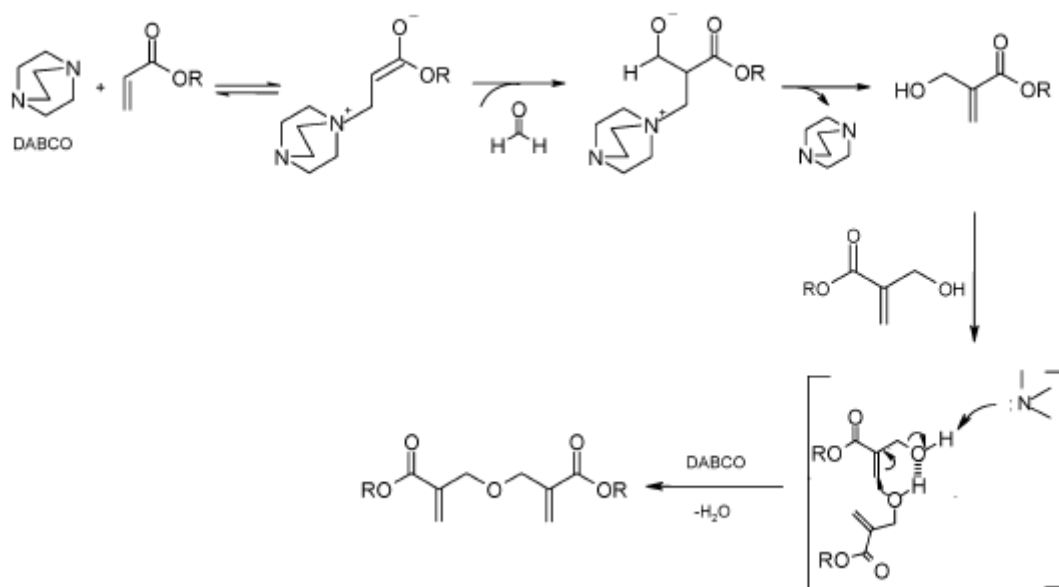


Figure 4.6. Synthesis of RHMA ether dimers by Baylis-Hillmann reaction.

Conversion of RHMA to ether dimer is sensitive to water. Since water is liberated in the formation of the ether dimer, the presence of water causes the cleavage of the ether

back to RHMA. Therefore, if water were removed during the later stages of the synthesis, overall reaction yield would be probably higher [35].

In this study, ether dimers of adamantyl- and cyclohexyl  $\alpha$ -(hydroxymethyl)acrylates ether dimers were synthesized successfully.

#### **4.1.4. Characterization of RHMA Ether Dimers**

As in the reactions of acrylates, reactions were monitored by TLC. It was observed that as reaction proceeded, formation of two products was observed. This observation proved the reaction mechanism. One spot belonged to the RHMA and the other belonged to the RHMA ether dimer. During the reaction, concentration of the RHMA decreased and that of the RHMA ether dimer increased. NMR spectra of the pure 1-adamantyl- and cyclohexyl-  $\alpha$ -(hydroxymethyl)acrylate ether dimers are shown in Figure 4.7-10.

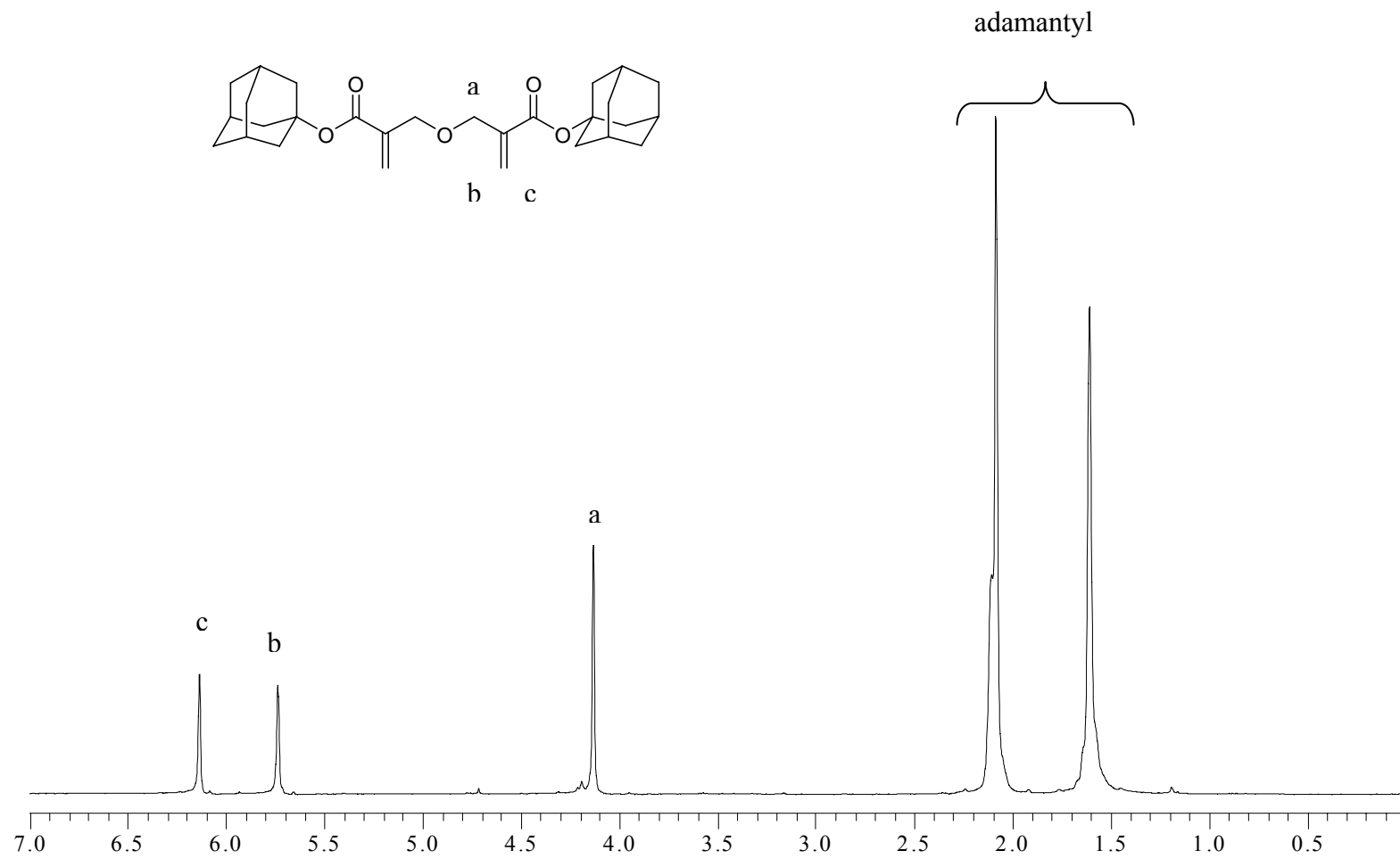


Figure 4.7.  $^1\text{H-NMR}$  of 1-adamantyl  $\alpha$ -(hydroxymethyl)acrylate ether dimer

