SYNTHESIS OF TELECHELIC ALIPHATIC CYCLOPOLYMERS BY CONTROLLED RADICAL POLYMERIZATION

by

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To My Family

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ABSTRACT

SYNTHESIS OF TELECHELIC ALIPHATIC CYCLOPOLYMERS BY CONTROLLED RADICAL POLYMERIZATION

Powder coating is a growing industry which has many application areas for many surfaces. The coating mixture has many different ingredients. The highest percentage of a powder coating mixture in terms of both volume and weight is the resin which is a crosslinkable polymer with specific properties. Some of the important properties are processability, stability, reactivity. Beside these properties a powder coating resin has to have certain physical properties which affect the coating quality and manufacturing process. Among many, the most important one is a given T_g range. For example for a curing temperature of 140-150 ^{0}C the T_g of the resin has to be adjusted to 55-60 ^{0}C. Generally reaching these values is possible only using relatively high molecular weight aliphatic polyesters (10,000-20,000 g/mol). Having similar properties with low molecular weight aliphatic polymers has not been investigated previously.

Aliphatic cyclopolymers derived from tert-butyl α-(hydroxymethyl)acrylate dimer(TBHMA) were synthesized via atom transfer radical polymerization (ATRP) to be used as potential base resins for powder coating applications. A variety of polymers were synthesized with various molecular weights and glass transition temperatures (T_g). To reach the desired T_g's, two new di-initiators containing di- and tetra-ethylene glycol soft units were synthesized and used in the cyclopolymerization of tert-butyl a-(hydroxymethyl)acrylate (TBHMA). Polymerizations were carried out in xylene. Cu(I)Br/PMDETA was chosen as the active catalyst complex. It was found that molecular weights of polymers directly affected the T_g in the molecular weight range that was chosen. Using the new soft-block containing di-initiators, the T_g of the polymers were decreased to the desired scales (55-60 ^{o}C). Also low polydispersities and high conversions were achieved via ATRP. Two alternative studies were chosen for functionalization: pendant crosslinking and end functional crosslinking units. For pendant approach, glycidyl acrylate and methacrylate units tried to incorporate to the polymer system either directly as the monomer or indirectly to the macro monomer. By the help of living nature of ATRP, end

group functionalization studies were done via using allyl alcohol and undeconoic acid under ATRP conditions. Characterization of all these cyclopolymers and copolymers were also investigated.

ÖZET

KONTROLLÜ RADİKAL POLİMERLEŞME İLE HALKALI ALİFATİK TELEKELİK POLİMER SENTEZİ

Pudra kaplamacılık(Toz boya) değişik yüzeylere uygulanabilen, birçok kullanım alanı olan ve günümüzde giderek büyümekte olan bir sektör haline gelmektedir. Pudra kaplama karışımının hacmen ve kütle olarak en büyük yüzdeye sahip kısmı kendine has özellikleri olan ve çapraz bağlanabilen polimer olan reçinedir. Bu özelliklerden bazıları işlenebilirlik, dayanıklılık, reaktif olmalarıdır. Bu özellikler dışında bir pudra kaplama reçinesinde olması gereken kaplama kalitesini ve üretim işleyişini etkileyen bazı fiziksel özellikler bulunmalıdır. Bunların arasında en önemlisi verilen T_g aralığıdır. Örnek olarak pişirme sıcaklığı 140–150 ^{0}C olan bir baz reçinenin T_g aralığının 55–60 ^{0}C olarak ayarlanması gerekir. Bu özelliklere ulaşmanın yolu genellikle sadece kısmen yüksek moleküler ağırlıkta alifatik polyester kullanmasıyla mümkündür(10,000–20,000 gr/mol). Benzer özelliklere sahip düşük moleküler ağırlıkta alifatik halkalı polimer eldesi şu ana kadar incelenmemiştir.

T-bütil α-(hidroksimetil) eter dimerlerinden ATRP yöntemi ile üretilen alifatik halkalı polimerler pudra kaplama uygulamalarında potansiyel baz reçine olarak kullanılmak üzere sentezlenmiştir. Değişik moleküler ağırlıklara ve camsı geçiş sıcaklığına(T_g) sahip çeşitli polimerlerin sentezi yapıldı. İstenilen T_g'lere ulaşmak için di- ve tetra-etilen glikol yumuşak birim içeren iki yeni çift taraflı başlatıcı sentezi yapılmış ve t-bütil α-(hidroksimetil) eter dimerlerinin (TBHMA) halkalı polimerleşmesinde kullanılmıştır. Polimerleşmeler ksilen içinde gerçekleştirilmiştir. Cu(I)Br/PMDETA aktif katalizör sistemi seçilmiştir. Seçilen moleküler ağırlık aralığında, polimerlerin moleküler ağırlığının T_g'leri direkt olarak etkilediği bulunmuştur. Yeni yumuşak blok içeren çift başlatıcılar kullanılarak polimerlerin T_g'leri istenilen oranlara düşürülmüştür(55–60 ^{o}C). Ayrıca düşük moleküler ağırlık ve yüksek dönüşüm ATRP ile sağlanmıştır. İki farklı çalışma fonksiyonelleşme için seçildi: polimer zincire asılı çapraz bağlanabilen birimler ve uç fonksiyonel çapraz bağlanma. Polimer zincire asılı çapraz bağlanma için glisidil akrilat ve metakrilat birimleri ya direkt monomer ya da dolaylı makro monomer olarak polimer yapısına kopolimerleşme

yöntemiyle dahil edilmeye çalışıldı. ATRP yönteminin sağladığı “yaşayan” olma özelliği sayesinde uç grup fonksiyonelleştirme çalışmaları ATRP koşulları içerisinde alil alkol ve undekanoik asit kullanılarak yapıldı. Sentezlenen polimerlerin fiziksel özellikleri, özellikle de T_g’lerine bakıldı.

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LIST OF ABBREVIATIONS

ATRP	Atom Transfer Radical Polymerization
RHMA	Alkyl α-(hydroxymethyl)acrylate
TBHMA	Tert-butyl α-(hydroxymethyl)acrylate
GHMA	Glycidyl α-(hydroxymethyl)acrylate
PMDETA	*N*,*N*,*N*,*N*',*N*'-pentamethyldiethylenetriamine
DABCO	1,4-Diazabicyclo[2.2.2]octane
EB*i*B	Ethyl 2-bromoisobutyrate
DEG	Di-ethylene glycol di initiator
TEG	Tetra-ethylene glycol di initiator
GPC	Gel Permation Chromatography
NMR	Nuclear Magnetic Resonans Spectroscopy
T_g	Glass Transition Temperature
TLC	Thin Layer Chromatography
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
SEC	Size Exclusion Chromatography

1. INTRODUCTION

1.1. Powder Coating

Coating industry has two backbone principal technologies:

- Liquid coating technology (wet), which has been applied for more than two centuries
- Powder coating technology (dry), which has been applied on an industrial scale for some 30 years [1].

Environmentally, the advantages of powder coating over liquid, solvent-based paint are obvious. Powder coating requires less energy and emits virtually no volatile organic compounds (VOCs) or hazardous air pollutants (HAPs), eliminating the need for expensive pollution control equipment. In addition, powder overspray can be recovered or reused, the process generates little or no hazardous waste compared with the problematic sludge left over by liquid paint [2].

In powder coating, finely-ground electro statically-charged coating particles are sprayed onto electrostatically-grounded surfaces, where they adhere. Then the dry powder layer is heated and permanently fused to the surface in an oven known as the curing process [2].

1.2. Powder Coating Process

Powder coating process can be divided into two: Manufacturing and application.

1.2.1. Powder Manufacturing

Powder Coating may contain up to 12-15 different components. The basic ones are resin, hardener, pigments and additives. An even distribution of these components in every

coating particle is essential for a good coating quality. In order to achieve this, several steps have been introduced in the manufacturing of the powder coatings (Figure 1.1).

