EFFECT OF THE ESTER (R) GROUPS ON THE CONTROLLED/LIVING ATRP CYCLOPOLYMERIZATION OF ALKYL ALPHA-(HYDROXYMETHYL) ACRYLATE (RHMA) ETHER DIMERS

by

Sezgin Bayrak

B.S., Chemistry, Boğaziçi University, 2006

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

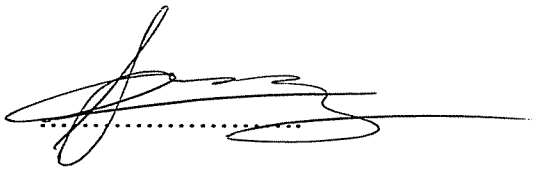
Boğaziçi University

2009

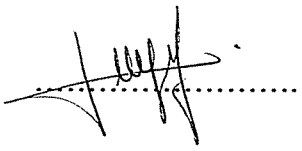
EFFECT OF THE ESTER (R) GROUPS
ON THE CONTROLLED/LIVING ATRP CYCLOPOLYMERIZATION OF
ALKYL ALPHA-(HYDROXYMETHYL) ACRYLATE (RHMA) ETHER DIMERS

APPROVED BY :

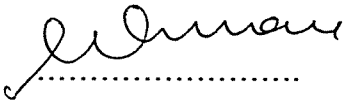
Assoc. Prof. A.Ersin Acar
(Thesis Supervisor)



Prof. Duygu Avcı



Prof. Ümit Tunca



DATE OF APPROVAL : 10.02.2009

To my lovely

FAMILY

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor Assoc. Prof. A. Ersin ACAR. I am indebted to him. Special thanks go to him for all the help, guidance, patience, encouragement, and motivation during my Ms. Thesis.

I would like to thank Prof. Duygu AVCI and Prof. Ümit TUNCA for being my committee members. I appreciate the time they spent for evaluating this thesis.

I would like to thank Aydın Can, a chemsick fellow, who conduced me to join Acar's Group. I am also grateful to, Ahmet Köseoğlu, Erhan Özkal, Cüneyt Bağcıoğlu, Hikmet Karayel, Gökhan Abi and Cem Öztürk for their friendship and help during my study. I wish to thank to my laboratory friends, Selda Erkoç and Engin Doğan for their support and friendship. I would like to extend my thanks to all members of Chemistry Department and the secretary of the department, Hülya Metiner, for their help and kindness.

I would like to thank special persons in this world, my Dad (Kemal Bayrak) and my Mom (Serpil Bayrak). Besides, I would like to thank my brother (Yusuf) and the loveliest sister in this world (Yeşim). For all of them I dedicate the thesis.

Above all, special thanks for my Chamomel, Nihan Sevinç. She is the person who stood beside me and encouraged me constantly. This accomplishment is as much as hers as it is mine. Without her this journey would have looked so much more intimidating.

I would like to thank Ali VATANSEVER from KordSA Global for the financial aid during my research. This project has been supported by Bogazici University Research Fund (BAP) with 04HB505 project number and The Scientific and Technological Research Council of Turkey (Tübitak) with 104M201 project number.

ABSTRACT

EFFECT OF THE ESTER (R) GROUPS ON THE CONTROLLED LIVING ATRP CYCLOPOLYMERIZATION OF ALKYL α-(HYDROXYMETHYL) ACRYLATE (RHMA) ETHER DIMERS

Previous cyclopolymerization studies of alkyl α-(hydroxymethyl) acrylate (RHMA) ether dimers showed that they are superior to non-cyclic linear ones due to improved thermal stability and high glass transition temperatures.

Cyclopolymerizations of RHMA ether dimers via controlled living ATRP have been formerly investigated in the literature where smaller alkyl groups such as ethyl, *n*-butyl and *tert*-butyl and bulkier groups such as; adamantyl and cyclohexyl groups were used as the alkyl group. It was found out that as the bulkiness of the alkyl group (R) increased, cyclization efficiency and polydispersities were improved up to certain size (*t*-butyl), but became worse when the size was increased further. However, the present study with another bulky group, isobornyl, exhibited polydisperties as low as the ones obtained with smaller *t*-butyl derivative, indicating that the ATRP process was more controlled than other bulky groups such as adamantyl. In addition to this, smaller isopropyl derivative was also studied and polydisperties was found to be much higher than the monomers with bulkier isobornyl and *t*-butyl groups, indicating that the ATRP polymerization was less controlled.

In this study, CuBr/PMDETA catalyst system was employed and cyclopolymerizations of isobornyl and isopropyl α-(hydroxymethyl) acrylate ether dimers were carried out in xylene. Cyclopolymers of IBHMA and IPHMA ether dimers were employed as macroinitiators in copolymerization studies with *t*-butyl acrylate comonomer in order to prove the livingness. SEC analysis showed that the cyclopolymers obtained were all living. Fortcoming studies on the physical properties of the cyclopolymers were also carried out and high T_g values and thermal stabilities were investigated.

ÖZET

ESTER (R) GRUPLARININ ALKİL α-(HİDROKSİMETİL) AKRİLAT (RHMA) ETER DİMERLERİNİN KONTROLLÜ YAŞAYAN ATRP HALKALI POLİMERİZASYONU ÜZERİNDEKİ ETKİLERİ

Önceki halkalı polimerizasyon çalışmalarında, alkil α-(hidroksimetil) akrilat (RHMA) eter dimerlerin, halkalı olmayan düz polimerlere göre daha yüksek ısısal dayanıklığa ve camsı geçiş sıcaklığına sahip oldukları görülmüştür.

Daha önce literatürde hacimce daha küçük alkil (R) gruplarına sahip; etil, *n*-butil ve *tert*-butil ve bunlara ek olarak hacimce daha büyük adamantil ve siklohekzil α-(hidroksimetil) akrilatların kontrollü yaşayan ATRP yöntemi kullanılarak halkalı polimerleşmeleri araştırılmıştır. Bağlı olan alkil (R) gruplarının hacimce büyümesinin, halkalaşma etkinliğini ve moleküler ağırlık dağılımını belirli bir hacme kadar (*t*-butil) iyileştirdiği, fakat daha sonrasında hacmin daha da büyütülmesinin bu değerleri kötü yönde etkilediği gözlemlenmiştir. Bu tezde hacimce büyük olan diğer bir grup, isobornil ile yapmış olduğumuz çalışmalar, moleküler ağırlık dağılımının hacimce daha küçük *t*-butil türevinin sahip olduğu kadar küçük olduğunu ortaya koymuştur. Bu, ATRP sisteminin, adamantil'dekinden daha kontrollü olduğunu göstermiştir. Ayrıca hacimce küçük olan isopropil grubu da çalışılmış olup, moleküler ağırlık dağılımının, hacimce büyük isobornil ve hacimce benzer *t*-butil gruplarından çok daha yüksek olduğu görülmüştür. Bu ATRP polimerizasyonunun daha az kontrollü olduğunu göstermektedir.

Bu araştırmada, CuBr/PMDETA katalizör olarak kullanılmış olup, isobornil ve isopropil α-(hidroksimetil) akrilat eter dimerlerin siklopolimerizasyonları ksilende gerçekleştirilmiştir. Polimerlerin yaşayan olma özelliğini ispat etmek için IBHMA ve IPHMA eter dimerlerin halkalı polimerleri, *t*-butil akrilat komonomerleriyle kopolimerleşme çalışmalarında, makrobaşlatıcı olarak kullanılmıştır. SEC analizleri tüm halkalı polimerlerin yaşayan özelliğe sahip olduğunu göstermiştir. Halkalı polimerler üzerinde yapılan fiziksel çalışmalar, polimerlerin yüksek camsı geçiş sıcaklığına (T_g) ve oldukça yüksek ısısal dayanıklılığa sahip oldukları gözlemlenmiştir.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS iv
ABSTRACT v
ÖZET vi
LIST OF FIGURES ix
LIST OF TABLES xii
LIST OF SYMBOLS / ABBREVIATIONS xiii
1. INTRODUCTION 1
1.1. What is Powder Coating and its Requirements? 1
1.2. Aliphatic Cyclopolymers with High Glass Transition Temperatures Derived from Alkyl α-(Hydroxymethyl) Acrylate (RHMA) Ether Dimers 2
1.3. Controlled/Living Radical Polymerization 3
1.3.1. Atom Transfer Radical Polymerization (ATRP) 4
1.3.2. Components in ATRP 4
1.3.3. Mechanism and Kinetics of ATRP 6
1.4. Factors Affecting the Cyclopolymerizations of Alkyl α-(Hydroxymethyl) Acrylate (RHMA) Ether Dimers 7
1.4.1. Steric Interaction of the Ester Functionality in Conventional Free Radical Cyclopolymerization 7
1.4.2. Steric Factors in Controlled/Living Cyclopolymerization via ATRP . 8
1.4.3. Effect of Temperature in Free Radical Cyclopolymerization 9
1.4.4. Effect of Temperature and Reaction Time in ATRP 10
1.5. Cyclopolymerizations of Alkyl α-(Hydroxymethyl) Acrylate (RHMA) Ether Dimers via ATRP 11
2. OBJECTIVE 12
3. EXPERIMENTAL 13
3.1. Methods and Materials 13
3.2. Instrumentation 13
3.3. Synthesis of Monomers 14
3.3.1. Synthesis of Isopropyl Acrylate 14

3.3.2. Synthesis of Isobornyl α-(Hydroxymethyl) Acrylate (IBHMA) Ether Dimer . . . 14
3.3.3. Synthesis of Isopropyl α-(Hydroxymethyl) Acrylate (IPHMA) Ether Dimer . . . 15
3.4. Polymer Synthesis . . . 16
3.4.1. The Procedure for the Solution ATRP of RHMA Ether Dimers . . . 16
3.4.2. ATRP of Isobornyl α-(Hydroxymethyl) Acrylate (IBHMA) Ether Dimer . . . 17
3.4.3. ATRP of Isopropyl α-(Hydroxymethyl) Acrylate (IPHMA) Ether Dimer . . . 17
3.4.4. Bulk Copolymerization of poly(RHMA ether dimer)s . . . 18
3.4.5. The Procedure for the Purification of the Resulting Cyclopolymers 20
4. RESULTS AND DISCUSSION . . . 21
4.1. Synthesis of the Monomers . . . 21
4.1.1. Synthesis of Isopropyl Acrylate . . . 21
4.1.2. Characterization of Isopropyl Acrylate . . . 22
4.1.3. Synthesis of RHMA Ether Dimers . . . 22
4.1.4. Characterization of RHMA Ether Dimers . . . 25
4.2. Cyclopolymerization of RHMA Ether Dimers by ATRP . . . 26
4.2.1. Steric Effect of R-group of Ester Substituent . . . 35
4.2.2. Effect of Temperature on ATRP Cyclopolymerization . . . 45
4.2.3. Physical Properties of the Cyclopolymers . . . 46
4.3. Block Copolymerizations of poly(RHMA ether dimer)s . . . 46
5. CONCLUSION . . . 53
REFERENCES . . . 55

LIST OF FIGURES

Figure 1.1. Example of aliphatic cyclopolymer obtained by cyclopolymerization of 1,6 dienes 2

Figure 1.2. Cyclopolymerizations of alkyl α-(hydroxymethyl) acrylate (RHMA) ether dimers 3

Figure 1.3. Various alkyl (R) groups that were used in cyclopolymerizations . . . 3

Figure 1.4. The metal complex exemplified with Cu(I) as the catalyst and 2,2'-bipyridine as ligand 5

Figure 1.5. ATRP Mechanism. RX: dormant species (alkyl halide); M_t^n /L : activator (metal complex); $R^{\cdot}$: propagating radical; X-M_t^{n+1} /L: deactivator; M: monomer; P:Dead chain 6

Figure 1.6. Intra- and intermolecular cyclization pathways of RHMA ether dimers 7

Figure 1.7. Steric factors on monomers in ATRP system 9

Figure 4.1. Synthesis of isopropyl acrylate 21

Figure 4.2. ^{1}H-NMR spectrum of isopropyl acrylate in $CDCl_3$ 23

Figure 4.3. ^{13}C-NMR spectrum of isopropyl acrylate in $CDCl_3$ 24

Figure 4.4. Synthesis of RHMA ether dimers by Baylis-Hilmann reaction 25

Figure 4.5. ^{1}H-NMR spectrum of isobornyl α-(hydroxymethyl) acrylate (IBHMA) ether dimer in $CDCl_3$ 27

Figure 4.6. ^{13}C-NMR spectrum of isobornyl α-(hydroxymethyl) acrylate (IBHMA) ether dimer in $CDCl_3$ 27

Figure 4.7. ^{1}H-NMR spectrum of isopropyl α-(hydroxymethyl) acrylate (IPHMA) in $CDCl_3$ 28

Figure 4.8. ^{13}C-NMR spectrum of isopropyl α-(hydroxymethyl) acrylate (IPHMA) in $CDCl_3$ 29

Figure 4.9. IR Spectrum of isopropyl α-(hydroxymethyl) acrylate (IPHMA) . . . 30

Figure 4.10. ^{1}H-NMR spectrum of isopropyl α-(hydroxymethyl) acrylate (IPHMA) ether dimer in $CDCl_3$ 32

Figure 4.11. IR Spectrum of isopropyl α-(hydroxymethyl) acrylate (IPHMA) ether dimer 33

Figure 4.12. ^{13}C-NMR spectrum of isopropyl α-(hydroxymethyl) acrylate (IPHMA) ether dimer in $CDCl_3$ 34

Figure 4.13. Cyclopolymerization of RHMA ether dimers via ATRP 34

Figure 4.14. ^{1}H-NMR spectrum of poly(IBHMA ether dimer) in $CDCl_3$ 38

Figure 4.15. ^{13}C-NMR spectrum of poly(IBHMA ether dimer) in $CDCl_3$ 39

Figure 4.16. ^{1}H-NMR spectrum of poly(IPHMA ether dimer) in $CDCl_3$ 40

Figure 4.17. ^{13}C-NMR spectrum of poly(IPHMA ether dimer) in $CDCl_3$ 41

Figure 4.18. Kinetic study of IBHMA ether dimer cyclopolymerization via ATRP at 70 ^{o}C. Increase of M_n and evolution of PDI as a function of conversion 42

Figure 4.19. First-order kinetic plot of IBHMA ether dimer cyclopolymerization via ATRP at 70 ^{o}C. 42

Figure 4.20. SEC traces of kinetic study of IBHMA ether dimer cyclopolymerization at 70 ºC. Molecular weights increases from left to right 43

Figure 4.21. First-order kinetic plot of IPHMA ether dimer cyclopolymerization via ATRP at 70 ^{o}C. 44

Figure 4.22. Kinetic study of IPHMA ether dimer cyclopolymerization via ATRP at 70 ^{o}C. Increase of M_n and evolution of PDI as a function of conversion 44

Figure 4.23. SEC traces of kinetic study of IPHMA ether dimer cyclopolymerization at 70 ºC. Molecular weights increases from left to right 44

Figure 4.24. TGA thermograms of poly(IBHMA ether dimer)s 48

Figure 4.25. TGA thermograms of poly(IPHMA ether dimer)s 49

Figure 4.26. DSC traces of poly(IPHMA ether dimer)s 50

Figure 4.27. SEC traces of the copolymerization study showing poly(RHMA ether dimer) macroinitiators (right) and the obtained block cyclopolymers (left) 52

Figure 5.1. The Effect of R group size on ATRP cyclopolymerization 54

Figure 5.2. Evolution of effectiveness of ATRP cyclopolymerization as a function of R group size 54

LIST OF TABLES

Table 4.1. Results from the ATRP of IBHMA and IPHMA ether dimers at 70 °C[a,b] 37

Table 4.2. Results from kinetic study of ATRP of IBHMA ether dimer at 70 °C[a,b] 42

Table 4.3. Results from kinetic study of ATRP of IPHMA ether dimer at 70 °C[a,b] 43

Table 4.4. Results from the ATRP of IBHMA and IPHMA ether dimers at 100 °C[a,b] 45

Table 4.5. Results from the ATRP of IBHMA and IPHMA ether dimers at 50 °C[a,b] 45

Table 4.6. Glass transition temperatures (T_g) of the cyclopolymers with various molecular weights and polydispersities synthesized at 50, 70 and 100 °C by ATRP 47

Table 4.7. Thermogravimetric analysis of IBHMA and IPHMA ether dimer cyclopolymers with various molecular weights and polydispersities synthesized at 50, 70 and 100 °C via ATRP 47

Table 4.8. Synthesis of copolymers by ATRP in bulk using the RHMA ether dimer-cyclopolymers as macroinitiator[a,b] 51

LIST OF SYMBOLS / ABBREVIATIONS

T_g	Glass Transition Temperature
k_{act}	Activation Rate Constant
k_{deact}	Deactivation Rate Constant
k_{eq}	Equilibrium Rate Constant
k_p	Propagation Rate Constant
k_t	Termination Rate Constant
ATRP	Atom Transfer Radical Polymerization
ADHMA	Adamantyl α-(Hydroxymethyl) Acrylate
CHHMA	Cyclohexyl α-(Hydroxymethyl) Acrylate
DABCO	1,4-diazabicyclo[2.2.2] octane
DSC	Differential Scanning Calorimetry
EB*i*B	Ethyl 2-bromoisobutyrate
EHMA	Ethyl α-(Hydroxymethyl) Acrylate
IBHMA	Isobornyl α-(Hydroxymethyl) Acrylate
IPHMA	Isopropyl α-(Hydroxymethyl) Acrylate
GPC	Gel Permation Chromatography
NMP	Nitroxide Mediated Polymerization
NMR	Nuclear Magnetic Resonans Spectroscopy
PDI	Polydispersity Index
PMDETA	N,N,N,N',N'-pentamethyldiethylenetriamine
RAFT	Reversible Addition–Fragmentation Chain Transfer
RHMA	Alkyl α-(Hydroxymethyl) Acrylate
SEC	Size Exclusion Chromatography
TGA	Thermogravimetric Analysis
TLC	Thin Layer Chromatography
UV	Ultra Violet

1. INTRODUCTION

1.1. What is Powder Coating and its Requirements?

Since introduction in North America almost 40 years ago, powder coating has become the fastest growing finishing technology in use today. Powder coating is entirely a dry finishing process for applying coatings on a substrate using heat fusible powders. Materials used in the process are referred as coating powders, finely divided particles of organic polymer, either thermoplastics or thermosetting, which usually contain pigments, fillers and other additives that are eloctrostatically charged and sprayed onto objects to be coated. After application to the substrate, the individual powder particles are melted in an oven where they coalesce to form a continuous film having decorative and protective properties associated with conventional organic coatings. The result is a uniform, durable, high quality finish. Compared to the other coating methods, powder technology offers a number of significant advantages. These coatings are essentially 100 per cent nonvolatile, ie, no solvents or other pollutants are given off during application and curing, and thus provide substantial economic savings [1].

Coating powders are based on both thermoplastic and thermosetting resins. Thermosetting powder coatings are the most commenly used. They undergo an irreversible chemical change during the curing process and will not soften back to the liquid phase when reheated. They are applied as thin-film decorative and corrosion resistant coatings, whereas thermoplastic powder coatings will repeatedly melt when subjected to heat, will solidify when cooled and are especially well suited for thick film applications where there are extreme performance requirements [1].

To be used as a powder coating, a resin should posseses: low melt viscosity, which affords a smooth continuous film; good adhesion to the substrate; good physical properties when properly cured, eg, high toughness and impact resistance; good heat and chemical resistance; and good weathering characteristics, ie, resistance to degradation by sun light,

hydrolytic stability, and low environmental pollutants; a sufficiently high glass-transition temperature (T_g), at a minimum of ~40 ºC and preferably >50 ºC so as to resist sintering and clumping during transportation, handling and storage [1].

Today, the most commonly used termosetting powder coatings all around the world are based on polyesters, those either aliphatic or aromatic. These powders have their disadvantages as well as their advantages, for example aromatic polyester resins have high T_g's, but due to the aromatic unit in the backbone they lack UV resistance and therefore are not recommended for outdoor applications. On the other hand, aliphatic polyester resins exhibit superior weathering stability, but have low T_g's and in order to overcome this problem their molecular weight should be increased which generally results in poor mechanical properties due to the loss in crosslink density [1].

Thus, previous studies showed that aliphatic cyclopolymers with high glass transition temperatures (>135 ºC) derived from alkyl α-(hydroxymethyl) acrylate (RHMA) ether dimers can satisfy these requirements and can be used in powder coating applications [2].

1.2. Aliphatic Cyclopolymers with High Glass Transition Temperatures Derived from Alkyl α-(Hydroxymethyl) Acrylate (RHMA) Ether Dimers

Aliphatic cyclopolymers of 1,6-dienes owing high degrees of cyclization exhibit excellent thermal stability, high glass transition temperatures compared to non-cyclic linear counterparts (Figure 1.1) [2, 3]. Consequently, these features make them more eligible for powder coating applications.

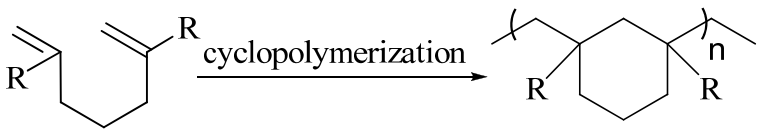
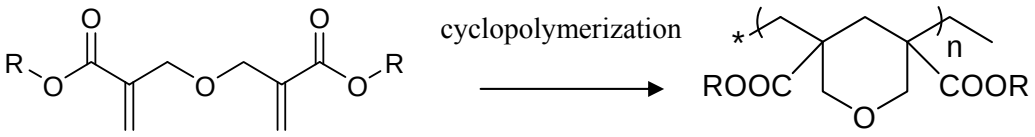


Figure 1.1. Example of aliphatic cyclopolymer obtained by cyclopolymerization of 1,6 dienes

Cyclopolymerization can be carried out by conventional free radical polymerization [4-8], or by more promising techniques such as controlled living ATRP [9] and RAFT [10]. In principle, simply throughout all radical cyclopolymerization systems, symmetrical 2,6-disubstituted 1,6-dienes undergo sequential intramolecular-intermolecular propagation reactions to give soluble cyclopolymers under appropriate conditions. For example cyclopolymers of alkyl α-(hydroxymethyl) acrylate ether dimers containing very stable six-membered tetrahydropyran repeat units in their backbone with various R groups have been successfully cyclopolymerized (Figure 1.2 and 1.3).