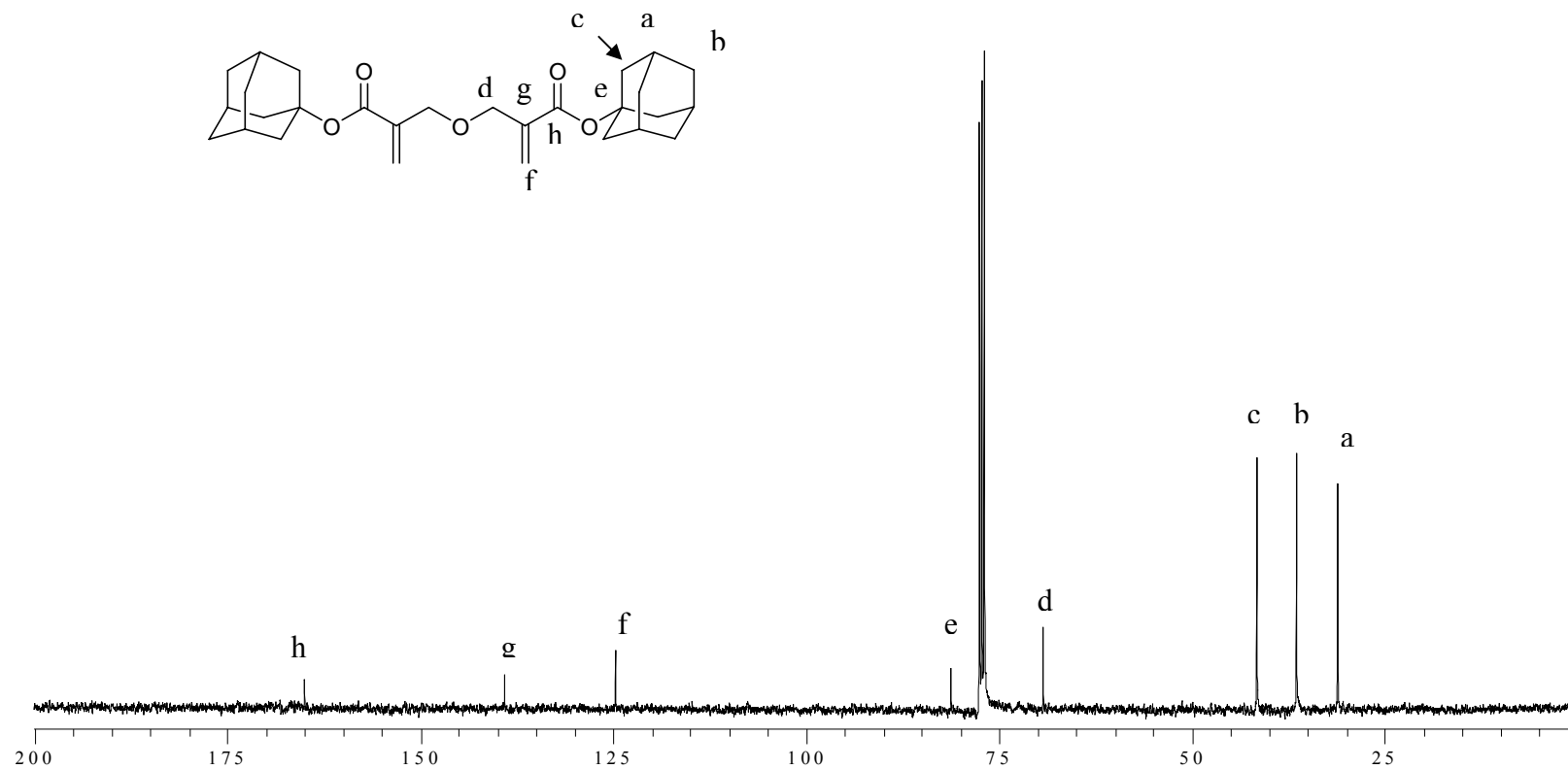


Figure 4.8.  $^{13}\text{C}$ -NMR of 1-adamantyl  $\alpha$ -(hydroxymethyl)acrylate ether dimer

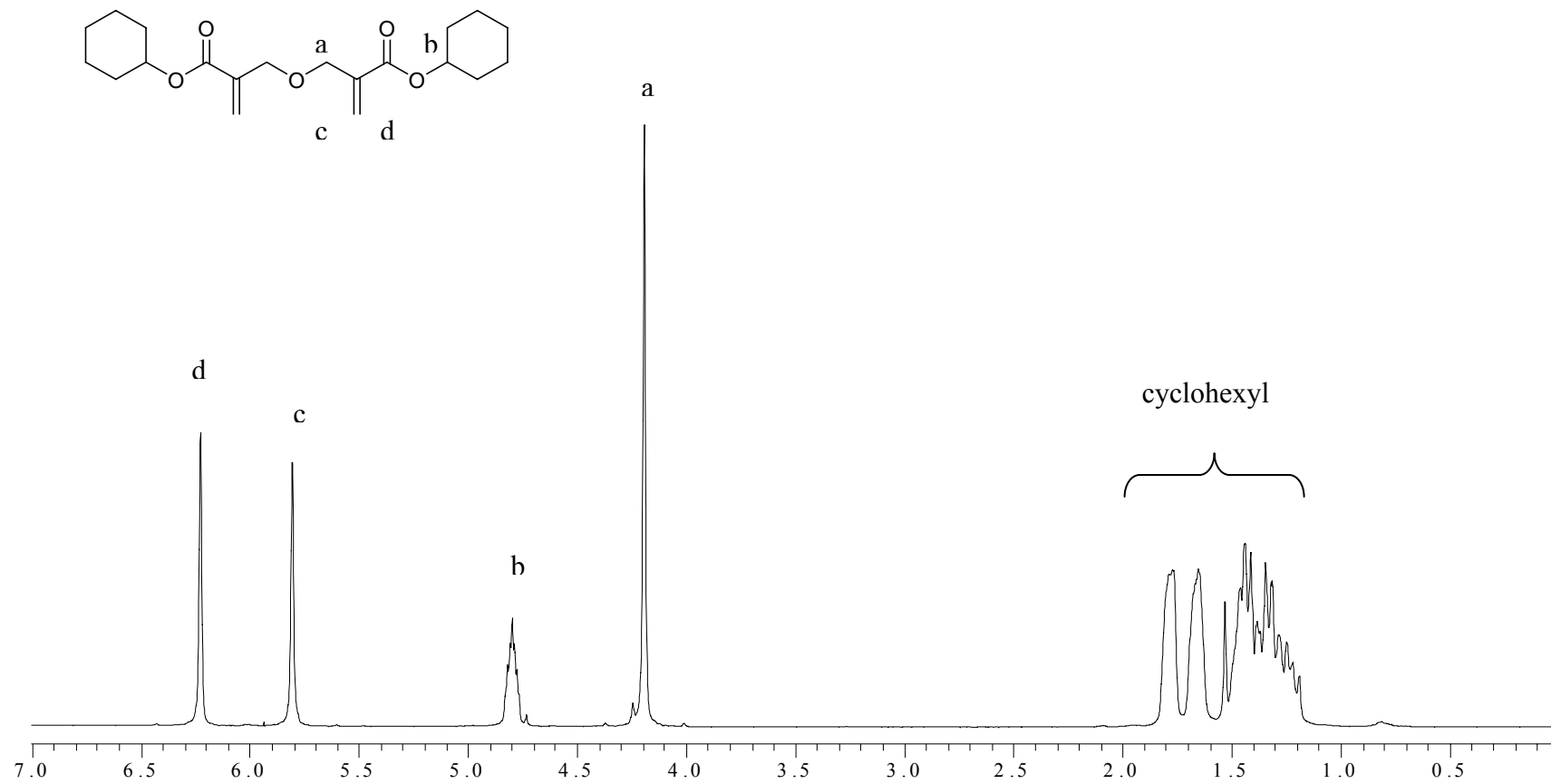


Figure 4.9.  $^1\text{H-NMR}$  spectrum of cyclohexyl  $\alpha$ -(hydroxymethyl)acrylate ether dimer