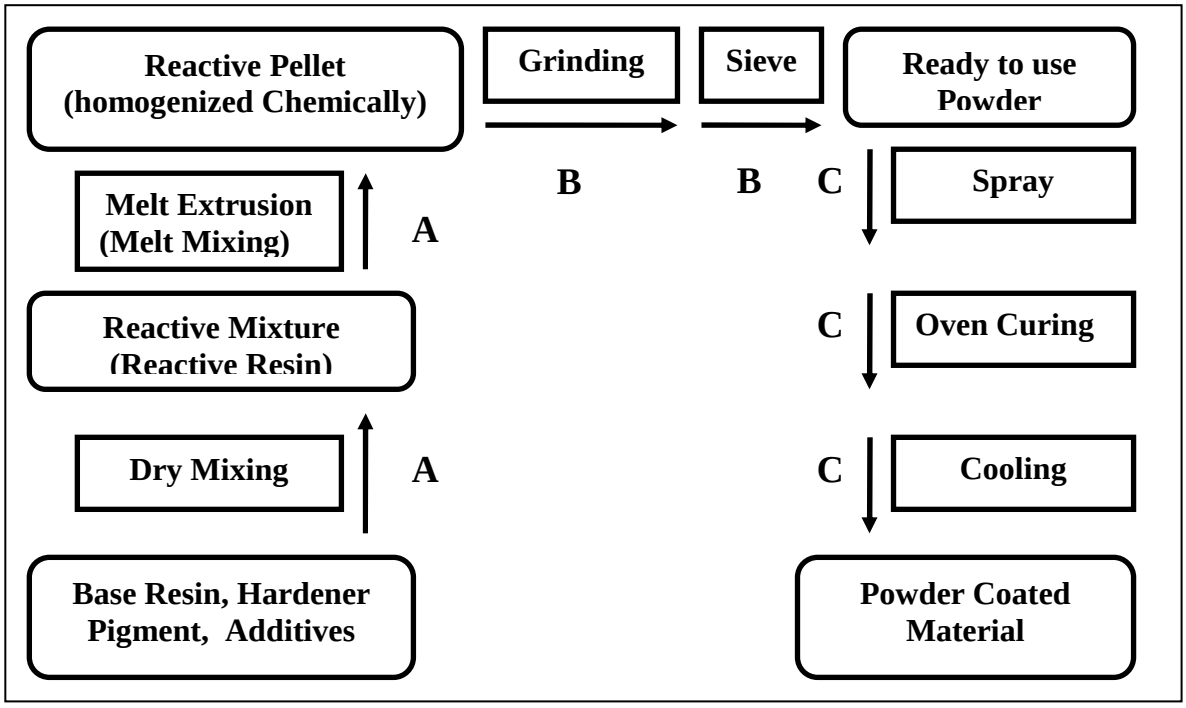

Figure 1.1. Simplified model for powder coating process.

The process shown in Figure 1.1 makes every powder particle exactly same with their counterparts. At each stage in the process, the powder coating material should be checked so that there won't be any further change or adjustment. As shown in Figure 1.1. in step A, raw materials which are resin, hardener, pigment and additives are weighed precisely. Then, all components are placed in the dry mixing container and are allowed to mix together until the desired specifications, in terms of physical properties, are reached. Continuing with the melt extrusion (melt mixing), the mixed materials are fed into the extruder which is heated to a predetermined temperature. The temperature is set only to liquefy all the components and to mix them in the barrel. Throughout step A, all the components are dispersed and wetted by the resin which makes a homogenous reactive pellet. At this point, it is very important not to have too high temperature in the extruder barrel which may cause low melt viscosity, low shear forces, poor pigment dispersion and a low gloss coating. The resin and hardener may also pre-react within the extruder which will also affect the product performance. At the step B, the molten mass is forced to cool down via a cooling-transporting devise. The solidified material is broken up and reduced

into smaller size (5 to 10) through a crusher. Continuing with step B, grinding and sieving, chips are ground to the desired powder size in a grinding mill. The grinding continues until the final powder coating material is obtained. To reach the optimal size and homogeneity in the powder, further treatment may be done which may consist of cycloning, classifying, filtering or sieving.

1.2.2. Coating Application

The powder coating is then applied using a powder coating gun which charges the powder coating particles electrostatically. These charged particles are sprayed over the coating substrate which is ground. Finally the substrate is subjected to the heat where it is cured in an oven. The curing temperature varies according to the powder coating used but generally it ranges from 160-210 ^{0}C.

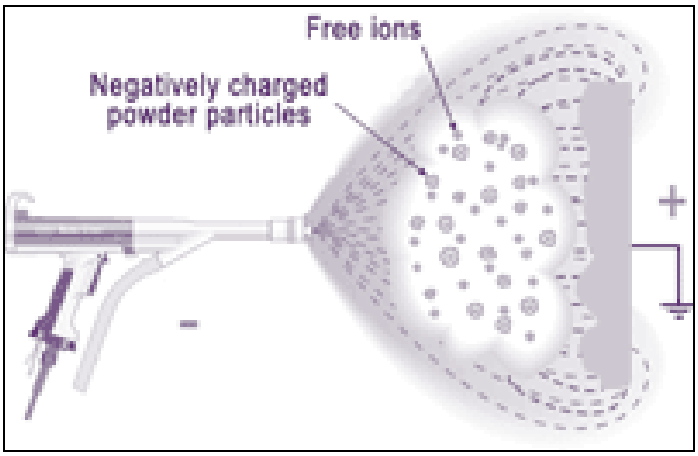

Figure 1.2. An example of spray gun.

1.3. Material Requirements for Powder Coatings

Before dealing with the chemistry of powder coating, it is very crucial to identify and investigate the physical aspects of powder coating technology. From powder handling to film formation there are several requirements to be met for a good powder coating.

To start with, it will be helpful to concentrate more closely on how the resin properties affect the film formation in powder coatings. During the application of the powder coating, powder particles which are 25-100 µm in size are electro-statically

sprayed onto a grounded substrate and the thickness of the uncured powder layer that is formed is in the range of 200-250 µm. Thicker films are difficult to form because of the reduced electrostatic attraction between the incoming particles and the substrate. In addition, it is difficult to achieve thinner films since uniformity of the film becomes a problem [3]. When heated to curing temperatures, the powder layer melts down to a final film thickness close to 75-125 µm.