RHMA ether dimer Poly(RHMA ether dimer)

Figure 1.2. Cyclopolymerization of alkyl α-(hydroxymethyl) acrylate (RHMA) ether dimers

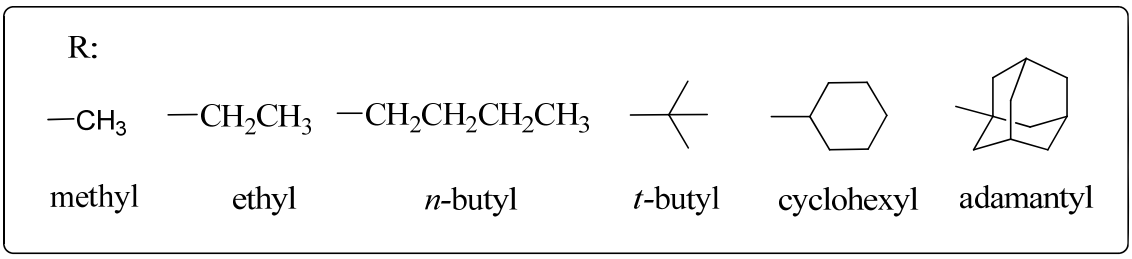


Figure 1.3. Various alkyl (R) groups that were used in cyclopolymerizations

1.3. Controlled/Living Radical Polymerization

Due to ease of processibility, free radical polymerization is the most widely used radical polymerization method in the industry. However, the high amount of termination reactions as a result of coupling, H-abstraction, disproportination or possible chain transfer reactions caused by relatively high concentration of reactive free radicals lead to branching, poor control over the molecular weight and high polydispersities which directly affect the

mechanical and physical properties of the resulting polymer. Moreover, it is desirable to control moleculer weights as accuratly as possible and produce polymers with desired functional-end groups which are difficult in free radical polymerization. Consequently, in order to obtain polymers with the properties mentioned above, a special technique that enables more control is needed.

Controlled/living polymerization is the method, ideally where no termination takes place and the polymerization proceeds in a controlled manner and continues until all the monomers are consumed. Thus, it enables to obtain well-defined polymers with tunable molecular weights and low polydispersity indexes (PDIs) [10-16]. Atom transfer radical polymerization (ATRP) [17-23], reversible addition fragmentation chain transfer (RAFT) [24-27] and the nitroxide mediated free radical process (NMP) [28] are the leading controlled radical polymerization techniques employed today. The basic principle in controlled living radical polymerization is to keep concentration of the free radicals at considerably low levels and adjust a dynamic equilibrium between active and dormant species.

1.3.1. Atom Transfer Radical Polymerization (ATRP)

Today, ATRP is one of the most promising controlled radical polymerization method which was first introduced independently by Matyjaszewski and Wang and Sawamoto *et al.* in 1995 [39,30].

1.3.2. Components in ATRP

Various vinyl monomers, such as styrenes, (meth)acrylates, acrylonitriles, and (meth)acrylamides can be homopolymerized with ATRP. An initiator that is an activated alkyl halide, that has both a radical stabilizing substituent; most commonly aryl, carbonyl or allyl groups and a weakly bonded, easily transferable halide on the α-carbon. Catalyst system is composed of a transition metal having at least two oxidation states to accept the halide; copper is the most widely used one. A suitable ligand that complexes with the metal, see example Figure 1.4 which enhances its solubility in organic media and controls

selectivity by steric effect and affects redox chemistry by electronic effect. The ligands are usually nitrogen-based (Figure 1.5) [31,32].

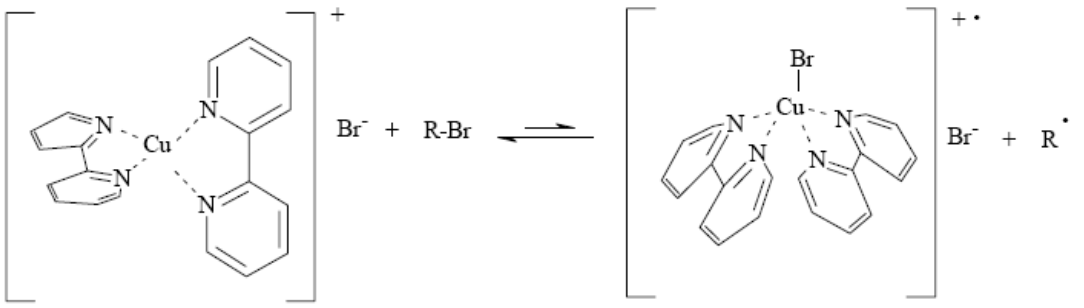


Figure 1.4. The metal complex exemplified with Cu(I) as the catalyst and 2,2'-bipyridine as ligand

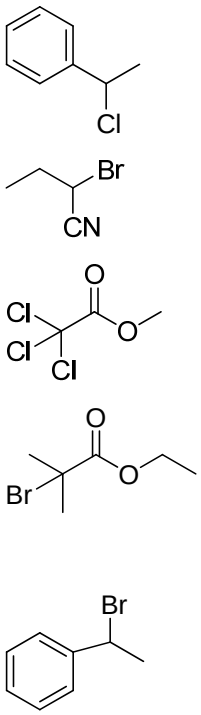
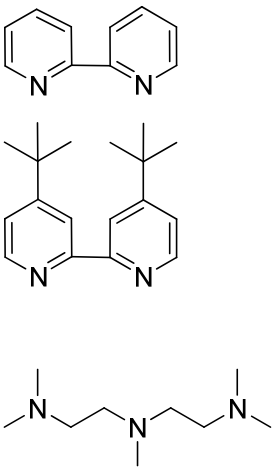
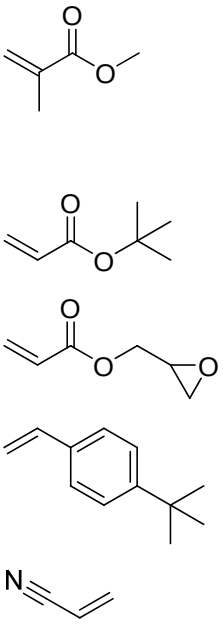
Initiators	Metal Halide	Ligand	Monomers
	CuCl CuBr		

Figure 1.5. Some ATRP system components

1.3.3. Mechanism and Kinetics of ATRP

In ATRP, the first step (initiation/activation) is transfer of the halide atom from initiator to catalyst complex to form a free radical (*R*•) and a metal halide $Mt^{n+1}X$ (deactivator) in its higher oxidation state. It is immediately followed by deactivation step to form dormant species (RX). The deactivation step should be faster than the activation step in order to keep free radical concentration low, and thus, establish the control on the polymerization. Then propagation takes place untill the monomer is consumed. Figure 1.6 shows a typical ATRP mechanism [31,32].

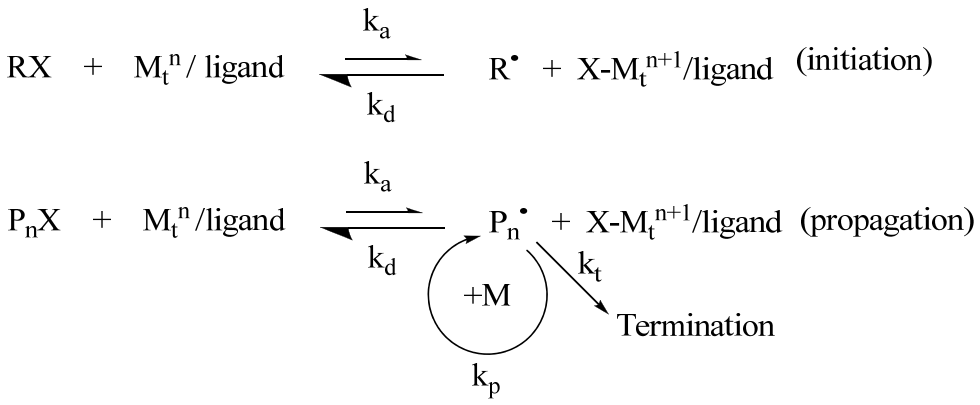


Figure 1.6. ATRP Mechanism. RX: dormant species (alkyl halide); M_t^n/L : activator (metal complex); R· : propagating radical; X-M_t^{n+1} /L: deactivator; M: monomer; P:Dead chain

The fundemantal phenomena that offers the control of the ATRP are fast initiation, rapid reversible deactivation and the ratio between the activation and the deactivation rate constants where $K_{eq}=k_{act}/k_{deact}$ is the equilibrium constant. If the equilibrium constant (K_{eq}) is too small which means that deactivation (k_{deact}) is too high, ATRP will not occur or it will occur very slowly. In the contrary case, polymerization becomes uncontrolled. Furthermore, as the equilibrium constant increases, the concentration of radicals increases. In summary higher the deactivation rate (k_{deact}), the lower the concentration of propagating radicals and the better is the control of the ATRP process [31,32].

1.4. Factors Affecting the Cyclopolymerizations of Alkyl α-(Hydroxymethyl) Acrylate (RHMA) Ether Dimers

No matter what type of polymerization technique is used, cyclopolymerization attitudes of the RHMA ether dimers change by type of the solvent, monomer concentration, polymerization temperature, extend of polymerization and steric interaction of the ester (R) functionality with the other components in the media and the present study will be focused more on the following parameters: temperature, time and steric interaction of the ester (R) substituents [33,34].

1.4.1. Steric Interaction of the Ester Functionality in Conventional Free Radical Cyclopolymerization

Previous cyclopolymerization studies of alkyl α-(hydroxymethyl) acrylates ether dimers via conventional free radical polymerization have shown that cyclization efficiency was affected by the number of carbon atoms linked to the central ester carbon (which defines the 'effective' bulkiness) rather than by the 'apparent' bulkiness, which encompasses the total mass or size of the whole substituent [34]. In short, steric contribution of the ester substituent affects cyclization efficiency either by inhibiting intermolecular monomer addition or promoting intramolecular cyclization as shown in the Figure 1.7 Studies with conventioanal free radical polymerization showed that cyclization efficiency increased in the following order: methyl, ethyl, isobornyl, *t*-butyl, adamantyl.

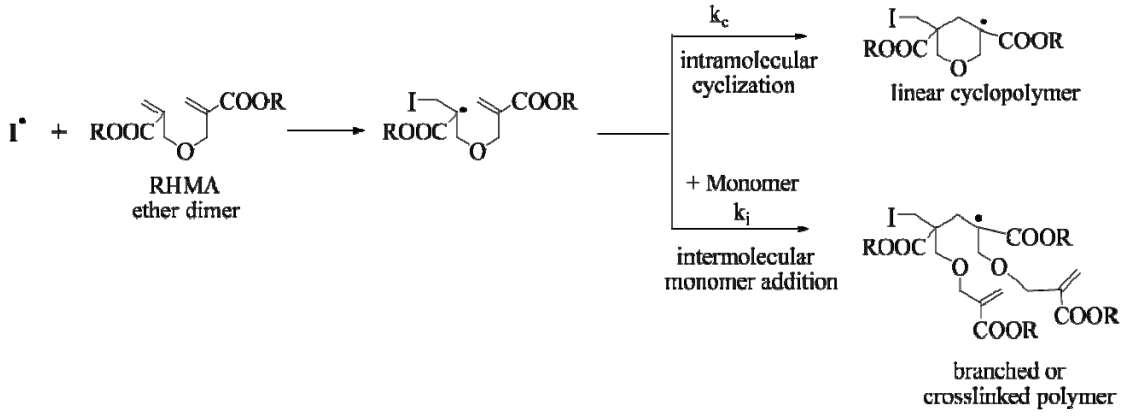


Figure 1.7. Intra- and intermolecular cyclization pathways of RHMA ether dimers

1.4.2. Steric Factors in Controlled/Living Cyclopolymerization via ATRP

As shown in Figure 1.8 the ATRP cyclopolymerization system is more complicated than the conventional free radical polymerization system. In the ATRP case the following parameters should be considered in order to figure out the optimum size of the ester substituents that fits best to the ATRP system. Firstly, steric interaction between monomer and catalyst system (ligand/metal halide) which may affect the activation/deactivation rate constants and thus the control of the ATRP. Secondly, steric contribution of ester functionality that effects intermolecular monomer addition / intramolecular cyclization ratio.

Furthermore, there has been two hypothesis; if the R group (ester substituent) is bulkier (which inhibits intermolecular monomer addition), cyclization is expected to be more favored. On the other hand, approach of the catalyst system (ligand/metal halide) will be worse which may influence the deactivation negatively and lead to the loss in control. Secondly, if the R group is smaller (which contributes intermolecular monomer addition), cyclization will be worse resulting in branching or crosslinking., but catalyst complex will easily approach the propagating chain or monomer which may enhance the deactivation in ATRP as shown in Figure 1.7 [35].

Cyclopolymerizations of RHMA ether dimers via ATRP method have been formerly investigated in our research group where for smaller alkyl groups; methyl, ethyl, *n*-butyl and *tert*-butyl and bulkier adamantyl and cyclohexyl groups were polymerized [35,36]. It was found out that starting from the smaller group, methyl, ethyl, going further to *n*-butyl and *t*-butyl groups, cyclization efficiency increased and polydispersities decreased ($1.05<PDI<1.23$) at 70 ^{o}C [35]. On the other hand, although the cyclization efficiencies were thought to be greater for bulkier cyclohexyl and adamantyl derivatives, they exhibited higher polydisperties at 70 ^{o}C [36]. In the case of the smaller alkyl (ester) substituents, except *t*-butyl derivative, crosslinking and pendant vinyl group in the polymer chain was observed. The *t*-butyl derivative gave the best results, where low polydispersities and high cyclization efficiency was observed at 70 ^{o}C. In summary, these studies suggests that the R group size is dramatically important and there should be an optimum size that best fits to

the ATRP system, that is to say *t*-butyl was the best candidate in ATRP cyclopolymerization so far [35,36].

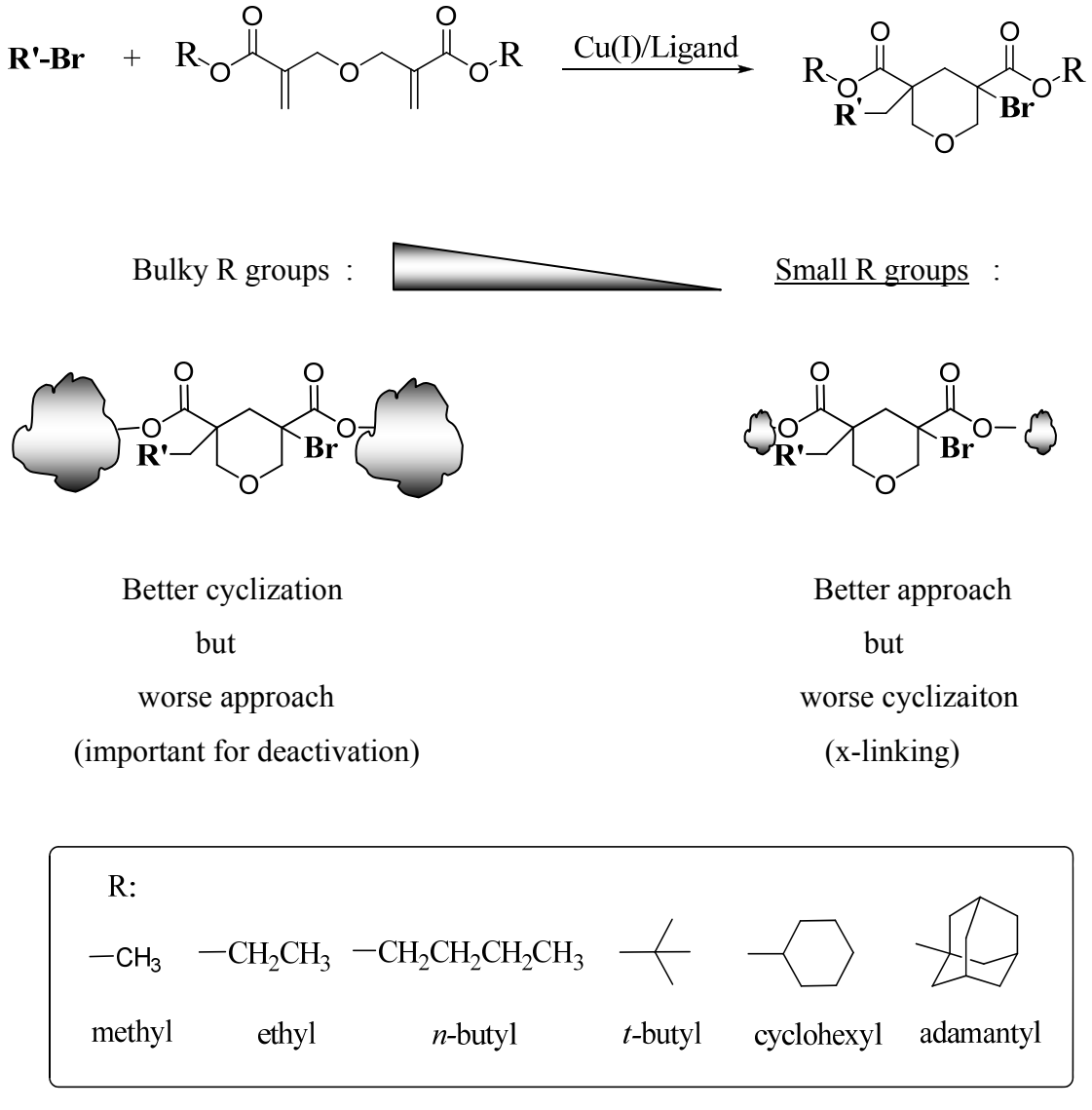


Figure 1.8. Steric factors on monomers in ATRP system

1.4.3. Effect of Temperature in Free Radical Cyclopolymerization

Cyclopolymerization temperature is also very important and should be considered together with the steric contribution of the ester substituent, since bulkiness is a disadvantage for activation energy of cyclization. Thus, in order to overcome the activation energy barrier for cyclization of bulky alkyl substituted monomers, cyclopolymerizations

should be carried out at higher temperatures. Shortly, the bulkier the ester (R) substituent the higher the temperature should be applied to promote cyclization [34].

1.4.4. Effect of Temperature and Reaction Time in ATRP

Since reaction rates are directly proportional to temperature, it is obvious that an increase in temperature should result in higher polymerization rate. Additionaly, radical propagation is more favored than termination by radical coupling or disproportionation at higher temperatures. Therefore, the higher the temperature is, the higher the k_p/k_t ratio gets. However, in ATRP systems dynamic equlibrium between the activator and deactivator (activation/deactivation ratio) should be established in order to control the polymerization. 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 the higher activation energy for the radical propagation than for the 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. Hence, temperature should be optimized by taking all the ATRP components into account to carry out a successful ATRP [31,32].

Furthermore, towards the end of the polymerization where almost all monomers are consumed, the k_p slows down, but the rate of side reactions are not affected significantly due to their monomer concentration independence. Moreover, complete polymerization is not desired due to the end group loss. For that reason, in order to accomplish polymerizations with high end-group-functionality, conversions must not exceed 95 per cent in order to avoid end group loss [31,32].

1.5. Cyclopolymerizations of Alkyl α-(Hydroxymethyl) Acrylate Ether Dimers via ATRP

Taking everything mentioned so far into account, ATRP method was preferred to conventional free radical polymerization due to its controlled nature (polymers with desired molecular weights), livingness (polymers with functional end groups) and low polydispersities ($1.0<M_w/M_n<1.5$). The main focus of the present study was to understand behaviours of different ester substituents in the ATRP system.

In this perspective, ATRP cyclopolymerization of five different alkyl α-(hydroxymethyl) acrylate ether dimers have been previously studied in our research group. These alkyl groups were smaller ethyl, *n*-butyl and *t*-butyl groups and bulkier cyclohexyl and adamantyl groups. In these studies, the effect of bulkiness and the temperature on cyclization efficiency were investigated [35,36].

It was found that, cyclization efficiency was favored by the increase in bulkiness of the ester substituent in the ATRP system. The *t*-butyl derivative seemed to be the best that fits to the ATRP system. Monomers with smaller ester group such as ethyl gave crosslinked material whereas bulkier derivatives gave cylopolymers containing six-membered tetrahydropyran units with higher polydisperties [35,36].

2. OBJECTIVE

ATRP of RHMA ether dimers with ethyl, *n*-butyl, *tert*-butyl, cyclohexyl and adamantyl as alkyl groups has been previously studied in our research group. Cyclization efficiency was found to increase with bulkiness of the ester substituent group in RHMA ether dimers. However, cyclopolymerization of isobornyl and isopropyl α-(hydroxymethyl) acrylate ether dimers by ATRP were not studied.

In this study, the goal is to get highly cyclized polymers with reasonable polydispersities and predictable molecular weights using bulkier isobornyl and smaller isopropyl groups. The cyclopolymerizations were carried out in xylene using CuBr/PMDETA as the ATRP catalyst complex and ethyl 2-bromoisobutyrate (EB*i*B) as the initiator.

The effect of temperature on the ATRP was investigated. Since livingness is an important characteristic of ATRP, copolymerization studies were performed to prove the livingness of the obtained polymers. Thermal properties of the obtained polymers were also investigated.