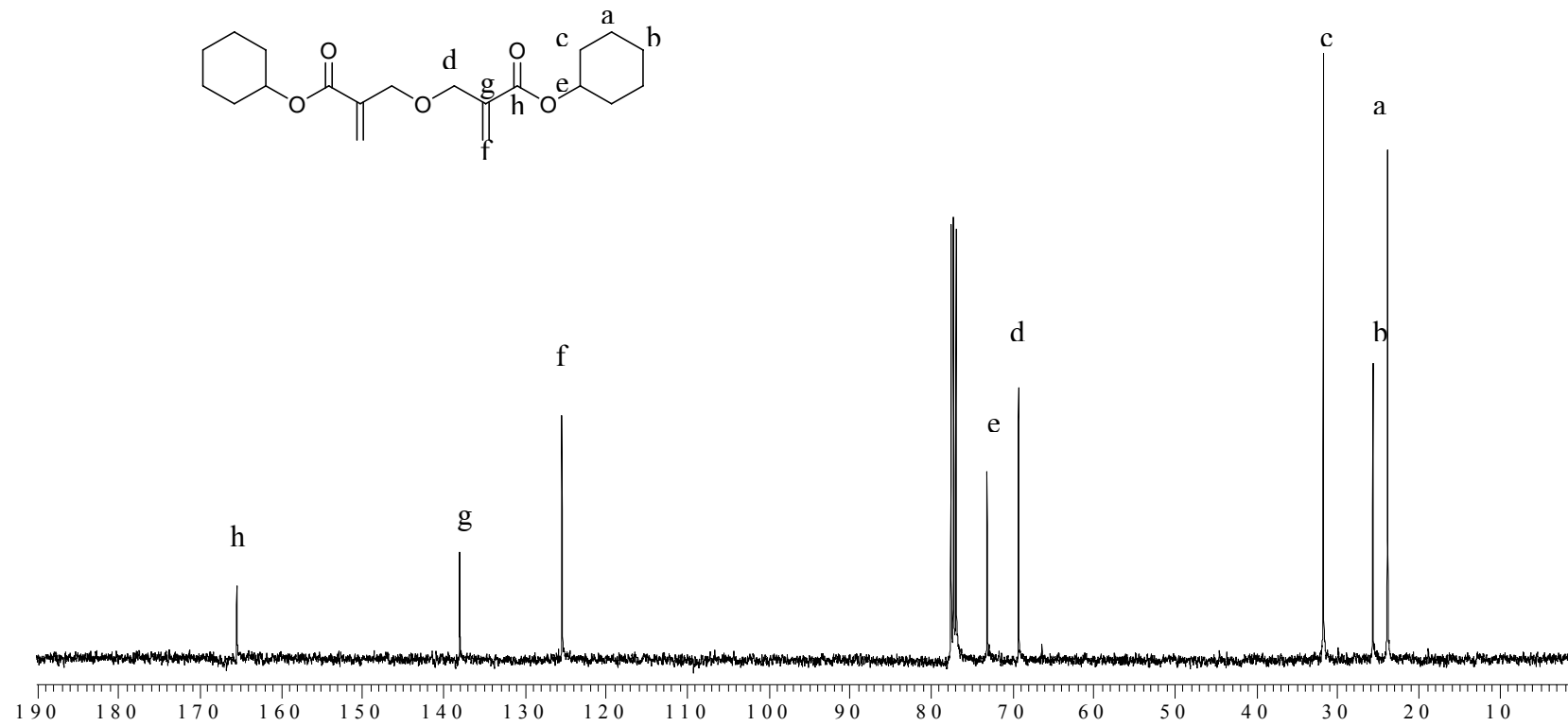


Figure 4.10.  $^{13}\text{C}$ -NMR of cyclohexyl  $\alpha$ -(hydroxymethyl)acrylate ether dimer



### 4.2.1. Steric Effect of R-group of Ester Substituent

As mentioned before in the ATRP of RHMA ether dimers, there are two possible reaction pathways which are shown in Figure 4.12. Depending on the polymerization parameters, such as temperature, and the steric interaction of the ester functionality, either intermolecular 1,2-vinyl addition of the pendant group, which leads to crosslinked polymer, or intramolecular cyclization which leads to cyclopolymers can be observed [9]. It was previously proved by our research group that small R-groups in ATRP result in crosslinked polymers [32]. However, as the bulkiness is increased, cyclization efficiency increases. For example, while the ethyl derivative resulted in crosslinked polymers, the n-butyl derivative gave mostly the desired cyclic polymers together with small amounts of pendant double bonds as detected by NMR. When the bulkier t-butyl derivative was subjected to ATRP, this time no pendant double bond was detected, thus, full cyclization was achieved.

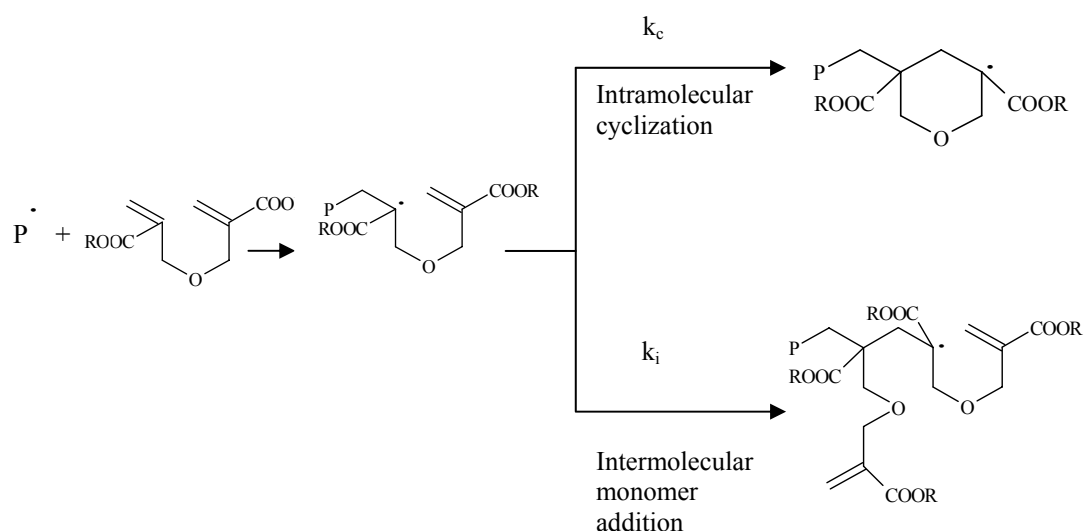


Figure 4.12. Inter- and intramolecular cyclization pathways of RHMA ether dimers

To the existing results obtained with ethyl, n-butyl and t-butyl derivatives of RHMA ether dimers, we wanted to add the cyclohexyl and adamantyl derivatives to observe the limits of the steric effect on ATRP and cyclization processes. Although bulky groups are desired for the cyclization pathway, they may alter the ATRP process. First, they could have an effect on the overall polymerization rate. Second, bulky groups may limit the access of the catalyst complex to the propagating site, and thus, they may negatively affect the control process in ATRP, in other words, the deactivation process.

Polymerizations were carried out with  $[M]:[EBiB]:[CuBr]:[Ligand]=100:1:1:1$  ratios in xylene at 80°C (Table 4.1). The concentrations of monomers in xylene were in between 0.91-0.97 M.

Table 4.1. Results from the ATRP of ADHMA and CHMA ether dimers at 80°C. <sup>a,b,c</sup>

Entry	Monomer	Time (h)	Conversion <sup>d</sup> (%)	$M_{n,cal}$ ( $10^3$ g/mol)	$M_{n,sec}$ ( $10^3$ g/mol)	PDI
1	t-butyl	8	36	10.7	10.9	1.19
2	ADHMA	3	58	22.7	10.9	1.50
3	ADHMA	4	38	17.2	9.2	1.41
4	ADHMA	4	52	23.0	10.3	1.46
5	ADHMA	5	30	13.8	6.3	1.40
6	CHMA	4	31	10.8	5.2	1.37
7	CHMA	5	48	16.8	7.6	1.39
8	CHMA	5	65	22.8	12.4	1.52

<sup>a</sup> All polymers were soluble in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> Conversions were calculated after second precipitation

<sup>c</sup> All monomers were ester ether dimers of the corresponding groups.

<sup>d</sup> Measured by gravimetric methods (weight of polymer / weight of polymer from 100% conversion).

