SYNTHESIS OF END-FUNCTIONALIZED ALKYL α-(HYDROXYMETHYL) ACRYLATE ESTER ETHER DIMER DERIVED POLYMERS VIA ATOM TRANSFER RADICAL POLYMERIZATION

by

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To my family

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ABSTRACT

SYNTHESIS OF END-FUNCTIONALIZED ALKYL α-(HYDROXYMETHYL) ACRYLATE ESTER ETHER DIMER DERIVED POLYMERS VIA ATOM TRANSFER RADICAL POLYMERIZATION

In this research, end group modification, hydroxylation, of the cyclic polymers obtained by the atom transfer radical polymerization of the alkyl- α-(hydroxymethyl) acrylate ester dimers (RHMA) were targeted. The dimers were synthesized from the corresponding acrylates using the Extented Baylis-Hilman reaction. The RHMA derived cyclopolymers were then block copolymerized with acrylate comonomers and then allyl alcohol was added, both under atom transfer radical polymerization (ATRP) conditions, to obtain hydroxyl containing end-groups. This sequence of reactions was not successful in obtaining the desired hydroxyl containing cyclopolymers. The hydroxyl content of the polymers was analyzed by ^{31}P-NMR. Since the above hydroxylation method failed with the cyclic polymers, to check the validity of the approach, the addition of allyl alcohol was carried out directly on the linear analogues of the dimers, t-butyl- and isobornyl acrylate. In the case of t-butyl acrylate end group modification seemed to be efficient, however the exact quantification of the end group needs further studies. The method seems to fail with the more bulky isobornyl acrylate.

ÖZET

FONKSİYONEL UÇ GRUPLU ALKİL α-(HİDROKSİMETİL) AKRİLAT (RHMA) ETER DİMER TÜREVI POLİMERLERIN ATOM TRANSFER RADİKAL POLİMERİZASYONU (ATRP) YÖNTEMİ İLE SENTEZI

Bu çalısmada atom transfer radikal polimerleşme, ATRP, yöntemiyle elde edilen alkil α-(hidroksimetil) akrilat (RHMA) eter dimer halkalı polimerlerinin uç gruplarının modifikasyonu, hidroksilleme, amaçlanmıştır. Dimerler ilgili akrilatlarından uzatılmış Baylis-Hilman reaksiyonu ile sentezlenmiştir. RHMA eter dimerlerinden elde edilmiş siklopolimerler akrilat komonomerleri ile blok kopolimerleştirilmiş, daha sonra alil alkol eklenmiştir, bu iki işlem de hidroksil içeren uç grup elde etmek için atom transfer radikal polişmerleşme (ATRP) ile yapılmıştır. Bu reaksiyon dizisi istenilen hidroksil uç grup içeren siklopolimerler elde etmekte başarılı olmamıştır. Polimerin hidroksil içeriği ^{31}P-NMR ile analiz edilmiştir. Yukarıdaki hidroksilleme metodu siklopolimerlerde başarısız olunca, yöntemin yürürlülüğünü denetlemek için, alil alkol doğrudan *t*-butil akrilat ve isobornil akrilat dimerlerin lineer analoglarına eklenmiştir. *t*-Butil akrilat durumunda son grup modifikasyonu etkili görülmüştür, fakat son grupların daha detaylı kantitatif hesaplamaları için daha fazla araştırma gerekmektedir. Metodun daha büyük isobornil akrilat monomeri ile başarısız olduğu görülmüştür.

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LIST OF ABBREVIATIONS

ATRP	Atom Transfer Radical Polymerization
CRP	Controlled Radical Polymerization
DABCO	1,4-diazabicyclo[2.2.2] octane
EB*i*B	Ethyl 2-bromoisobutyrate
GPC	Gel Permation Chromatography
HEBIB	2-Hydroxyethyl 2-bromoisobutyrate
IBHMA	Isobornyl α-(Hydroxymethyl)acrylate
NMR	Nuclear Magnetic Resonans Spectroscopy
PDI	Polydispersity Index
PMDETA	N,N,N,N',N'-pentamethyldiethylenetriamine
RHMA	Alkyl α-(Hydroxymethyl)acrylate
TBHMA	tert-Butyl α-(Hydroxymethyl)acrylate
TEG	Tetra-ethylene glycol di initiator
T_g	Glass Transition Temperature
TLC	Thin Layer Chromatography
UV	Ultra Violet

1. INTRODUCTION

1.1. Atom Transfer Radical Polymerization (ATRP)

The development of controlled living radical polymerization (CRP) is one of the most significant advances in polymer chemistry. Several methods allowing control of radical polymerization have been reported. Most widely used and studied CRP methods are atom transfer radical polymerization (ATRP) [1-4], reversible addition-fragmentation chain transfer (RAFT) [5, 6] and nitroxide-mediated polymerization (NMP) [7]. Atom transfer radical polymerization (ATRP) like most CRP methods enables to synthesize polymers with predetermined molecular weight, narrow molecular weight distribution, as well as desired composition and molecular architecture. Additionally, polymers obtained by ATRP are suitable for various post-polymerization modifications and serve as macroinitiators for block copolymers thanks to their living end group [8, 9].

ATRP is based on a simple concept, equilibrium between a low concentration of active propagating chains and a predominant amount of dormant chains, which are incapable to propagate or self-terminate. This attenuates the probability of bimolecular termination reactions and thus, radical polymerization becomes a living system. Fundamental mechanism of ATRP is homolytic cleavage of an alkyl halide bond R-X by a transition metal complex Mt^n and to generation of the corresponding higher oxidation state metal halide complex $Mt^{n+1}X$ and an alkyl radical $R^{\bullet}$ (Figure 1.1) [10]. The generated radical $R^{\bullet}$ then can propagate with a vinyl monomer, terminate by either coupling or disproportionation, or can be reversibly deactivated in the equilibrium by the catalyst system. Compared to conventional radical polymerization radical termination is minimized to great degree as a result of persistent radical effect that strongly shifts the equilibrium towards the dormant species ($k_{act} << k_{deact}$).

A good initiator should initiate fast and quantitatively. Generally, alkyl halides (RX) with activating substituent on the R-carbon, such as aryl, carbonyl, or allyl groups can potentially be used as the initiator for ATRP. The polymerization is first order with respect

to the concentration of RX. The main role of the initiator is to determine the number of growing polymer chains.

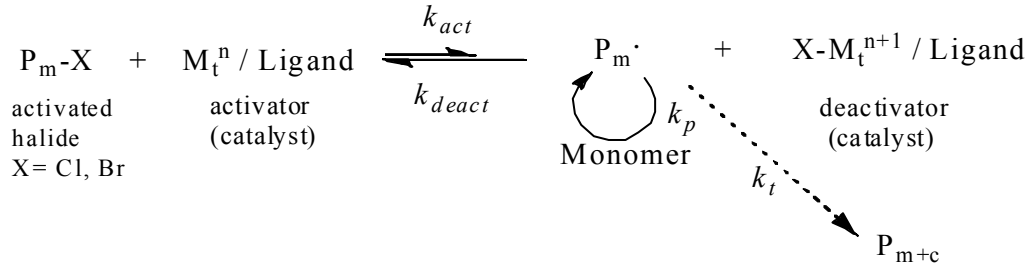


Figure 1.1. Mechanism of ATRP.

The number of growing chains is constant and equal to the initial initiator concentration when initiation is fast and transfer and termination are negligible. To obtain well-defined polymers with narrow molecular weight distribution, the halide group, X, must rapidly and selectively migrate between the growing chain and transition-metal complex [11, 12].

The successful initiation strongly depends on the choice of the catalyst, which is the most critical component of ATRP since it determines the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. The ideal catalyst should be highly selective for atom transfer and should not participate in other reactions. Catalyst system reversibly activates dormant species or a terminal carbon-halogen bond, where it undergoes a one-electron oxidation/reduction followed by abstraction/release of a halogen. Thus, central metals should afford formation of at least two valence states with one valence different and should posses a moderate halogen affinity.

Ligands serve several purposes. The main role of the ligand in ATRP is to solubilize the transition-metal salt in the organic media and to adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer [13].

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used for different monomers. Solvent

choice depends on minimum chain transfer to solvent, interaction between solvent and the catalyst system and catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper based ATRP) [13]. In addition, solvent-assisted side reactions [14] should be minimized.

Increasing the temperature increases both the atom transfer equilibrium constant and the radical propagation rate constant which would increase the rate of polymerization in ATRP. Increase in temperature generally increases the solubility of the catalyst but, catalyst decomposition and chain transfer and other side reactions become more pronounced as well. The optimal temperature depends mostly on monomer, the catalyst and the targeted molecular weight [14].

1.2. Monomer Synthesis

1.2.1. DABCO-Catalyzed Synthesis of the IBHMA Ether Dimers

Baylis-Hillman reaction enables formation of IBHMA monomers. The reaction of formaldehyde with acrylate esters is catalyzed by 1,4-diazabicyclo[2.2.2] octane (DABCO) [15] . The mechanism of the Baylis-Hillman is a tertiary amine-catalyzed coupling of an α,β-unsaturated carbonyl compound with an aldehyde, as shown in Figure 1.2. The most significant step is the formation of nucleophilic anion after the addition of DABCO to an α,β-unsaturated ester. Attack of this anionic nucleophile to formaldehyde initiates formation IBHMA where elimination of amine moiety also takes place.

In the presence of DABCO conversion of RHMA ether dimers is thermodynamically favorable and simply requires heating of the reaction mixture. However, this conversion reaction is very sensitive to water. The presence of water liberated during IBHMA ether dimer formation can actually cleave the ether bond back to the IBHMA. Thus, water must be removed in the later stages of the RHMA ether dimer synthesis to facilitate the reaction and to obtain higher overall yields of ether dimer. Similarly, the formation of acetal derivatives of RHMA is also reversible and is gradually driven back to the alcohol and then to the ether as the reaction is forced to completion or final equilibrium [12].

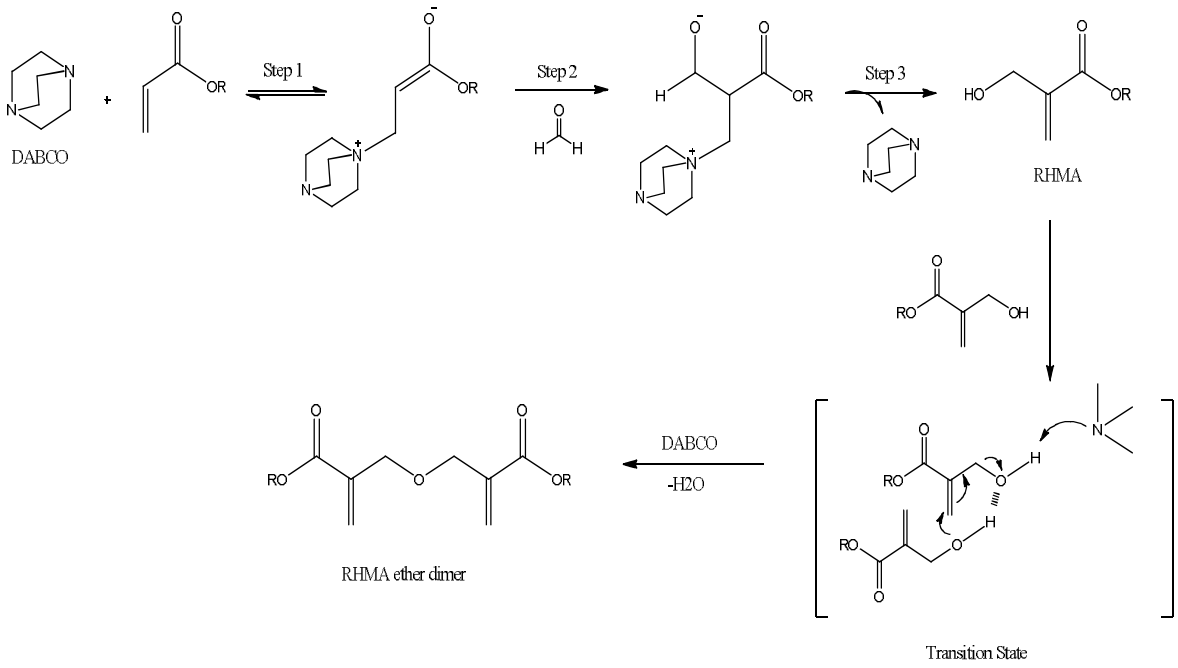


Figure 1.2. Synthesis of IBHMA ether dimer monomer.