3. EXPERIMENTAL

3.1. Methods and Materials

2-Propanol (Merck, ≥99.8%), isobornyl acrylate, acryloyl chloride (96%, Merck), paraformaldehyde (Sigma Aldrich), triethylamine (TEA) (Merck, ≥99%), 1,4-diazabicyclo[2.2.2]octane (DABCO) (Fluka, ≥95%), *tert*-butyl alcohol (Merck, 99%), hydrochloric acid (HCl) (Sigma-Aldrich, 37%), ethyl-2-bromoisobutyrate (EB*i*B) (Fluka, ≥97%), copper (I) bromide (CuBr) (Aldrich, 99.999%), copper (I) chloride (CuCl) (Aldrich, 99.995+%and pentamethyldiethylene triamine (PMDETA) (Aldrich, 99%) were used as received without purification. Tetrahydrofurane (THF, 99.8%, J.T. Baker) and xylene (mixture of isomers) (Merck) was purified by distillation over Na metal and benzophenone. Dichloromethane, hexane, methanol, ethyl acetate, *n*-pentane and acetone were all obtained from Merck were used as received without purification.

3.2. Instrumentation

^{1}H-NMR and ^{13}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 μm MIXED-C Column that was calibrated against polystyrene standards. T_g values were determined with a TA Instruments Differential Scanning Calorimeter (DSC Q100).

TGA scans were performed under nitrogen flow using a TA Q50 at a heating rate of 10 ^{o}C/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 Isopropyl Acrylate

The synthesis was carried out under inert atmosphere using nitrogen. Isopropanol (30.00 g, 0.50 mol), TEA (65.72 g, 0.65 mol) and dichloromethane (250 mL) were added to a 500 mL three necked round bottom flask fitted with a condenser, magnetic stirrer and addition funnel. The reaction bath temperature was adjusted to 0 ^{o}C using ice. Acryloyl chloride (54.00 g, 0.60 mol) was added dropwise by addition funnel to the reaction flask. The mixture was stirred for 3 hours. The reaction progress was monitored by thin layer chromatography (TLC) using silica gel plates and CH_2Cl_2 as the eluting and diluting solvent. At the end of the 3 hours, the mixture was diluted with 100 mL dichloromethane and filtered to remove small amount of insoluble material, washed twice with 100 mL of 5 per cent HCl and then with 100 ml of distilled water. The organic layer was separated and CH_2Cl_2 evaporated to give crude product as an oil. The oily mixture was passed through silica column prepared with dichloromethane : *n*-pentane mixture 4:1 (v/v). Evaporation of the solvent gave 52.44 g pure product as a clear liquid in 92 per cent yield. ^{1}H NMR ($CDCl_3$) δ 1.23 (d, 6H, C*H*$_3$), 5.03 (m, 1H, C*H*-O), 5.74 (d, 1H, C*H*=CH), 6.05 (dd, 1H, C*H*=CH$_2$), 6.34 (d, 1H, C*H*=CH) ppm. ^{13}C NMR ($CDCl_3$) δ 21.91 (*C*H$_3$), 67.95 (*C*H-O), 129.30 (*C*H$_2$=CH), 130.06 (*C*H=CH$_2$), 165.78 (*C*=O) ppm.

3.3.2. Synthesis of Isobornyl α-(Hydroxymethyl) Acrylate (IBHMA) Ether Dimer

Isobornyl acrylate (52.00 g, 0.25 mol), paraformaldehyde (7.50 g, 0.25 mol), DABCO (3.75 g, 4.8 wt per cent) and *t*-butanol (15 g, 19.2 wt per cent) were added to a 250 mL three necked round bottom flask fitted with a condenser and magnetic stirrer. The reaction bath temperature was adjusted to 80 ^{o}C. The mixture was stirred for 7 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. At the end of the 7 days the mixture was poured into 700 ml of methanol and placed in a refrigerator at -15 ^{o}C overnight. The precipitant was filtered and washed with 100 ml of cold methanol, then dried in vacuo to

give pure white solid in 67 per cent yield. ^{1}H NMR ($CDCl_3$) δ 6.27 (s, 2H, (C*H*=CH), 5.87 (s, 2H, C*H*=CH), 4.75 (t, 2H, C*H*-O), 4.24 (s, 4H, CH_2-O), 1.7-1.9 (m, 4H, CH_2-CH-O), 1.57 (m, 2H, C*H*-CH_2), 1.05-1.25 (m, 8H, CH_2-CH_2), 1.02 (s, 6H, CH_3), 0,86 (s, 12H, CH_3) ppm. ^{13}C NMR ($CDCl_3$) δ 165.0 (*C*=O), 137.5 (*C*=CH_2), 125.2 (*C*H_2=C), 81.2 (*C*H-O), 68.9 (*C*H_2-O), 48.8 (*C*-CH_3), 46.9 [*C*-(CH_3)$_2$], 45.0 (*C*H-CH_2), 38.7 (*C*H_2-CH), 33.6 (*C*H_2-C), 27.0 (*C*H_2-CH_2), 20.1 (*C*H_3), 19.9 (*C*H_3), 11.5 (*C*H_3) ppm.

3.3.3. Synthesis of Isopropyl α-(Hydroxymethyl) Acrylate (IPHMA) Ether Dimer

It was a two-step synthesis. Both steps were carried out under dry conditions using $CaCl_2$ tube. In the first step, isopropyl acrylate (57.00 g, 0.50 mol), paraformaldehyde (15.00 g, 0.50 mol), DABCO (3.75 g, 4.80 wt per cent) and t-butanol (15.00 g, 19.20 wt per cent) were added to a 250 mL three necked round bottom flask fitted with a condenser and magnetic stirrer. The reaction bath temperature was adjusted to 60 ^{o}C. The mixture was stirred 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. At the end of the 4 days the mixture was diluted with 100 mL dichloromethane and washed twice with 50 mL of 5 per cent HCl and then with 50 ml of distilled water. The organic layer was separated and CH_2Cl_2 evaporated to give crude product as an oil. The oily mixture was passed through silica column prepared with *n*-hexane : ethyl acetate mixture 6:1 (v/v). Evaporation of the solvent gave the pure product, isopropyl α-(hydroxymethyl) acrylate (IPHMA) as a clear liquid in 60 per cent yield.^{1}H NMR ($CDCl_3$) δ 1.20 (d, 6H, CH_3), 3.20 (br, 1H, O*H*), 4.22 (s, 2H, CH_2-C), 5.00 (m, 1H, C*H*-O), 5.75 (s, 1H, C*H*=C), 6.14 (s, 1H, C*H*=C) ppm. ^{13}C NMR ($CDCl_3$) δ 166.0 (*C*=O), 140.3 (*C*=CH_2), 124.9 (*C*H_2=C), 68.5 (*C*H-O), 62.0 (*C*H_2-O), 21.9 (*C*H_3) ppm. In the second step, isopropyl α-(hydroxymethyl) acrylate (IPHMA) (23.00 g, 0.16 mol), DABCO (2.00 g, 6.60 wt per cent) and *t*-butanol (5.00 g, 16.60 wt per cent) 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 85 ^{o}C. The mixture was stirred for 3 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. At the end of the 2 days the mixture was diluted with 100 mL dichloromethane and washed with 50 mL of 5% HCl and then with 50 ml of distilled water. The organic

layer was separated and CH_2Cl_2 evaporated to give crude product as an oil. The oily mixture was passed through silica column prepared with *n*-hexane : ethyl acetate mixture 99:1 (v/v). Evaporation of the solvent gave the pure product, isopropyl α-(hydroxymethyl) acrylate (IPHMA) ether dimer, as a clear liquid in 35 per cent yield. ^{1}H NMR ($CDCl_3$) δ 1.25 (d, 12H, C*H*$_3$), 4.24 (s, 4H, C*H*$_2$-O), 5.07 (m, 2H, C*H*-O), 5.86 (s, 2H, C*H*=CH), 6.27 (s, 2H, C*H*=CH) ppm. ^{13}C NMR ($CDCl_3$) δ 22.02 (*C*H$_3$), 68.36 (*C*H$_2$-O), 69.12 (*C*H-O), 125.44 (*C*H$_2$=C), 137.77 (*C*=CH$_2$), 165.49 (C=O) 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 120 ^{o}C and purged with nitrogen before use. All liquid chemicals were purged with nitrogen for at least 10 minutes prior to use. The solution polymerization of RHMA ether dimers was conducted in a one-necked round bottom flask using xylene as the solvent. The reaction flask fitted with a stirring bar and monomer in it, was sealed with rubber septa, xylene (the amount of xylene added is calculated by fixing monomer concentrations 1 M ± 0.01 and substracting the amount of xylene used in CuBr transfer step) was added to dissolve it.and purged with nitrogen for 15 minutes. Then CuBr was weighted in a 5 mL vial fitted with a stirring bar and sealed with a rubber septa and purged with nitrogen for 10 minutes, then 2 mL of deoxyganated xylene was added.by syringe. Then, PMDETA was added to vial by a microsyringe and the heteromixture was heated and stirred till all the CuBr was dissolved. Afterwards, solution was transferred to the main reaction flask by a deoxygenated syringe. Then the flask was immersed into a preheated oil bath. Ethyl α-bromoisobutyrate (EB*i*B) was introduced into the reaction flask by microsyringe. The final polymers were precipitated twice into acetone (for isobornyl derivative) and 5:1 methanol/water mixture (for isopropyl derivative) and dried in a vacuum 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 (RI) detector with poly(styrene) (PS) standards. Characterization of the polymer samples has been performed by ^{1}H-NMR and ^{13}C-NMR spectroscopy.

3.4.2. ATRP of Isobornyl α-(Hydroxymethyl) Acrylate (IBHMA) Ether Dimer

A typical ATRP cyclopolymerization procedure is as follows. IBHMA ether dimer (1.55 g, 3.38 mmol) was polymerized in 3.40 mL xylene (1 M ± 0.01) by using CuBr (4.85 mg, $3.38x10^{-5}$ mol) and PMDETA (7 μL, $3.38x10^{-5}$ mol) catalyst system and ethyl-α-bromoisobutyrate (5 μL, $3.38x10^{-5}$ mol) initiator taccording to the given procedure. The polymerization was carried out at 70 ^{o}C for 1 hour. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially colorless and clear and turned light green, pale green and deep green with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer precipitated twice into 50 mL acetone and dried in a vacuum oven overnight. The obtained polymer was powder, soluble, 0.29 g, in a 19 per cent yield. Serious of cyclopolymerizations were performed at various temperatures (50, 70, 100 ^{o}C) for various periods of time applying the same procedure above.

A typical kinetic study of ATRP cyclopolymerization is as follows. IBHMA ether dimer (3.40 g, 7.42 mmol) was polymerized in 7,5 ml xylene (1 M ± 0.01) by using CuBr (10,65 mg, $7.42x10^{-5}$ mol) and PMDETA (16 μL, $7.42x10^{-5}$ mol) catalyst system and ethyl α-bromoisobutyrate (11 μL, $7.42x10^{-5}$ mol) initiator according to the given procedure. The polymerization was carried out in a three-necked round bottom flask at 70 ^{o}C. 1 mL samples were periodically removed using a syringe purged with nitrogen to monitor conversion (gravimetrically) and evolution of molecular weights (SEC). The resulting polymers were precipitated twice into 50 ml of acetone and dried in vacuum overnight.

3.4.3. ATRP of Isopropyl α-(Hydroxymethyl) Acrylate (IPHMA) Ether Dimer

A typical ATRP cyclopolymerization procedure is as follows. IPHMA ether dimer (0,70 g, 2.59 mmol) was polymerized in 2.6 mL xylene (1 M ± 0.01M) by using CuBr (3.72 mg, $2.59x10^{-5}$ mol) and PMDETA (6 μL, $2.59x10^{-5}$ mol) catalyst system and ethyl-α-bromoisobutyrate (4 μL, $2.59x10^{-5}$ mol) initiator according to the given procedure. The polymerization was carried out at 70 ^{o}C for 0.5 hour. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially colorless and

clear and turned light green, pale green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 2 ml methylene chloride and precipitated twice into 50 mL methanol/water (5:1 v/v) mixture and dried in a vacuum oven overnight. The obtained polymer was white powder, soluble, 0.33 g, in a 47 per cent yield. Serious of cyclopolymerizations were performed at various temperatures (50, 70, 100 ^{o}C) for various periods of time applying the same procedure above.

A typical kinetic study of ATRP cyclopolymerization is as follows. IPHMA ether dimer (2.00 g, 7.42 mmol) was polymerized in 7,5 ml xylene (1 M ± 0.01 M) by using CuBr (10,65 mg, 7.42x10^{-5} mol) and PMDETA (16 μL, 7.42x10^{-5} mol) catalyst system and ethyl α-bromoisobutyrate (11 μL, 7.42x10^{-5} mol) initiator according to the given procedure. The polymerization was carried out in a three-necked round bottom flask at 70 ^{o}C. 1 mL samples were periodically removed using a syringe purged with nitrogen to monitor conversion (gravimetrically) and evolution of molecular weights (SEC). The resulting polymer was precipitated twice into 50 mL methanol/water (5:1 v/v) mixture and dried in a vacuum oven overnight

3.4.4. Bulk Copolymerization of poly(RHMA ether dimer)s

A typical ATRP block copolymerization of IBHMA ether dimer and *tert*-BA is as follows. All liquid chemicals were purged with nitrogen for at least 20 min prior to use. The copolymerization was conducted in a one-necked 25 mL round-bottom flask. The solid macroinitiator poly(IBHMA ether dimer) (0.15 g, 1.34x10^{-5} mol) (Table 4.1, Entry 10) was added to a reaction flask fitted with a stirring bar and which had been sealed with rubber septa and purged with nitrogen for 15 min. *tert*-BA (4 mL) was added to the reaction flask by syringe. The resulting mixture was stirred and degassed until the macroinitiator dissolved. Then, the solution was degassed for an additional 30 min and immersed into a preheated oil bath at 80 ^{o}C. CuBr (3.84 mg, 2.68x10^{-5} mol) was put in a separate vial sealed with a rubber septum and 2 mL of *tert*- BA was added to the CuBr and purged with nitrogen for 20 min. PMDETA (6 μL, 2.68x10^{-5} mol) was added to the vial and the resulting mixture was stirred and heated until the CuBr dissolved. The resulting

solution was then transferred into the reaction flask by syringe. Polymerization was carried out under nitrogen at 80 ^{o}C for 4 hours. The final polymer was dissolved in 3 mL of methylene chloride, precipitated into 50 mL methanol/water (5:1 v/v) mixture and dried in a vacuum oven overnight.

A typical ATRP block copolymerization of IPHMA ether dimer and *tert*-BA is as follows. All liquid chemicals were purged with nitrogen for at least 20 min prior to use. The copolymerization was conducted in a one-necked round-bottom flask. The solid macroinitiator poly(IPHMA ether dimer) (0.12 g, 9.66x10^{-6} mol) (Table 4.1, Entry 13) was added to a reaction flask fitted with a stirring bar and which had been sealed with rubber septa and purged with nitrogen for 15 min. *tert*-BA (4 mL) was added to the reaction flask by syringe. The resulting mixture was stirred and degassed until the macroinitiator dissolved. Then, the solution was degassed for an additional 30 min and immersed into a preheated oil bath at 80 ^{o}C. CuBr (2.77 mg, 1.93x10^{-5} mol) was put in a separate vial sealed with a rubber septum and 2 mL of *tert*- BA was added to the CuBr and purged with nitrogen for 20 min. PMDETA (5 μL, 1.93x10^{-5} mol) was added to the vial and the resulting mixture was stirred and heated until the CuBr dissolved. The resulting solution was then transferred into the reaction flask by syringe. Polymerization was carried out under nitrogen at 80 ^{o}C for 7 hours. The final polymer was dissolved in 4 mL of methylene chloride, and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight.

A typical ATRP block copolymerization of IBHMA ether dimer and iBA is as follows. All liquid chemicals were purged with nitrogen for at least 20 min prior to use. The copolymerization was conducted in a one-necked 25 mL round-bottom flask. The solid macroinitiator poly(IBHMA ether dimer) (0.14 g, 1.29x10^{-5} mol) (Table 4.1, Entry 9) was added to a reaction flask fitted with a stirring bar and which had been sealed with rubber septa and purged with nitrogen for 15 min. isobornyl acrylate (iBA) (4 mL) was added to the reaction flask by syringe. The resulting mixture was stirred and degassed until the macroinitiator dissolved. Then, the solution was degassed for an additional 30 min and immersed into a preheated oil bath at 80 ^{o}C. CuBr (3.70 mg, 2.58x10^{-5} mol) was put in a separate vial sealed with a rubber septum and 2 mL of iBA was added to the CuBr and purged with nitrogen for 20 min. PMDETA (5.5 μL, 2.58x10^{-5} mol) was added to the vial

and the resulting mixture was stirred and heated until the CuBr dissolved. The resulting solution was then transferred into the reaction flask by syringe. Polymerization was carried out under nitrogen at 80 ^{o}C for 6 hours. The final polymer was dissolved in 3 mL of methylene chloride, precipitated into 50 mL methanol/water (5:1 v/v) mixture and dried in a vacuum oven overnight.

A typical ATRP block copolymerization of IBHMA ether dimer and *tert*-BA using Cu(I)Cl is as follows. All liquid chemicals were purged with nitrogen for at least 20 min prior to use. The copolymerization was conducted in a one-necked 25 mL round-bottom flask. The solid macroinitiator poly(IBHMA ether dimer) (0.32 g, 2.56x10^{-5} mol) (Table 4.1, Entry 11) was added to a reaction flask fitted with a stirring bar and which had been sealed with rubber septa and purged with nitrogen for 15 min. *tert*-BA (4 mL) (4 mL) was added to the reaction flask by syringe. The resulting mixture was stirred and degassed until the macroinitiator dissolved. Then, the solution was degassed for an additional 30 min and immersed into a preheated oil bath at 70 ^{o}C. CuCl (5.07 mg, 5.12x10^{-5} mol) was put in a separate vial sealed with a rubber septum and 2 mL of *tert*-BA was added to the CuCl and purged with nitrogen for 20 min. PMDETA (11 μL, 5.12x10^{-5} mol) was added to the vial and the resulting mixture was stirred and heated until the CuCl dissolved. The resulting solution was then transferred into the reaction flask by syringe. Polymerization was carried out under nitrogen at 70 ^{o}C for 6 hours. The final polymer was dissolved in 3 mL of methylene chloride, precipitated into 50 mL methanol/water (5:1 v/v) mixture and dried in a vacuum oven overnight.

3.4.5. The Procedure for the Purification of the Resulting Cyclopolymers

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-d for NMR analysis and tetrahydrofuran (THF) for GPC analysis.

4. RESULTS AND DISCUSSION

The aim of this project was to synthesize well defined cyclopolymers with predictable molecular weights and then to investigate the effect of bulkiness of the ester (R) substituents on the ATRP cyclopolymerization. In this study, monomers with apparently bulkier isobornyl and smaller isopropyl group were used. These monomers are not reported yet in the literature.

Here, we will discuss the synthesis and characterization of the monomers first and then give the results of a series of cyclopolymerizations carried out at different temperatures in order to figure out the cyclization behaviors of the mentioned monomers within the ATRP system. Furthermore, physical properties of the corresponding cyclopolymers will be reported and finally living nature of the ATRP cyclopolymerization will be discussed by giving results on the copolymerization studies.

4.1. Synthesis of the Monomers

4.1.1. Synthesis of Isopropyl Acrylate

A typical acrylate synthesis is as follows. It was synthesized via nucleophilic addition / elimination reaction in high yields by addition of acryloyl chloride dropwise to isopropyl alcohol in the presence of triethylamine (TEA) as the acid scavenger and the CH_2Cl_2 as the solvent [37].

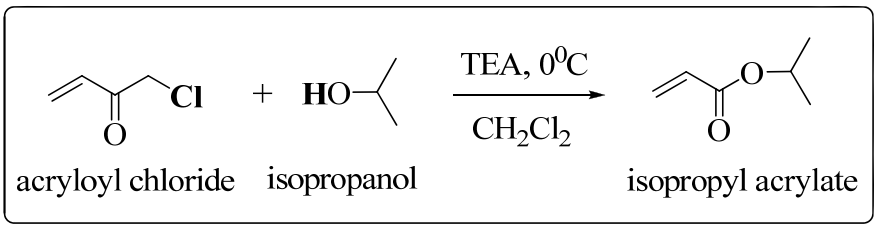


Figure 4.1. Synthesis of isopropyl acrylate

4.1.2. Characterization of Isopropyl Acrylate

^{1}H-NMR and ^{13}C-NMR spectra of the pure isopropyl acrylate are presented (Figure 4.2 and Figure 4.3). 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 isopropyl acrylate.

4.1.3. Synthesis of RHMA Ether Dimers

RHMA ether dimers were synthesized by using very well known extended Baylis-Hillman reaction according to the given literature procedure [34] in good yields. The Baylis-Hillman reaction, which is a tertiary amine-catalyzed coupling of an α, β-unsaturated carbonyl compound with an aldehyde, is among the most useful C-C bond forming reactions in organic synthesis [37]. 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 4.4. The addition of formaldehyde to acrylate ester is catalyzed by 1,4-diazabicyclo[2.2.2]octane (DABCO). The key step is the addition of the amine catalyst, DABCO, to α, β-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 is thermodynamically favorable [34].

The synthesis of IPHMA ether dime was conducted in two steps due to the extensive side product formation. In the first step isopropyl α-(hydroxymethyl) acrylate (IPHMA) was synthesized keeping the reaction temperature low at 60 ºC for 4 days. After the purification process, ether dimer of IPHMA was synthesized at 85 ºC for 3 days. The yields would have been higher if the reaction time was extended, however reformation of paraformaldehyde on the reaction flask's wall and formation of isopropyl acrylate was observed upon extended reaction time, which means that the reaction was reversible. In addition, extensive side product formation was observed. Therefore, in order to avoid side product formation, the reaction time was shortened.