The results obtained by the polymerization of bulky 1-adamantyl and cyclohexyl  $\alpha$ -(hydroxymethyl)acrylate ether dimers showed that, as the bulkiness was increased further, molecular weight distribution increased. Comparison of the results show that the molecular weight distribution increases when going from t-butyl- to cyclohexyl- then to adamantyl- ether dimers. This may be due to the fact that, the available free space around the propagating radical was occupied mostly by the bulky substituent. Therefore, the metal

catalyst could not get close enough to the propagating site to promote the formation of the dormant species. In other words, the deactivation rate constant decreased as the size of the substituents increased, giving rise to less controlled ATRP process. In all polymerizations, precipitation of the copper-catalyst, most probably Cu(II), was observed after about 1 hour and the amount of the precipitate increased with time. This may be another reason for high polydispersities because as Cu(II) precipitates out, the rate of reversible deactivation decreases and the amount of irreversible termination increases, generating more Cu(II). The nature of precipitate was not quite known, but from its dark green color, it appeared to be Cu(II)-based.

Molecular weights obtained were lower than the theoretical values for both adamantyl and cyclohexyl substituents. This was attributed to hydrodynamic volume difference between the resulting polymers and polystyrene standards which was used to calibrate the GPC. Further NMR studies will be carried out to clarify the differences observed.

First indication that cyclizations were efficient was that all polymers obtained were soluble in organic solvents such as dichloromethane. Also both  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectroscopies proved that cyclizations were efficient with RHMA ether dimers with the bulky R groups (Figure 4.13-16). In the  $^{13}\text{C-NMR}$  characterizations, the spectrum clearly shows peaks characteristic of backbone carbons, cyclic ether groups, ester carbonyls. The backbone quaternary carbon is at 45 ppm and ether methylenes of the cyclopolymer are at 72 ppm. The peaks of ester alkyls are at the same positions as those in the  $^{13}\text{C-NMR}$  spectroscopies of corresponding RHMA ether dimers. The ester group on the ring is at 174 ppm. For both cyclohexyl and adamantyl derivatives, there were no evidence of the presence of uncyclized-pendant double bonds in the polymers. This suggesting that full cyclization was achieved. In other words, once the radical was formed, intramolecular cyclization was favored over intermolecular addition reaction.

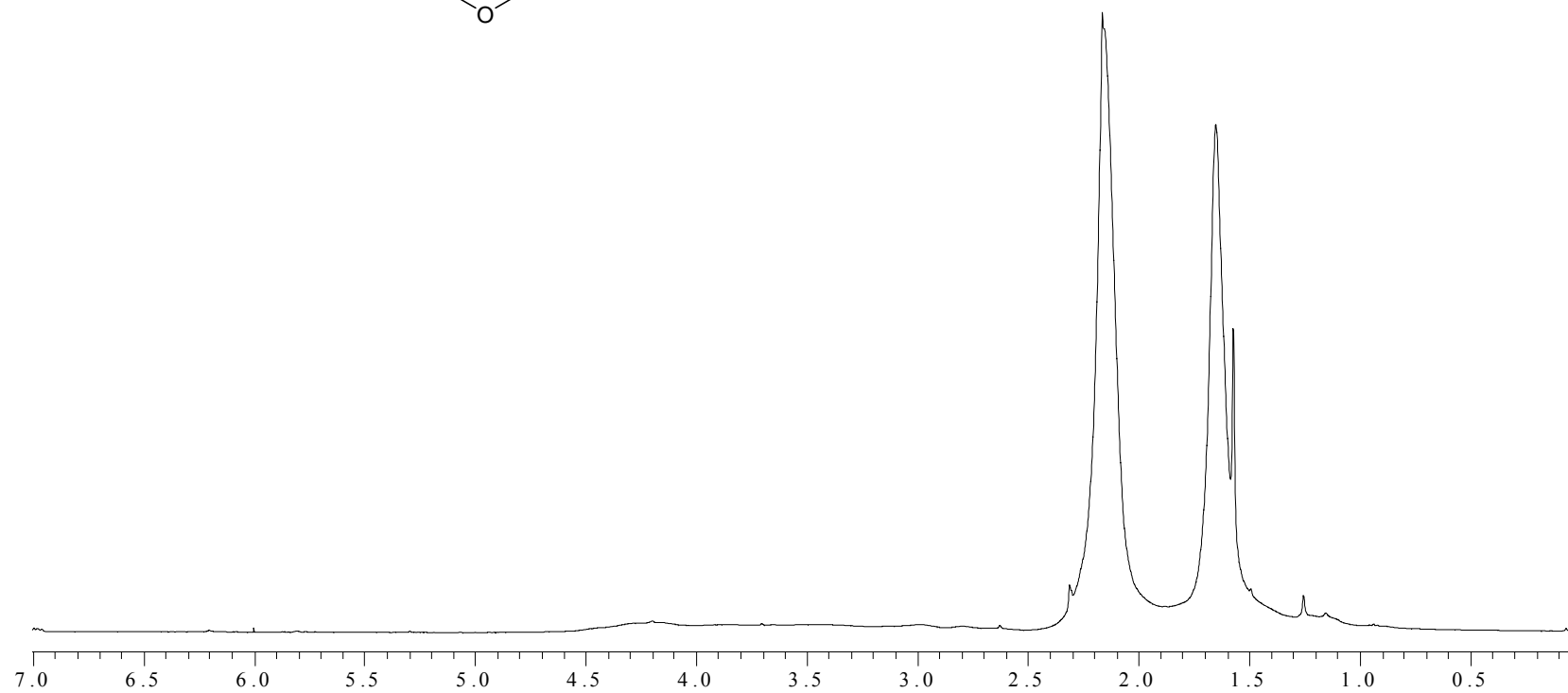
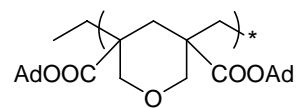


Figure 4.13.  $^1\text{H-NMR}$  of poly(ADHMA ether dimer)

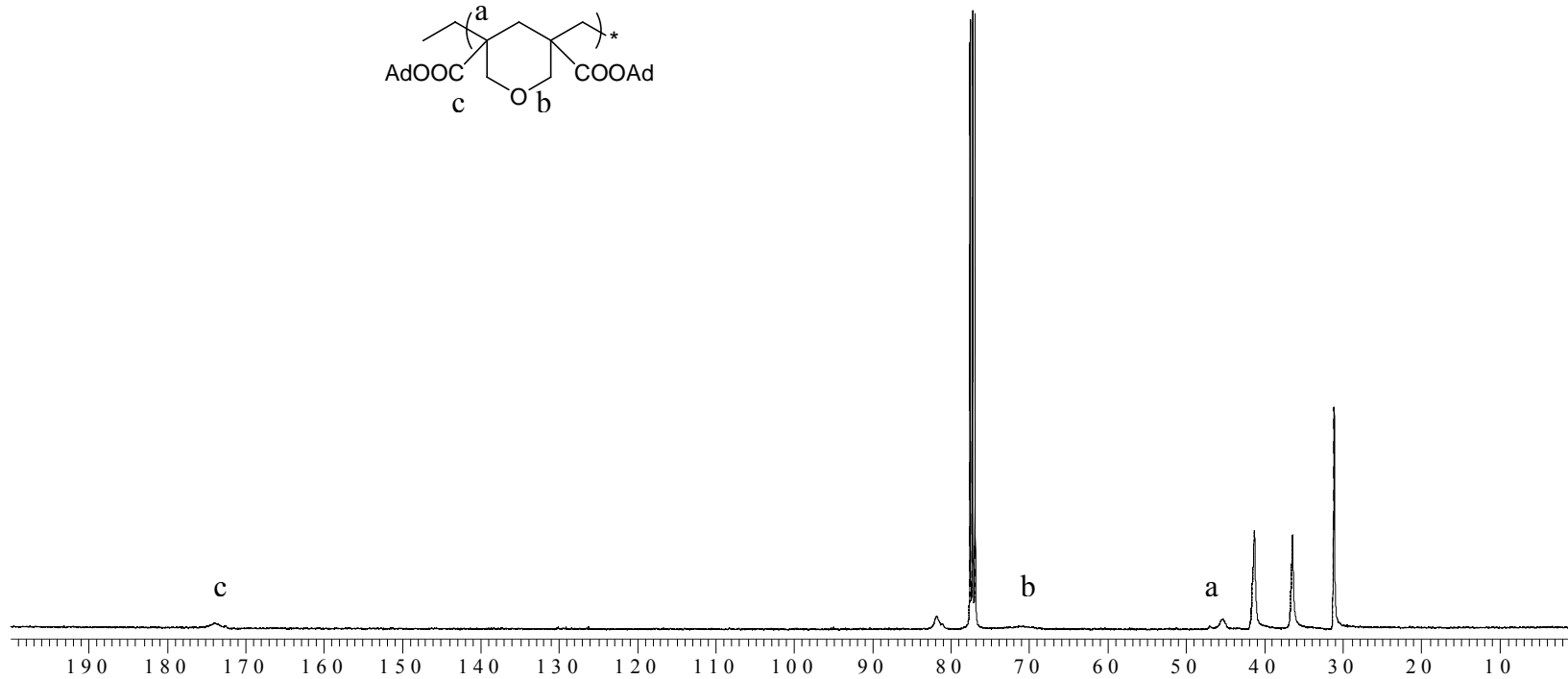
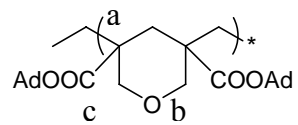