1.3. Cyclopolymerization of RHMA Ether Dimers via ATRP

ATRP was successfully adjusted to the controlled cyclopolymerization of several types of alkyl á-(hydroxymethyl) acrylate ether dimers in our research group formerly [16, 17]. Cyclopolymers of RHMA ether dimers are desirable because of their high glass transition temperatures, low shrinkage during polymerization and excellent thermal stabilities [18]. To attain end functional and low polydisperse cyclopolymers ATRP technique has been used (Figure 1.3).

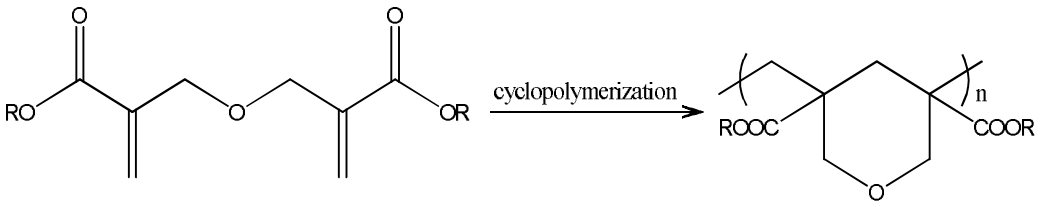


Figure 1.3. Cyclopolymerization of RHMA ether dimers.

Previously investigated alkyl á-(hydroxymethyl) acrylate ether dimers in our research group vary in substituted alkyl groups from small to bulky ones. Small alkyl groups are ethyl, *n*-butyl and *t*-butyl. Bulkier alkyl groups are cyclohexyl, adamantyl,

isobornyl and isopropyl. These researches conducted in ATRP showed that increase in bulkiness of the ester substituent enhances the cyclization efficiency. The *t*-butyl and isobornyl derivatives of RHMA ether dimers display best result in ATRP conditions. Monomers with smaller ester group (ethyl, isopropyl) resulted in crosslinked material. Lastly, monomers with bulkier derivatives (adamantyl, cyclohexyl) gave cyclopolymers with higher polydispersities [19].

Depending on the reaction conditions, such as temperature and the steric interactions of the substituted alkyl group at ester functionality there are two possible pathways for polymerization reaction of RHMA ether dimers. ATRP of RHMA ether dimers either form cyclopolymers by intramolecular cyclization or form crosslinked polymers by intermolecular 1,2-vinyl addition of the pendant group [12]. These two phenomena are shown in Figure 1.4.

Studies in our research group have established that as the bulkiness of the R group increased cyclization efficiency increased. Still, smaller R groups result in crosslinked polymers [13-15]. For instance, when ATRP was applied to ethyl derivatives ended up with crosslinked polymers, and *n*-butyl derivatives showed expected cyclopolymers with pendant double bonds. When *t*-butyl derivative was subjected to ATRP desired cyclization was observed and no pendant double bond residuals were detected in NMR spectra. Cyclopolymers of *t*-butyl α-(hydroxymethyl) acrylate ether dimer were with narrow polydispersities ($1.05<PDI<1.23$) and well defined thus proving that full cyclization of *t*-butyl was successful. Further increase of the bulkiness displayed no pendant double bonds, but gave cyclopolymers with high polydispersities. Bulky groups complicates the access of the catalyst/ligand complex to propagating site, so with bulky groups such as cyclohexyl and adamantyl groups control was lost over ATRP process.

To sum up, polydispersity index increased when smaller substituent groups were used such as ethyl, *n*-butyl and isopropyl. A decrease was observed for t-butyl and isobornyl ester substituents, giving best polydispersity results. However, polydispersity index increased for bulkier groups like adamantyl.

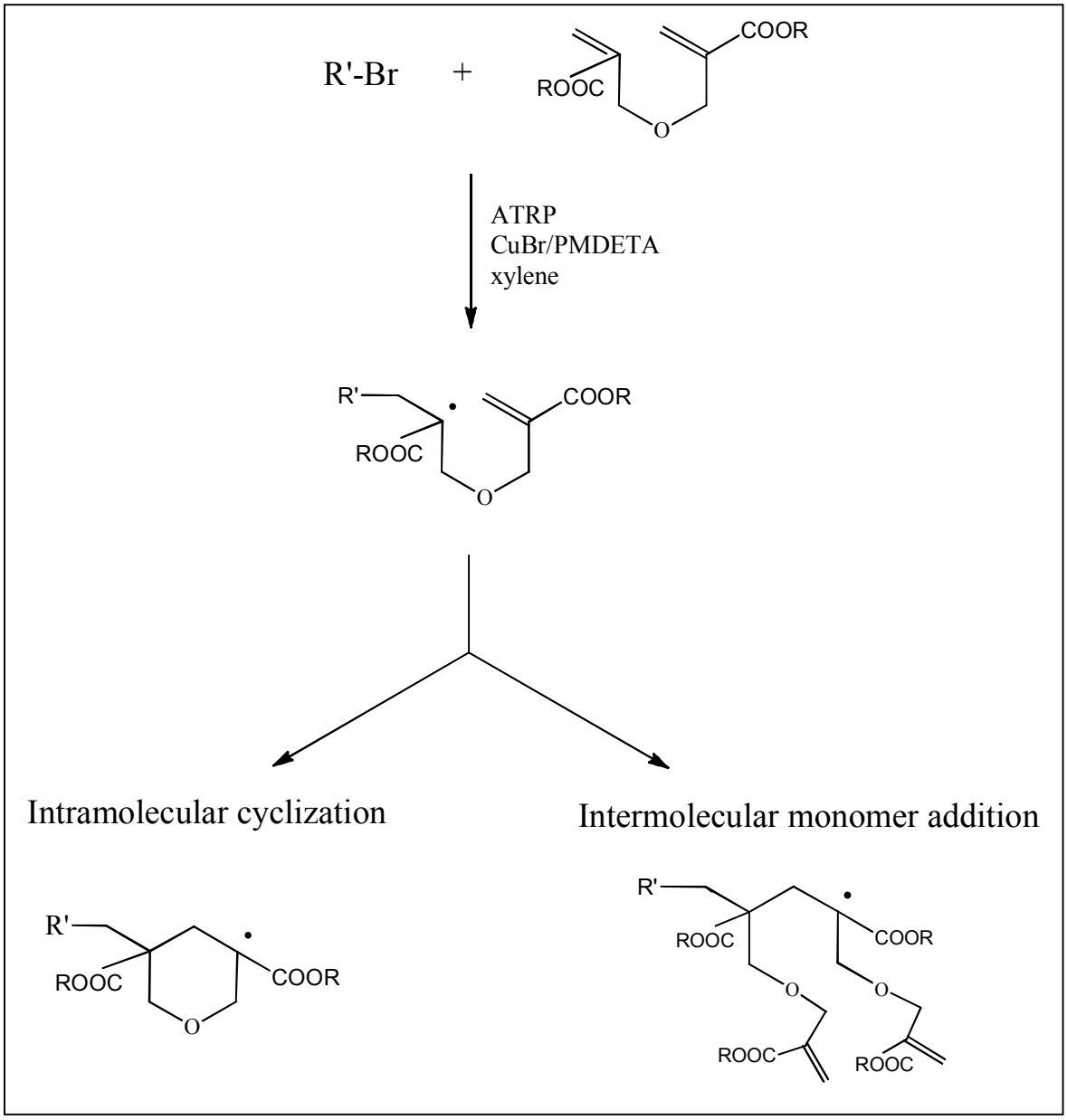


Figure 1.4. Intramolecular cyclization and intermolecular monomer addition.

1.4. End Group Functionalization of Polymers

Polymers with high degree of end-group functionality can be prepared under less demanding reaction conditions by controlled/living radical polymerization (CRP). ATRP has the advantages of a radical polymerization and benefits of a controlled polymerization process. To attain functionalized polymers with ATRP there are different approaches, it is either through monomer itself or by the modification of chain ends. To obtain polymers with functional side groups functional monomers such as poly (2-hydroxyethyl

methacrylate) [20], poly (2-hydroxyethyl acrylate) [21], poly (dimethylaminoethyl methacrylate) [22] has been reported.

One of the most effective way to obtain the terminal functionality is to use initiators bearing hydroxyl or other functional groups [23-27]. The nature of the initiators used defines the end groups of the polymers prepared via ATRP. When alkyl halide is used as an initiator, one end-group of the polymer chain is the alkyl group of the initiator, whereas the other end-group is the halide. However, being one-step process using functional initiator have disadvantages, it has limited choice of initiating entities and they should be inert to polymerization reactions.

Another way of introducing functional group to the polymer chain ends is transformation of the halogen end group into other functional groups using standard organic procedures, such as nucleophilic substitution, electrophilic addition, and radical reactions. In the literature Matyjaszewski first reported post functionalization of a poly(acrylate) to obtain hydroxyl terminated polymer [28, 29]. Post polymerization modification of the polymers via ATRP which was new to the literature, was done on poly(methyl acrylate). Methyl acrylate was polymerized via Cu catalyst system by ATRP then at the high monomer conversion excess amount of allyl alcohol was introduced to the reaction flask (Figure 1.5). Alcohol groups at the ω-end of the poly(methyl acrylate) were identified and analyzed by ^{1}H-NMR and ESI-MS.

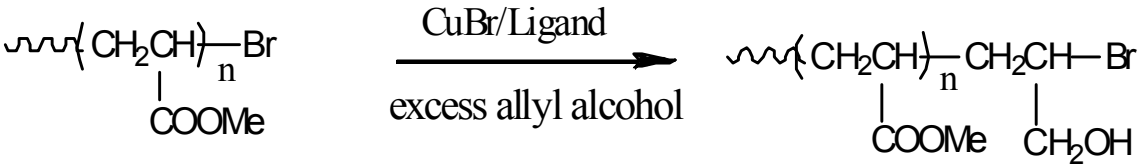


Figure 1.5. Allyl alcohol addition to the chain end of poly(methyl acrylate).

In this method, by adding the less reactive non-polymerizing allyl alcohol functionalization of polymer chain end groups was attained (Figure 1.6). Radical addition of allyl alcohol takes places via ATRP but it does not lead to polymerization. Addition of allyl alcohol to the active chain end generates a radical that is not efficiently stabilized, which then becomes deactivated to the corresponding dormant brominated species. Due to the absence of a stabilizing group near the radical center reactivation of the resulting halide

becomes impossible. Hence, usage of these polymers as a macroinitiator for futher copolymerization by ATRP is impossible. The resulting hydroxyl functional polymers are very valuable since they can be incorporated in subsequent reactions to form esters, carbonates, urethanes and etc.