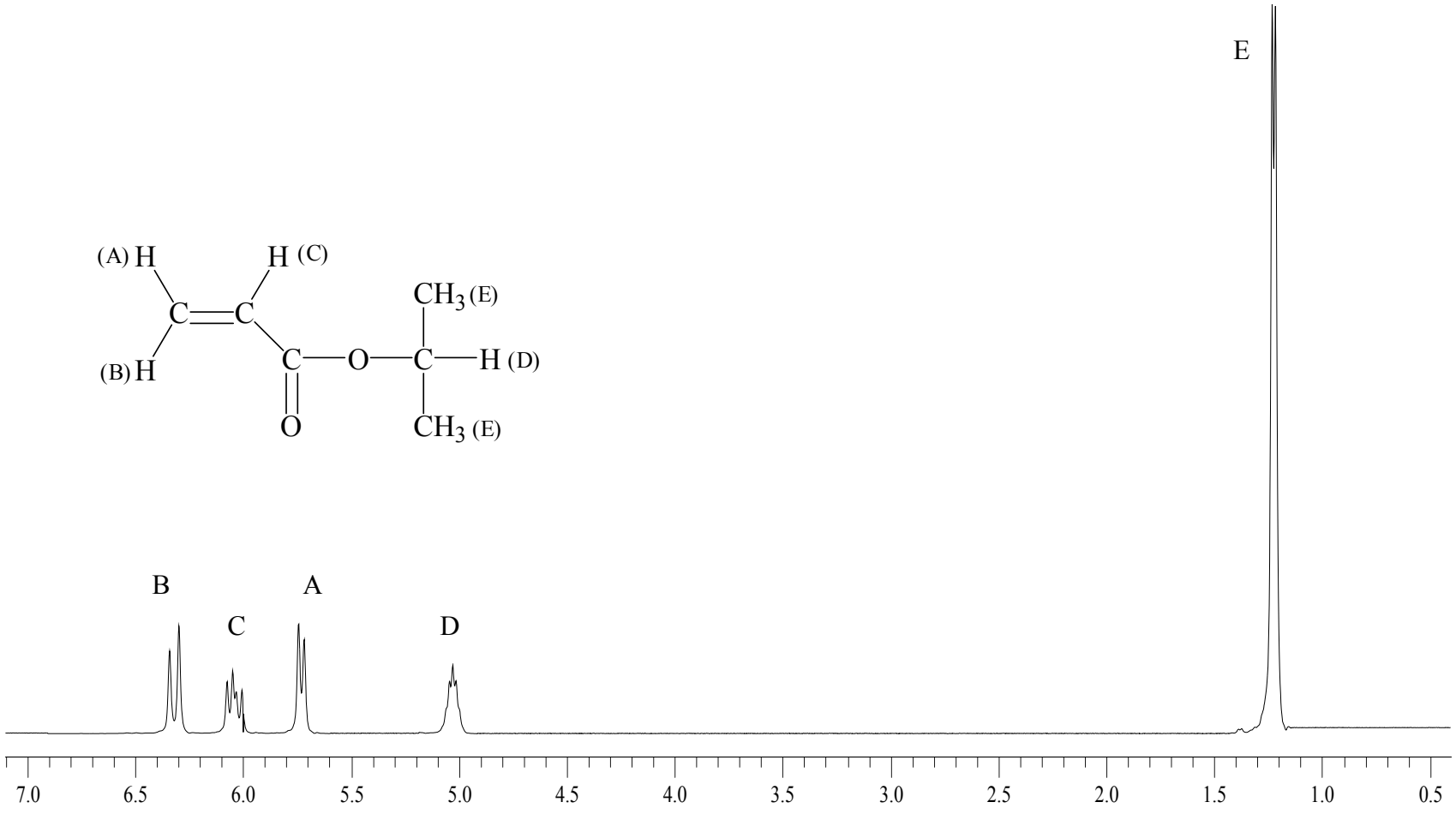


Figure 4.2. ^{1}H-NMR spectrum of isopropyl acrylate in $CDCl_3$

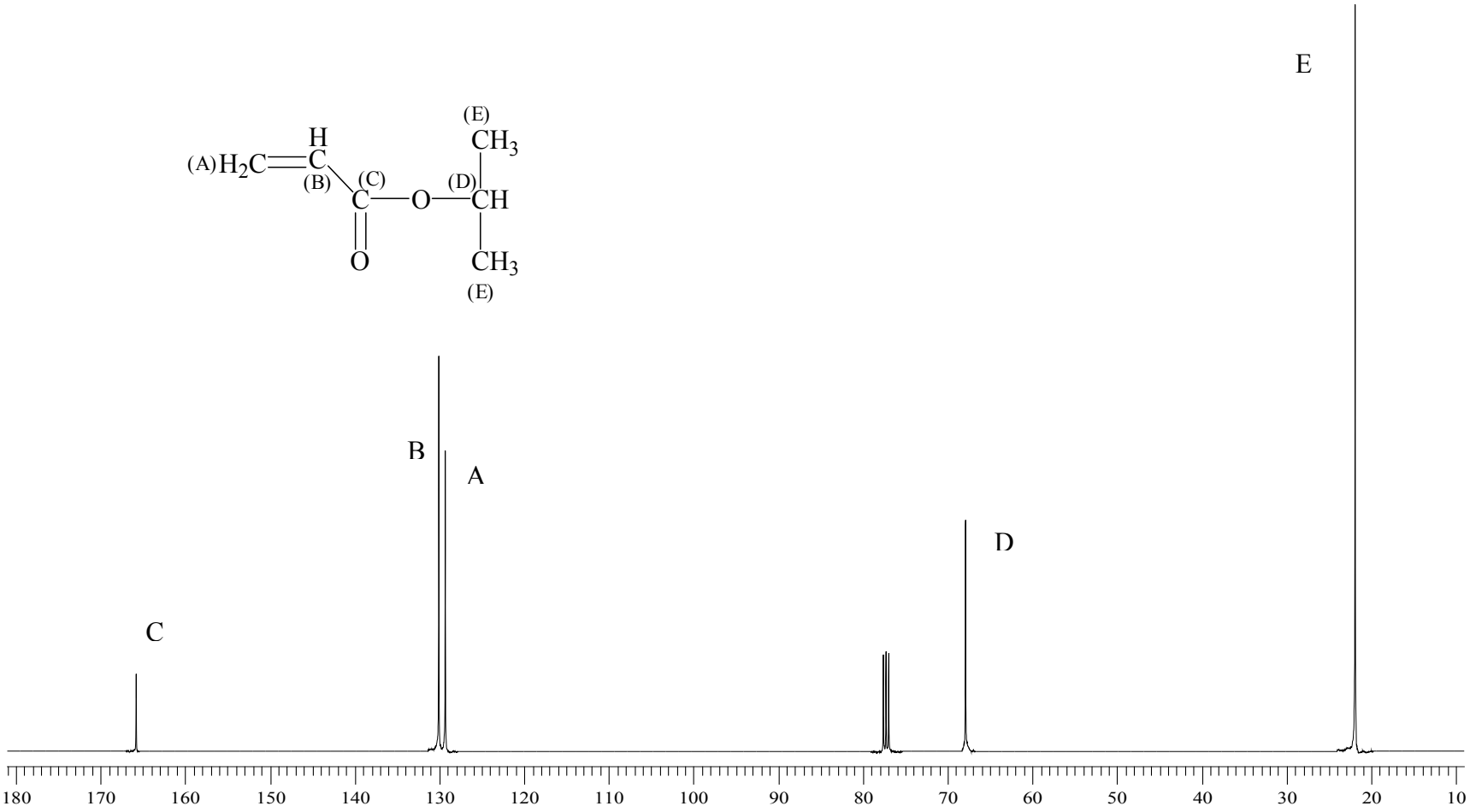


Figure 4.3. ^{13}C-NMR spectrum of isopropyl acrylate in $CDCl_3$

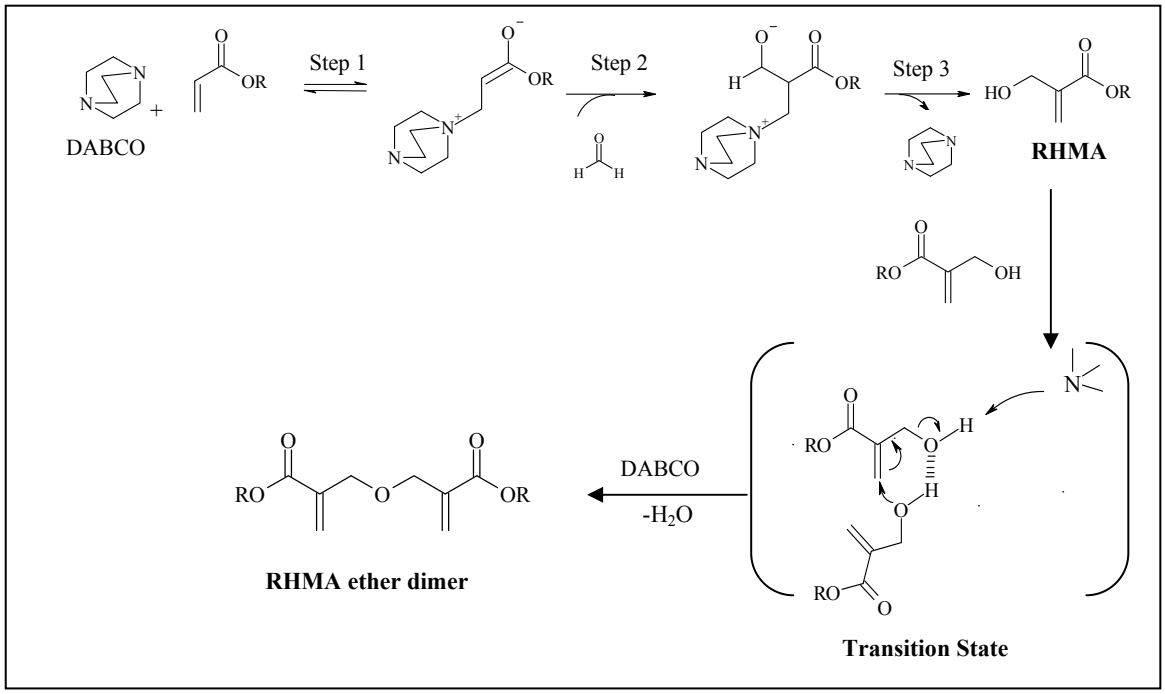


Figure 4.4. Synthesis of RHMA ether dimers by Baylis-Hilmann reaction

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, the removal of the water increases the yield [34].

4.1.4. Characterization of RHMA Ether Dimers

All the reactions were tracked by the most widely used method, TLC, using silica gel plate. During the reactions, formation of RHMA and then formation of ether dimer of RHMA were detected as evidenced by the decrease in the intensity of RHMA and acrylate spots. In ^{1}H-NMR spectra, the formation of new peak at around 4.24 ppm for both monomers (Figure 4.5 and 4.10) and in ^{13}C-NMR , the peak at 168.9 and 168.36 (α-methylene) that belongs to IPHMA and IBHMA ether dimers respectively were detected (Figure 4.6 and 4.12).

In the IR spectrum of isopropyl alpha-(hydroxylmethyl)acrylate (IPHMA) the main peaks at 1711.90 cm^{-1} (ester C=O stretch), triplet at 2982.40 cm^{-1}, 2938.02 cm^{-1} and 2882.32 cm^{-1} (aliphatic C-H stretch), 1055.02 cm^{-1} (strong CH_2-OH stretch), 1108. 85 cm^{-1}

(CH_2 stretch of CH_2-O), 1633 cm^{-1} and 949.04 (C=CH_2 stretch), peaks at 1386.75 cm^{-1} and 1375.19 cm^{-1} (CH_3 bend of isopropyl group), 1455.82 cm^{-1} (CH_2 bend of CH_2-C=C) were observed (see Figure 4.9).

Moreover, in the IR spectrum of the IPHMA ether dimer, disappearance of the broad OH stretch at 3435.14 cm^{-1} and strong stretching peak at 1055.02 cm^{-1} were observed. The main peaks at 1709.08 cm^{-1} (ester C=O stretch), 1090.95 cm^{-1} (CH_2-O stretch of C-O-C), 1373.69 cm^{-1} (CH_3 bend of isopropyl group), 1638.16 cm^{-1} and 948.97 cm^{-1} (C=CH_2 stretch), triplet at 2872.54 cm^{-1} 2980.30 cm^{-1} and 2933.08 cm^{-1} (aliphatic CH stretch), 1463.07 cm^{-1} (CH_2 bend of CH_2-C=C) were identified (Figure 4.11).

4.2. Cyclopolymerization of RHMA Ether Dimers by ATRP

The ATRP method was preferred throughout this study, due to the ability to obtain well defined polymers with narrow polydisperties and desired molecular weights. The components of the system were choosen to be PMDETA/Cu(I)Br as the catalyst system in order to obtain polymers with properties mentioned above as. EBiB (ethyl 2-bromoisobutyrate) was used as the initiator capable of forming tertiary radical that leads to fast initiation.

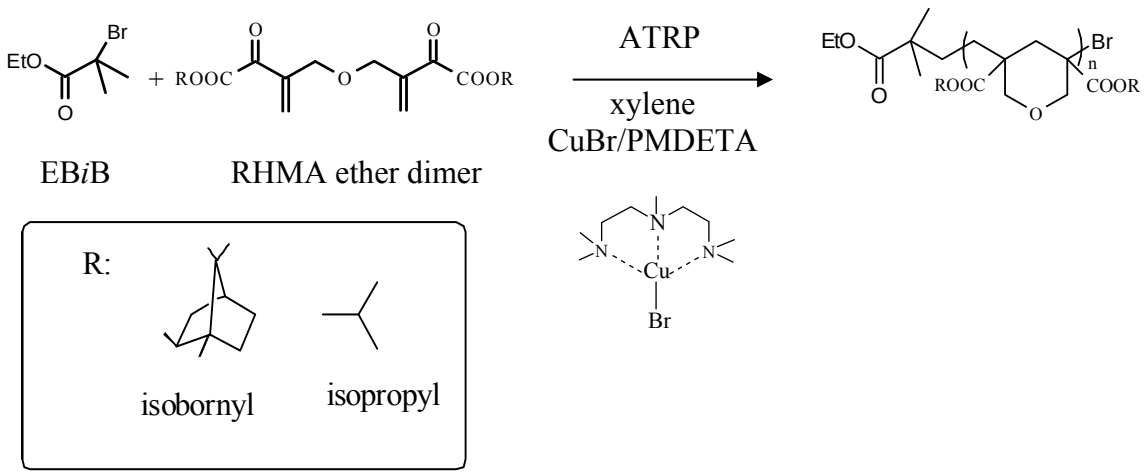


Figure 4.5. Cyclopolymerizations of RHMA ether dimers via ATRP

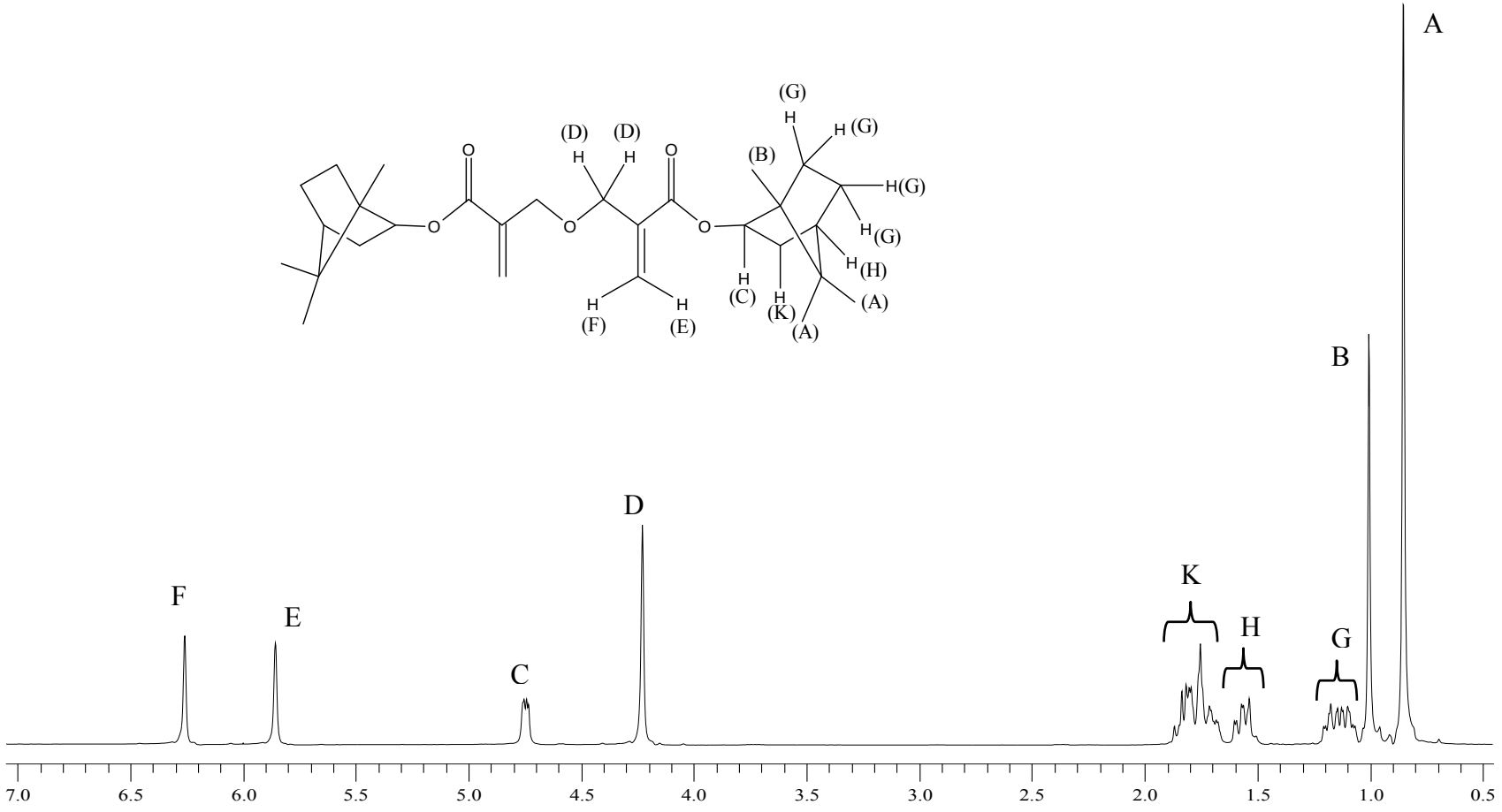


Figure 4.6. ^{1}H-NMR spectrum of isobornyl α-(hydroxymethyl) acrylate (IBHMA) ether dimer in $CDCl_3$

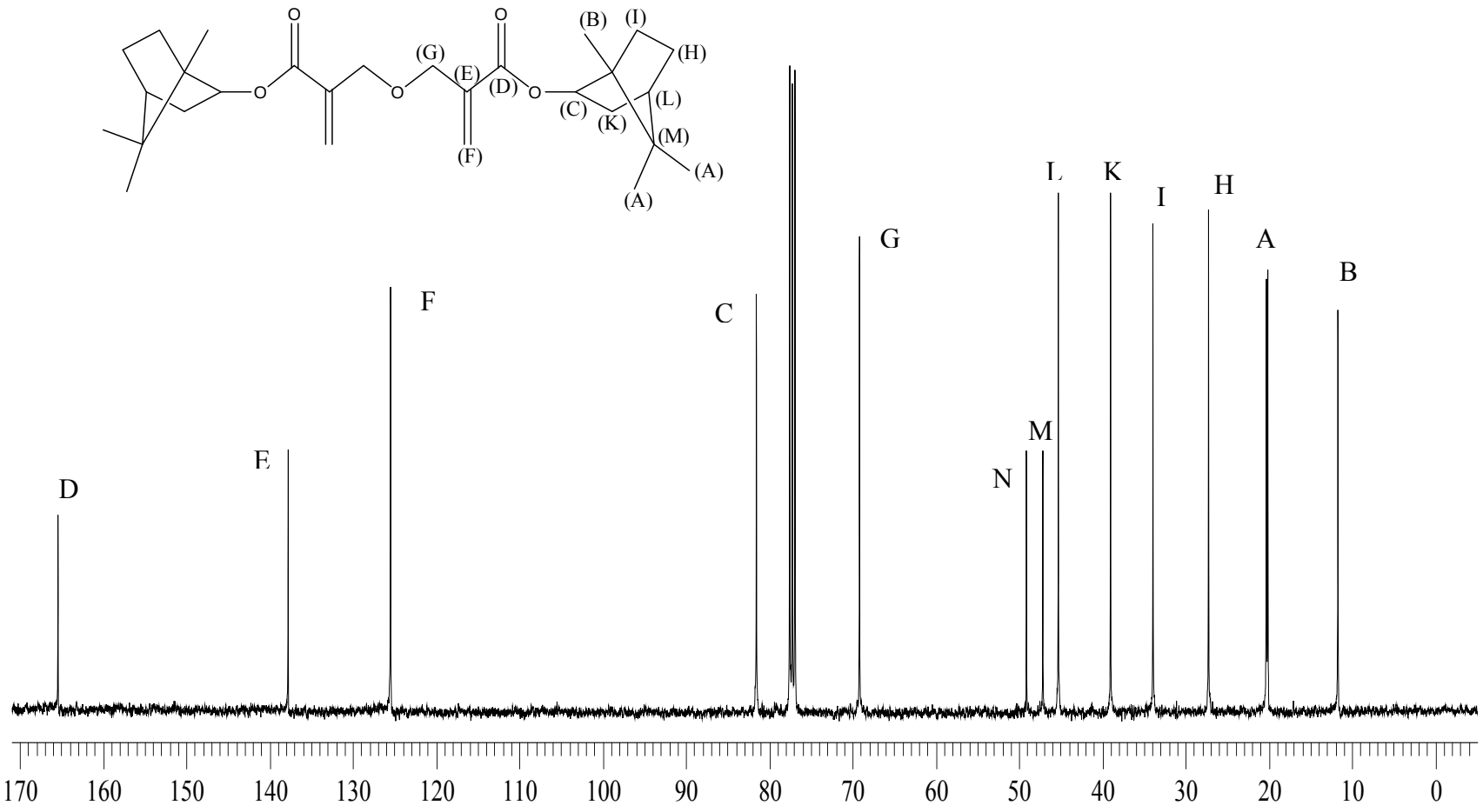


Figure 4.7. ^{13}C-NMR spectrum of isobornyl α-(hydroxymethyl) acrylate (IBHMA) ether dimer in $CDCl_3$