Figure 4.14.  $^{13}\text{C}$ -NMR of poly(ADHMA ether dimer)

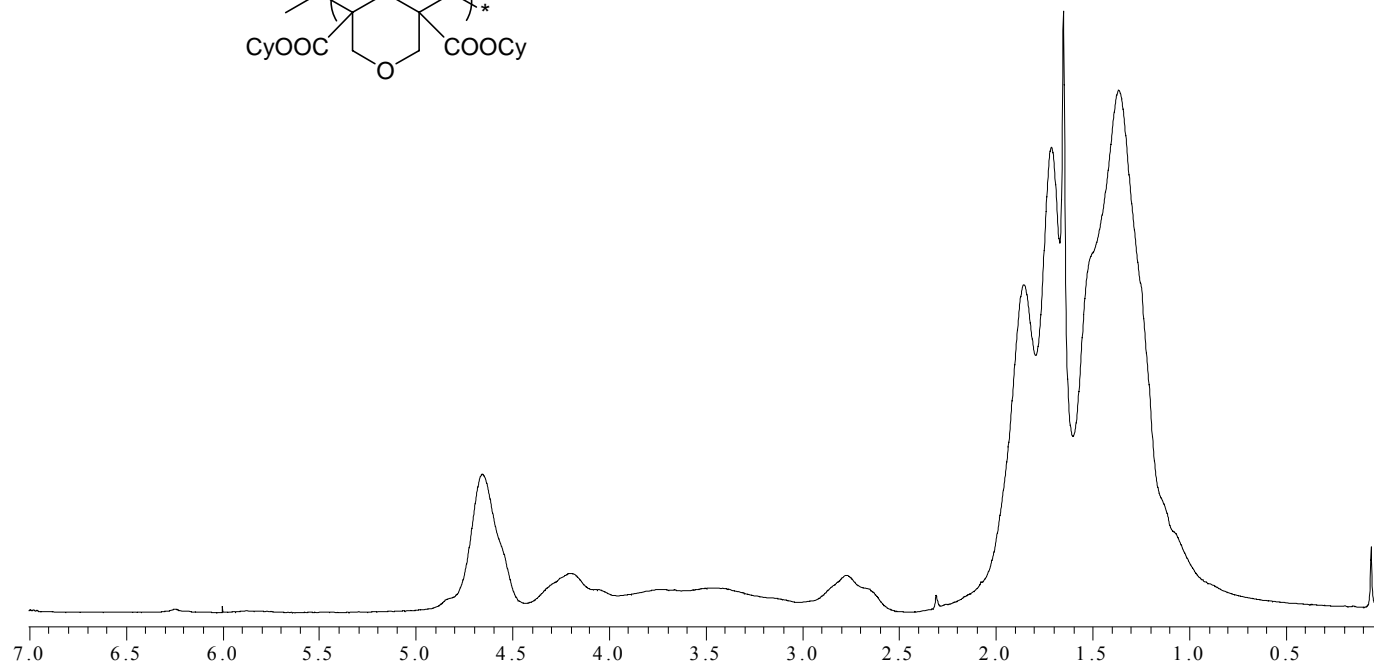
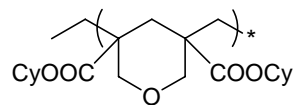


Figure 4.15.  $^1\text{H-NMR}$  of poly(CHMA ether dimer)

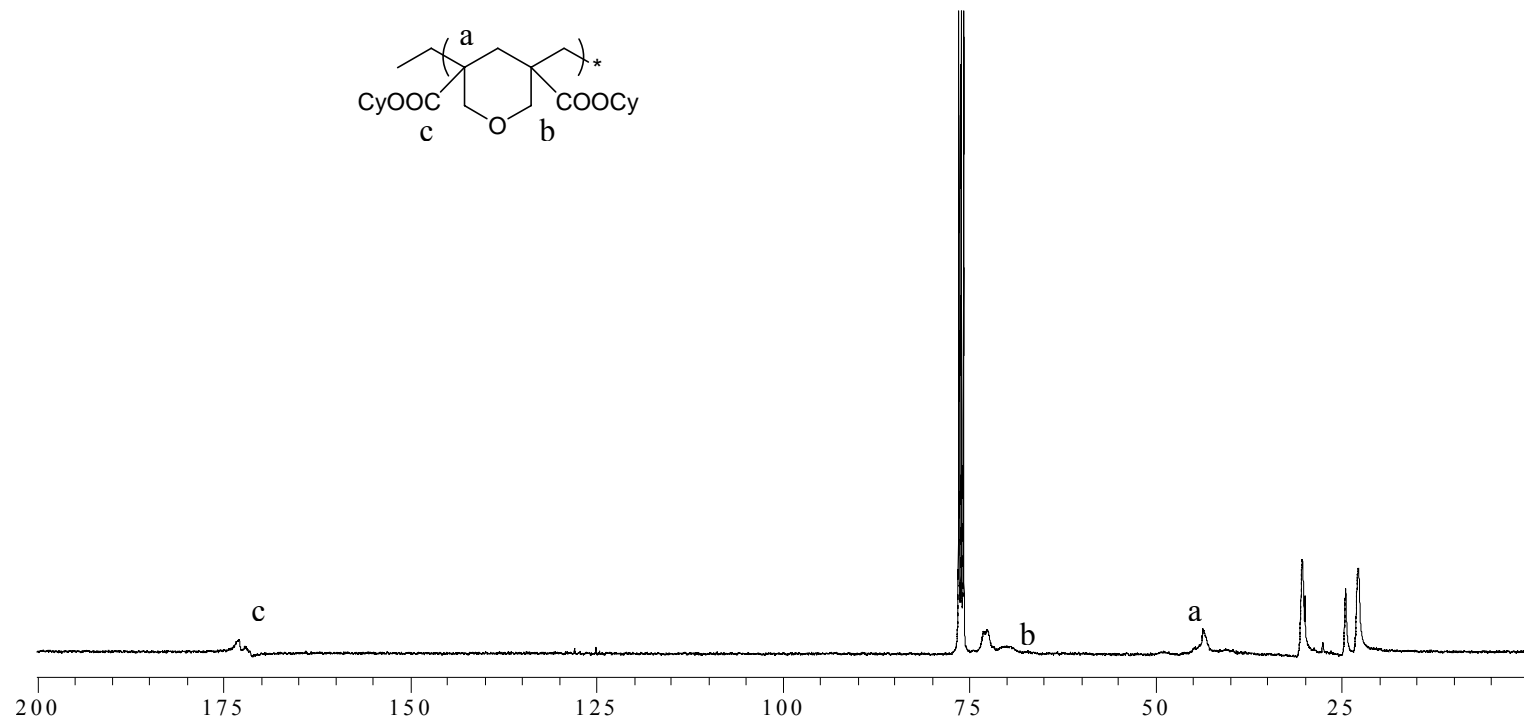


Figure 4.16.  $^{13}\text{C}$ -NMR of poly(CHMA ether dimer)

The results of the kinetic study of cyclopolymerization of CHMA ether dimers at 80°C is shown in Table 4.2 (Figure 4.17-18). The data indicates that molecular weights increased with the conversion linearly. Molecular weight distribution was low initially but it increased with time and conversion. The increase in polydispersity may result from the poor controlled ATRP process which becomes more apparent as the conversion increases. Also, this might be due to terminations of the propagating chains with oxygen which might diffuse into the reaction flask during the slow polymerization process or while taking samples.