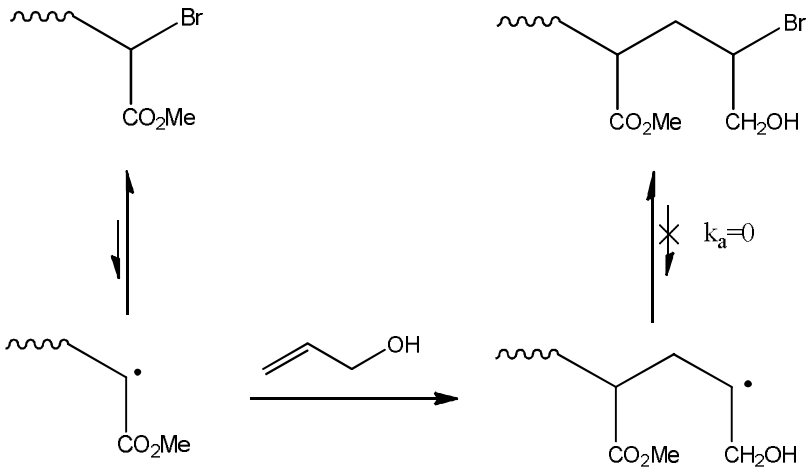


Figure 1.6. End group functionalization by addition of allyl alcohol.

2. OBJECTIVES

The aim of this study is to obtain hydroxyl functional polymers with controlled molecular weights and low polydispersities. Former investigation done in our research group showed that functional co-monomer addition to TBHMA ether dimer derived cyclopolymer was not successful. The aim of this research is to modify the cyclopolymers with acrylate comonomer and then functionalize them with the addition of allyl alcohol to the hydroxyl end groups. Adding acrylate comonomer provides secondary bromide instead f tertiary bromide and reduces the steric hindrance caused by the cyclic repeat units. By adding a small amount of acrylate comonomer to the IBHMA derived cyclopolymer functionalization of end groups and quantitative analysis of these functional groups were expected.

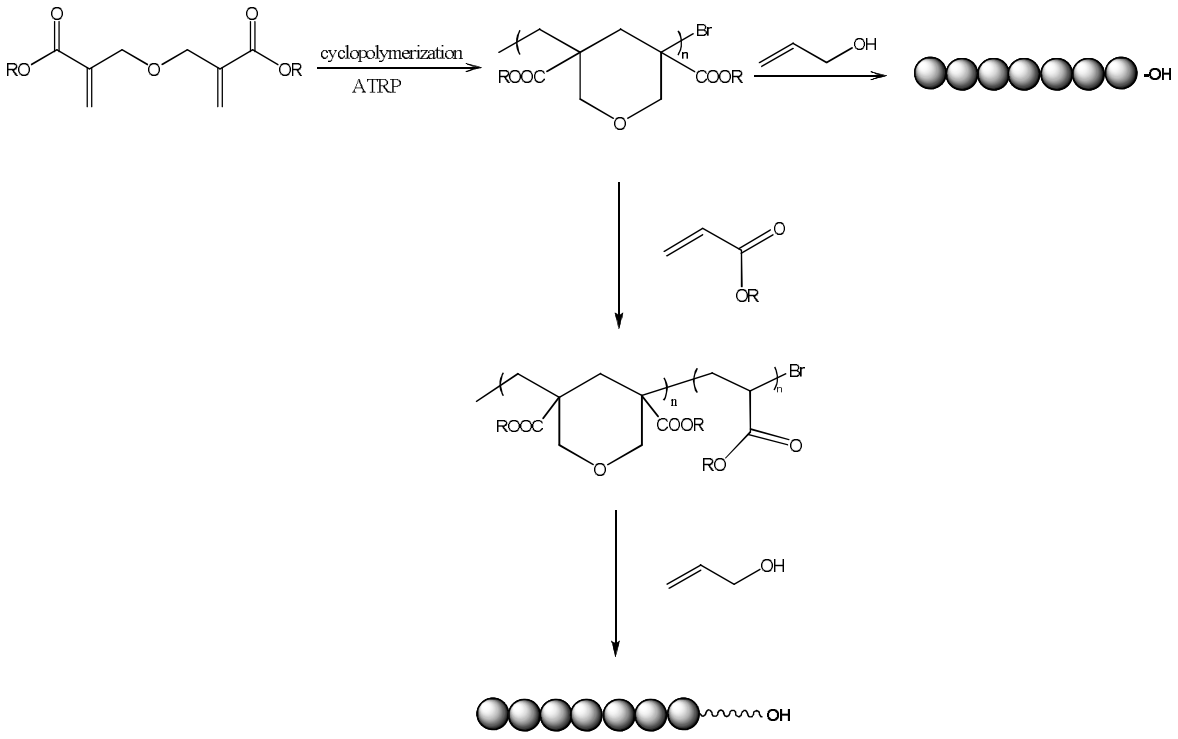


Figure 2.1. The General approach Used in the Hydroxyl functionalization of the cyclopolymers.

3. EXPERIMENTAL

3.1. Methods and Materials

t-Butyl acrylate (Acros Organics, 99%), paraformaldehyde (Sigma-Aldrich), 1,4 diazabicyclo[2.2.2]octane (DABCO) (Fluka, >95.0%), *t*-butyl alcohol (Merck, 99%), isobornyl acrylate, paraformaldehyde (Sigma Aldrich), triethylamine (TEA) (Merck, ≥99%), 1,4-diazabicyclo[2.2.2]octane (DABCO) (Fluka, ≥95%), ethyl-2-bromoisobutyrate (EB*i*B) (Fluka,≥97%), copper (I) bromide (CuBr) (Aldrich, 99.999%), and pentamethyldiethylene triamine (PMDETA) (Aldrich, 99%) were used as received without purification. Xylene (mixture of isomers) (Merck) was purified by distillation over Na metal and benzophenone. The solvents; methylene chloride (CH_2Cl_2), hexane, methanol, acetone and tetrahydrofuran (THF) were all obtained from Merck and used as received.

3.2. Instrumentation

Infrared spectroscopy was carried out on Thermo Scientific Nicolet 380 FT-IR spectrophotometer. ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra's were recorded using a Varian Gemini 400 MHz spectrometer at the Advanced Technologies Research and Development Center at Boğaziçi University.

3.3. Monomer Synthesis

3.3.1. 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 mixture was stirred for 7 days at 80 ^{0}C. The reaction progress was monitored by thin layer chromatography (TLC) using silica gel plates and CH_2Cl_2 as the eluting and diluting solvent. The mixture was poured into 700 mL of methanol and placed in a refrigerator at -

15 ^{0}C overnight. Obtained precipitant was filtered and washed with cold methanol, then dried in vacum to give pure white solid with 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. 13C NMR ($CDCl_3$) δ 165.0 (*C*=O), 137.5 (*C*=CH_2), 125.2 (*C*H_2=C), 81.2 (*C*HO), 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.

3.3.2. Synthesis of 2-Hydroxyethyl 2-Bromoisobutyrate (HEBIB)

All reagents were weighed and put into 100 mL round bottom flask with magnetic stirrer and condenser fitted into it. 20 fold excess ethylene glycol (62 g, 0.999 mol), triethyl amine (2.85 g, 0.028 mol), 4-dimethylaminopyridine (DMAP) (0.1174g, 5 mol%), and 30 mL THF were added into reaction flask which is in ice bath left for cooling. 4.8245 g (0.021 mol) of 2-Bromo-2- methylpropionyl bromide in 20 mL of THF was cooled in a ice bath and added into the reaction flask via addition funnel with a rate of one drop per second. The reaction progress was monitored by thin layer chromatography (TLC) using silica gel plates and CH2Cl2 as the eluting and diluting solvent. TLC plates were visualized using potassium permanganate solution. At the end of two hours, the mixture was diluted with 250 mL methylene chloride, extracted firstly three times with 75 mL of 0.5 N HCl, then six times with 100 mL distilled water. To obtain crude product organic layer was separated and evaporated under reduced pressure. Evaporation of the solvent gave the pure initiator as a light brown liquid in around 60 per cent yield.

^{1}H NMR ($CDCl_3$): □= 1.92 (s, 6H, CH3), 3.71 (t, 2H, OCH2), 4.27 (t, 2H, OCH2), 5.27 (t, 1H, OH) ppm.

3.4. Polymer Synthesis

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

All glassware, needles and stirring bars were dried in 120 ^{0}C oven overnight and purged with nitrogen before use. All chemicals were purged with nitrogen at least 20 minutes. RHMA ether dimer was weighed and put into 250 mL round bottom flask. The reaction flask was sealed with rubber septa and was left under nitrogen. Solvent of solution polymerization, xylene, was measured so that monomer concentration is 1 M ± 0.01. Degassed xylene was transfered to the reaction flask by degased syringe and purged with nitrogen for 15 minutes. Then CuBr was weighed and purged with nitrogen for 15 minute in a 5mL vial. 2 mL of calculated xylene and PMDETA was added into vial containing CuBr and to homogenize solution it was stirred and heated. Dissolved CuBr solution was transferred into reaction flask wich is then immersed into preheated oil bath. The initiator was added into the reaction flask with microsyringe. Transfer of all chemicals was carried out by degassed syringe. Polymerizations were done under nitrogen and required temperatures. The resulting polymers were precipitated in acetone and dried under vaccum overnight. Monomer conversion was determined by gravimetric methods. The determination of the molar masses and molecular weight distributions has been carried out by size exclusion chromatography (SEC) with a refractometer detector with polystyrene (PS) standards. Characterization of the polymer samples has been performed by proton and carbon NMR spectroscopy.

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

The ATRP of IBHMA ether dimer was performed using following ratio:$[IBHMA]_0$/ $[EbiB]_0$/ $[CuBr]_0$/ $[PMDETA]_0$ = 100/ 1/ 1/ 1 in xylene. IBHMA ether dimer (3 g, 6.76 mmol) was polymerized in 6.70 mL xylene (1 M ± 0.01) by using CuBr (9.7 mg, $6.76x10^{-5}$ mol) and PMDETA (14 µL, $6.76x10^{-5}$ mol) catalyst system and ethyl-α-bromoisobutyrate (EB*i*B) (10µL, $6.76x10^{--5}$ mol) initiator. All the glassware were cleaned thoroughly then dried in a 120 ^{0}C oven before use. The chemicals were purged with nitogen for at least 20 minutes. The polymerization was carried out at 70 ^{0}C for 2 hour. 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 white powder, soluble, 0.6 g, in a 20 per cent yield.

3.4.3. Block Copolymerization with t-Butyl Acrylate

Block copolymerization of IBHMA ether dimer cyclopymer with tert-butyl acrylate is as following. Solid macroinitiator p(IBHMA ether dimer) ($5.75x10^{-5}$ mol) was dissolved in 2 mL of xylene and put into a round bottom flask and sealed with rubber septa and was purged with nitrogen for 20 minutes (16 mg, $11.15x10^{-5}$ mol) of CuBr was put into separate vial and fitted with rubber septa, 2mL of degassed xylene was put into it and purged with nitrogen for15 minutes. PMDETA (24 μL, $8.07x10^{-5}$ mol)was transefed with degassed microsyringe into CuBr solution. The solution was heated to dissolve CuBr, when homogenous solution was obtained it was transferred into main reaction flask, which is then immersed to the preheated oil bath. *t*-butyl acrylate (0.25 mL,$172.5x10^{-5}$ mol) which previously degassed with nitrogen was transferred into the reaction flask by the help of syringe. Polymerization was done under 80 ^{0}C for 3 hours. The polymer product was precipitated into 60mL 5:1 methanol: water twice and dried in vaccum oven overnight.