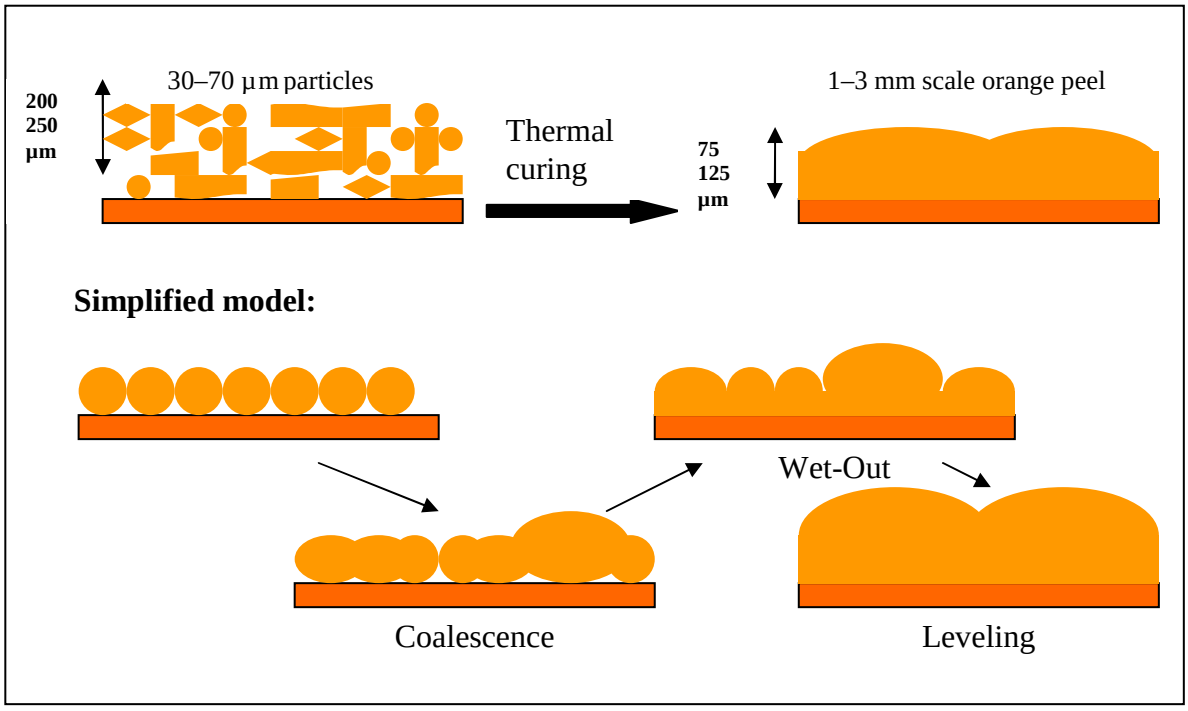

Figure 1.3. Powder coating film formation (top) and simplified elements (bottom) for analyzing resin properties.

As can be seen from Figure 1.3., the complex geometry of the stacked powder particles is reduced to a single layer of spherically shaped particles during the curing process at which the particles melt out. The melting process can be separated into three different stages such as particle coalescence, substrate wetting, and film leveling. It's known that rate of coalescence is related to the particle radius, the resin surface tension and viscosity [4]. The main criterion for powder coating is that the rate is directly proportional to the surface tension and inversely proportional to the viscosity. The substrate wetting depends on the interfacial energies between the surface, air and the resin. The resin wet-out is best achieved by minimizing the surface energies of the resin with both the solid and the air. If controllable, increasing the surface energy of the substrate is also beneficial. Like

coalescence, a lower resin viscosity and higher surface tension results in the formation of a smooth film. All these points out the need to minimize the resin viscosity while balancing opposing needs such as high resin surface energy (for coalescence and leveling) and a low surface energy (for substrate wetting)[4].

Although some powder coatings can be quite smooth most show a fair level of orange peel. This orange peel has a characteristic scale of 1-3 mm which is very similar to that seen in solvent applied paints.

Beside the resin size, viscosity and the surface tension which were discussed previously, there is also an indirect requirement or constrain for the glass transition temperature of the resin to be used in the powder coating. Depending on the curing temperature, the T_g must be in a given temperature range for the following reasons:

- Polymer T_g should be at least 10-20 ^{0}C higher than the maximum handling temperature of the powder coating to prevent early coagulation of the powder particles which in turn affects the film quality.
- Polymer T_g should be high enough so that dry mixing can be done efficiently without melting.
- The polymer T_g should be at least 30 to 50 ^{0}C below the melt extrusion temperature so

  that at the melt extrusion step all the components can be melt-mixed together homogeneously. In other words the melt extrusion temperature highly depends on the T_g. Since high temperatures in the melt extrusion process are not desired because they gave rise to early curing and crosslinking, one should decrease the T_g of the polymer to minimize the melt extrusion temperature. It is generally desirable to have the maximum gap between the melt extrusion temperatures and curing temperatures.

In summary, for a coating to be cured at 130-160 ^{o}C, the T_g should be at least 60-80 ^{0}C lower than the curing temperature. So, considering all these facts, the T_g window of the polymer must be chosen between 55 and 70 ^{0}C.

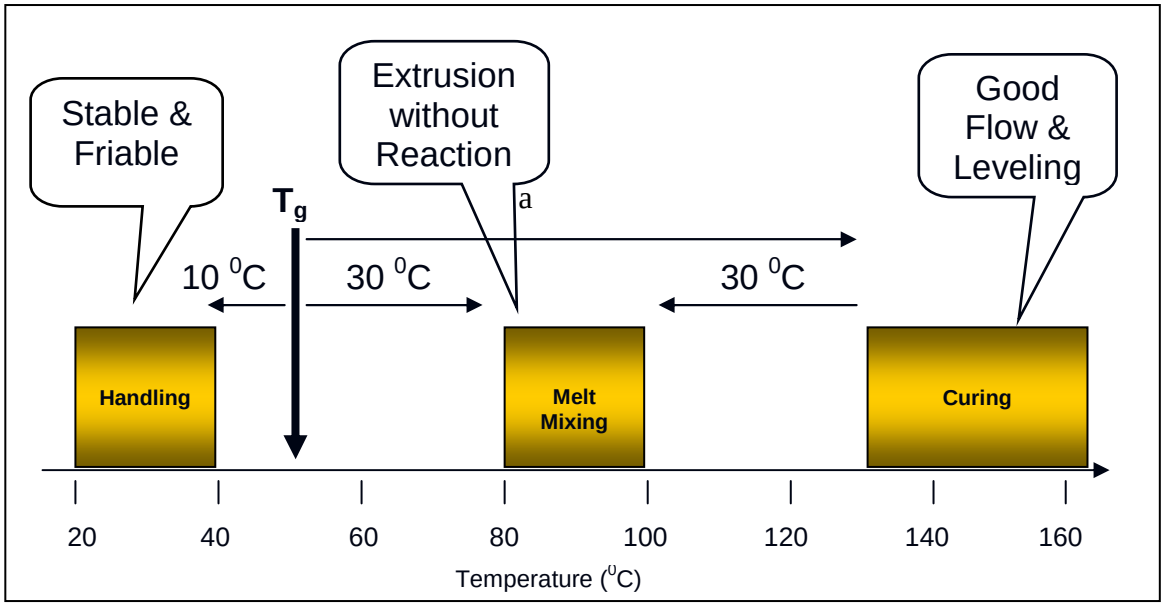

Figure 1.4. T_g requirement of the desired polymers.

1.4. Chemistry of Powder Coatings

1.4.1. Curing Reactions Used in Powder Coatings

There are two types of powder coating: thermoplastic and thermosetting coatings. Thermoplastic coatings do not react upon heating; in contrast they melt and flow out onto the substrate. Because of this property, they are used in coating wire, pipes and accessories. The thickness of such coating is around 250 microns.

Thermosetting coatings also melt upon heating but they undergo a simultaneous chemical reaction and polymerize through crosslinking into a resistant film. Once the chemical reaction has occurred, the powder coating film can not be remelted. These coatings are used in both the decorative and the industrial markets. The general film thickness of these coating are around 20 to 80 micron.

For all of the resins available, two types of thermoset chemistries are used in powder coating: There are based on acid-epoxy and alcohol-isocyanate reactions (Figure 1.5. and 1.6).

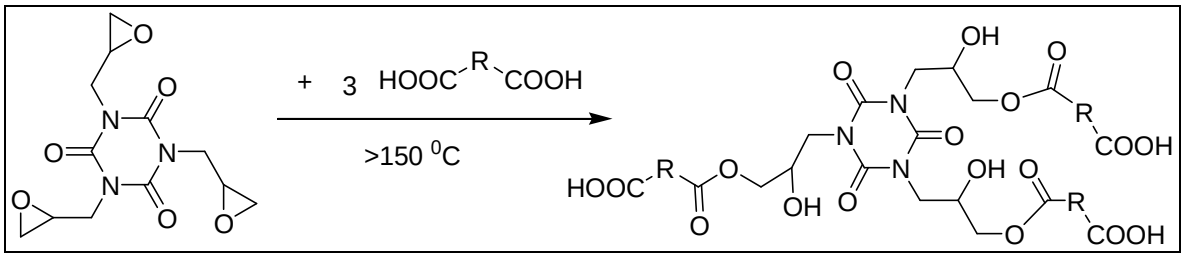

Figure 1.5. Acid-epoxy chemistry.