Table 4.2. Results from kinetic study of ATRP of CHMA ether dimer at 80°C.<sup>a,b</sup>

Entry	Monomer	Time (h)	Conversion <sup>c</sup> (%)	$M_{n,cal}$ ( $10^3$ g/mol)	$M_{n,sec}$ ( $10^3$ g/mol)	PDI
1	CHAD	0.75	39	13.6	9.2	1.47
2	CHAD	1.75	71	24.8	16.7	1.72
3	CHAD	3.00	80	28.0	19.6	2.02
4	CHAD	4.00	86	30.1	21.8	2.08

<sup>a</sup>Conditions:  $[M]_0:[I]:[CuBr]:[Ligand]=100:1:1:1$ ,  $[M]=0.96$  M in xylene.

<sup>b</sup>All polymers were soluble in  $CH_2Cl_2$ .

<sup>c</sup> Measured by gravimetric methods (weight of polymer / weight of polymer from 100% conversion).

A linear plot of  $\ln ([M]_0/[M])$  versus time was observed for the ATRP of CHMA ether dimer, which indicates that the number active species ( $k_p [P]$ ) remains essentially constant throughout the course of the cyclopolymerization ( Figure 4.17) Also linear evolution of molecular weight with conversion showed that although polydispersity increased, polymerization was still under some control (Figure 4.18).

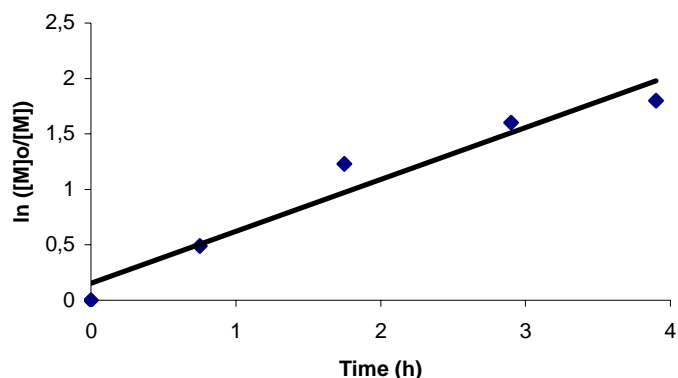


Figure 4.17. Plot of  $\ln ([M]_0/[M])$  versus time for CHMA ether dimer polymerization via ATRP. Conditions:  $80^\circ\text{C}$ ;  $[M]=0.96\text{M}$ ;  $[M]_0:[I]:[\text{Cu}]:[L]=100:1:1:1$

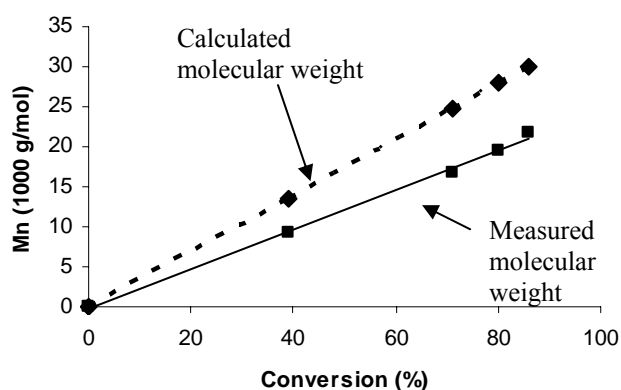


Figure 4.18. Plot of  $M_n$  versus conversion for CHMA ether dimer polymerization via ATRP. Conditions:  $80^\circ\text{C}$ ;  $[M]=0.96\text{M}$ ;  $[M]_0:[I]:[\text{Cu}]:[L]=100:1:1:1$

#### 4.2.2. Effect of Temperature on ATRP Cyclopolymerization

In the conventional free radical cyclopolymerization of the RHMA ether dimers, it is known that temperature affects the course of the cyclopolymerizations. At higher temperatures intramolecular cyclization becomes favored. Therefore, effect of temperature was investigated for the cyclopolymerization of 1-adamantyl and cyclohexyl  $\alpha$ -(hydroxymethyl)acrylate ether dimers and the results are presented in Table 4.3.

Table 4.3. Results from the ATRP of ADHMA and CHMA ether dimers at 100°C. <sup>a,b,c</sup>

Entry	Monomer	Time (h)	Conversion <sup>d</sup> (%)	$M_{n,cal}$ (10 <sup>3</sup> g/mol)	$M_{n,sec}$ (10 <sup>3</sup> g/mol)	PDI
1	ADHMA	4	28	12.0	5.2	1.41
2	ADHMA	4.5	30	13.6	6.2	1.48
3	CHMA	3	80	28.0	12.7	1.81
4	CHMA	4.5	87	30.4	15.5	2.00

<sup>a</sup> All polymers were soluble in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> Conversions were calculated after second precipitation

<sup>c</sup> All monomers were ester ether dimers of the corresponding groups.

<sup>d</sup> Measured by gravimetric methods (weight of polymer / weight of polymer from 100% conversion).

The results obtained at 100°C show that high temperature did not have a significant effect on the polydispersities and conversions in the ATRP of adamantyl  $\alpha$ -(hydroxymethyl)acrylate ether dimer. On the other hand, a temperature effect was observed with the cyclohexyl  $\alpha$ -(hydroxymethyl)acrylate ether dimer. These different behaviors of poly(ADHMA ether dimer) and poly(CHMA ether dimer) may result from the different responses of the activation and deactivation rate constants to temperature. Since each monomer has its own characteristic rate constants, effect of temperature may vary depending on the monomer.

#### 4.2.3. Physical Properties of the Cylopolymers

The glass transition temperatures of the resulting poly(ADHMA ether dimer) and poly(CHMA ether dimer) were around 240°C and 128°C, respectively (Figure 4.19-20).

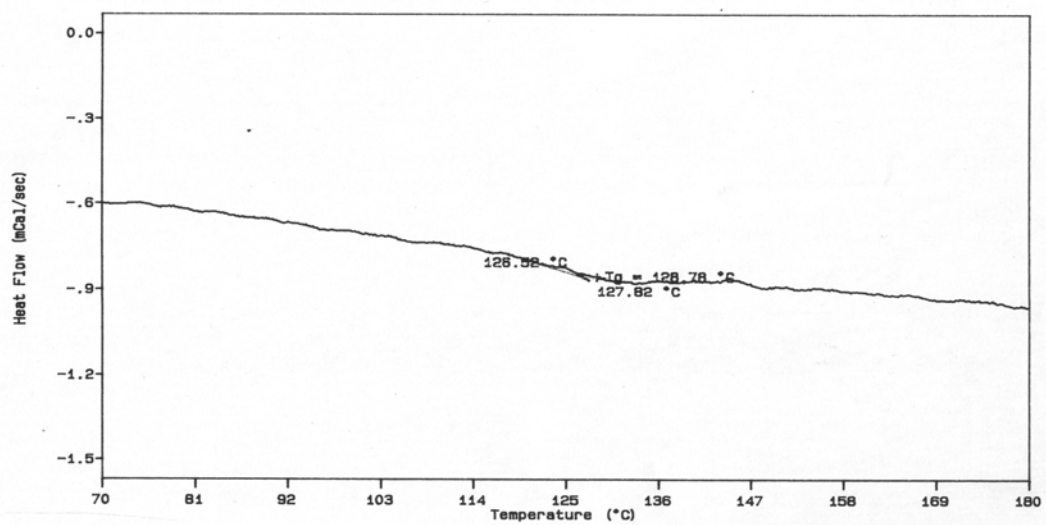


Figure 4.19. DSC of poly(CHMA ether dimer) at heating rates of 10°C/min.