3.4.4. Polymerization of Isobornyl Acrylate via ATRP

Isobornyl acrylate (3.99g, 18.9 mmol) was polymerized in 4 mL xylene (1 M ± 0.01 M) by using CuBr (27 mg, 0.188 mmol) and PMDETA (39.5 μL, 0.188 mmol) catalyst system and EB*i*B (28 μL, 0.188 mmol). The polymerization was carried out at 70 ^{0}C for 2 hours. All the chemicals were degassed with nitrogen at least for 20 minutes.The CuBr was dissolved in 2 mL xylene with PMDETA and heated to get homogenous solution. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dark green as the reaction proceeded. The reaction mixture was homogeneous during the polymerization. The resulting polymer was precipitated into 50 mL methanol and 10 mL water solution twice. It was then dried in vacuum oven overnight before further handling.

3.4.5. Purification of the Resulting Polymers

To purify the polymercs obtained all the products were dissolved in methyle chloride and passed through basic aluminum oxide column. The polymes were pricipitated into corresponding non solvent mixtures used. Then it was filtered and dried under vaccum oven overnight. The pure polymers were analyzed by GPC and NMR by dissolving in THF and chloroform respectively.

3.5. Radical Addition of Allyl Alcohol

IBHMA-tBA copolymer (0.45g, $2.52x10^{-5}$ mol) was dissolved in xylene in a round bottom flask and fitted with ruber septa and was purged with nitrogen for 20 minutes. (7.5mg $5.23x10^{-5}$ mol) CuBr was purged with nitrogen for 15 minutes in a separate 5mL vial. With the help of PMDETA (10 μL, $5.23x10^{-5}$ mol) and 2mL xylene CuBr was dissolved. Homogeneous CuBr solution was transferred into reaction flask wich is then emmersed into preheated oil bath. Excess allyl alcohol priorily degassed was added into reaction flask. The reaction was done at 50 ^{0}C for overnight. The product was precipitated into 50:1 methanol: water twice and dried in vacuum oven overnight.

3.6. Polymerization of Isobornyl Acrylate with HEBIB via ATRP

Isobornyl acrylate (3.99g, 18.9 mmol) was polymerized in 2 mL xylene (% 50 by volume) by using CuBr (27 mg, 0.188 mmol) and PMDETA (39.5 μL, 0.188 mmol) catalyst system and HEBIB (57.8 mg, 0.188 mmol). The polymerization was carried out at 70 ^{0}C for 2 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dark green as the reaction proceeded. The reaction mixture was homogeneous during the polymerization. The resulting polymer was precipitated into 50 mL methanol and 10 mL water solution twice. It was then dried in vacuum oven overnight before further handling.

4. RESULTS AND DISCUSSION

4.1. Phosphorus-31 NMR

4.1.1. Phosphorus-31 NMR

Phosphorus-31 NMR (^{31}P-NMR) is a powerful analytical technique that is applied for the identification and analysis of the organic compounds containing phosphorus. ^{31}P is the most stable isotope of phosphorus (P). Thus, all species bearing phosphorus in a sample can be determined by the means of the NMR spectroscopy. ^{31}P nucleus also has a rather high gyromagnetic ratio, a spin of ½, which simplifies obtaining and interpretation of the NMR spectroscopy [30].

^{31}P-NMR can be successfully employed for the analysis of the functional group when it is appropriately derivatized with an active nucleus. Therefore, ^{31}P-NMR is the proper method to inspect and quantify functional groups (eg. end –OH groups) in polymers even in ppm level.

Derivatization of the functional group is done with active nucleus containing compound that gives reaction with functional group. For polymers with OH end groups 1,2-phenylene phosphochloridite was used as ^{31}P derivatizing agent [31]. –OH groups reacts with 1,2-phenylene phosphochloridite and gives quantitatively the corresponding derivatives at room temperature, Figure 4.1.

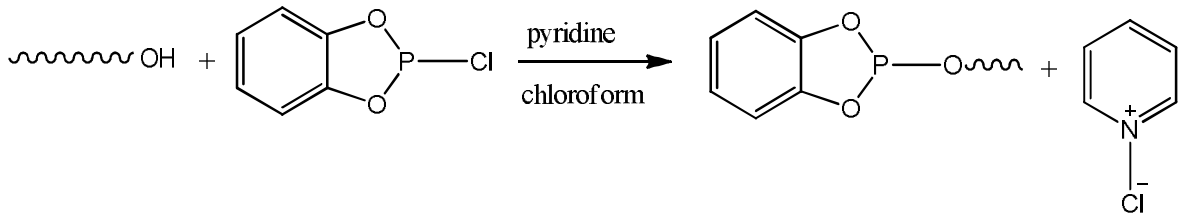


Figure 4.1. ^{31}P Derivatization of polymers with –OH end group.

4.1.2. ^{31}P- NMR Spectra Interpretation

In order to avoid complications spectra of solvent and reagents used were studied. From the ^{31}P-NMR spectra assignment of the peaks were done initially. Figure 4.2 shows spectra of chloroform-d with 1,2-phenylene phosphochloridite (a) in it where 173.6ppm corresponds to 1,2-phenylene phosphochloridite. (b) Shows spectra of chloroform-d, 1,2-phenylene phosphochloridite and pyridine: at 131.5ppm appears internal standard and at 129.2ppm complex of pyridine with phosphorus reagent is observed. Spectra at the top (c) contains the same reagents as (b) but extra water is added. In this spectrum all peaks drastically diminished whereas peak at 121.2ppm increased which is the indication that it is for water in the media.

In the light of these spectra chemical shifts for the used chemicals during phosphorus derivatization were assigned. In brief, chemical shifts of the reagents are as follows:

extra 1,2-phenylene phosphochloridite	173.6ppm
internal standard	131.5ppm
pyridine complex	129.2ppm
water	121.2ppm

4.1.3. ^{31}P-NMR spectrum of Phosphorus Derivatized n-Butanol

Prior to the functionalization of the polymers with hydroxyl group, the ^{31}P-NMR of primary –OH group was examined. The spectrum of the pshosphorus derivatized pure n-butanol was obtained. Figure 4.3. displays peak at 127. 4ppm indicating phosphorus derivatized –OH end group.

4.1. End Group Modification Studies on the p(IBHMA)

As mentioned earlier end group functionalization was previously investigated in our group [32] where end group functionalization of RHMA cylopolymers by adding allyl

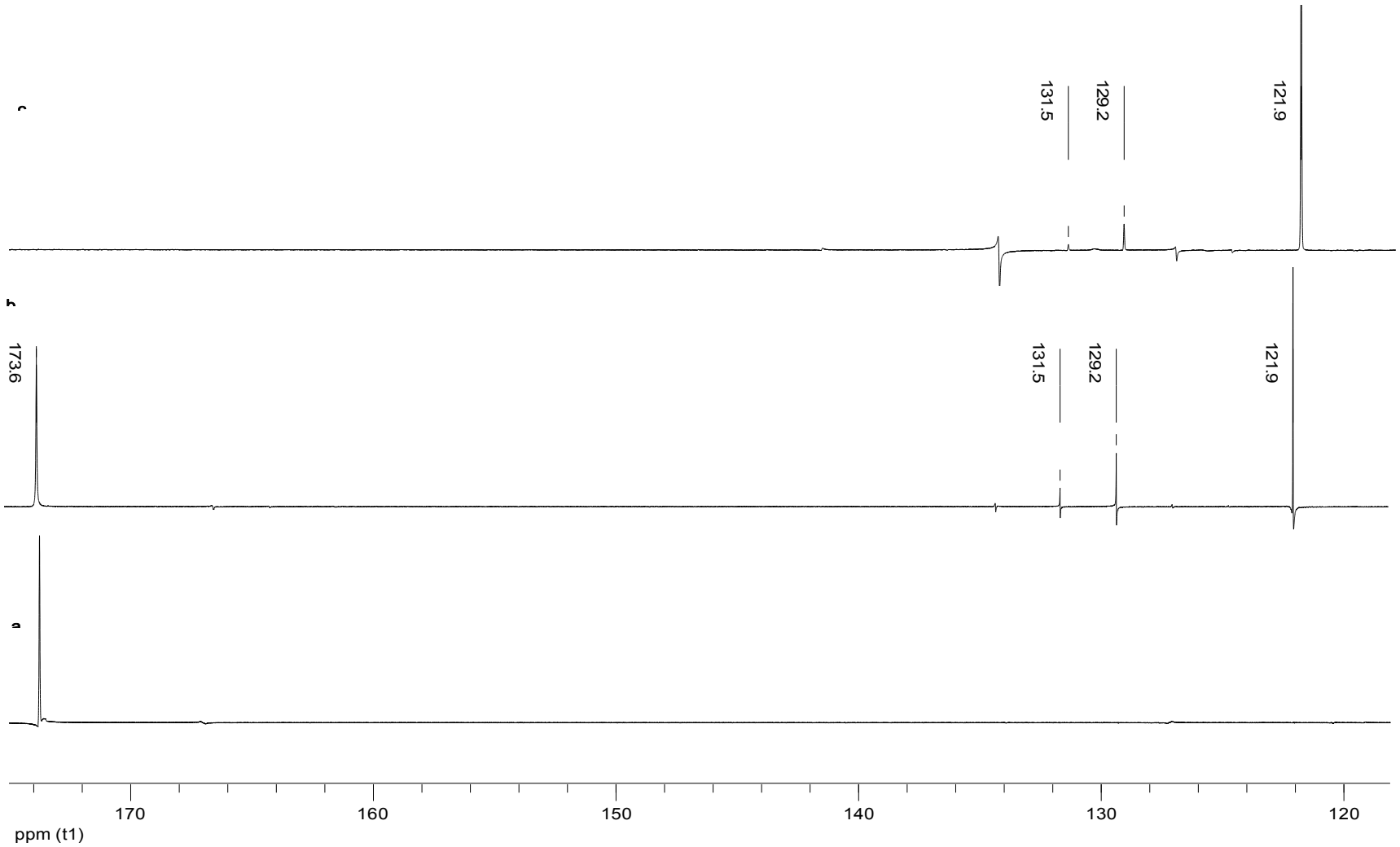


Figure 4.1. ^{31}P-NMR spectra of the blank control experiments.