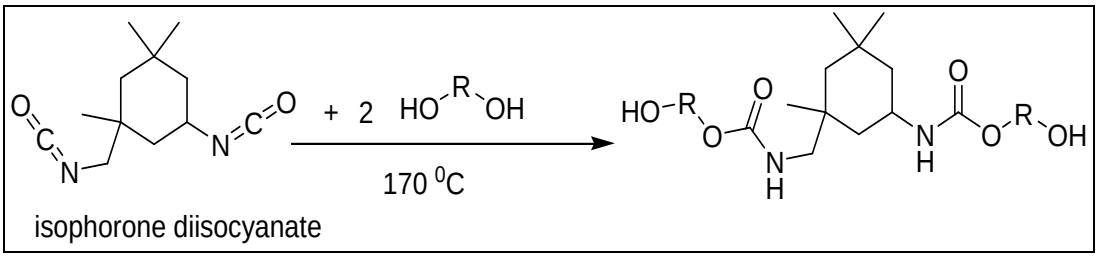

Figure 1.6. Urethane chemistry.

1.4.2. Resins Used in Powder Coatings

There are five different powder coating mixtures available commercially. The powder coating is chosen with respect to the properties needed. Each coating has different properties and therefore different area of application. Their comparison is given in Table 1.1:

Table 1.1. Main properties of different types of thermoset powder coatings [5].

	EPOXY	ACRYLIC	POLYESTER	HYBRID	URETHANE
Weatherability	Poor	Excellent	Excellent	Poor	Good
Corrosion resistance	Excellent	Good	Very good	Very good	Very good
Chemical resistance	Excellent	Very good	Good	Very good	Very good
Heat resistance	Very good	Good	Good	Good	Very good
Impact resistance	Very good	Fair	Good	Very good	Very good
Hardness	HB-5H	HB-4H	HB-4H	HB-2H	HB-3H
Flexibility	Very good	Fair	Very good	Very good	Very good
Adhesion	Excellent	Fair	Excellent	Excellent	Very good

In powder coating, both aliphatic and aromatic structures have been used in epoxy, urethane, acrylic and polyester formulations separately or at the same time (hybrids). Aromatic structures generally provide rigidity and thus may help to achieve certain desired properties for the powder coating resins. However, they are not very useful for outdoor applications since the aromatic unit is susceptible to UV or sun light photodegradation. In contrast, aliphatic ones are resistant to UV and sunlight but they require high molecular weights to meet the T_g requirements. This generally results in poor mechanical properties and low chemical resistance. Therefore, in this project syntheses of new aliphatic polymers which have higher T_g's were targeted.

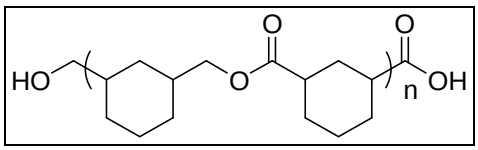

Figure 1.7. Aliphatic polyester.

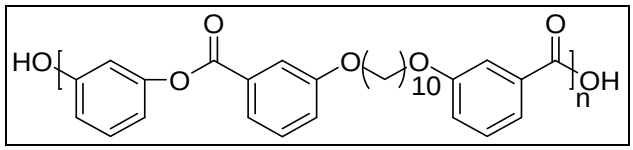

Figure 1.8. Aromatic polyester.

1.4.3. Cyclopolymers as Potential Resins for Powder Coatings

Cyclopolymers can be used as an alternative base resin polymer. They are rigid enough to replace the aromatic resins. Also they don't have double bond. Several cyclopolymers are reported in the literature. They are synthesized by conventional free radical methods. But for powder coating we should have control on both molecular weight and also on end groups. The first is needed for adjusting the desired T_g; the second is needed for the crosslinking reactions in the curing step. So the desired cyclopolymers should be synthesized via controlled polymerization and they should also have reactive end groups for functionalization. Therefore for the synthesis of reactive cyclopolymers with desired molecular weights atom transfer radical polymerization technique was investigated.

1.5. Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is one of the most efficient controlled/living radical polymerization (CRP) method [6]. It has gained increasing interest due to the relatively mild reaction conditions, availability of plenty of monomers, initiators and catalysts, and in particular its versatility in the synthesis of polymers with predictable

molecular weights, low polydispersities with specific functionalities and various architectures.

1.5.1. Kinetics and Mechanism of ATRP

The general mechanism of ATRP is shown in Figure 1.9. The dormant species are the activated alkyl halides, and the active species are the propagating radical chains. Since the halide and the radical species before and after the addition of the monomers possess comparable reactivities, the activation-addition-deactivation cycle repeats itself until all of the monomer present is consumed. This process results in a chain-growth polymerization [7].

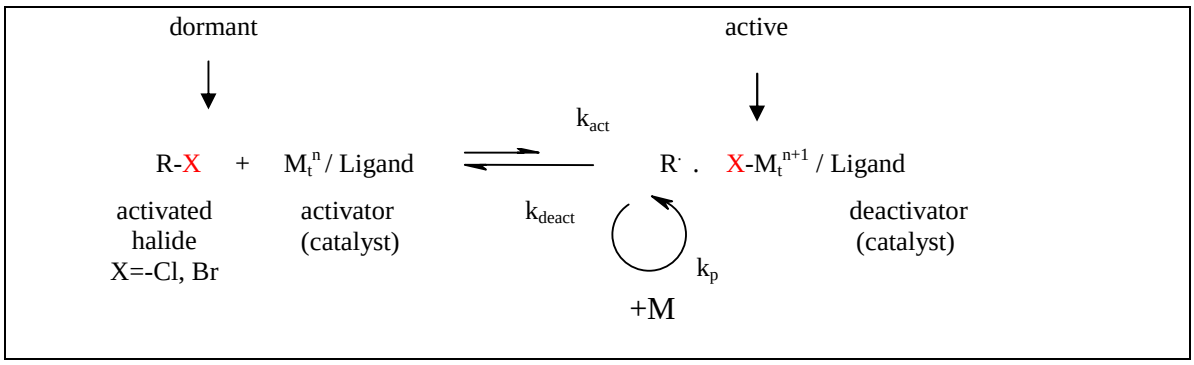

Figure 1.9. The mechanism of ATRP.

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

The rate of ATRP shows first-order kinetic with respect to the monomer, initiator and transition metal complexes. The degree of control in ATRP is strongly affected by the position of the equilibrium ($K_{ATRP}=k_{act}/k_{deact}$) and by all rate constants. K_{ATRP} depends on the solvent, temperature, monomer (i.e. structures PX and P•), and structure of Cu/Ligand complexes [7].

In a successful ATRP, the number of added monomer molecules at one activation step is limited so that polymers with low polydispersities can be obtained. This means $k_{act}<k_{deact}$. This also reduces the probability of side reactions such as termination reactions. Actually, termination as a side reaction in any radical polymerization is unavoidable; however, the activation-deactivation cycle in ATRP minimizes termination by creating a steady, low concentration of short-lived, active radical chain ends [8]. This provides the livingness of most of the polymer end groups and low polydispersity. In addition, since the initiator is consumed at early stages of the ATRP process, the molecular weight distribution of the resulting polymers are low.

1.5.2. Components of ATRP

ATRP is a multi-component system and the successful control depends on the right balance between them. Generally, ATRP technique requires four main components; monomer, initiator, transition metal and ligand. Solvent and sometimes additives may be used. For successful ATRP, temperature and reaction time should also be considered [6].