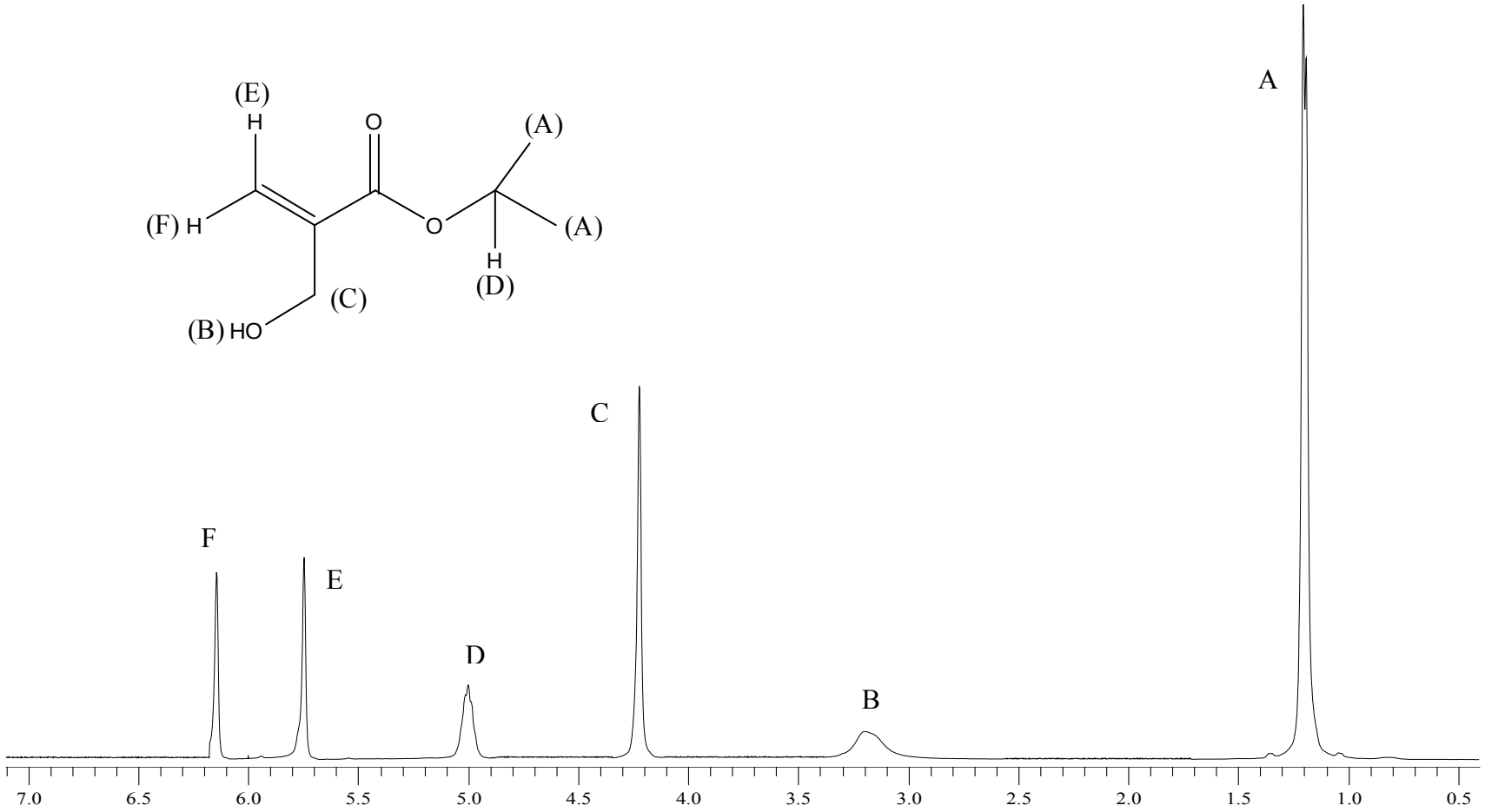


Figure 4.8. ^{1}H-NMR spectrum of isopropyl α-(hydroxymethyl) acrylate (IPHMA) in $CDCl_3$

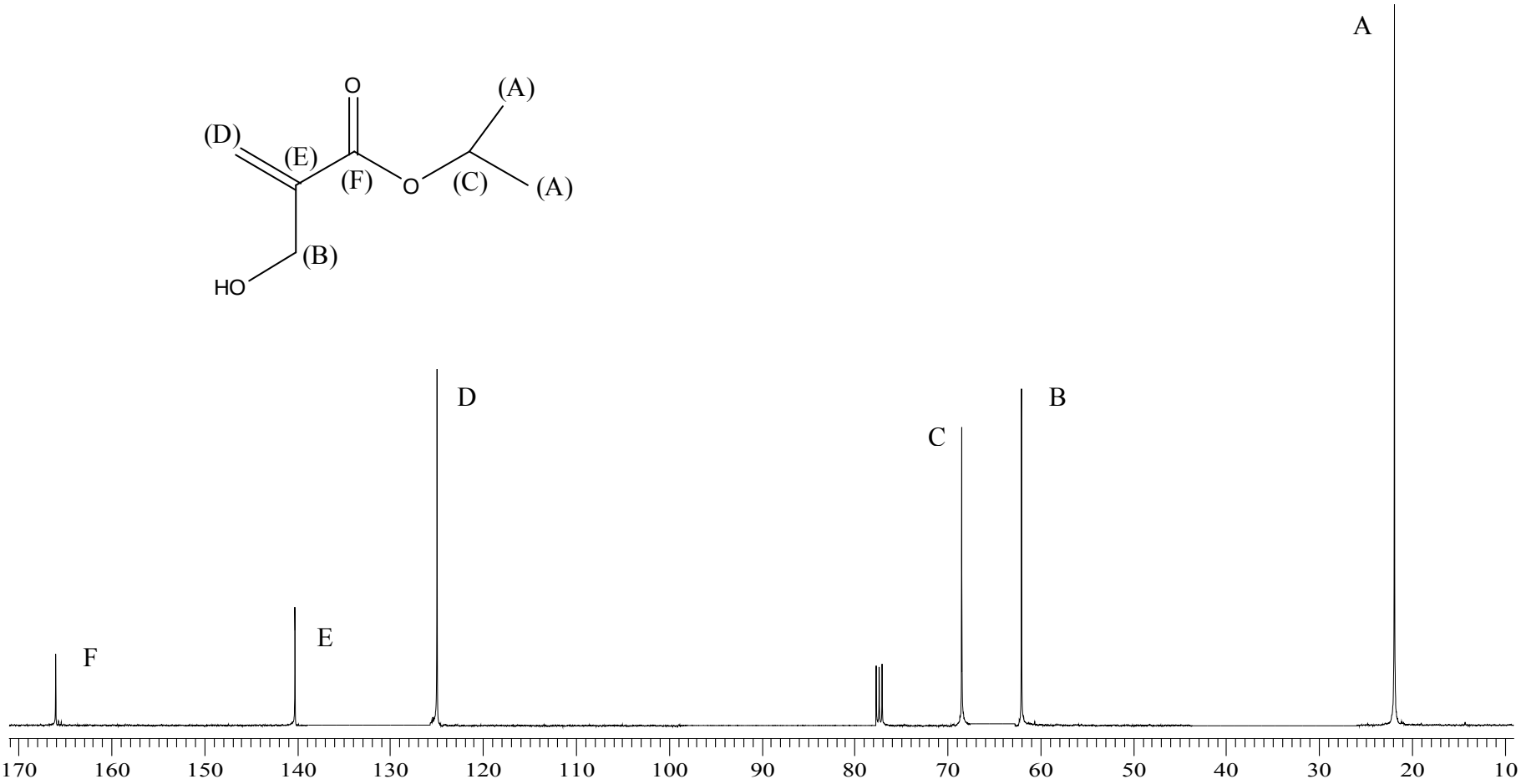


Figure 4.9. ^{13}C-NMR spectrum of isopropyl α-(hydroxymethyl) acrylate (IPHMA) in $CDCl_3$

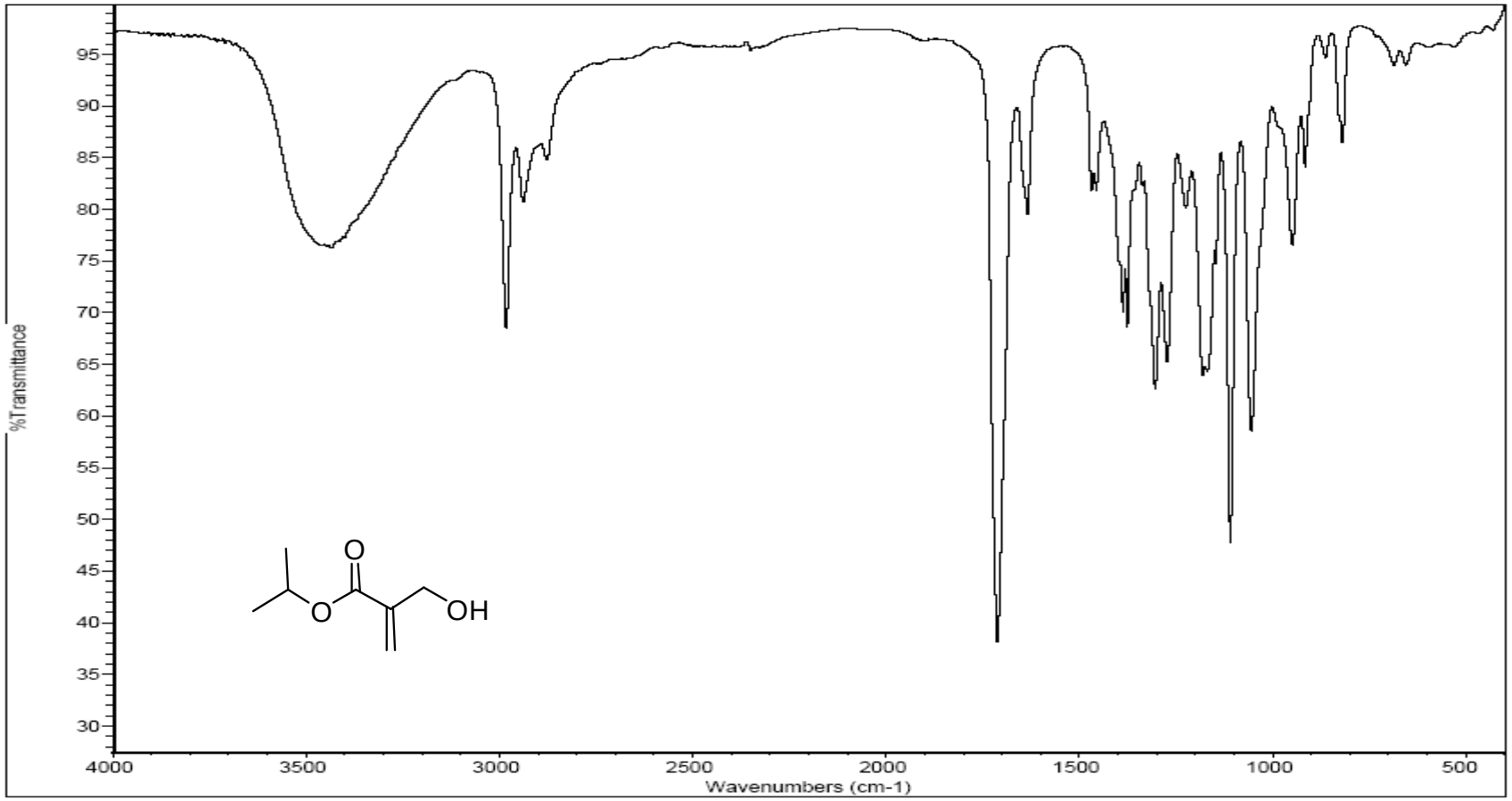


Figure 4.10. IR Spectrum of isopropyl α-(hydroxymethyl) acrylate (IPHMA)

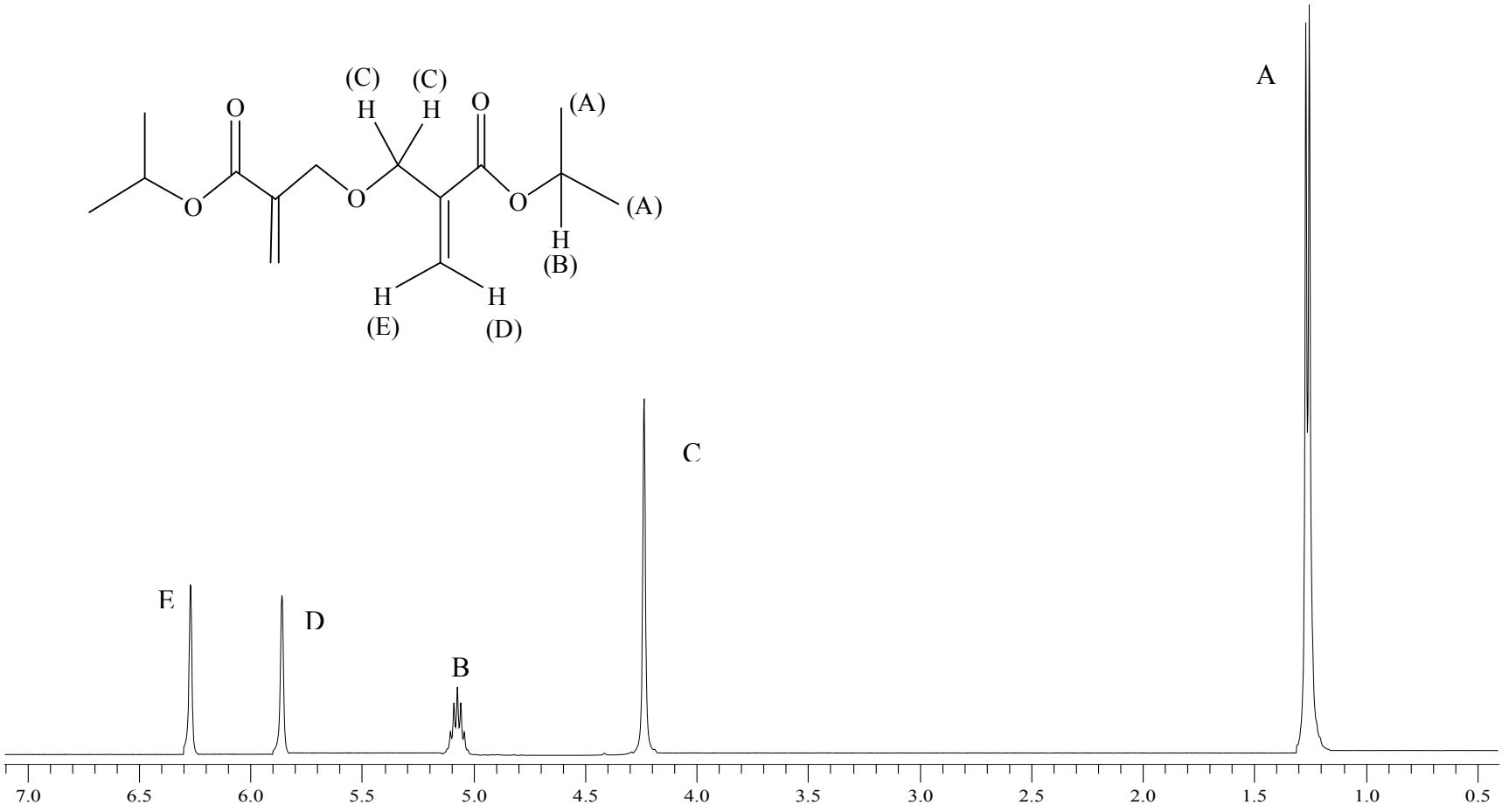


Figure 4.11. ^{1}H-NMR spectrum of isopropyl α-(hydroxymethyl) acrylate (IPHMA) ether dimer in $CDCl_3$



Figure 4.12. IR Spectrum of isopropyl α-(hydroxymethyl) acrylate (IPHMA) ether dimer

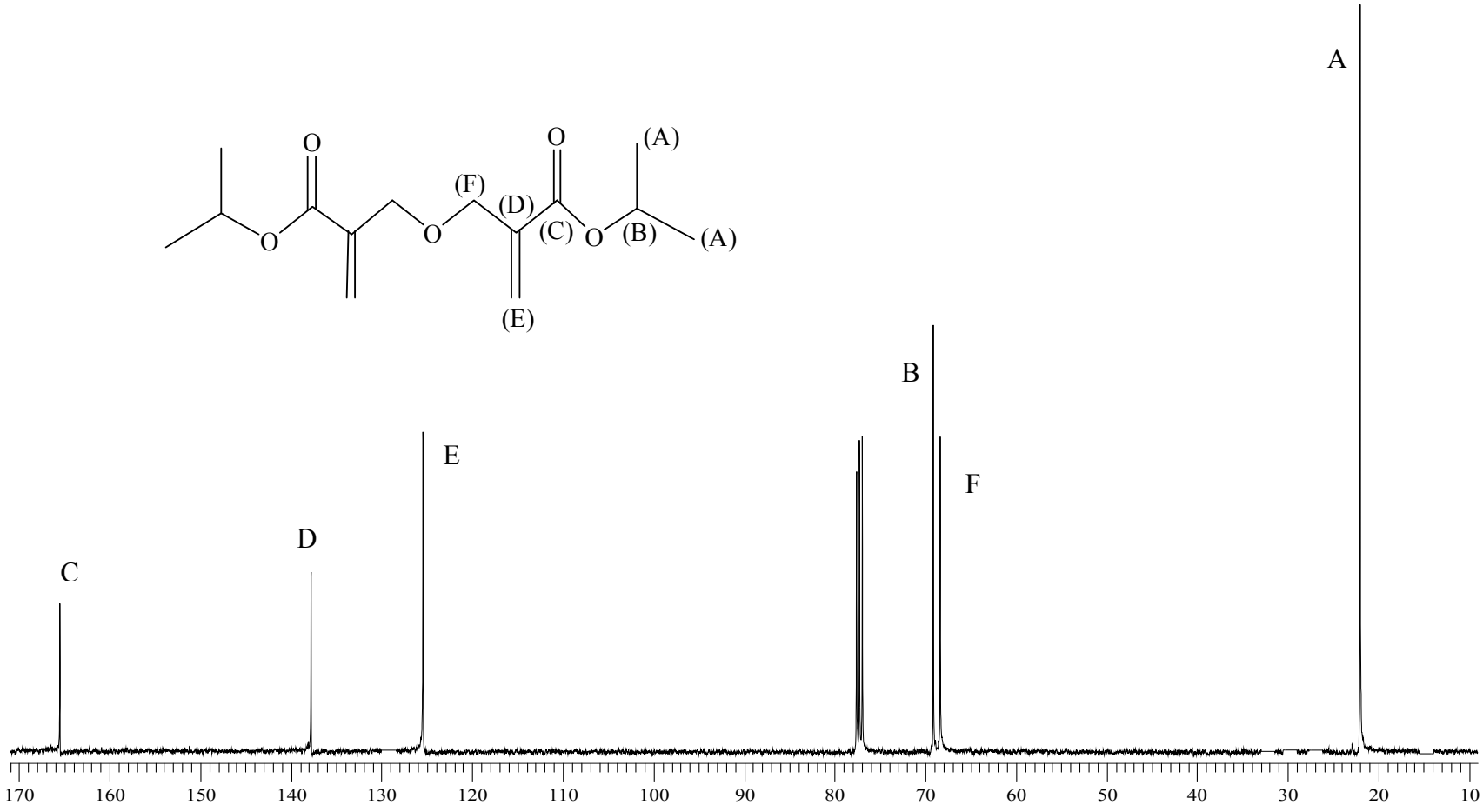


Figure 4.13. ^{13}C-NMR spectrum of isopropyl α-(hydroxymethyl) acrylate (IPHMA) ether dimer in $CDCl_3$

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 1.6. 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 cylopolymers can be observed [4]. It was previously proved by our research group that small R-groups in ATRP result in crosslinked polymers [9,35]. 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. Then, when the *t*-butyl derivative was subjected to ATRP, this time no pendant double bond was detected, cycloplymers were well defined with considerably narrow polydisperties ($1.05<PDI<1.23$) thus, full cyclization was achieved. In addition to this, further increase in bulkiness to cyclohexyl and adamantyl groups have lead to increase in polydisperties exhibiting no double bond residuals in NMR spectra proving full cyclization. In these systems the increase in polydisperities were attributed to loss of control in ATRP process due to the increase in bulkiness which makes the approach or access of the catalyst/ligand complex harder to the propagating site, and thus influencing deactivation negatively. Polymerizations were carried out with $[M]_0$:[EB*i*B]$_0$:$[CuBr]_0$:$[Ligand]_0$=100:1:1:1 ratios in 1 M ±0.01xylene at 70 ^oC (Table 4.1).