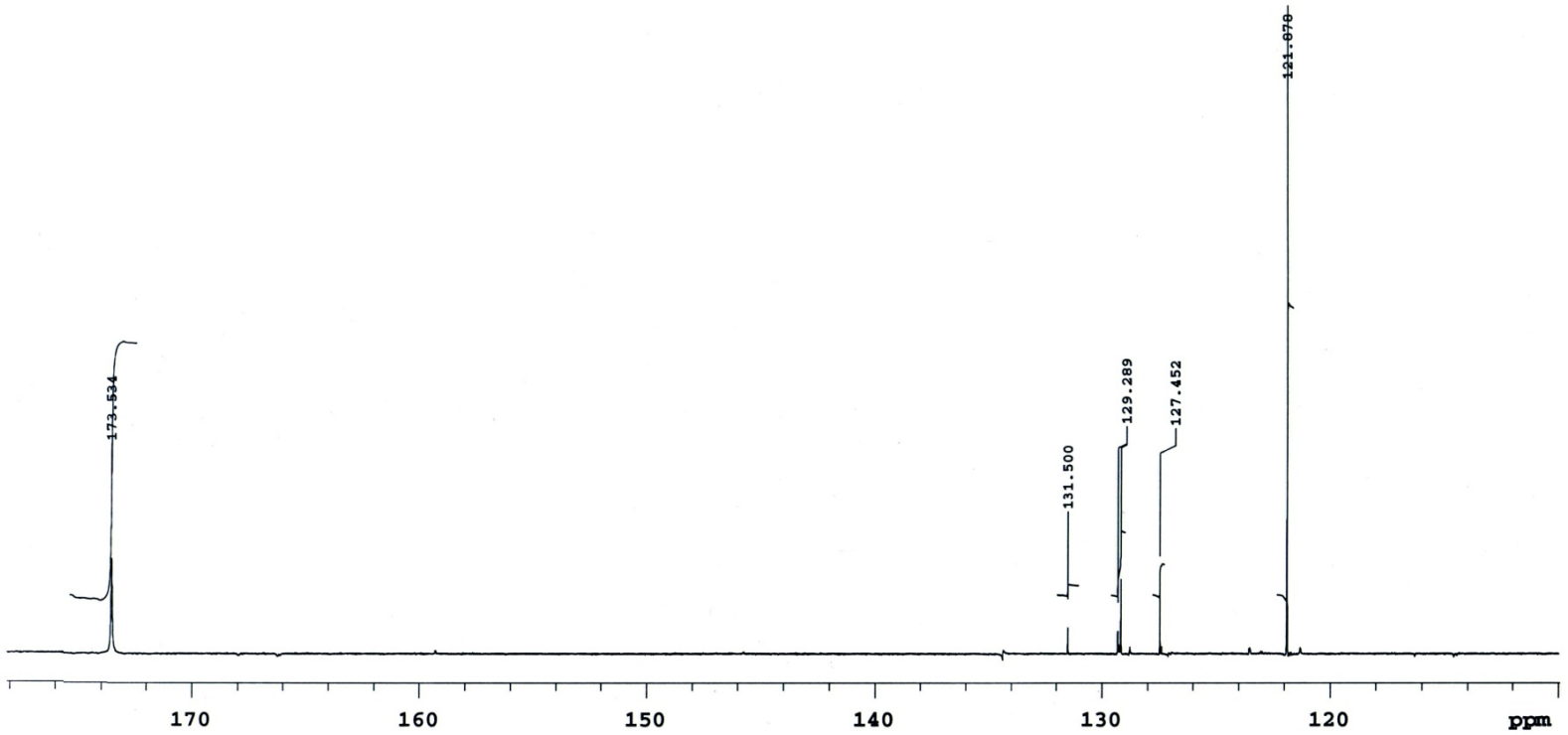


Figure 4.2. ^{31}P-NMR spectra of phosphorus derivatized n-butanol.

alcohol under ATRP conditions was not successful. Hence, the main idea of this project was to modify cyclopolymer end groups to get hydroxyl functional polymers. In the previous work the addition was done directly on the TBHMA ether dimer derived cylopolymers. These cyclopolymers had hindered terminal tertiary bromides. The radicals that formed at the end groups most probably were relatively stable to react with the double bond of the allyl alcohol and ^{31}P-NMR data showed very little conversion of the end groups to alcohol functionality. As a result, in this present study, adding a more reactive, secondary radical generating acrylate as comonomer at the end of the cyclopolymers is proposed for better end group functionalization with the allyl alcohol. Unlike the RHMA ester ether dimers the acrylates added were monofunctional to overcome the potential steric crowding effect of the cyclic repeat units and thuş a better addition of allyl alcohol was expected thanks to the less bulky but more reactive end groups.

4.1.1. Synthesis of the IBHMA ether dimers

The DABCO catalyzed synthesis of the IBHMA ether dimer is thermodynamically favorable and carried out at mild reaction conditions. The reaction was stirred for 7 days at 80 ^{0}C. The product was poured into cold methanol and placed in a refrigerator at 15 ^{0}C and then the solid precipitate was filtered.

The monitoring of the reaction was done with thin layer chromatography (TLC) by using silica gel (SiO_2) plates and CH_2Cl_2 as the elution and dilution solvent. With the help of TLC the actual time for the reaction completeness and reaction intermediates were monitored.

4.1.2. Cyclopolymerization of RHMA Ether Dimers by ATRP

N,N,N',N',N''–pentamethyldiethylenetriamine (PMDETA), a tridentate ligand has high activity towards Cu(I)Br metal center. Thus, Cu(I)Br/PMDETA was employed as the active catalyst complex. The favored fast initiation is accomplished by using ethyl 2-bromoisobutyrate (EB*i*B) as an initiator since tertiary activated alkyl halides give fast initiation.

Figure 4.4 shows the cyclopolymerization of RHMA ether dimers via ATRP with the active catalyst complex and the initiator.

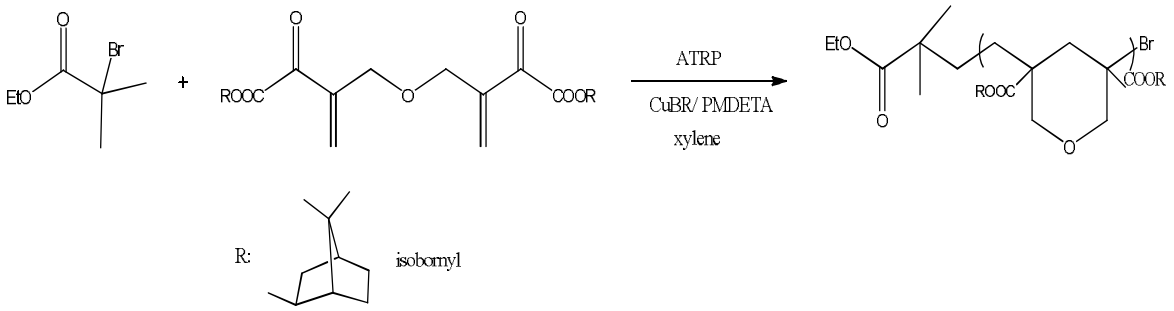


Figure 4.3. Cyclopolymerization of RHMA ether dimer via ATRP.

4.1.3. Cyclopolymerization of IBHMA Ether Dimers by ATRP

The cyclopolymerization of isobornyl α-(hydroxymethyl) acrylate ether dimer via ATRP was studied previously in our research group [14]. Isobornyl derivatives showed similar results to *t*-butyl derivatives; low polydispersity and high degree of intramolecular cyclization of the monomers. All the polymerization reactions of IBHMA ether dimers were carried out at 70 ^{0}C. Study on temperature effect on ATRP of RHMA ether dimers [13,14] has showen that PDIs and monomer conversions increases as temperature increases up to certain point, since reaction rate increases in accordance with the temperature. Although, high reaction temperature facilitates the solubility of the transition metal catalyst complex, it may also decompose the catalyst system giving rise to higher polydispersities. On the other hand, at low reaction temperatures polydispersities of the cyclopolymers obtained were higher. The optimum reaction temperature for IBHMA ether dimer was reported to be 70 ^{0}C (Table 4.1). Polymerizations were carried out with $[M]_0$:$[EBiB]_0$:$[CuBr]_0$:$[Ligand]_0$=100:1:1:1 ratios in 1 M ±0.01 xylene at 70 ^{0}C. Polymers with different molecular weights, and relatively low polydispersities and low monomer conversions were targeted.

4.2. Changing the Activity and Steric Hindrance of the p(IBHMA) End Groups

4.2.1. Block Copolymerization of p(IBHMA) with t-Butyl Acrylate

To get acrylic sequence at the end of RHMA ether dimer derived polymeric chain copolymerizations were done. After successful cyclopolymerization of IBHMA ether dimers, cyclopolymers were further polymerized with *t*-butyl acrylate (Table 4.1). The copolymerizations were carried out by using CuBr/PMDETA catalyst system in xylene.

Table 4.1. Results of block copolymer study.

	pIBHMA[a]			pIBHMA-ptBA[b]		pIBHMA-ptBA + allyl alcohol[c]	
Entry	Monomer conv. (%)	$M_{n,sec}$ (g/mol)	M_w/M_n	$M_{n,sec}$ (g/mol)	M_w/M_n	$M_{n,sec}$ (g/mol)	M_w/M_n
1	68	19970	1.37	23170	1.39		
2	30	21920	1.43	24350	1.36	25420	1.41
3	59	19800	1.31	22940	1.44	27380	1.45
4	38	14400	1.23	17840	1.33	18100	1.38
5	67	17940	1.26	20000	1.37	21300	1.37

a: Conditions: $[M]_0:[EBiB]_0:[Cat]_0$=100:1:1 concentration ratio, solvent: xylene

b: $[tBA]_0:[In]_0:[CuBr]_0:[L]_0$=30:1:2:2 concentration ratio, solvent: xylene

c: At 50 C^0, $[Allyl\ alcohol]_0/[In]_0/[CuBr]_0/[L]_0$ excess/1/2/2,overnight

Comonomer, t-butyl acrylate, was polymerized at 80 ^{0}C for 3 hours to obtain the blockcopoymers of IBHMA with the linear acrylic co-monomer. At the end of the block copolymerization, the tertiary active bromine end, should in principle, will become secondary bromine and be still active for future ATRP reactions. Table 4.1. shows the data of the cyclic homopolymers of IBHMA ether dimer and their corresponding block copolymers with *t*-butyl acrylate.

4.2.2. End Group Functionalization of the Cyclopolymers

End group modification of the polymer chain via ATRP is done either by using functional initiator [26-30] or by exploitation of simple chemistry on terminal halide [33].In the first strategy functional moiety of the initiator will be transferred to the α-chain end of the polymer. The second process that is also named as post polymerization modification requires the addition of functional groups by replacing halide group of the polymers (addition of functional comonomer like allyl alcohol [31, 32], functionalization by click chemistry [34-36] and functional group will end up at the ω-end of the polymer chain.

4.2.3. End Group Functionalization by Using Functional Comonomer

For the functionalization of the ω-chain end, allyl alcohol radical addition was done on copolymers under ATRP conditions. Copolymers shown in the Table 4.1 are IBHMA cylopolymers with *t*-butyl acrylate, which provides secondary Br at the chain ends. This active bromine with enough reactivity towards radical addition of allyl alcohol should end up with hydroxyl functional groups [31]. However, ^{31}P-NMR spectra (Figure 4.5.) showed no alcohol peak, which should appear at 127.4 ppm as proven by the ^{31}P-NMR spectra of the phosphorus derivatized *n*-butanol.

^{31}P-NMR results showed that allyl alcohol addition to comonomer was not successful. To check the validity if the method, the addition of allyl alcohol to the secondary radical formed at the chain ends, simple linear acrylate polymers were studied instead of RHMA ether dimer derived cyclopolymer and copolymer. Linear polymers of *t*-butyl acrylate and isobornyl acrylate were investigated for end group functionalization. *t*-Butyl acrylate was polymerized using ATRP techniques in xylene (Table 4.2). To obtain relatively low molecular weight polymers and to avoid loss of end group, low monomer conversion was preferred. Polymerization reactions were carried out at 80 ^{0}C for 3 hours, with $[tBA]_0$:$[EBiB]_0$:$[CuBr]_0$:$[PMDETA]_0$ ratio equal to 100:1:1:1. Allyl alcohol addition to p(tBA) were done overnight at 40 ^{0}C, with excess concentration of the allyl alcohol for the completion of the reaction.