1.5.2.1. Monomers

Almost all monomers used in free radical polymerizations have been successfully polymerized via ATRP, e.g. styrene derivates, (meth) acrylates, (meth)acrylamides, (meth)acrylic acid salts, vinylpyridine and acrylonitrile. Various monomers can also be used in the copolymerization using ATRP, for instance isobutene, isobutyl vinyl ether, maleimides, vinylchlorides and vinylacetate (Figure 1.10).

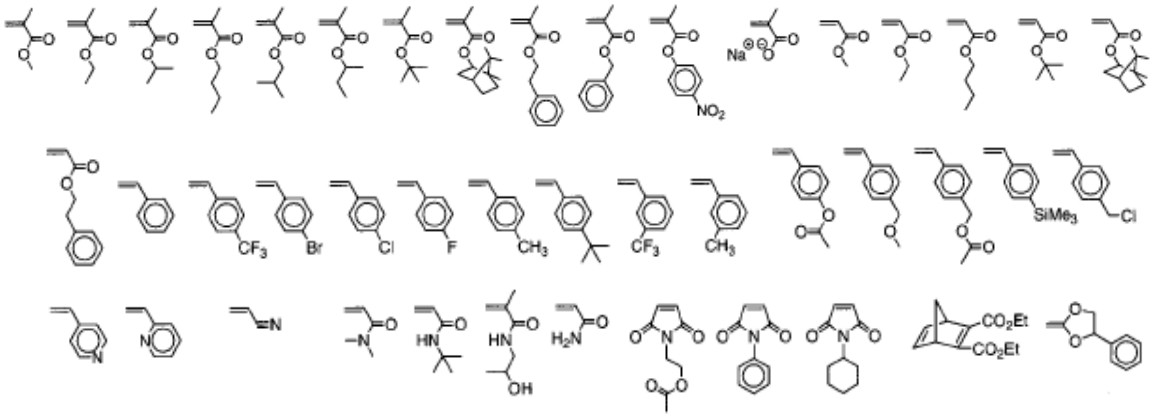

Figure 1.10. Monomers used in ATRP.

Monomers often have a major effect on the ATRP reaction, several variables can be listed for the influence of the used monomer, including:

1. The solubility characteristics of the monomer and the copper-complex
2. The kp of the monomer will affect the polymerization rate. When a monomer with a high polymerization rate is used, multiple monomer additions per activation/deactivation step can occur causing a broadening of the molecular weight distribution, especially at low conversion and low initiator efficiency.
3. Each monomer used in a polymerization will result in an alkyl halide with a specific redox potential. This will influence the atom transfer equilibrium constant (Keq), the (de)activation constant, and thereby change the radical concentration present in the system.
4. Some halide containing polymer end-groups can have, aside from halogen atom exchange, specific interactions with the copper species present in the reaction [9].

1.5.2.2. Initiators

In ATRP initiators can be selected from a broad range of halogen containing compounds including alkyl halides with activated substituents on the α-carbon, arenesulfonyl chlorides [10,11] and polyhalogenated compounds. Macro-initiators can also be employed; including polymers prepared using ATRP, halogen containing polymers or halogen end functionalized polymers [12].

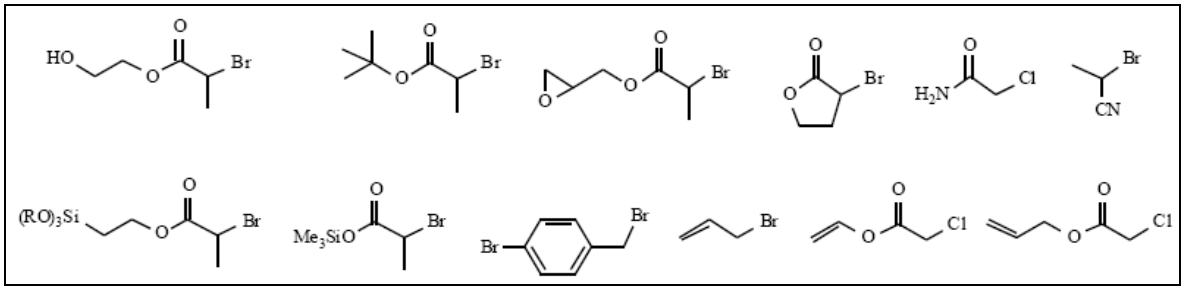

Figure1.11. Some of the ATRP initiators.

An efficient control over the molecular weight and polydispersity in ATRP is reached if the contribution of side-reactions is low, the initiation rate surpasses, or at least equals,

the observed propagation rate and if the initiation is quantitative. Many factors can influence the initiation rate, including: [13]

1. The bond strength of the carbon-halide bond. The bond strength of alkyl chlorides is generally higher than the one of alkyl bromides, thus lowering the activation coefficient (K_a) of alkyl chlorides.
2. The stability of the formed radicals. The stability of the formed radical will generally increase with the number of alkyl side-groups on the radical center, and will therefore be formed easier. Tertiary halides will be better initiators in that respect than secondary, which will be better than primary halides.
3. The effectiveness of the stabilizing groups. A rough classification of groups can be written, according to the stabilizing effect they have on the radical in the following order: CN>C(=O)R>C(=O)OR≈Ph>Cl>Me.
4. The possible formation of anions. When the initiators form very electron deficient radicals, outer sphere electron transfer could occur during activation, leading to radical anions susceptible for side reactions.

It can not be unambiguously stated that a fast carbon-halogen bond cleavage will lead to better results. Fast initiation will generally produce radicals that are more stable and this could lead to a less efficient initiation and may increase the susceptibility for side reactions. Moreover the high initial radical flux will induce bimolecular ‘irreversible’ termination, and the concentration of CuII species will rapidly increase at the beginning of the polymerization thereby decreasing the polymerization rate. The disadvantage of fast initiation is frequently overcome by a slow addition of the initiator (ca. 5 min.).

1.5.2.3. Transition Metals

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

later, the oxidized metal center donates the halogen back to the growing radical where reduction of the metal center occurs.

The requirements for the catalyst efficiency are [13]:

- The metal complex must have an accessible one-electron redox couple to promote atom transfer.
- Upon one-electron oxidation, the coordination number of the metal center must increase by one in order to adapt a new ligand. For example, in most systems with the copper-based ATRP, the lower oxidation state of the metal is assumed to be tetra coordinate and the higher oxidation state is presumed to be penta coordinate.
- The catalyst must show selectivity for atom transfer and therefore possess a low affinity for alkyl radicals and the hydrogen atoms an alkyl groups. If not, then the transfer reactions, such as β-H elimination and the formation of organometallic derivatives, may be observed.
- The metal center must not be a strong Lewis acid; otherwise the ionization of certain initiators/end groups to carbocations may occur.

There are plenty of transition metal complexes including complexes based on early, middle and late transition metals(e.g. Ru, Fe, Ni, Pd, Rh, Re) [[14],[15]] that have been studied and enhanced as efficient ATRP catalyst [16]. Of all the transition metals studied, copper appears to be the most satisfactory in terms of price and versatility. A variety of monomers including styrene and its derivatives, (meth)acrylic esters and acrylonitrile can be polymerized in controlled fashion[17].

1.5.2.4. Ligands

The ligand plays an important role in the activation/deactivation equilibrium in ATRP.