Recent cyclopolymerization studies with the bulkier isobornyl derivative exhibited polydisperties as low as the one obtained from smaller *t*-butyl derivative. On the other hand, parallel studies with smaller isopropyl derivative gave cyclopolymers with higher molecular weight distributions. And the whole data obtained so far was collected, and it was found that polydispersity indexes decreases from smaller ester substituents, such as ethyl, *n*-butyl and isopropyl and keeps decreasing and reaches to a minima with *t*-butyl and isobornyl groups and then going through cyclohexyl and adamantyl, it starts increasing and finally reaches to a maxima. In the light of the NMR data obtained so far, the most probable scenario is the following, as the ester substituent gets bulkier, the amount of

branched pendant vinyl double bonds leading either to crosslinking or high PDIs decreases, that is to say intermolecular monomer addition decreases with increasing bulkiness [4]. In the case of relatively bulky adamantyl and cyclohexyl groups approach of the catalyst/ligand complex became harder which causes loss of control (decrease in deactivation rate) in ATRP system resulting in cyclopolymers with higher PDI values.

Number average molecular weights (M_n) values obtained were lower than the theoretical values for isobornyl derivate which was attributed to hydrodynamic volume difference between the resulting polymers and polystyrene standards which was used to calibrate the GPC. On the other hand, both calculated and theoretical M_n values of cycpolymers obtained from isopropyl derivative were in good match.

Absence of uncyclized-pendant double bonds in both ^{1}H-NMR and ^{13}C-NMR spectra of poly(IBHMA ether dimer) (Figure 4.14 and 4.15) confirmed the full cyclization. However, existence of the double bond residuals in ^{1}H-NMR of poly(IPHMA ether dimer) (Figure 4.16) around 6 ppm was the indication of branching due to uncyclized pendant vinyl group(s) on the polymer chain that is consistent with the higher PDI values.

Furthermore, the data obtained from the kinetic study of IBHMA ether dimer cyclopolymerizations at 70 ^{o}C (Table 4.2) showed a linear relationship between conversion and M_n values (Figure 4.18). Kinetic plot of $\ln([M]_0/[M])$ versus time (Figure 4.19) were linear which confirmed that the polymerization rate was first- order with respect to monomer concentration and the concentration of radicals was constant throughout the cyclopolymerization. Cyclopolymers with well defined GPC traces (Figure 4.20) and narrow polydisperties ($1.16<PDI<1.37$) were obtained. An increase in PDIs were also observed with conversion, which might be the result of the control loss due to the increased number of termination reactions towards the end of the cyclopol ymerization.

On the other hand, although there was a relationship between conversion and molecular weight in the kinetic study of the cyclopolymers obtained using IPHMA ether dimer (Table 4.3), PDIs were considerably higher ($1.26<PDI<2.04$) for the ATRP process. The occurrence of the shoulder as shown in Figure 4.23 at high moleculer weight region might be the reason for the higher polydispersities observed. It is possible that two or more

propagating polymer chains having uncyclized-pendant vinyl groups couples and the molecular weights doubles, triples etc. and causes the occurrence of the shoulder at high molecular weights, as a result an increase in the polydispersity is observed eventhough the ATRP process is controlled.

Table 4.1. Results from the ATRP of IBHMA and IPHMA ether dimers at 70 °C[a,b]

Entry	Monomer[c,d]	Time (h)	Conversion (%)	$M_{n,cal}$[e] (10^3.g.mol^{-1})	$M_{n,sec}$[f] (10^3.g.mol^{-1})	PDI
1	EHMA	5	x-link	x-link	x-link	x-link
2	TBHMA	2	29	8.6	8.6	1.05
3	TBHMA	8	36	10.7	10.9	1.19
4	BHMA	6	13	3.9	17.6	1.90
5	ADHMA	3	58	22.7	10.9	1.50
6	CHHMA	1	30	10.5	9.1	1.28
7	CHHMA	3	55	19.3	18.8	1.45
8	IBHMA	1	19	8.7	10.5	1.15
9	IBHMA	1	22	10.1	10.8	1.16
10	IBHMA	2	49	22.4	11.4	1.17
11	IBHMA	2	47	21.5	12.4	1.19
12	IBHMA	4	81	37.1	18.6	1.25
13	IPHMA	0,5	47	12.7	12.2	1.32
14	IPHMA	2	75	20.3	19.7	1.51

[a]All polymers were soluble in CH_2Cl_2. [b]$[M]_0$:$[EBiB]_0$:$[CuBr]_0$:$[Ligand]_0$=100:1:1:1 ratios in 1 M ±0.01 xylene at 70 °C. [c]All monomers were ester ether dimers of the corresponding groups. [d]Entry 1-4 belongs to [9,35] and entry 5-7 belongs to [36]. [e]Measured by gravimetric methods. [f]Relative to polystyrene standarts.

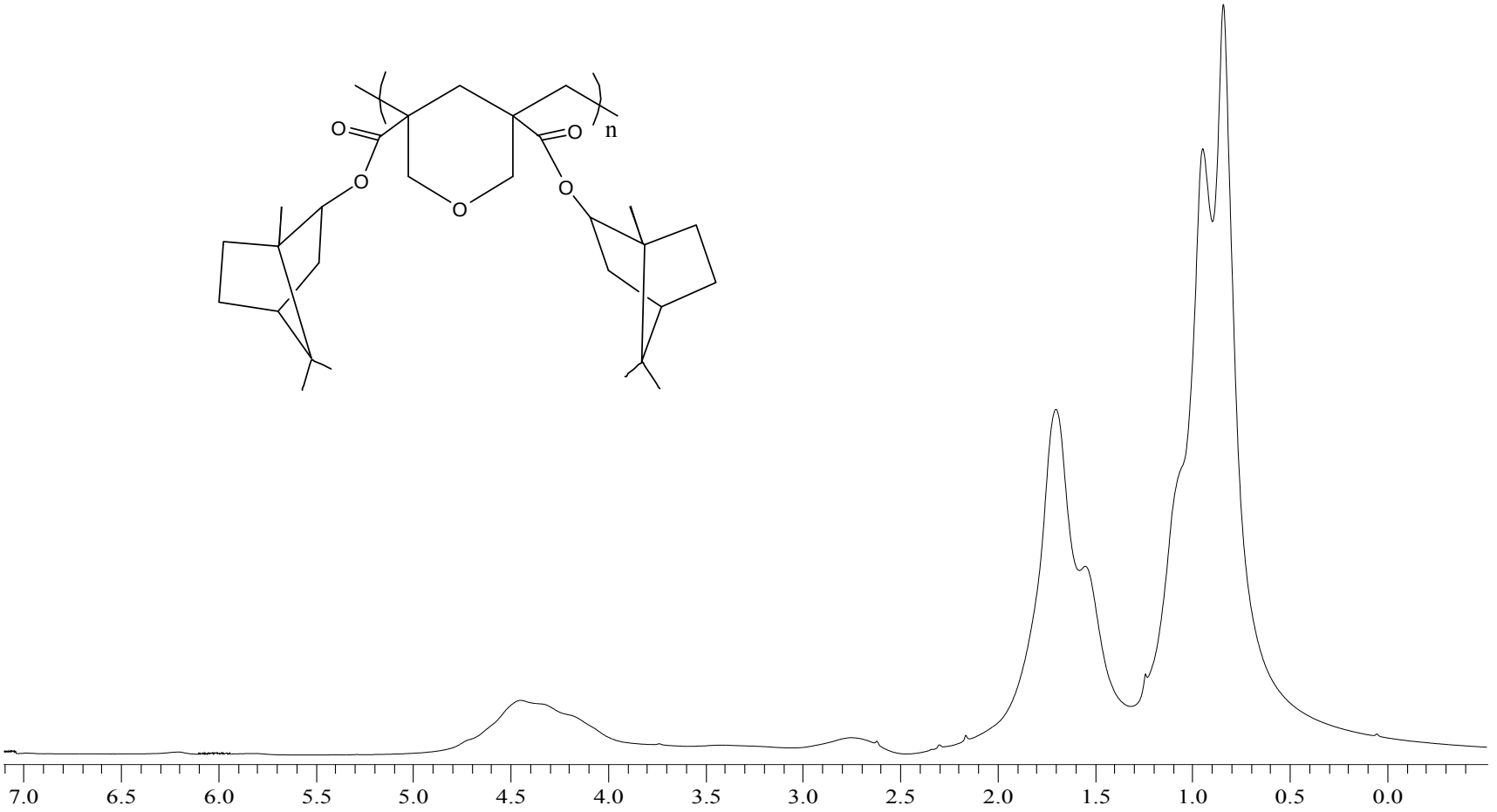


Figure 4.14. ^{1}H-NMR spectrum of poly(IBHMA ether dimer) in $CDCl_3$

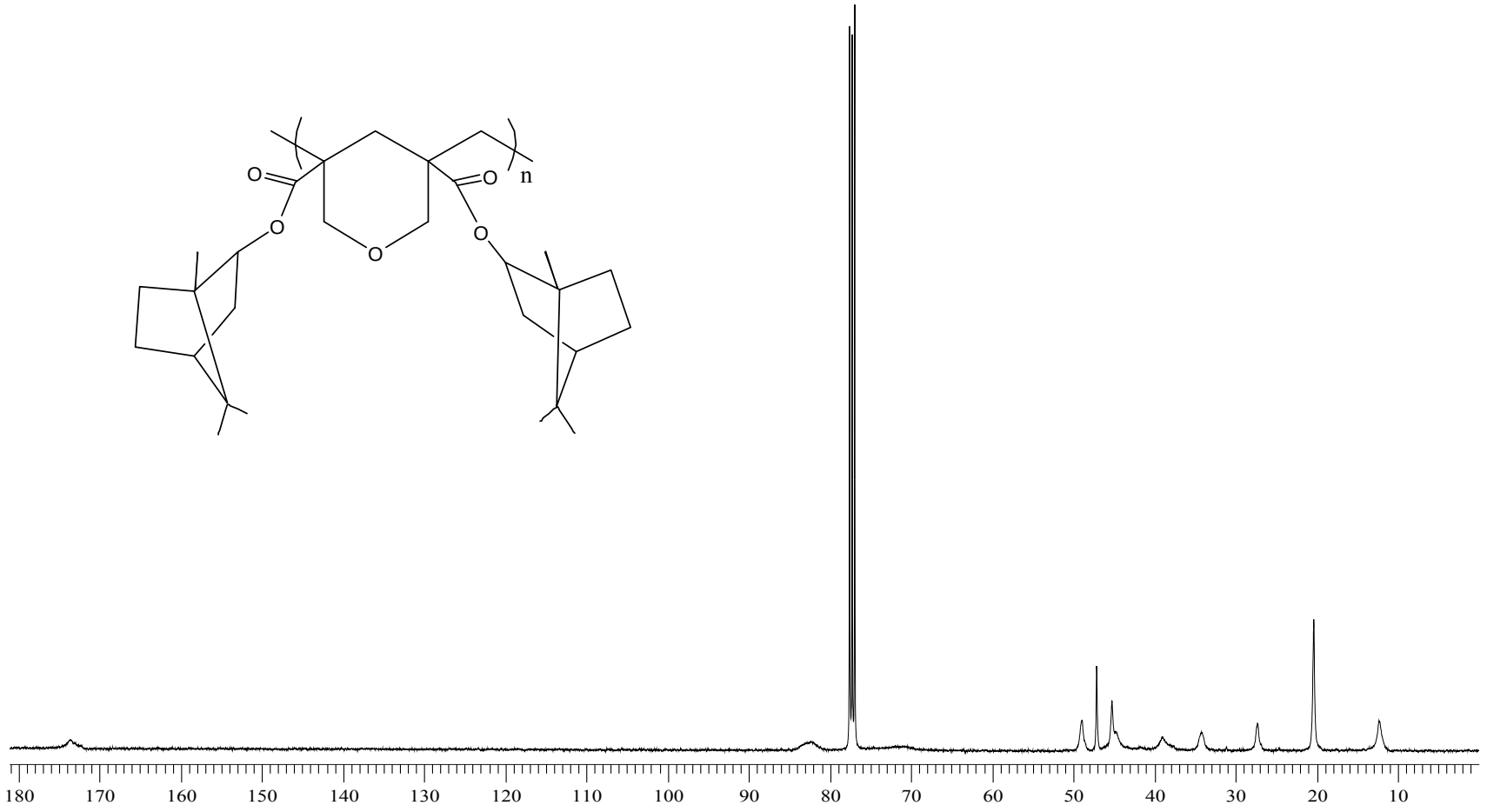


Figure 4.15. ^{13}C-NMR spectrum of poly(IBHMA ether dimer) in $CDCl_3$

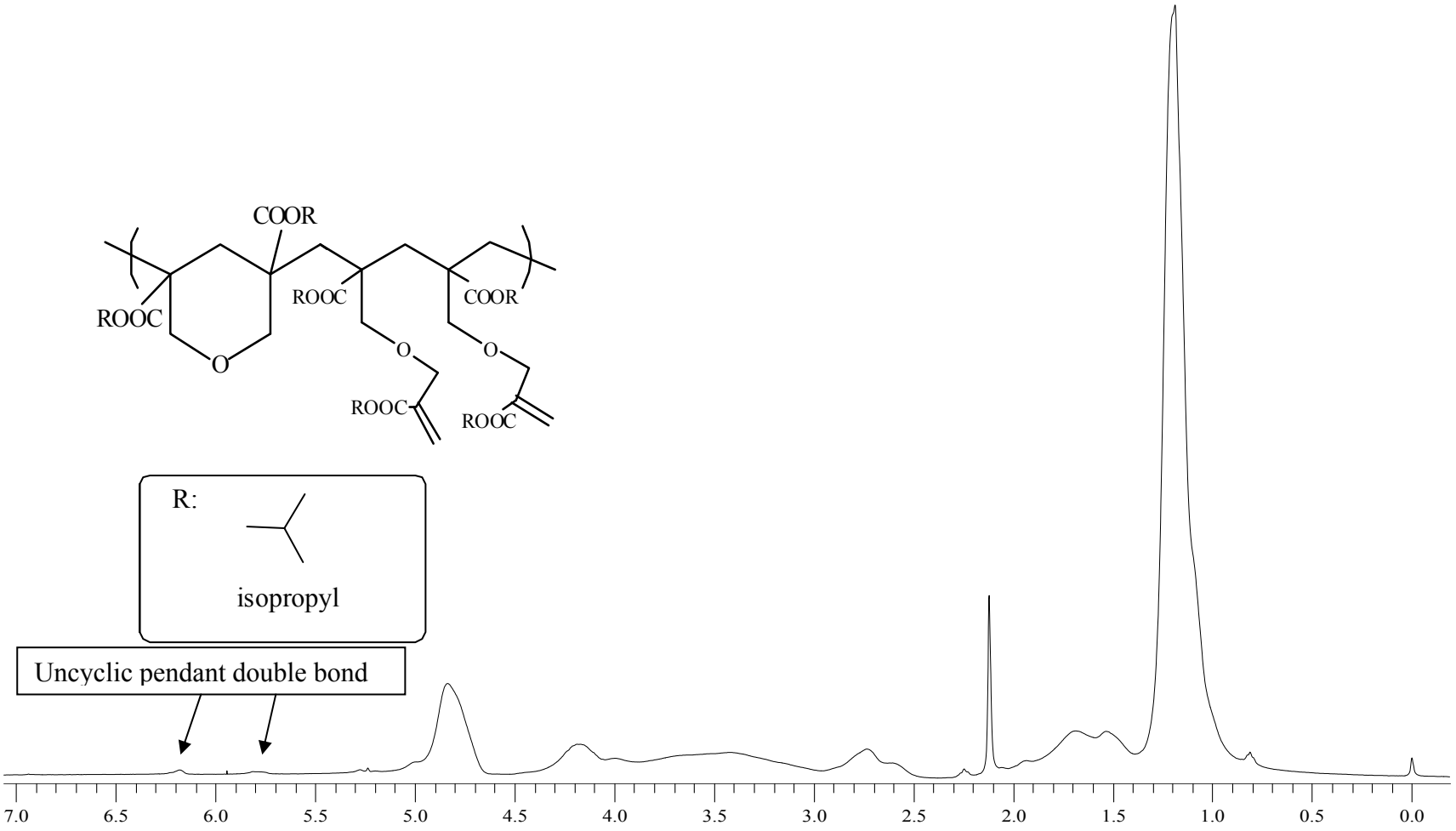


Figure 4.16. ^{1}H-NMR spectrum of poly(IPHMA ether dimer) in $CDCl_3$

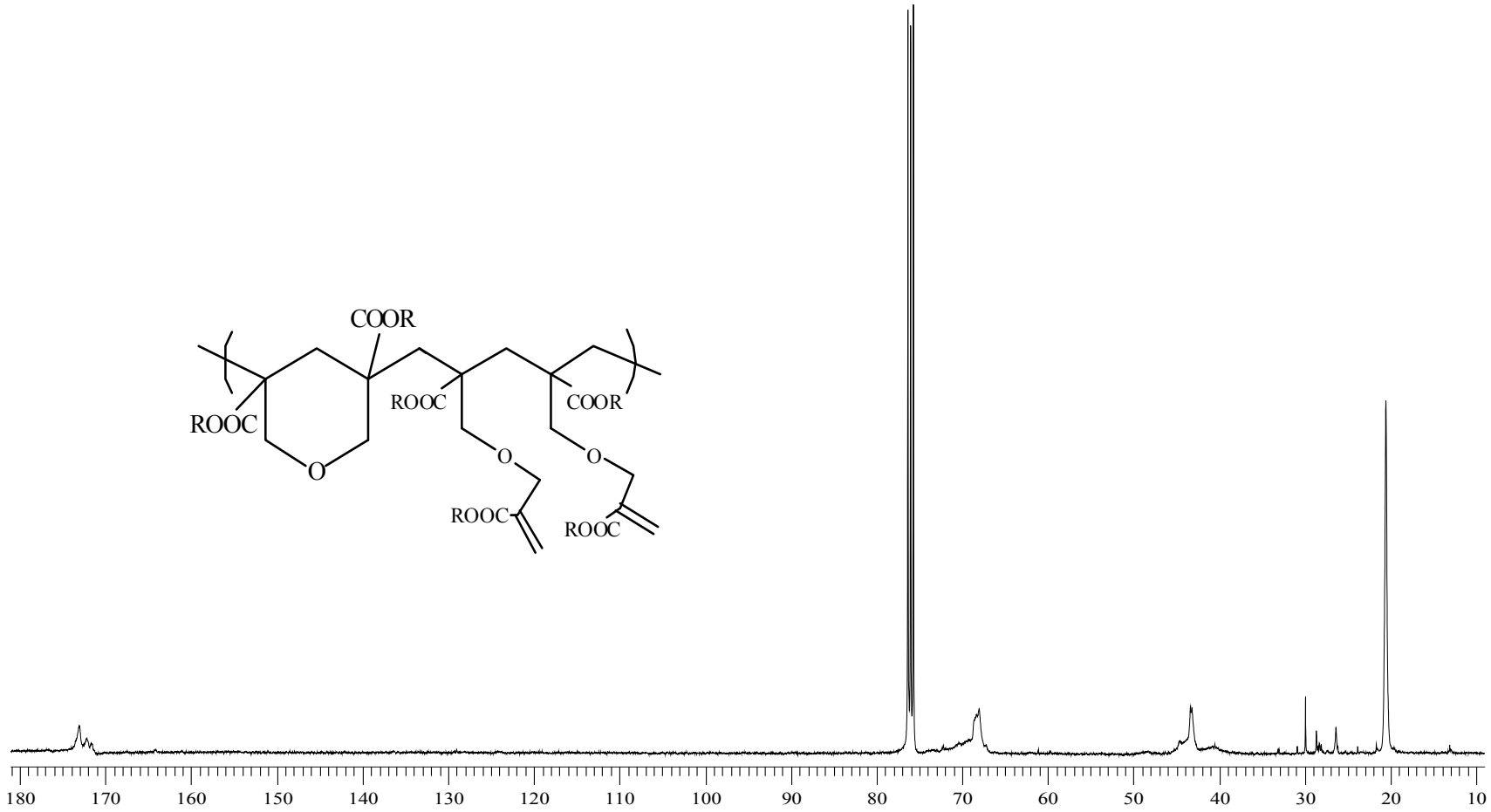


Figure 4.17. ^{13}C-NMR spectrum of poly(IPHMA ether dimer) $CDCl_3$

Table 4.2. Results from kinetic study of ATRP of IBHMA ether dimer at 70 °C[a,b]

Entry	Time (hour)	Conversion (%)	$M_{n,cal}$[c] (10^3.g.mol^{-1})	$M_{n,sec}$[d] (10^3.g.mol^{-1})	M_w/M_n
1	2	41	18.6	8.9	1.16
2	3	62	28.2	14.1	1.19
3	4	74	33.8	17.8	1.27
4	5	81	37.0	20.4	1.32
5	6	85	38.9	21.5	1.37

[a]Conditions: $[M]_o$:[I]:[CuBr]:[Ligand]=100:1:1:1, [M]=0.99 M in xylene. [b]All polymers were soluble in CH_2Cl. [c]Measured by gravimetric methods. [d]Relative to polystyrene standarts.