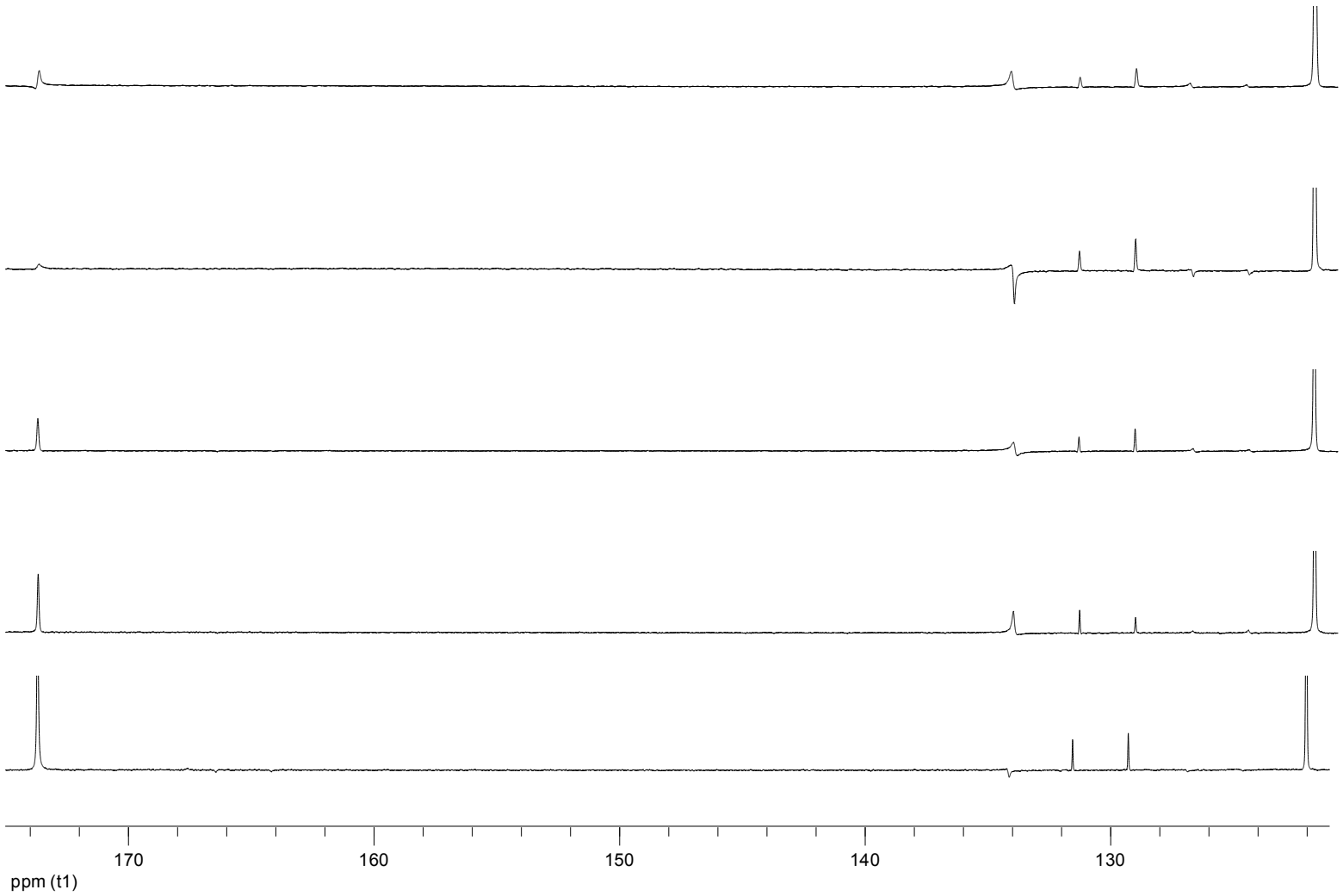


Figure 4.5. ^{31}P-NMR Results of the –OH end functionalization attempt on the copolymers.

Table 4.2. Results of the *t*-butyl acrylate study.

	ptBA[a]			ptBA+ allyl alcohol[b]	
Entry	Conversion (%)	$M_{n,sec}$,(g/mol)	M_w/M_n	$M_{n,sec}$(g/mol)	M_w/M_n
1	40	10100	1.23	10100	1.23
2	34	14200	1.29	13980	1.27
3	56	7600	1.19	7700	1.19
4	68	9540	1.23	9740	1.24

a: At 80 C^0, $[tBA]_0/[In]_0/[CuBr]_0/[L]_0$ 100/1/1/1, 3 h.

b: At 40 C^0, overnight, $[Allyl\ alcohol]_0/[In]_0/[CuBr]_0/[L]_0$ excess/1/2/2.

Isobornyl acrylate was polymerized by using EBiB as an initiator, Cu(I)Br/ PMDETA as catalyst system in 50% by volume xylene under ATRP conditions. Polymers with low monomer conversion and low molar mass were targeted to yield high functionality (Table 4.3). Radical addition of allyl alcohol to the poly(isobornyl acrylate) gave small change in M_n values.

Table 4.3. Results from the poly-isobornyl acrylate study.

	piBoA[a]			piBoA+ allyl alcohol[b]	
Entry	Conversion. (%)	$M_{n,sec}$ (g/mol)	M_w/M_n	$M_{n,sec}$ (g/mol)	M_w/M_n
1	68	12190	1.49		
2[b]	68	12190	1.49	12890	1.45
3[c]	68	12190	1.49	13140	1.45

a : At 90 ^{0}C, 2h, $[iBoA]_0/[In]_0/[CuBr]_0/[L]_0$ 100/1/1/1, in 50% vol xylene

b: At 40 ^{0}C,overnight, $[Allyl\ acohol]_0/[In]_0/[CuBr]_0/[L]_0$, excess/1/1/1

^{31}P-NMR spectra (Figure 4.6) of p(tBA) indicates allyl alcohol addition to polyacrylates. As seen from the spectra there are peaks of internal standard (131.5 ppm), pyridine complex (129.2ppm), water remained (121.2 ppm) and excess phosphorus reagent (173.6 ppm) and expected hydroxyl peak at around 127.4 ppm. Quantitative calculations according to these spectra are shown in the Table 4.4.

Table 4.4. ^{31}P-NMR study results of poly(*t*-butyl acrylate).

	ptBA			ptBA+ allyl alcohol				
Entry	Conver. (%)	$M_{n,sec}$, (g/mol)	M_w/M_n	$M_{n,sec}$, (g/mol)	M_w/M_n	Exp (ppm)	Theo (ppm)	Yield ppm (%)
1	40	10100	1.23	10100	1.23	1206.70	1680.50	71
2	34	14200	1.29	13980	1.27	1509.00	1191.70	126

Post polymer modification on IBHMA-tBA copolymer with hydroxyl group was not successful. The same procedure of allyl alcohol addition to poly(t-butyl acrylate) in ATRP system ended up with high percent converstion to the hydroxyl end group.

4.2.4. Post Copolymerization Study on the Allyl Alcohol Added Block Copolymers

Theoretically, if the end group functionalization with the allyl alcohol is accomplished, then further ATRP reactions should not be possible with the allyl alcohol added end groups. According to the given mechanism for the allyl alcohol radical addition reaction [29-32] the resulting chain end should be non-active for further ATRP (Figure 4.7.). Therefore, the other way to check whether the addition of allyl alcohol was achieved or not, was to perform further ATRP reaction with the obtained polymers and an acrylate and check if there was any molecular weight change under ATRP conditions. If the allyl alcohol addition is not attained then polymer chain should still be active for ATRP and should give rise to an increase in molecular weight.

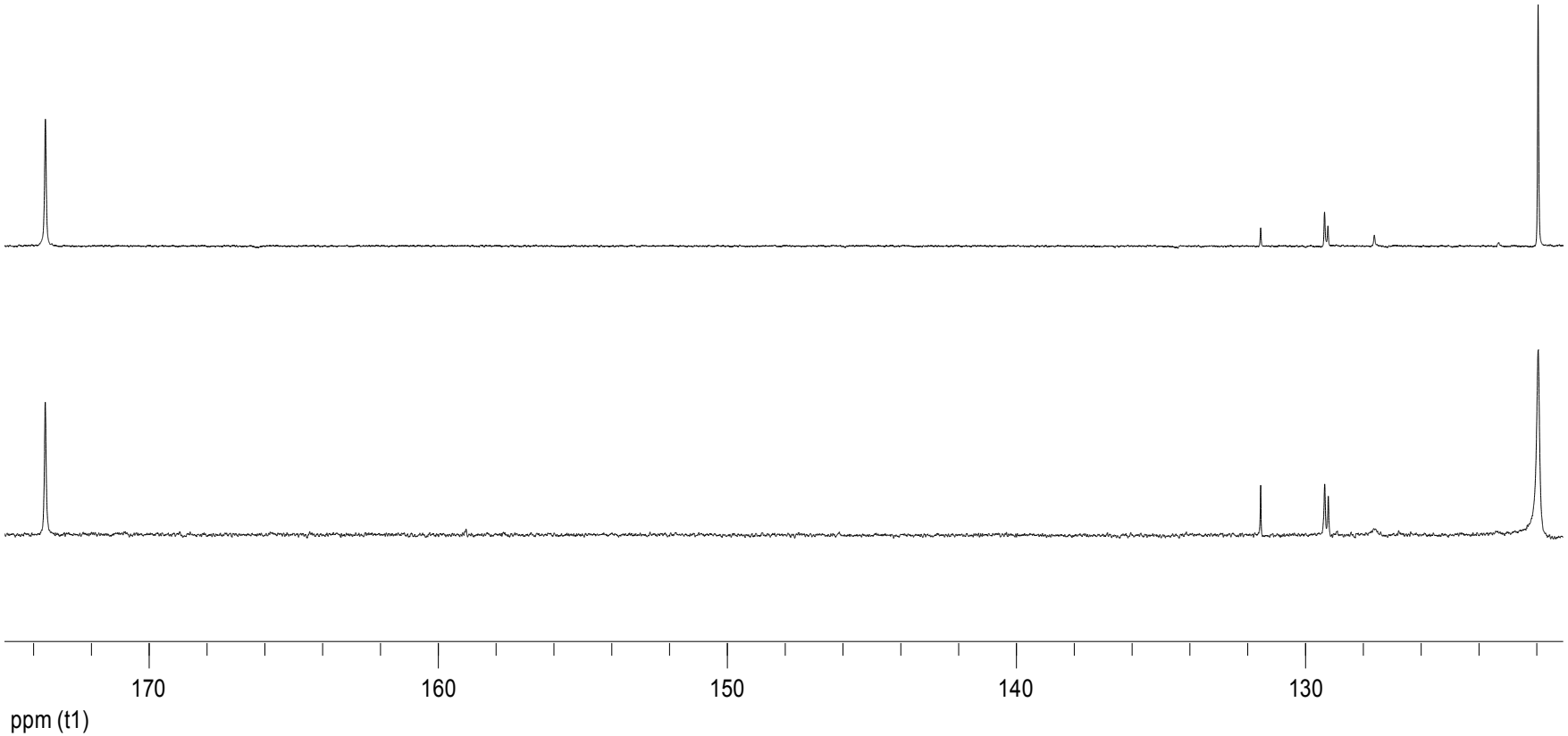


Figure 4.6. ^{31}P-NMR Results of the –OH end functionalization attempt on poly(*t*-butyl acrylate).

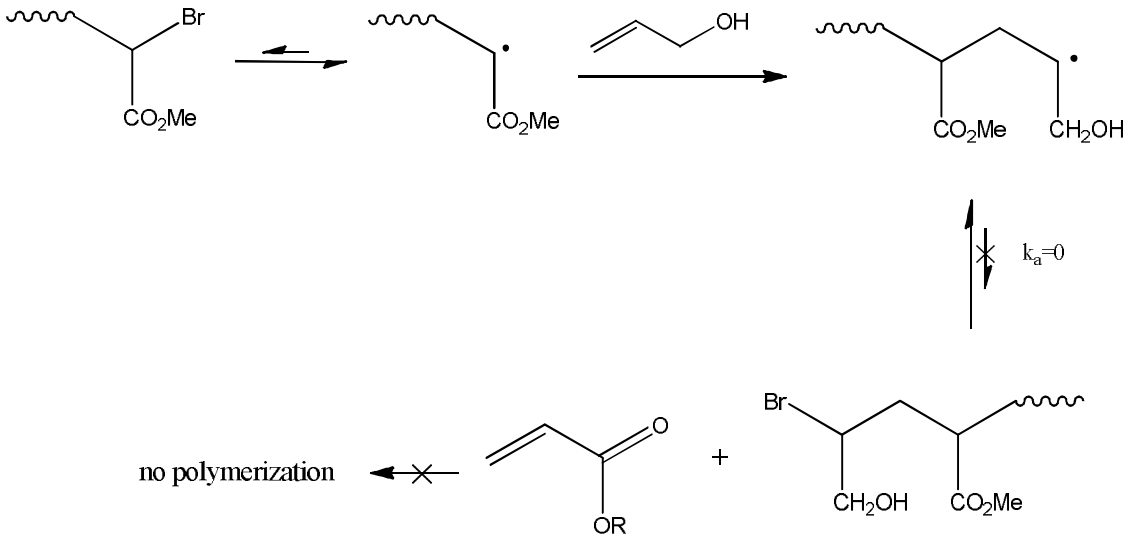


Figure 4.7. Further polymerization reaction on polymers after allyl alcohol addition.