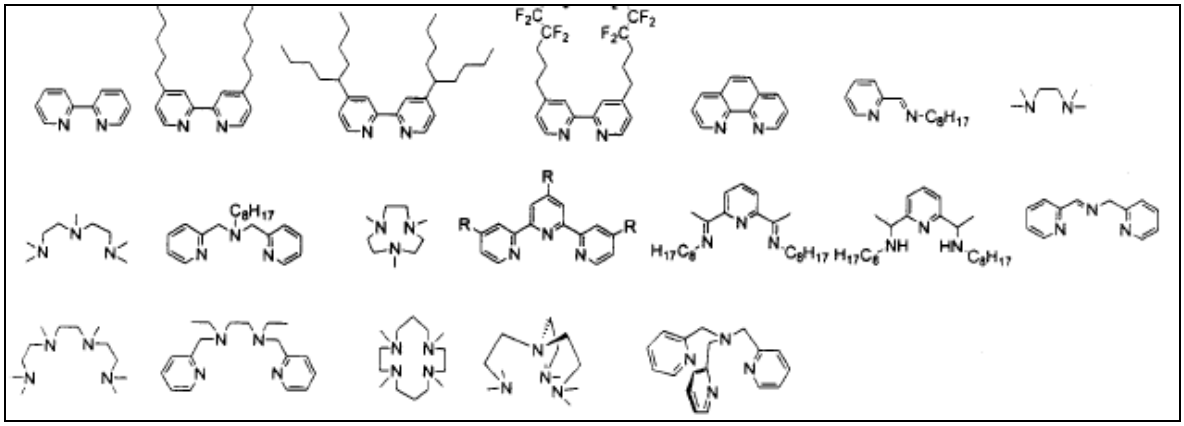

Figure 1.12. Examples of ligands used in ATRP.

Factors affecting the activity include:

1. The electronic effect. The combination of the copper species and the ligand has a large influence on the activation and deactivation coefficients. The complex must have an accessible one-electron redox couple to promote the atom transfer reaction, but should not be a very strong Lewis acid to prevent ionization of the end-groups. The electronic effect of the complex is shown by a significant decrease of the polymerization rate when electron withdrawing substituents are used as R-groups in a ligand. An electron withdrawing ligand will destabilize the complex involving the metal at its higher oxidation state and thereby increase the deactivation constant and decrease the polymerization rate. Also extensive studies on the structure-activity relation of tri-[18] and quadridentate [19] amine ligands have been performed using cyclic voltammetry [20]. From these studies it could be concluded that the activity of the complex increased in the order of aryl amine<arylimine<<alkyl imine<pyridine≈alkylamine as complex promoting sites of the ligand.

2. The solubility of the complexes with the metal at different oxidation states. When one of the oxidation states of the complex is less soluble, a heterogeneous system can originate, changing the rate of polymerization. Moreover, if the complex at its higher oxidation state is less soluble, deactivation will decrease which can result in higher polymerization rates and in an increase of the fraction of irreversibly terminated ‘dead’ chains. The solubility (parameters) of the ligand can be changed, by the choice of the side-groups (R).

3. Steric effects. They can influence the equilibrium by blocking the space for the halogen atom transfer, for example 6,6’ disubstituted bipyridine can totally inhibit

ATRP [12]. To enable halogen transfer the coordination number of the complex must also be able to increase by one to accommodate the incoming halogen atom.

4. The activity of the copper/ligand complex depends on the number of sites of the ligand available for complexation with the metal species. The activity decreases with an increasing number of active sites. The number of carbon atoms linking the active sites has also an effect on the activity of the copper/ligand complex, decreasing with the number of connecting carbon atoms, 2>3>>4 [21].

To promote ATRP for industrial purposes new systems are evaluated with recoverable copper complexes. Systems that are investigated include fluorinated ligands in which the copper/ligand complex separates from the polymerization mixture at low temperatures [22], polymer based ligands [23,24], and the immobilized ligands [25], [26] Ionic liquids can also be used as a medium for polymerization, and the polymer can be recovered by extraction with a conventional solvent [27].

1.5.2.5. Solvents

ATRP can be performed in bulk, in solution and in heterogeneous systems (e.g. emulsion and suspension). The solvent can have a large influence on the polymerization reaction, both on the reaction rate and the final properties of the prepared polymer. Matyjaszewski *et al.* [28] the polymerization of butyl acrylate, with 1- phenylethyl-1-bromide as initiator and Cu(I)Br/bipyridine complex as catalytic system, in different solvents. Their research showed that the solvent largely influences the polymerization rate which decreased in the order: ethylene carbonate>bulk>anisole>1,4- dimethoxy benzene>biphenyl ether>propylene carbonate. The influence of solvents on the reaction rate is attributed to a change in the copper complex and/or a change in the solubility of the copper complex.

1.6. Cyclopolymerization of Tert-butyl α-(Hydroxymethyl)acrylate Ether Dimers via ATRP

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

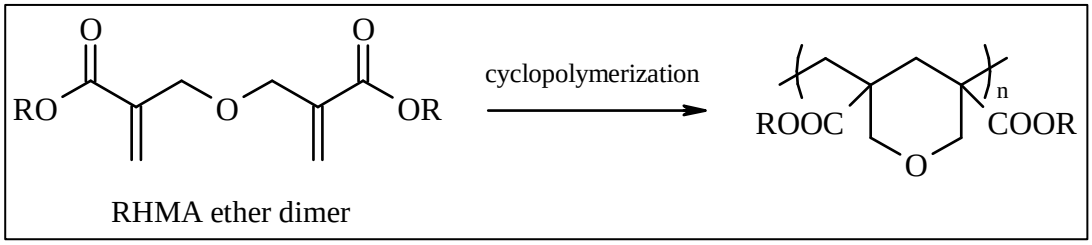

Figure 1.13. Cyclopolymerization of RHMA ether dimers.

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

The results showed that as the bulkiness increases, cyclization efficiency increases.[32] For example, the polymerization of ethyl α-(hydroxymethyl)acrylate ether dimer gave crosslinked polymers while the monomer with t-butyl group gave cyclopolymers with six-membered tetrahydropyran units. These results are consistent with the results obtained on the cyclization efficiency in conventional radical polymerization [29,30].

1.7. End Group Functionality of Polymers

In order to get telechelic polymers via ATRP, there are two main approaches used. The first approach is to use a functional group containing initiator which will allow

obtaining a polymer with monofunctional end-group. The other end group which is halogen can also be turned into the same functionality by simple organic reactions. The second approach is to use a di functional initiator that will make both ends halogen group and after that the ends can be turned easily to the desired functionality by a simple organic reaction.

The halogen atom can be replaced via several reactions which lead to end functional polymers (Figure 1.14.) [31].