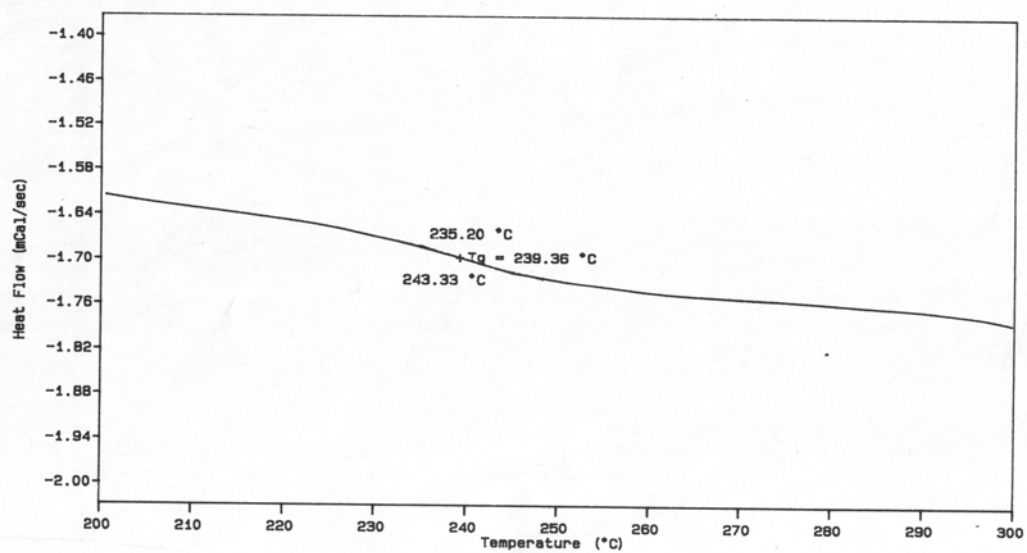


Figure 4.20. DSC of poly(ADHMA ether dimer) at heating rates of 10°C/min.

Thermal stability of the polymers were investigated by thermogravimetric analysis (TGA) under nitrogen. Figure 4.21 shows the TGA thermograms of poly(ADHMA ether dimer).

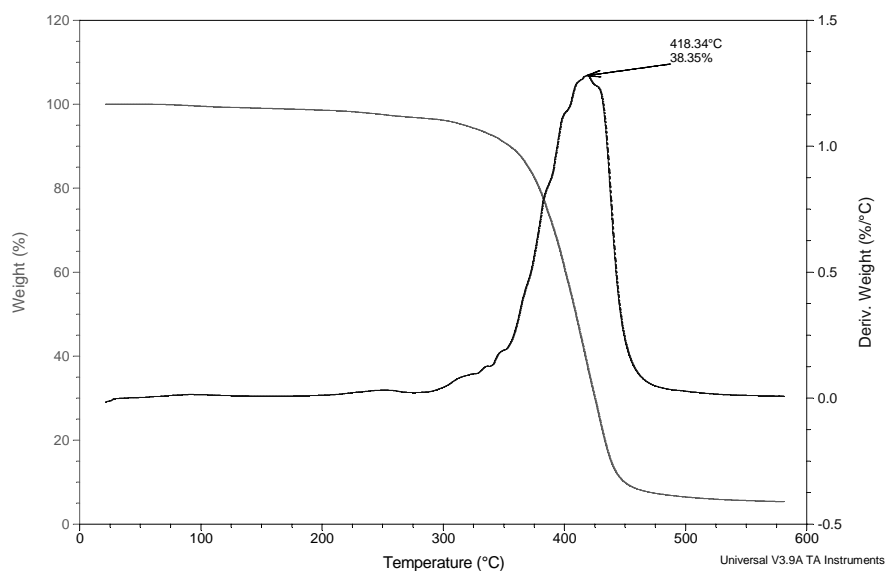


Figure 4.21. TGA thermograms of poly(ADHMA ether dimer).

The polymer containing adamantyl group showed high thermal stability. The decomposition was observed at 418°C which probably belongs to chain decomposition. In the TGA thermogram of poly(CHMA ether dimer), a two step decomposition was observed (Figure 4.22). First at 328°C which most probably belongs to cyclohexyl decomposition and second at 424°C which belongs to chain decomposition.

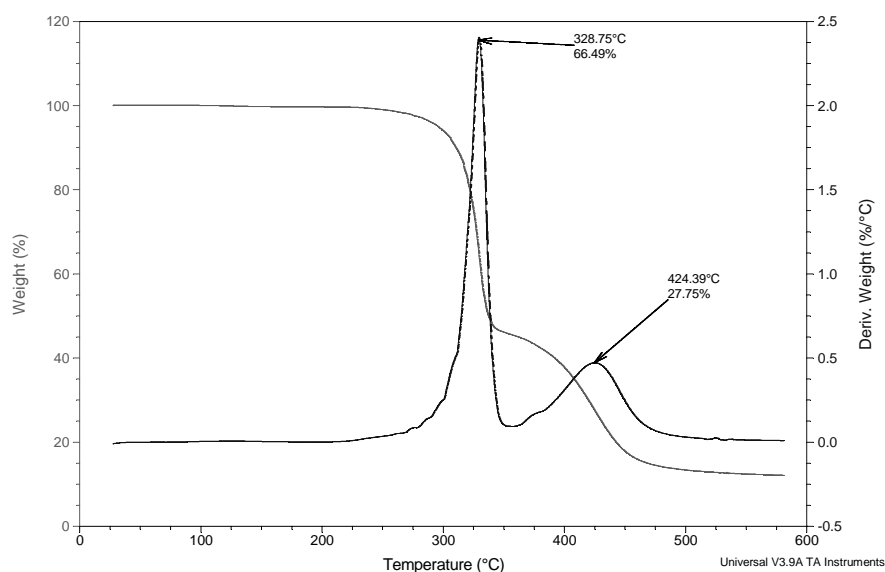


Figure 4.22. TGA thermograms of poly(CHMA ether dimer).

### 4.3. Block Copolymerizations of poly(ADHMA ether dimer) and poly(CHMA ether dimer)

Copolymerization studies were performed to prove the livingness of the cyclopolymers obtained. The copolymerizations were carried out with both CuBr/PMDETA and CuCl/PMDETA catalyst complexes at 80°C in bulk using the obtained cyclopolymers as macroinitiators. The second monomer, *t*-butyl acrylate or *n*-butyl acrylate depending on the monomer type, was used as the solvent. For both copolymerizations, increase in molecular weights were observed (Table 4.4).

Table 4.4. Synthesis of copolymers by ATRP in bulk at 80°C.<sup>a,b,c</sup>

Entry	Macroinitiator	Time (hour)	Catalyst	Mn,macroinitiator (103 g/mol)	Mn,sec Copolymer (103 g/mol)	PDI
1	Poly(ADHMA ether dimer)	5	CuBr	11.2	20.7	2.2
2	Poly(ADHMA ether dimer)	5.5	CuCl	11.2	15.7	1.6
3	Poly(CHAD ether dimer)	5	CuBr	7.5	15.8	1.8
4	Poly(CHAD ether dimer)	6	CuCl	5.2	16.2	2.2

<sup>a</sup> Monomers were *n*-butyl acrylate for entry 1-2, *tert*-butyl for 3 and 4.