The post copolymerization was carried out with *t*-butyl acrylate (Entry 4, Table 4.1, M_n=18 100g/mol, PDI=1.38). The GPC results exhibited a small increase in both M_n and PDI values (M_n=19 380 g/mol, PDI=1.45). ^{31}P-NMR (Figure 4.8.) spectra taken after comonomer addition, as expected, showed no hydroxyl group.

When all results are considered it is obvious that the alcohol group is not present at the polymer end. Although the slight increase in molecular weight may indicate that the allyl alcohol is not added to the polymer chain ends, the change in molecular weight was not as high as expected. This data might be consistent with the recent papers [37, 38] that report the hydrogen abstraction from the polymers from the PMDETA ligand and the formation of hydrogen-functionalized polymers which was shown by using MALDI-TOF. In conclusion, radical addition of allyl alcohol using the ATRP technique seems to be not an efficient way to obtain alcohol end groups with the RHMA derived cyclopolymers.

4.2.5. End Group Functionalization by Using Functional Initiator

In ATRP, polymers synthesized by using an initiator with a given functional group results in polymers with that specific end group [39]. Choosing an initiator bearing hydroxyl group should in principle give polymer chains with mono hydroxyl functionality

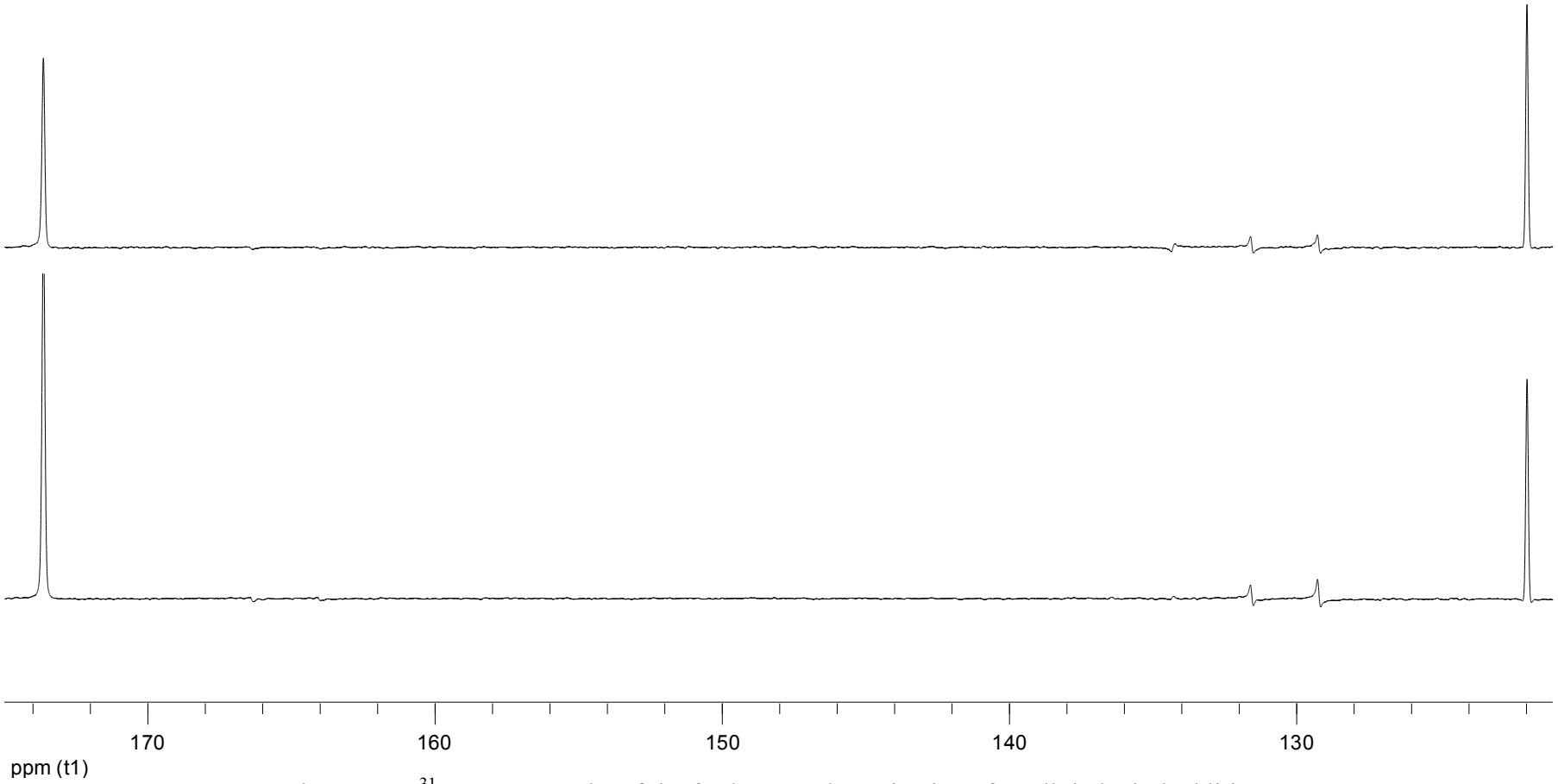


Figure 4.8. ^{31}P-NMR Results of the further copolymerization after allyl alcohol addition.

at the α-end. Hydroxyethyl bromo isobutyrate (HEBIB) as a functional initiator is suitable for the ATRP conditions. It is fast for initiation, easily accessible, soluble in most organic solvents. It was thought that this could be the most precise way of synthesizing hydroxyl functional polymers and these polymers with known alcohol end group should allow the determination of alcohol peak in ^{31}P-NMR spectra. Polymerizations reactions of isobornyl acrylate and IBHMA ether dimer with HEBIB were carried out with $[M]_0$:$[HEBIB]_0$:$[CuBr]_0$:$[Ligand]_0$=50:1:1:1 ratios in 1 M ±0.01 xylene at 70 ^{0}C (Table 4.4). Obtained products were reasonable in polydispersity and molar mass.

Table 4.5. Results of p(iBoA) and p(IBHMA) synthesized with HEBIB.

Entry	Monomer	Conversion (%)	$M_{n,sec}$ (g/mol)	M_w/M_n
1	iBoA	10	14000	1.39
2	iBoA	34	13700	1.42
3	iBoA	57	11400	1.42
4	IBHMA	14	9320	1.34
5	IBHMA	31	8620	1.75

^{31}P-NMR spectra of polymers initiated with HEBIB should give nice peaks of hydroxyl group at 127.4 ppm. However, from Figure 4.9 it is obvious that there are very small peaks related to the hydroxyl end group. Quantitative data from the ^{31}P-NMR spectra of the Entries 3 and 5 from Table 4.5 illustrate very low percent yield for hydroxyl end group (Table 4.6).

The reason for the low ppm of the hydroxyl group could be the high reaction temperature, polymerization reactions were performed at 70 ^{0}C. At elevated temperature –OH group could undergo transesterification reaction which leads to the loss of functional end groups. The shortest way to check this phenomena is to compare $M_{n,cal}/M_{n,sec}$ ratios of the same polymers initiated with hydroxylated initiator and polymers initiated with no hydroxyl bearing initiator. When $M_{n,cal}/M_{n,sec}$ ratios of the poly(isobornyl acrylate) derived

Table 4.6. ^{31}P-NMR study results of the polymers synthesized with hydroxyl functional initiator.

Entry	Monomer	Conversion (%)	$M_{n,sec}$ (g/mol)	M_w/M_n	Exp (ppm)	Theo (ppm)	Yield ppm (%)
3	iBoA	57	11400	1.42	30.49	1489.14	2
5	IBHMA	31	8620	1.75	255.93	1970.10	13

from EBiB (Entry 4) is compared to the poly(isobornyl acrylate) initiated with hydroxyl functional initiator (HEBIB) (Entries 1-3) it demonstrates that the first three have much higher values. This is the indication of possible transesterification reactions in hydroxylated polyacrylates. Still, this option needs to be checked by further experimentation.

Table 4.7. Results of poly(isobornyl acrylate) initiated with HEBIB and EBiB.

Entry	Monomer	Conversion (%)	$M_{n,cal}$ (g/mol)	$M_{n,sec}$ (g/mol)	M_w/M_n	$M_{n,cal}/ M_{n,sec}$
1	iBoA[a]	10	1440	14027	1.39	9.74
2	iBoA[a]	34	4894	13712	1.42	2.80
3	iBoA[a]	57	8064	11416	1.42	1.41
4	iBoA-EBiB	68	14164	12193	1.49	0.86

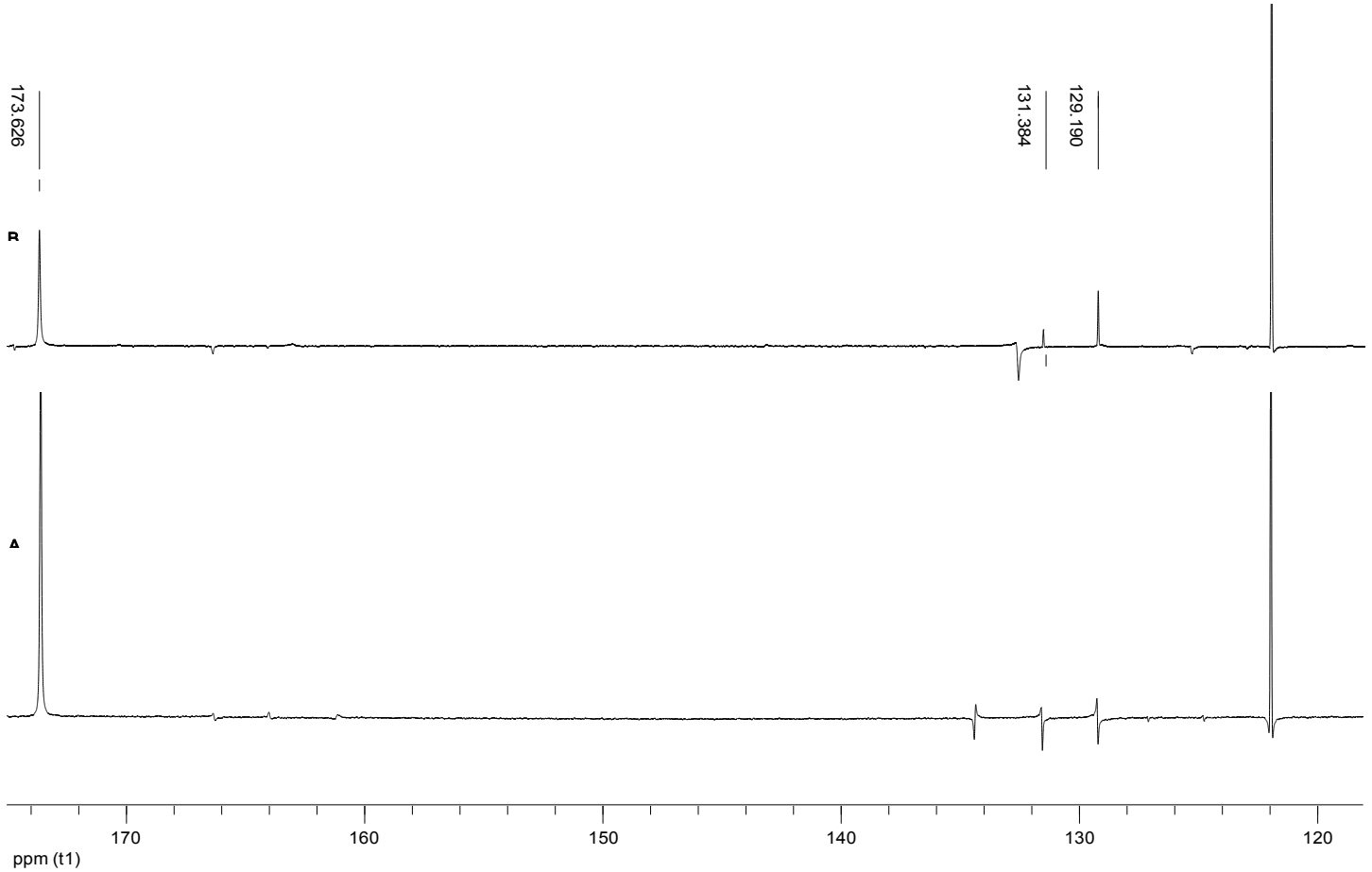


Figure 4.9. ^{31}P-NMR spectra of polymers synthesized with HEBIB.