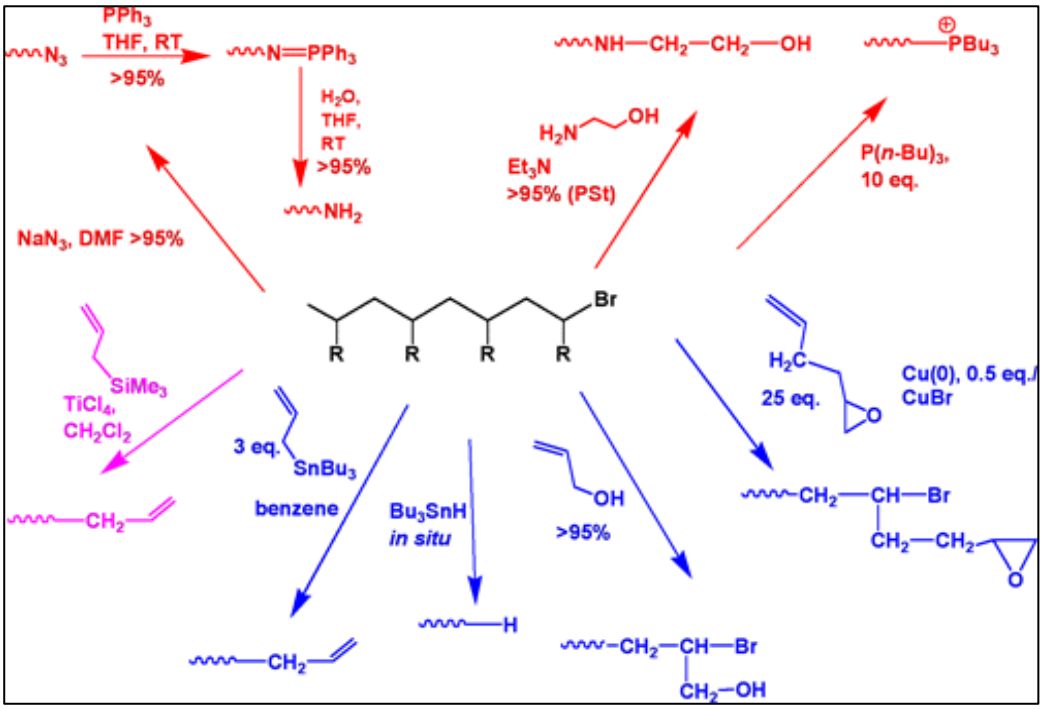

Figure 1.14. End group transformation of polymers prepared by ATRP.

1.8. Objective of the Study

ATRP of TBHMA ether dimers has been previously reported by our research group. However, optimization studies such as control of molecular weights and the tuning of the glass transition temperature for powder coating were not studied. Also end groups modifications were not investigated previously.

In this study, the aim is to get living cyclic polymers with reasonable polydispersities with specific molecular weights (Mw 5000-7000) and T_g (60-80 ^oC) for powder coating applications. For these cyclopolymers it was also desirable to have reactive end groups or pendant groups for crosslinking (curing) process. Thus, studies targeting the synthesis of reactive polymers were also undertaken.

2. EXPERIMENTAL PART

2.1. Monomer Synthesis

2.1.1. Materials

Tert-butyl acrylate (Acros Organics, 99%), paraformaldehyde (Sigma-Aldrich), 1,4diazabicyclo[2.2.2]octane (DABCO) (Fluka, >95.0%), t-butyl alcohol (Merck, 99%), hydrochloric acid (HCl) (Sigma-Aldrich, 37%), potassium permanganate ($KMnO_4$), Sodium Bicarbonate ($NaHCO_3$) (Riedel-de Haen, 99%), Diethylene glycol (Fisher, 98%), Tetra ethylene glycol (Fisher, 98%), 2-Bromo-2- methylpropionyl bromide (Acros, 98%), Triethyl amine (TEA) (Merck, 99%), 4-Dimethylaminopyridine (DMAP) (Acros, 99%) were used as received without purification. The solvents; methylene chloride (CH_2Cl_2), hexane, methanol, tetra hydro furan (THF) were all obtained from Merck and used as received.

2.1.2. Apparatus

^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra's were recorded using a Varian Gemini 400 MHz spectrometer.

2.1.3. Synthesis of Tert-Butyl α-(Hydroxymethyl)acrylate Ether Dimer

t-Butyl acrylate (137.80 g, 1.09 mol), Para formaldehyde (32.3 g, 1.08 mol), 1,4-diazabicyclo[2.2.2]octane (DABCO) (5.38 g, 2.9 wt%) and t-butyl alcohol (8.70 g, 4.7wt%) were added into a 250 mL three-necked round-bottom flask fitted with a condenser and a magnetic stirrer. The mixture was stirred at 95 ^{o}C for 4 days. The reaction progress was monitored by thin layer chromatography (TLC) using silica gel plates and CH_2Cl_2 as the eluting and diluting solvent. TLC plates were visualized using potassium permanganate solution. At the end of the fourth day, the mixture was diluted with 200 mL of methylene chloride, extracted three times with 100 mL of 3% HCl, and then with 100 mL of distilled water. The organic layer was separated and evaporated under reduced

pressure to give crude monomer. The pure monomer was obtained from silica column eluted by hexane/methanol mixture (99/1) as a clear liquid in 60-80 per cent yield.

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

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

2.1.4. Synthesis of Diethylene Glycol di Initiator (DEG)

Diethylene glycol (1.88 g, 0.018 mol), triethyl amine (4.34 g, 0.043 mol), 4-dimethylaminopyridine (DMAP) (0.12g, 5 mol%), and 30 mL THF were added into a 100 mL three-necked round-bottom flask fitted with a condenser and a magnetic stirrer. Using ice bath for cooling, 10.66 g of 2-Bromo-2- methylpropionyl bromide and 10 mL of THF were added 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 CH_2Cl_2 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 200 mL methylene chloride, extracted firstly two times with 100 mL of distilled water, then three times with 100mL of 0.5 N HCl, three times with 100 mL of saturated sodium bicarbonate ($NaHCO_3$) solution and then two times with 100 mL distilled water. The organic layer was separated and evaporated under reduced pressure to give crude monomer. Evaporation of the solvent gave the pure DEG initiator as a light brown liquid in around 80 per cent yield.

^{13}C-NMR ($CDCl_3$): δ= 30.95 (CH_3), 55.40 (C-(*C*H_3)$_2$), 65.28 (CH_2-O), 69.02 (CH_2-O), 171.73 (C=O) ppm.

^{1}H-NMR ($CDCl_3$): δ= 2.00 (s, 12H, CH_3), 3.70 (t, 4H, OCH_2), 4.30 (t, 4H, OCH_2) ppm.

2.1.5. Synthesis of Tetra Ethylene Glycol di Initiator (TEG)

Tetra ethylene glycol (3.49 g, 0.017 mol), triethyl amine (4.30 g, 0.041 mol), 4-dimethylaminopyridine (DMAP) (0.12g, 5 mol%), and 30 mL THF were added into a 100 mL three-necked round-bottom flask fitted with a condenser and a magnetic stirrer. Using ice bath for cooling 11.19 g of 2-Bromo-2- methylpropionyl bromide and 10 mL of THF were added 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 CH_2Cl_2 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 300 mL methylene chloride, extracted firstly three times with 100 mL of distilled water, secondly three times with 150mL of 0.5 N HCl, thirdly three times with 120 mL of saturated Sodium Bicarbonate ($NaHCO_3$) solution and then two times with 120 mL distilled water. The organic layer was separated and evaporated under reduced pressure to give crude initiator. Evaporation of the solvent gave the pure TEG initiator as a light brown liquid in 85 per cent yield.

^{13}C-NMR ($CDCl_3$): δ= 30.89 (CH_3), 55.88 (C-(CH_3)$_2$), 65.22 (CH_2-O), 67.96 (CH_2-O), 69.96 (CH_2-O), 70.76 (CH_2-O), 171.56 (C=O) ppm.

^{1}H-NMR ($CDCl_3$): δ= 1.95 (s, 12H, CH_3), 3.62 (m, 8H, OCH_2), 3.71 (t, 4H, OCH_2), 4.30 (t, 4H, OCH_2) ppm.

2.1.6. Synthesis of glycidyl α-(Hydroxymethyl)acrylate Ether Dimer

TBHMA ether dimer (30.00 g, 0.1mol) was added into a 100 mL three-necked round-bottom flask fitted with a condenser and a magnetic stirrer. Thionyl chloride ($SOCl_2$) (70 ml, 0.96 mol) was added 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 CH_2Cl_2 as the eluting and diluting solvent. TLC plates were visualized using potassium permanganate solution. At the end of two hours, reaction heated to 45 ^{0}C and after 36 hours reaction stopped. Excess $SOCl_2$ was evaporated via N_2 by using strong base

solution containing tramps. The obtained product was 36 g and used without further purification.