<sup>b</sup> Conditions: [I]<sub>0</sub>: [CuX]<sub>0</sub>: [PMDETA] = 1:2:2

<sup>c</sup> Macroinitiators were Br-terminated

In the SEC traces, although an increase in molecular weight was observed, bimodal peaks were detected for the copolymerization of poly(ADHMA ether dimer) with CuBr/PMDETA catalyst (Figure 4.23-24). In the copolymerization of poly(CHMA ether dimer) with CuBr/PMDETA catalyst system, a new peak at higher molecular weight was observed as in the poly(ADHMA ether dimer) with a slight shoulder (Figure 4.21). We believe that the bimodal or larger molecular weight distribution is due to the slow initiation from the bulky cyclic structure, and faster propagation of the acrylates. When CuCl was used to perform a halogen exchange to slow down the propagation rate, similar results were obtained. Further studies are needed to understand the copolymerization behavior. The use of the CHMA or ADHMA ether dimers as the monomers for the so called copolymerization study, may help to understand whether or not the bimodal peak distribution is due to slow initiation and fast propagation rates.

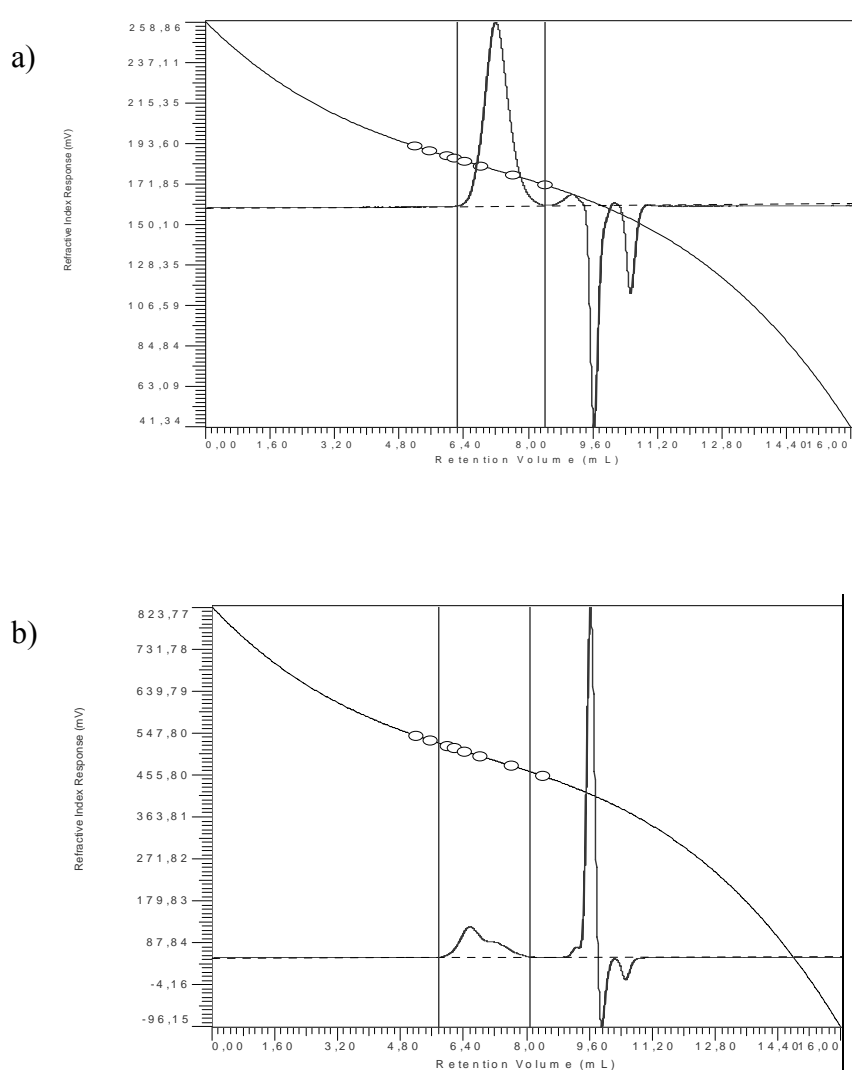


Figure 4.23. SEC traces of polymers a) Poly(ADHMA ether dimer) macroinitiator  
b) Copolymer of poly(ADHMA ether dimer)

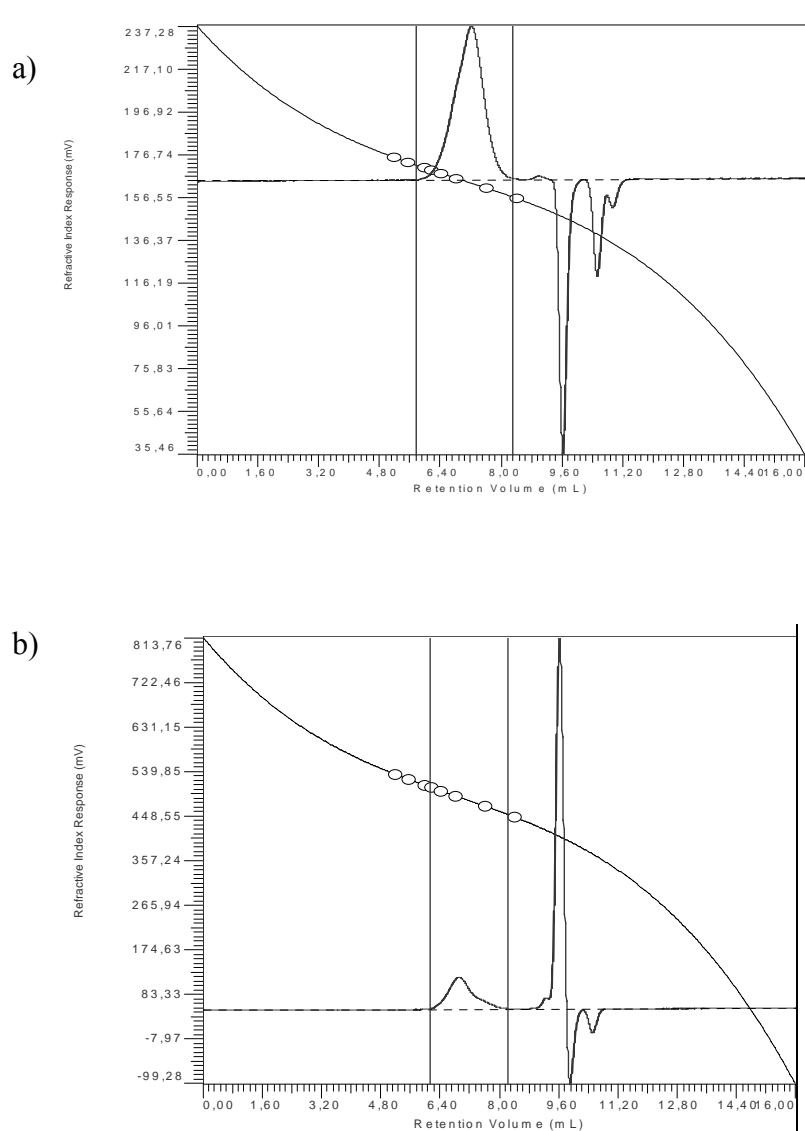


Figure 4.24. SEC traces of polymers a) Poly(CHMA ether dimer) macroinitiator  
b) Copolymer of poly(CHMA ether dimer)

## CONCLUSION

As a summary, steric effect of alkyl groups on ATRP cyclopolymerization was investigated by increasing bulkiness of substituent groups. In the cyclopolymerization of both adamantyl and cyclohexyl  $\alpha$ -(hydroxymethyl)acrylate ether dimers cyclization efficiency was high enough to give fully cyclic polymers, on the other hand, control was poorer with increasing bulkiness. At higher temperature, both polydispersity and conversion increased in ATRP of cyclohexyl  $\alpha$ -(hydroxymethyl)acrylate ether dimers, however, the ATRP of the adamantyl  $\alpha$ -(hydroxymethyl)acrylate ether dimers was not affected much.

Livingness of the obtained polymers was investigated by copolymerization with *n*-butyl and *tert*-butyl acrylates. Increase in molecular weight was observed but peaks belonged to copolymers had always shoulders. This showed the livingness of the obtained polymers, but high propagation and slow initiation rate constants probably resulted in copolymers with less defined structures. Thermal properties of the homopolymers were also determined. Both polymers had excellent thermal stabilities and high glass transition temperatures.

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