A. p(iBoA) initiated with HEBIB.

B. p(IBHMA) initiated with HEBIB.

5. CONCLUSION

In this study end group functionalization of the polymer chain was investigated. Aliphatic cyclopolymers derived from alkyl α-(hydroxymethyl)acrylate ether dimer (IBHMA) were synthesized via Atom Transfer Radical Polymerization (ATRP). To get less hindered active halide cyclopolymers were copolymerized with *t*-butyl acrylate. Post-polymerization functionalization technique was employed to get the desired reactive end groups by the addition of allyl alcohol using Cu/PMDETA catalyst system according to the literature.

Experiments show that allyl alcohol addition by using ATRP is not an efficient way to get hydroxyl end group at the polymer chains of IBHMA ether dimer derived cyclopolymer block copolymerized with tBA. Allyl alcohol addition to the linear poly(*t*-butyl acrylate) gave high percent yield. Wherease, polymerization reaction of both IBHMA ether dimer derived cyclopolymer and poly(isobornyl acrylate) with hydroxyl containing initiator (HEBIB) gave very low percent yield of –OH functionalization. The quantitative analysis was carried out by ^{31}P-NMR.

6. FUTURE WORK

To achieve functionality at the end of the polymer chain various experiments can be proposed. First target may be the synthesis of polymers *via* ATRP with functional initiator (eg. HEBIB) at lower temperature and with lower M_n values. In order to prevent the transesterification reactions of the hydroxyl end groups low reaction temperature might be essential.

ATRP MALDI-TOF analysis of copolymers and polyacrylates functionalized via allyl alcohol addition may give clear understanding of H-abstraction, if exists, caused by the excess PMDETA in the media.

REFERENCES

1. Matyjaszewski, K., T. P. Davis, *Handbook of Radical Polymerization*, Wiley, Hoboken, 2002.

2. Kamigaito, M., T. Ando., M. Sawamoto, "Metal-Catalyzed Living Radical Polymerization", *Chem. Rev*. Vol. 101, pp. 3689-3745, 2001.

3. Matyjaszewski, K., J. Xia, "Atom Transfer Radical Polymerization", *Chem. Rev*, Vol. 101, pp. 2921-2990, 2001.

4. Coessens, V., T. Pintauer, K. Matyjaszewski, "Functional Polymers by Atom Transfer Radical Polymerization", *Prog. Polym. Sci*., Vol. 26, pp. 337-377, 2001.

5. Chiefari, J., Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. 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.

6. Moad, G., J. Chiefari, Y. K. Chong, J. Krstina, T. A. R. Mayadunne, A. Postma, E. Rizzardo, H. S. Thang, *Polym Int.*, Vol. 49, pp. 993-1001, 2000.

7. Craig, J. H., W. A. Bosman, E. Harth, "New Polymer Synthesis by Nitroxiade Mediated Living Radical Polymerizations", *Chem. Rev*., Vol. 101, pp. 3661-3688, 2001.

8. Moad, G., D. H. Solomaon, "The Chemistry of Free Radical Polymerization", Pergamon, Oxford, 1995.

9. Kamigaito, M., T. Ando, M. Sawamoto, "Metal-catalyzed living radical polymerization: Discovery and development", *Chem. Rev*., Vol. 4, pp. 159-175, 2004.

10. Queffelec, J., G. S. Gaynor, K. Matyjaszewski, "Optimization of Atom Transfer Radical Polymerization Using Cu(I)/Tris(2(dimethylamino)ethyl)amine as a Catalyst", *Macromolecules* 2000, Vol. 33, pp. 8629-8639, 2000.

11. Kato, M., M. Kamigaito, 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.

12. Nanda, K. A., 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. 1487-1493, 2003.

13. Matyjaszewski, K., T. E. Patten, J. J. Xia, "Controlled/ "Living" Radical Polymerization. Kinetics of the Homogeneous Atom Transfer Radical Polymerization of Styrene", *Am. Chem. Soc*, Vol. 119, pp. 674-680, 1997.

14. Matyjaszewski, K., K. Davis, T. Patten, M. Wei, "Observation and Analysis of a Slow Termination Process in the Atom Transfer Radical Polymerization of Styrene", *Tetrahedron*, Vol. 53, pp. 15321-15329, 1997.

15. Tsuda, T., L. Mathias, "Cyclopolymerization of Ether Dimers of α-(Hydroxymethyl)acrylic Acid and its Alkyl Esters: Substituent Effect on Cyclization Efficiency and Microstructures", *Polymer*, 35, 3317-3328, 1994.

16. Erkoc, S., Cyclopolymerization of Alkyl α- (Hydroxymethyl) Actylate (RHMA) Ether Dimers via Atom Transfer Radical Polymerization, M.S. Thesis, Bogazici University, 2005.

17. Bayrak, S., Effect of the Ester Groups on the Controlled/ Living ATRP Cyclopolymerization of α- (Hydroxymethyl) Actylate (RHMA) Ether Dimers, M.S. Thesis, Bogazici University, 2009.

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

19. 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.

20. Beers, K. L., S. Boo, K. Matyjaszewski, "Preparation of Poly(2-Hydroxyethyl Methacrylate) by Controlled Radical Polymerization", *Polym. Mat. Sci. Eng.* Vol. 79, pp. 407-408, 1998.

21. Coca, S., C. B. Jasieczek, K. L. Beers, K. Matyjaszewski, "Polymerization of Acrylates by Atom Transfer Radical Polymerization. Homopolymerization of 2-Hydroxyethyl Acrylate", *J. Polym. Sci., Part A: Polym. Chem.* Vol. 36, pp. 1417-1424, 1998.

22. Zang, X., J. Xia, K. Matyjeszewski, "Controlled/ "Living" Radical Polymerization of 2-(Dimethylamino)Ethyl Methacrylate", *Macromolecules*, Vol. 31, pp. 5167-5169, 1998.

23. DeSimone, J. M., A. M. Hellstern, E. J. Siochi, S. D. Smith, T. C. Ward, P. M. Gallagher, V. J. Krukonis, J. E. McGrath, *Makromol. Chem., Macromol. Symp.*, 683, 1990.

24. Radke, W., A. H. E. Muller, *Makromol. Chem., Macromol. Symp*., Vol. 54, pp. 583, 1992.

25. Haddleton, D. M., C. Waterson, P. J. Derrick, C. Jasieczek, B. Shooter, "Monohydroxy Terminally Functionalised Poly(Methyl Methacrylae) from Atom Transfer Radical Polymerization", *Chem. Commun*., pp. 683-683, 1997.

26. Gaynor, S. G., K. Matyjaszewski, *ACS Symp. Ser.*,Vol. 685, pp. 396, 1998.

27. Schon, F., M. Hartenstein, A. H. E. Muller, "New Strategy for the Synthesis of Halogen-Free Acrylate Macromonomers by Atom Transfer Radical Polymerization", *Macromolecules*, Vol. 34, pp. 5394-5397, 2001.

28. Coessens, V., K. Matyjaszewski, "Synthesis of Amino End Groups by Atom Transfer Radical Polymerization", *J. Macromol. Sci., Pure Appl. Chem.* 1999, A36, pp. 811-826, 1999.

29. Coessens, V., J. Pyun, P. J. Miller, S. G. Gaynor, K. Matyjaszewski, "Functionalization of Polymers Prepared by ATRP Using Radical Addition Reactions", *Macromol. Rapid Commun.*, Vol. 21, pp. 103-109, 2000.

30. Kühl, O., "Phosphorus-31 NMR spectroscopy", Springer: Berlin, 2008.

31. Dhara,D., A. A. G. Shaiki, G. Chatterjef, C. Seetharaman, inventors; Aliphatic Diols Polycarbonates and their preparation. 2005 July. 21. PCT WO 2005/066239 A1.

32. Ozkal, E., Synthesis of Alkyl α- (Hydroxymethyl) Actylate (RHMA) Ether Dimer Derived Polymers and Their Potential Use in Powder Coating, M.S. Thesis, Bogazici University, 2008.

33. Boyer. C., H. A. Soeriyadi. J. P. Roth. R. M. Whittaker. P. T. Davis, "Post-Functionalization of ATRP Polymers Using Both thiol/Ene and Thiol/Disulfide Exchange Chemistry", *Chem. Commun.*, Vol. 47, pp. 1318–1320, 2011.

34. Kolb, H. C., M. G. Finn, K. B. Sharpless, "Click Chemistry: Diverse Chemical Function from a Few Good Reactions", *Angew. Chem., Int. Ed.*, Vol. 40, pp. 2004−2021, 2001.

35. Díaz, D. D., S. Punna, P. Holzer, A. K. McPherson, K. B. Sharpless, V. V. Fokin, M. G. Finn, "Click Chemistry in Material Synthesis. 1. Adhesive Polymer from Copper-Catalyzed Azide-Alkyne Cycloaddition", *J. Polym. Sci., Part A:Polym. Chem.*, Vol. 42, pp. 4392−4403, 2004.

36. Tsarevsky, N. V., K. V. Bernaerts, B. Dufour, F. E. Du Prez, K. Matyjaszewski, "Well-Defined (Co)polymers with 5-Vinyltetrazole Units via Combination of Atom Transfer Radical (Co)polymerization of Acrylonitrile and "Click Chemistry"-Type Postpolymerization Modification", *Macromolecules*, Vol. 37, pp. 9308−9313, 2004.

37. Pioge, S., L. Fontaine, J. C. Soutif, E. Nicol, S. Pascual, "A new Strategy for the Synthesis of Methacrylate End-Functionalized Macromonomers by ATRP", *J. Polym. Sci. Part A: Polym Chemy*, Vol. 48, pp. 1526–1537, 2010.

38. Bednarek, M., T. Biedron, P. Kubisa, "Studies of Atom Transfer Radical Polymerization (ATRP) of Acrylates by MALDITOF Mass Spectroscopy", *Macromol Chem Phys.*, Vol. 201, pp. 58-66, 2000.

39. Percec. V., B. Barboiu, J. H. Kim, "Arenesulfonyl Halides: A Universal Class of Functional Initiators for Metal-Catalyzed "Living" Radical Polymerization of Styrene(s), Methacrylates, and Acrylates", *J. Am. Chem. Soc.* , Vol. 120, pp. 305-316, 1998.