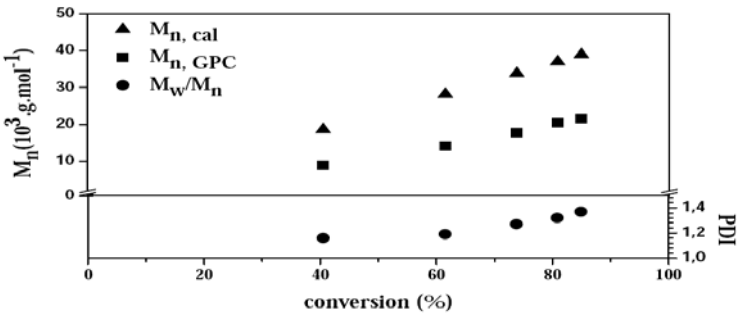


Figure 4.18. Kinetic study of IBHMA ether dimer cyclopolymerization via ATRP at 70 °C. Increase of M_n and evolution of PDI as a function of conversion

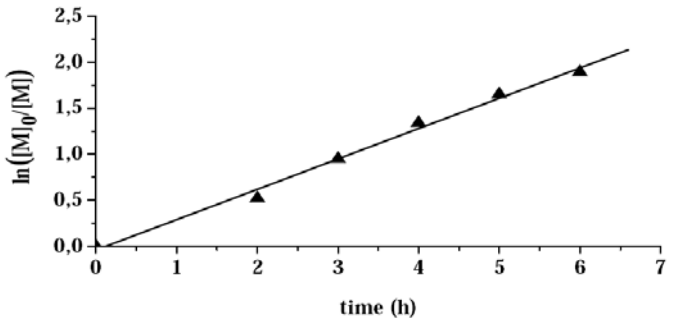


Figure 4.19. First-order kinetic plot of IBHMA ether dimer cyclopolymerization via ATRP at 70 °C

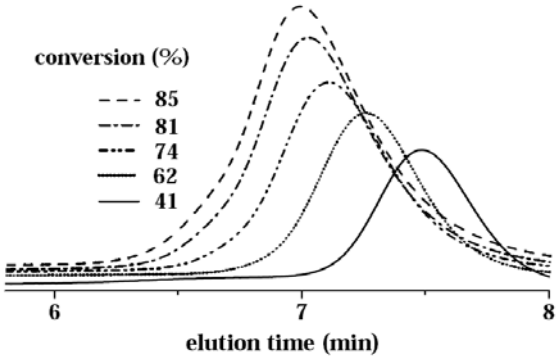


Figure 4.20. SEC traces of kinetic study of IBHMA ether dimer cyclopolymerization at 70 ºC. Molecular weights increases from left to right

Table 4.3. Results from kinetic study of ATRP of IPHMA ether dimer at 70 $^{o}C^{a,b}$

Entry	Time (hour)	Conversion (%)	$M_{n,cal}{}^{c}$ (10^3.g.mol^{-1})	$M_{n,sec}{}^{d}$ (10^3.g.mol^{-1})	M_w/M_n
1	0.5	36	9.7	9.2	1.26
2	1	62	16.7	15.1	1.42
3	1.5	73	19.7	19.2	1.57
4	2	84	22.6	21.7	1.83
5	2.5	92	24.8	23.8	2.04

[a]Conditions: $[M]_0:[I]_0:[CuBr]_0:[Ligand]_0$=100:1:1:1, [M]=0.99 M ± 0.01 in xylene.[b]All polymers were soluble in CH_2Cl.[c]Measured by gravimetric methods. [d]Relative to polystyrene standarts.

In addition to this, slopes of the first order kinetic plots of the cyclopolymerizations (Figure 4.19 [slope: 0.32] and Figure 4.21 [slope: 0.96]) showed that ATRP polymerization of the IPHMA ether dimer was much faster than that of IBHMA ether dimer. Kinetic plot of $\ln([M]_0/[M])$ (Figure 4.21) versus time were linear for the IPHMA ether dimer which confirmed that the polymerization rate was first- order with respect to monomer concentration and that the concentration of radicals was constant throughout the cyclopolymerization.

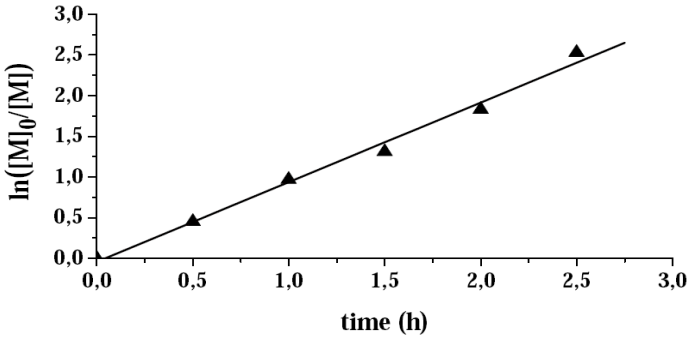


Figure 4.21. First-order kinetic plot of IPHMA ether dimer cyclopolymerization via ATRP at 70 °C

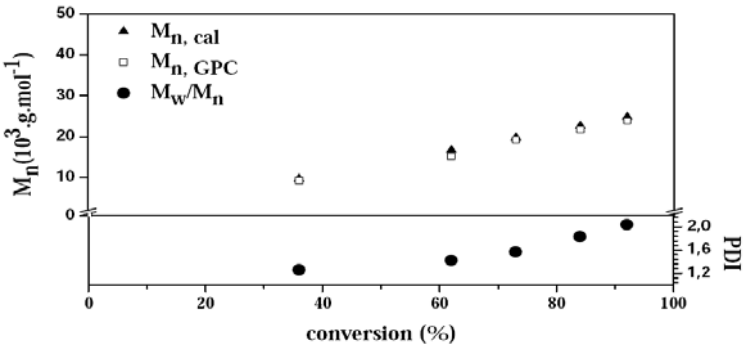


Figure 4.22. Kinetic study of IPHMA ether dimer cyclopolymerization via ATRP at 70 °C. Increase of M_n and evolution of PDI as a function of conversion.

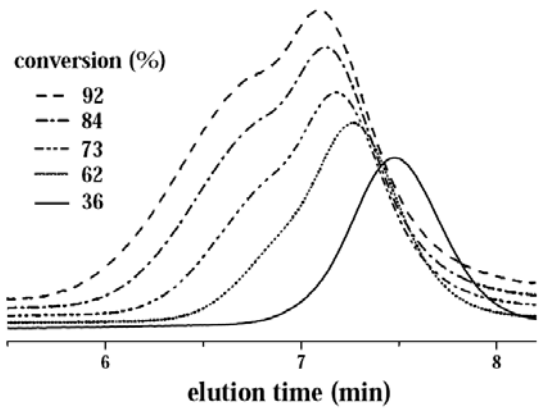


Figure 4.23. SEC traces of kinetic study of IPHMA ether dimer at 70 ºC. Molecular weights increases from left to right

4.2.2. Effect of Temperature on ATRP Cyclopolymerization

The cyclopolymerizations were carried out at various temperatures in order to investigate the effect of temperature on both IBHMA and IPHMA ether dimer cyclopolymerization. Studies at 100 ^{o}C (Table 4.4) showed that PDIs and conversions increased as the temperature increased. Since rate increases with the temperature increases, an increase in conversion was observed in cyclopolymerization of the RHMA ether dimers. However we believe that the increase in temperature may change the activation / deactivation rate constant ratio which may affect the polydispersities of the final polymers. In addition although in general higher temperatures enhance the solubility of the transition metal catalysts in the presence of the ligands, higher temperatures may also cause catalyst decompositions [32]. All reaction systems studied at 100 ^{o}C became heterogeneous, darker and greener towards the end of the polymerizations indicating the irreversible oxydation of the copper catalyst. It is more probable that all these factors contributed to the higher polydispersities observed at 100 ^{o}C.

Table 4.4. Results from the ATRP of IBHMA and IPHMA ether dimers at 50 ^{o}C[a,b]

Entry[c]	Monomer	Time (h)	Conversion (%)	$M_{n,cal}$[d] (10^3.g.mol^{-1})	$M_{n,sec}$[e] (10^3.g.mol^{-1})	M_w/M_n
1	IBHMA	9	33	15.1	9.4	2.30
2	IPHMA	26	57	15.4	14.6	1.60

[a]All polymers were soluble in CH_2Cl_2. [b]All monomers were ester ether dimers of the corresponding groups. [c]Conditions: $[M]_0:[I]_0:[CuBr]_0:[Ligand]_0$=100:1:1:1, [M]=0.99 M ± 0.01 in xylene. [d]Measured by gravimetric methods. [e]Relative to polystyrene standarts.

On the other hand, polydispersities of the cyclopolymers obtained at 50 ^{o}C were found to be higher (Table 4.5). In addition to this, tail and shoulder formation at high moleculer weight region of GPC traces was seen which might be due to the incomplete cyclization.

Table 4.5. Results from the ATRP of IBHMA and IPHMA ether dimers at 100 $^{o}C^{a,b}$

Entry[c]	Monomer	Time (h)	Conversion (%)	$M_{n,cal}$[d] (10^3.g.mol^{-1})	$M_{n,sec}$[e] (10^3.g.mol^{-1})	M_w/M_n
1	IBHMA	2	82	37.5	16.2	1.42
2	IBHMA	4	87	39.8	16.6	1.50
3	IPHMA	0.5	65	17.6	16.8	1.43

[a]All polymers were soluble in CH_2Cl_2. [b]All monomers were ester ether dimers of the corresponding groups. [c]Conditions: $[M]_0:[I]_0:[CuBr]_0:[Ligand]_0=100:1:1:1$, [M]=0.99 M ± 0.01 in xylene. [d]Measured by gravimetric methods. [e]Relative to polystyrene standarts.

4.2.3. Physical Properties of the Cyclopolymers

Differential scanning calorimetry (DSC) analysis of the cyclopolymers at various molecular weights were performed in order to find out the glass transition temperatures (T_g) of the cyclopolymers. T_g of the resulting poly(IPHMA ether dimer)s were around 110 ^{o}C, but T_g was not observed for poly(IBHMA ether dimer)s before decomposition temperature (see Table 4.7, Figure 4.26).

Thermogravimetric analysis (TGA) of the poly(RHMA ether dimer) cyclopolymers were done under nitrogen in order to investigate the thermal stability of the materials (Table 4.6). As seen in Figure 4.24 and 4.25 a-two segmental decomposition was observed for both of the cyclopolymers.

4.3. Block Copolymerizations of poly(RHMA ether dimer)s

Since ATRP is known as a living polymerization method, in order to prove the livingness of the cyclopolymers obtained, copolymerization studies were performed. The copolymerizations were carried out using CuBr/PMDETA as the catalyst system in bulk, the cyclopolymers obtained as the macroinitiator and *t*-butyl acrylate as the comonomer.

Table 4.6. Glass transition temperatures (T_g) of the cyclopolymers with various molecular weights and polydispersities synthesized at 50, 70 and 100 °C by ATRP

Entry	Cyclopolymer	Temp (ºC)	$M_{n,sec}$ (10^3.g.mol^{-1})	M_w/M_n	T_g (ºC)
1	Poly(IBHMA ether dimer)	50	9.4	2.30	-[a]
2	Poly(IBHMA ether dimer)	70	11.4	1.17	-[a]
3	Poly(IBHMA ether dimer)	100	18.7	1.26	-[a]
4	Poly(IPHMA ether dimer)	50	14.6	1.60	106.4
5	Poly(IPHMA ether dimer)	70	15.1	1.42	110.2
6	Poly(IPHMA ether dimer)	70	21.7	1.83	115.4
7	Poly(IPHMA ether dimer)	100	16.8	1.43	116.8

[a]Not determined before the decomposition temperature.

Table 4.7. Thermogravimetric analysis of IBHMA and IPHMA ether dimer cyclopolymers with various molecular weights and polydispersities synthesized at 50, 70 and 100 °C via ATRP

Entry	Cyclopolymer	Temp (ºC)	$M_{n,sec}$ (10^3.g.mol^{-1})	M_w/M_n	Temp (ºC) at % 5 dec
1	Poly(IBHMA ether dimer)	50	9.4	2.45	255.9
2	Poly(IBHMA ether dimer)	70	11.4	1.17	262.1
3	Poly(IBHMA ether dimer)	70	18.6	1.25	263.7
4	Poly(IBHMA ether dimer)	100	18.7	1.26	258.4
5	Poly(IPHMA ether dimer)	50	14.6	1.60	293.7
6	Poly(IPHMA ether dimer)	70	15.1	1.42	291.9
7	Poly(IPHMA ether dimer)	70	21.7	1.83	296.2
8	Poly(IPHMA ether dimer)	100	16.8	1.43	296.6

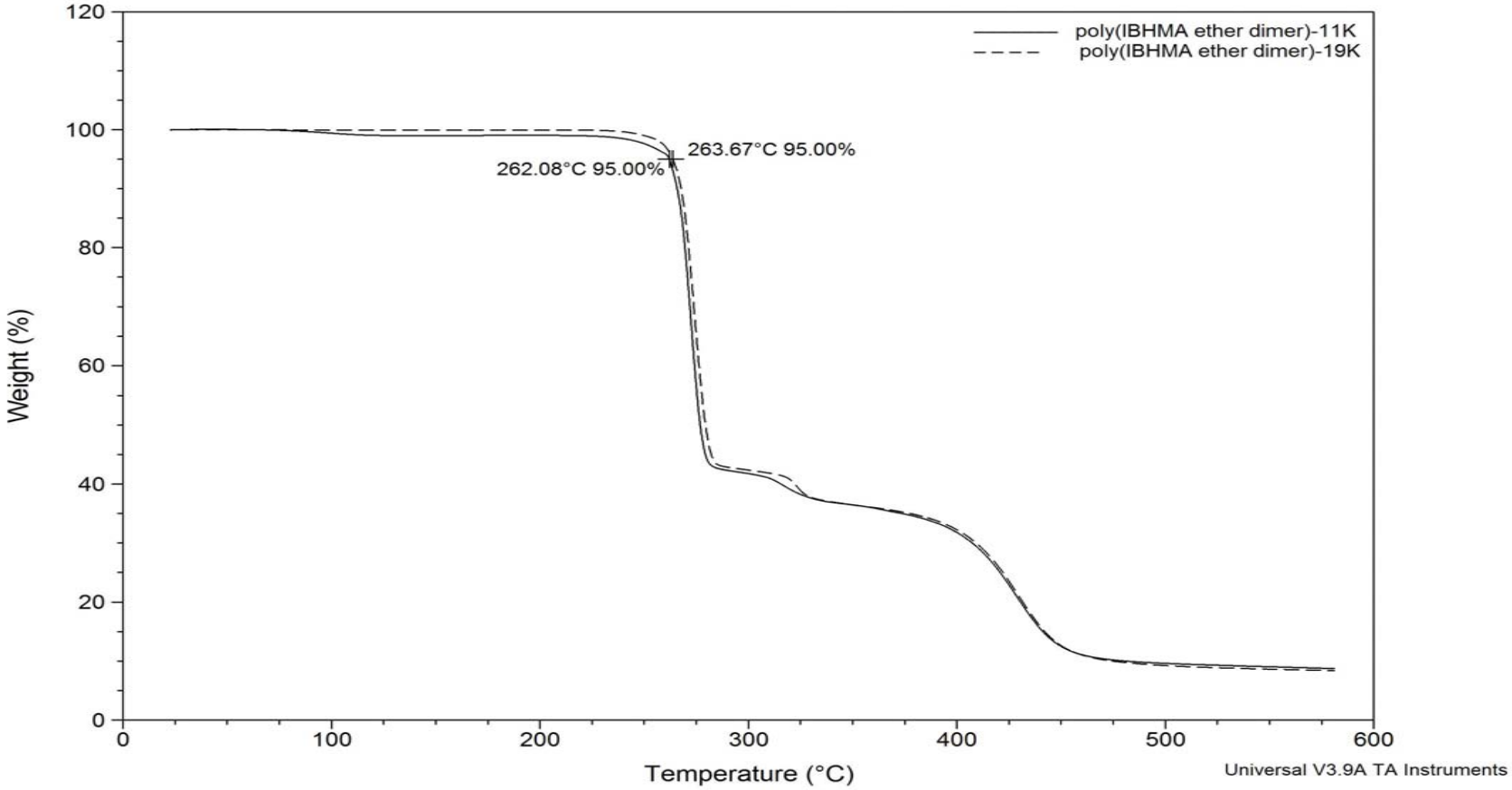


Figure 4.24. TGA thermograms of poly(IBHMA ether dimer)s

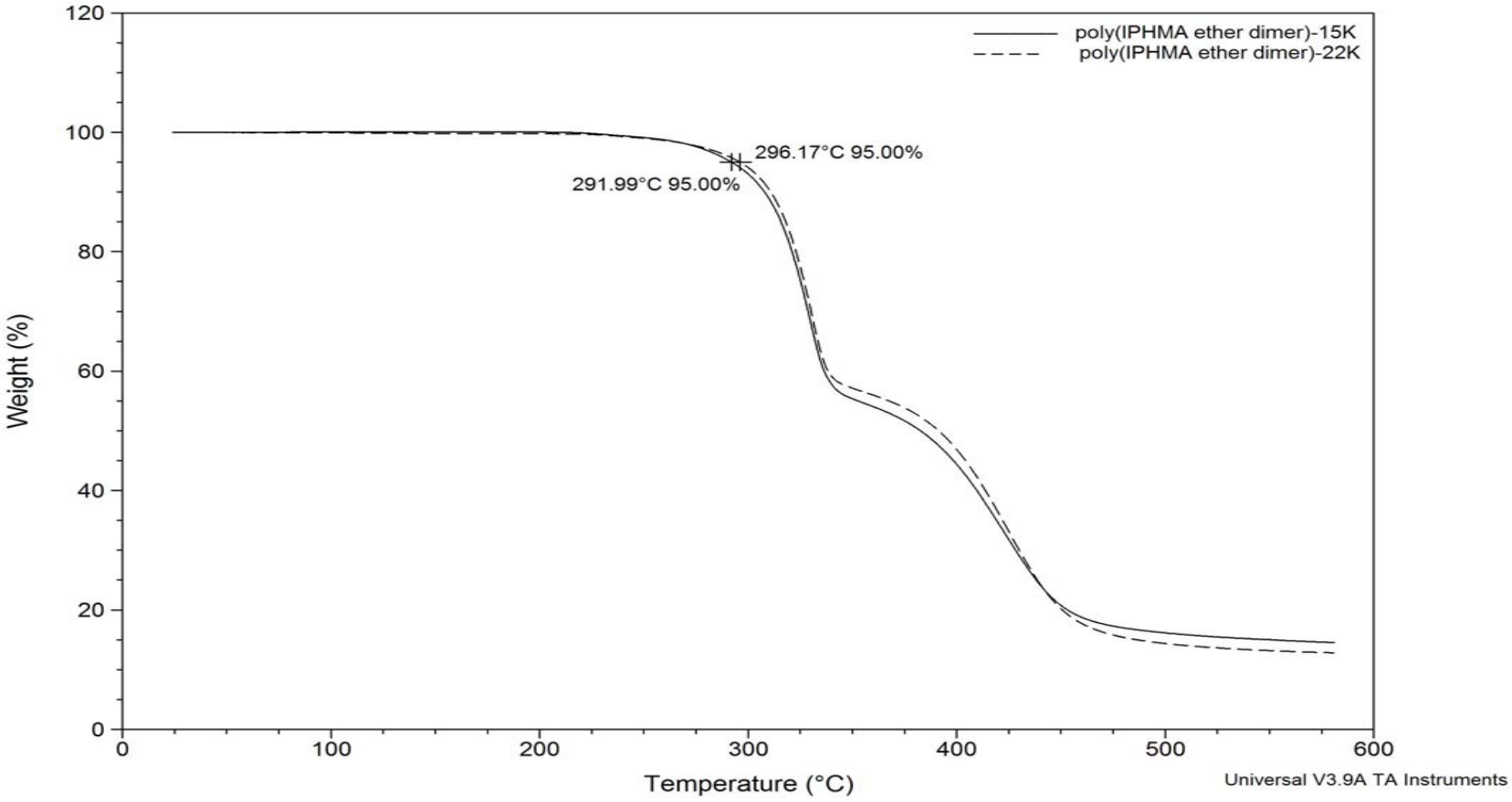


Figure 4.25. TGA thermograms of poly(IPHMA ether dimer)s

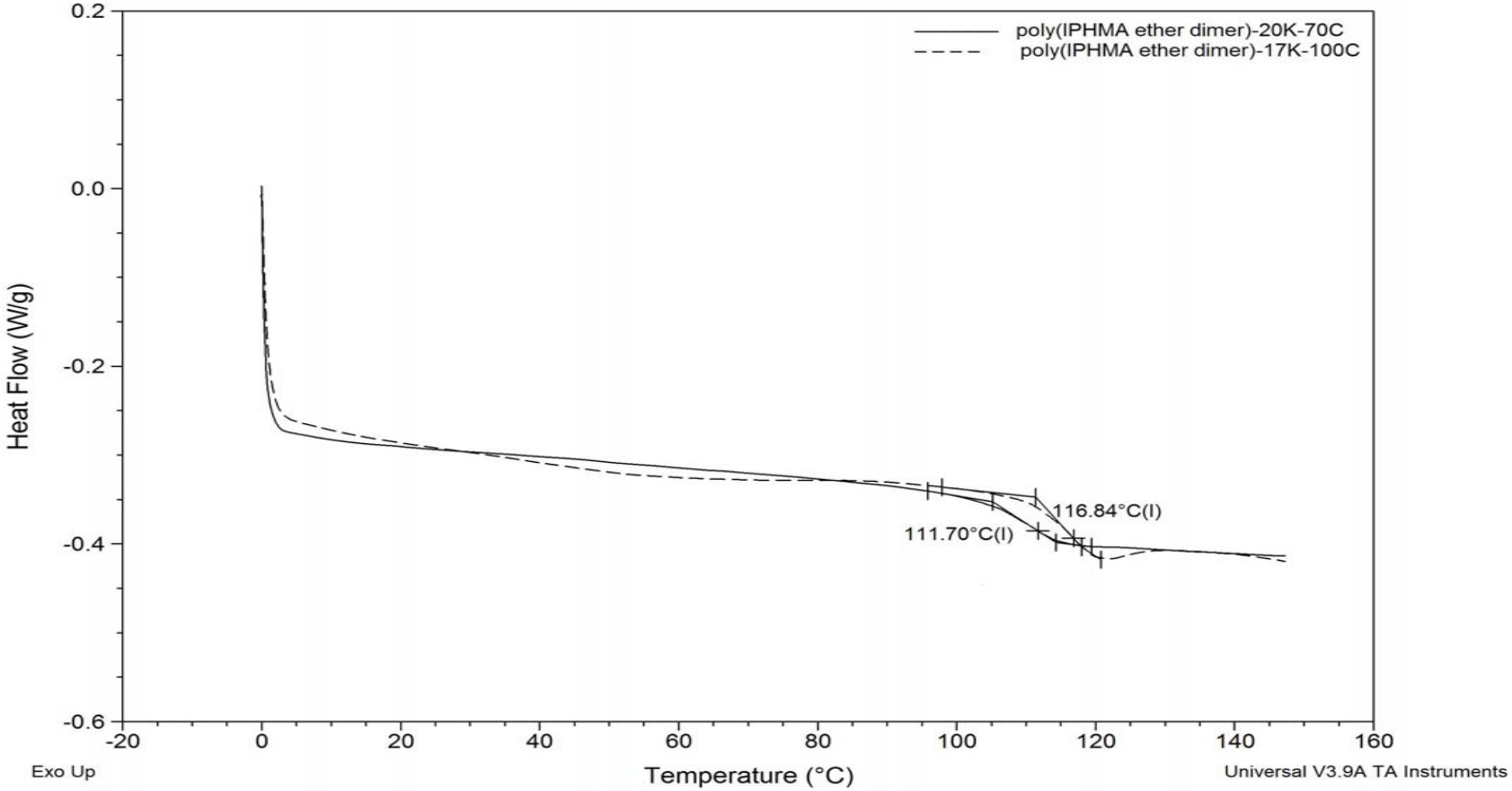


Figure 4.26. DSC traces of poly(IPHMA ether dimer)s

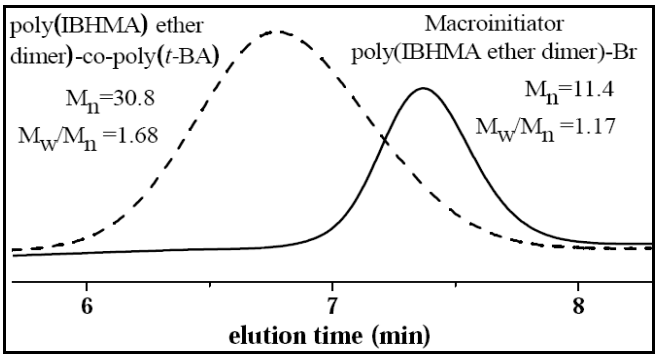
In the SEC traces, the peaks corresponding the poly(IBHMA ether dimer) and poly(IPHMA ether dimer) macroinitiators (Table 4.8) disappeared and new peaks at higher molecular weights were observed. Thus, this study suggests that cyclopolymers obtained by the ATRP technique with both monomers is fully living and capable of being used in block copolymerization studies (Figure 4.27).

In addition to this, polydisperties of the corresponding copolymers (especially poly(IBHMA ether dimer copolymer) were found to be higher than that of macroinitiators. We thought that larger molecular weight distribution was due to the slow initiation from the bulky cyclic structure and faster propagation of the acrylates. In order to slow down the propagation rate relative to initiation rate, bulky isobornyl acrylate was used as a comonomer (Table 4.8, Entry 2), but the obtained PDI value was much worse. Secondly, CuCl was used to perform a halogen exchange to slow down the propagation rate, and as a result molecular weight distribution was found to be improved (Table 4.8, Entry 3). Hence, this study proved our hypothesis.

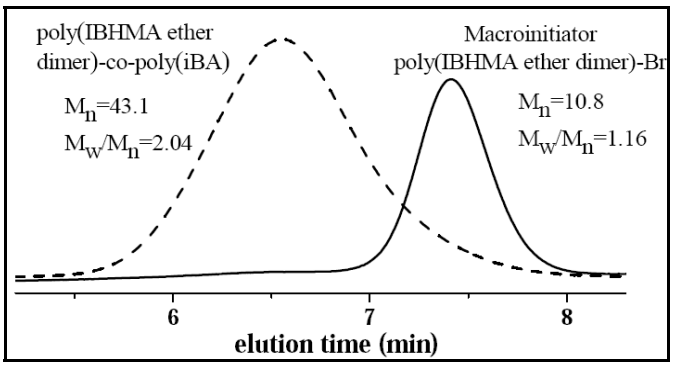
Table 4.8. Synthesis of copolymers by ATRP in bulk using the RHMA ether dimer-cyclopolymers as macroinitiator[a,b]

Entry[c,d,e]	Macroinitiator Poly(RHMA ether dimer)			Block Copolymer				
	R-	$M_{n,sec}$[f] (10^3.g.mol^{-1})	M_w/M_n	Comonomer	Time (h)	CuX	$M_{n,sec}$[f] (10^3.g.mol^{-1})	M_w/M_n
1	Isobornyl	11.4	1.17	*t*-BA	4	CuBr	30.8	1.68
2	Isobornyl	10.8	1.16	iBA	6	CuBr	43.1	2.04
3	Isobornyl	12.4	1.19	*t*-BA	5	CuCl	22.7	1.56
4	Isopropyl	12.2	1.32	*t*-BA	7	CuBr	25.6	1.43

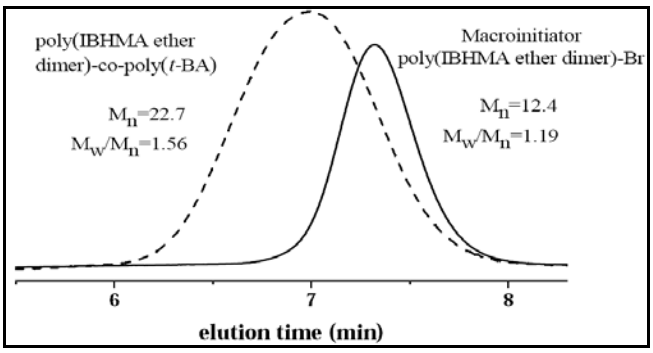
[a]Conditions: $[I]_0:[CuX]_0:[PMDETA]_0$ =1 :2:2. [b]Macroinitiators were Br terminated. [c]Cyclopolymerization temperature was 80 °C for Entries 1,2,4 and 70 °C for Entry 3. [d]*t*-butyl acrylate (*t*-BA) was used as the comonomer in Entries 1,2,4 and isobornyl acrylate (iBA) in Entry 3. [e]Cyclopolymers taken from (Table 4.1, Entry 10, 9, 11, 13) were used as macroinitiators respectively. [f]Relative to polystyrene standarts.



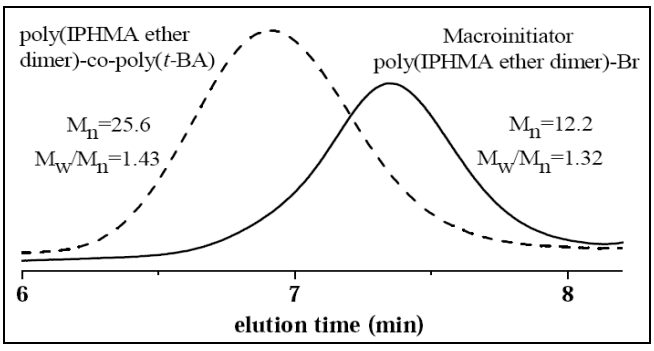
(Entry 1)



(Entry 2)



(Entry 3)



(Entry 4)

Figure 4.27. SEC traces of the copolymerization study showing poly(RHMA) ether dimer macroinitiators (right) and the obtained block copolymers (left)

5. CONCLUSION

In this study, the effect of ester (R) substituents on the control/living ATRP cyclopolymerizations of alkyl α-(hydroxymethyl) acrylates was investigated.

It was found that molecular weight distributions of the cyclopolymers obtained from bulky isobornyl derivatives (1.15<PDI<1.37) were as narrow as the one with *t*-butyl derivative (1.05<PDI<1.30) and these data together with the ^{1}H-NMR and ^{13}C-NMR which show no evidence of uncyclized pendant double bonds, are the indication of an efficient cyclization at 70 ^{o}C. However, cyclopolymers obtained from smaller isopropyl derivative exhibited higher molecular weight distributions (1.26<PDI<2.04). The reason is thought to be the coupling of propagating chains which contain the uncyclized pendant vinyl double bonds as evidenced by the existence of double bond in ^{1}H-NMR spectrum of the poly(IPHMA ether dimer).

Furthermore, linear relationship between conversions and molecular weights were observed and first order kinetic plots with respect to monomer concentrations were obtained upon kinetic studies of both IPHMA and IBHMA ether dimers proving the control nature of the ATRP process. The livingness of the cyclopolymers were proved by copolymerization studies using bromo terminated cyclopolymers as the macroinitiators and *t*-butyl acrylate as the comonomers.

Moreover, cyclopolymerization studies at 100 ºC showed that higher temperatures causses loss in ATRP control. On the other hand, cyclopolymers with higher polydispersities were obtained at 50 ^{o}C which means that this temperature was not enough for efficient cyclization and lead to branching as a result of incomplete cyclization.

All in all, if we combine all the data obtained here and before in our research group [9,36,37], we can say that starting from smaller methyl going further to isopropyl derivative both cyclization and ATRP efficiencies increases, and then an optimum size is reached with the *t*-butyl and more bulkier isobornyl derivative. Further increase in bulkiness (cyclohexyl and adamantyl) causes a decrease in the control. Thus, *t*-butyl and

isobornyl derivatives were found to be the best candidates that fit to the ATRP system as summarized in Figure 5.1 and 5.2.

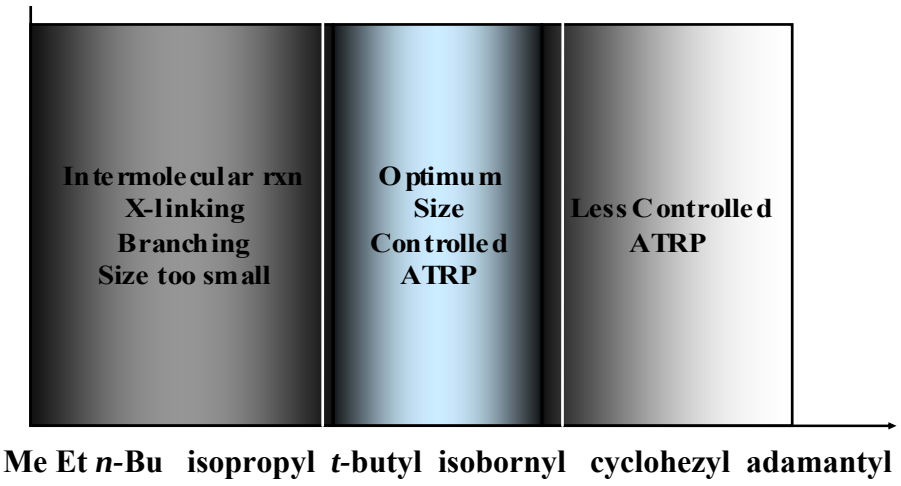


Figure 5.1. The Effect of R group size on ATRP cyclopolymerization

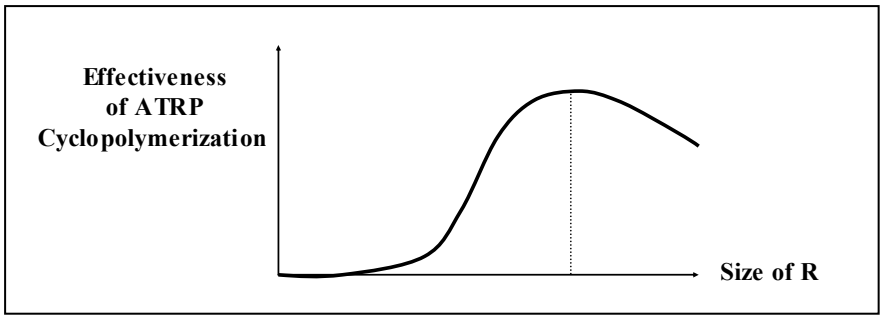


Figure 5.2. Evolution of effectiveness of ATRP cyclopolymerization as a function of R group size

REFERENCES

1. Othmer, K., "Coating Processes, Powder Technology", *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th Ed., Vol. 7, John Wiley, New York, 2001.

2. Lee, H. J., T. Kodaira, M. Urushisaki, T. Hashimoto, "Radical Polymerization of R-(2-Phenylallyloxy) methylstyrene: Synthesis of Highly Cyclized Polymers with High Glass Transition Temperatures and Thermal Stability", *Polymer,* Vol. 45, pp. 7505, 2004.

3. Butler, G. B., "Cyclopolymerization and Cyclocopolymerization", Marcel Dekker: New York, 1992.

4. Mathias L. J., R. M. Warren, and S. Huang, "*tert*-Butyl α-(Hydroxymethyl) acrylate and Its Ether Dimer: Multifunctional Monomers Giving Polymers with Easily Cleaved Ester Groups", *Macromolecules*, Vol. 24, pp. 2036-2042, 1991.

5. Avcı, D., K. Lemopulo and L. J. Mathias, "Cyclopolymerization of Allyl-Acrylate Quaternary Ammonium Salts with Diallyldimethylammonium Chloride", *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 39, pp. 640-649, 2001.

6. Duygu Avcı, C. Haynes and L. J. Mathias, "Cyclopolymerization of Amine-Linked Diacrylate Monomers", *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 35, pp. 2111-2121, 1997.

7. Mathias, L. J., S. H. Kusefoglu, A. O. Kress, S. Lee, C. W. Dickerson and S. F. Thames, "New Acrylate-Containing Dimers and Oligomers for Crosslinking Vinyl Polymers", *Polymer News*, Vol. 17, pp. 36-42, 1992.

8. Mathias, L. J., S. H. Küsefoglu, J. E. Ingram, "Cyclopolymerization of the Ether of Methyl α-(hydroxymethyl) acrylate", *Macromolecules* Vol. 21, pp. 545, 1988.

9. Erkoc S., L. J. Mathias, A. E. Acar, "Cyclopolymerization of *tert*-Butyl R-(Hydroxymethyl) Acrylate (TBHMA) Ether Dimer via Atom Transfer Radical Polymerization (ATRP)", *Macromolecules* Vol. 39, pp. 8936, 2006.

10. Erkoc, S., A. E. Acar, "Controlled/Living Cyclopolymerization of *tert*-Butyl α-(Hydroxymethyl) Acrylate Ether Dimer via Reversible Addition Fragmentation Chain Transfer Polymerization", *Macromolecules* Vol. 41, pp. 9019, 2008.

11. Sarbu, T., K. Lin, J. Spanswick, R. R. Gil, D. J. Siegwart and K. Matyjaszewski, "Synthesis of Hydroxy-Telechelic Poly(methyl acrylate) and Polystyrene by Atom Transfer Radical Coupling", *Macromolecules*, Vol. 37, pp. 9694, 2004.

12. He, T., D. Li, X. Sheng, B. Zhao, "Synthesis of ABC 3-Miktoarm Star Terpolymers from a Trifunctional Initiator by Combining Ring-Opening Polymerization, Atom Transfer Radical Polymerization, and Nitroxide-Mediated Radical Polymerization" *Macromolecules*, Vol. 37, pp. 3128, 2004.

13. Altintas, O., I. Yilmaz, G. Hizal, U. Tunca, "Synthesis of poly(methyl methacrylate)-*b*-polystyrene containing a crown ether unit at the junction point via combination of atom transfer radical polymerization and nitroxide mediated radical polymerization routes", *J. Polym. Sci.*, *Part A: Polym. Chem,* Vol. 44, pp. 3242, 2006.

14. Shemper, B. S., Shemper, A. E. Acar, L. J. Mathias, "Synthesis of Linear and Starlike Polymers from Poly(propylene glycol) Methacrylate Using Controlled Radical Polymerization", *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 40, pp. 334-343, 2002.

15. Zhang, H., X. Jiang, R. Linde, "Synthesis and Characterisation of Hydroxyl End-Capped Telechelic Polymers with Poly(methyl methacrylate)-*block*-poly*(n*-butyl acrylate) Backbones via Atom Transfer Radical Polymerisation", *Polymer*, Vol. 45, pp. 1455, 2004.

16. Cai, Y., S. P. Armes, "Synthesis of Well-Defined Y-Shaped Zwitterionic Block Copolymers via Atom-Transfer Radical Polymerization" *Macromolecules,* Vol. 38, pp, 271, 2005.

17. Kamigaito, M., T. Ando and M. Sawamoto, "Metal-Catalyzed Living Radical Polymerization", *Chem. Rev,* Vol. 101, pp. 3689, 2001.

18. Nanda, A. K., K. Matyjaszewski, "Effect of [PMDETA]/[Cu(I)] Ratio, Monomer, Solvent, Counterion, Ligand, and Alkyl Bromide on the Activation Rate Constants in Atom Transfer Radical Polymerization", *Macromolecules*, Vol. 36, pp. 1487, 2003.

19. Uegaki, H., Y. Kotani, M. Kamigaito, M. Sawamoto, "$NiBr_2(P$*n*$-Bu_3)_2$-Mediated Living Radical Polymerization of Methacrylates and Acrylates and Their Block or Random Copolymerizations", *Macromolecules,* Vol. 31, pp. 6756, 1998.

20. Haddleton, D. M., C. B. Jasieczek, M. J. Hannon, A. J. Shooter, "Atom Transfer Radical Polymerization of Methyl Methacrylate Initiated by Alkyl Bromide and 2-Pyridinecarbaldehyde Imine Copper(I) Complexes", *Macromolecules,* Vol. 30, pp. 2190-2193, 1997.

21. Chambard, G., B. Klumperman, and A. L. German, "Effect of Solvent on the Activation Rate Parameters for Polystyrene and Poly(butylacrylate) Macroinitiators in Atom Transfer Radical Polymerization", *Macromolecules*, Vol. 33, pp. 4417-4421, 2000.

22. Inoue, Y. and K. Matyjaszewski, "New Amine-Based Tripodal Copper Cataysts for Atom Transfer Radical Polymerization", *Macromolecules*, Vol. 37, pp. 4014, 2004.

23. A. E. Acar, M. B. Yagci, and L. J. Mathias, "Adventitious Effect of Air in Atom Transfer Radical Polymerization: Air-Induced (Reverse) Atom Transfer Radical Polymerization of Methacrylates in the Absence of an Added Initiator", *Macromolecules*, Vol. 33, pp. 7700-7706, 2000.

24. Chiefari, J., Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. Le, R. T. Mayadunne, G. F. Meijs, G. Moad, C. L. Moad, E. Rizzardo, S. H. Thang, "Living Free-Radical Polymerization by Reversible Addition−Fragmentation Chain Transfer: The RAFT Process", *Macromolecules*, Vol. 31, pp. 5559-5562, 1998, 31.

25. Moad, G., J. Chiefari, B. Y. Chong, J. Krstina, R. T. Mayadunne, A. Postma, E. Rizzardo, S. H Thang, "Living free radical polymerization with reversible addition-fragmentation chain transfer (the life of RAFT)", *Polym. In.t,* Vol. 49, pp. 993, 2000.

26. Moad, G., Y. K. Chong, A. Postma, E. Rizzardo, S. H. Thang, "Advances in RAFT polymerization: the synthesis of polymers with defined end-groups", *Polymer*, Vol. 46, pp. 8458-8468, 2005.

27. Barner-Kowollik, C., T. P. Davis, J. P. A. Heuts, M. H. Stenzel, P. Vana, M. J. J. Whittaker, "RAFTing down under: Tales of missing radicals, fancy architectures, and mysterious holes", *Polym. Sci., Part A: Polym. Chem*., Vol. 41, pp. 365-375, 2003

28. Hawker, C. J., A. W. Bosman, E. Harth, "New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations", *Chem Rev, Vol.101 pp. 3661,* 2001.

29. Wang, J. S., K. Matyjaszewski, "Controlled/Living Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes", *J. Am. Chem. Soc.*, Vol. 117, pp. 5614-5615, 1995.

30. Kato, M., K. Masami, M. Sawamoto, T. Higashimura, "Polymerization of Methyl Methacrylate with the Carbon Tetrachloride / Dichlorotris-(triphenylphosphine) ruthenium(II) / Methylaluminum Bis(2,6-di-tert-butylphenoxide) Initiating System: Possibility of Living Radical Polymerization", *Macromolecules*, Vol. 28, pp. 1721-1723, 1995.

31. Kamigaito, M., T. Ando, M. Sawamoto, "Metal-Catalyzed Living Radical Polymerization", *Chem Re.,*. Vol.101, pp. 3689, 2001.

32. Matyjaszewski, K., J. Xia, “Atom Transfer Radical Polymerization”, *Chem. Rev,.*Vol. 101, pp. 2921, 2001.

33. Stansbury, J. W., “Difunctional and Monofunctional Monomers Capable of Cyclopolymerization”, *Macromolecules*, Vol. 24, pp. 2029-2035, 1991.

34. Tsuda, T., L. J. Mathias, “Cyclopolymerization of ether dimers of α-(hydroxymethyl) acrylic acid and its alkyl esters: substituent effect on cyclization efficiency and microstructures”, *Polymer*, Vol. 35, pp. 3317-3328, 1994.

35. Erkoç, S., *Cylopolymerization of Alkyl α-(Hydroxymethyl)Acrylate (RHMA) Ether Dimers via Atom Transfer Radical Polymerization*, M.S. Thesis, Boğaziçi University, 2005

36. Kocasakal, G., *Structure-Reactivity Relationship of Acrylic Acid Ester Ether Dimers in ATRP*, M.S. Thesis, Boğaziçi University, 2007

37. Yu, C., L. Hu, “Successful Baylis-Hillman Reaction of Acrylamide with Aromatic Aldehydes”, *J. Org. Chem.*, Vol. 67, pp. 219-223, 2002.