The acid chloride dimer synthesized divided into two fractions. Acid chloride dimer (18 g, 0.08 mol), Triethyl amine (10.2 g, 0.1 mol), 4-Dimethylaminopyridine (DMAP) (1.3229g, 5 mol%), and 50 mL CH_2Cl_2were added into a 250 mL three-necked round-bottom flask fitted with a condenser and a magnetic stirrer. Using ice bath for cooling 35.2515 g of Glycidol and 50 mL of CH_2Cl_2 were added 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 CH_2Cl_2 as the eluting and diluting solvent. TLC plates were visualized using potassium permanganate solution. At the end of two hours, the mixture was extracted firstly three times with 50 mL of saturated Sodium Bicarbonate ($NaHCO_3$) solution, secondly three times with 50mL of 0.5 N HCl, thirdly two times with 50 mL of distilled water. The organic layer was separated and evaporated under reduced pressure to give a brown viscous liquid as the impure glycidyl dimer monomer. The pure monomer was obtained from silica column eluted by CH_2Cl_2 as a brown viscous liquid in 8 g. Because of wrong identification, wrong fraction was taken. So, from the second fraction of acid chloride dimer throughout the same procedure 1.4 g of pure monomer was obtained.

^{13}C-NMR ($CDCl_3$): δ= 44.82 (ring CH_2), 49.48 (ring CH), 65.41 (CH_2), 69.56 (CH_2-O), 127.00 (*C*=CH_2), 136.80 (*C*H_2=C), 165.54 (C=O) ppm.

^{1}H-NMR ($CDCl_3$): δ= 2.64 (q, 4H, ring CH_2), 2.83 (q, 4H, ring CH_2), 3.23 (m, 2H, ring CH), 4.00 (q, 4H, CH_2), 4.25 (s, 4H, OCH_2), 4.48 (q, 4H, CH_2), 5.93 (s, 2H, CH=C), 6.36 (s, 2H, CH=C) ppm.

2.2. Polymer Synthesis

2.2.1. Materials

Ethyl-2-bromoisobutyrate (Fluka, >97.0%), copper (I) bromide (CuBr) (Aldrich, 99.999%), and pentamethyldiethylene triamine (PMDETA) (Aldrich, 99%) were used as received without purification. The synthesized initiators (DEG and TEG) were used

directly. The solvents; methylene chloride and methanol were obtained from Merck and used as received. Xylene (mixture of isomers) was purified by distillation over Na metal and benzophenone.

2.2.2. Apparatus

^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Varian Gemini 400 MHz spectrometer. GPC analyses were done using a Viscotek GPCmax VE-2001Analysis System. PL Gel 5 µm MIXED-C Column 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 via basic aluminum oxide columns to remove the copper catalyst followed by two reprecipitations before NMR, GPC, DSC and TGA analyses.

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

All glassware, needles and stirring bars were dried overnight in an oven at 150 ^{o}C and purged with nitrogen gas before use. All liquid chemicals were purged with nitrogen for at least 20 minutes prior to use. The polymerization of RHMA ether dimers was conducted in a three-necked round bottom flask using xylene as the solvent. The reaction flask fitted with a stirring bar was sealed with rubber septa and purged with nitrogen for 15 minute. Then the monomer was dissolved in 7 mL xylene and transferred into the reaction flask by syringe. The solution was stirred and purged with nitrogen for 20 min. Then, the solution was immersed into a preheated oil bath. 2 mL of this solution was taken via syringe and added onto CuBr which was sealed with rubber septa in a vial and purged with nitrogen for 15 minute. PMDETA was added to this solution containing the CuBr. The resulting solution was stirred and heated until homogenous. This solution was then transferred into the reaction flask by syringe. The initiator was introduced into the reaction flask by syringe. Polymerizations were carried out under nitrogen at the proper temperature. The final polymers were dissolved in methylene chloride and precipitated into methanol/water and dried in a vacuum oven overnight.

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

2.2.4. The Procedure for the Purification of the Resulting Polymers

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

2.2.5. ATRP of *tert*-Butyl α-(Hydroxymethyl)acrylate Ether Dimer with EBiB

Experiment 1. TBHMA ether dimer (1.04 g, 3.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (9.8 mg, 0.068 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 70 ^{o}C for 6 hours. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially yellow and clear and turned yellow-green, dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 4 ml methylene chloride and precipitated into 40 mL methanol and 8 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.63 g, in a 63 per cent yield. Mw= 5800, PDI= 1,17.

Experiment 2. TBHMA ether dimer (2.02 g, 6.8 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (9.7 mg, 0.068 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) initiator according to the given procedure. The polymerization was carried out at 70 ^{o}C for 8 hours. The CuBr solution was colorless before transferring into the reaction flask. The reaction mixture was initially yellow and clear and turned yellow-green, dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer

was dissolved with 6 ml methylene chloride and precipitated into 40 mL methanol and 8 mL water and dried in a vacuum oven overnight. The obtained polymer was powder, soluble, 0.72 g, in a 36 per cent yield. Mw= 10900, PDI= 1,19.

2.2.6. ATRP of *tert*-Butyl α-(Hydroxymethyl)acrylate Ether Dimer with DEG

Experiment 1 TBHMA ether dimer (1.02 g, 3.4 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (11.2 mg, 0.078 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and DEG (11 μL, 0.041 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 5.5 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.38 g, in a 38 per cent yield. Mw= 8400, PDI= 1,14.

Experiment 2. TBHMA ether dimer (1.04 g, 3.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (12.2 mg, 0.085 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and DEG (6 μL, 0.022 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 6 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.47 g, in a 47 per cent yield. Mw= 19000, PDI= 1,20.

2.2.7. ATRP of *tert*-Butyl α-(Hydroxymethyl)acrylate Ether Dimer with TEG

Experiment 1. TBHMA ether dimer (1.01 g, 3.4 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (11.6 mg, 0.081 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (6 μL, 0.022 mmol) initiator according to the given procedure.

The polymerization was carried out at 80 ^{o}C for 6.5 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 1.02 g, in a 102 per cent yield.

Experiment 2. TBHMA ether dimer (1.03 g, 3.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (11.2 mg, 0.078 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (11 μL, 0.041 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 5 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.95 g, in a 95 per cent yield.

Experiment 3. TBHMA ether dimer (1.37 g, 4.6 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (11.2 mg, 0.078 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (4 μL, 0.014 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 6 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.87 g, in a 64 per cent yield.

Experiment 4. TBHMA ether dimer (1.03 g, 3.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (11.6 mg, 0.081 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (46 μL, 0.134 mmol) initiator according to the given procedure.

The polymerization was carried out at 80 ^{o}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 dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.54 g, in a 54 per cent yield. Mw= 4840, PDI= 1,16.

Experiment 5. TBHMA ether dimer (1.06 g, 3.6 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (10.4 mg, 0.072 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (11 μL, 0.074 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}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 dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.75 g, in a 75 per cent yield. Mw= 12342, PDI= 1,26.

Experiment 6 (Kinetic study). All glassware, needles and stirring bars were dried overnight in an oven at 150 ^{o}C and purged with nitrogen gas before use. Xylene and PMDETA were purged with nitrogen prior to use. TBHMA ether dimer (6.05 g, 20.3 mmol) was added to a three-necked round bottom flask. The reaction flask fitted with a stirring bar was sealed with rubber septa and purged with nitrogen for 30 minute. 21 mL xylene was transferred into the reaction flask by syringe. 4 mL xylene and PMDETA (108 μL, 0.513 mmol) were added onto CuBr (73.6 mg, 0.515 mmol) which was sealed with rubber septa in a vial and purged with nitrogen for 15 minute. The resulting solution was stirred and heated until homogenous. This solution was then transferred into the reaction flask by syringe. Then, the reaction flask was immersed into a preheated oil bath at 80 ^{o}C. 180 μL TEG was introduced into the reaction flask by syringe. The reaction mixture was green-brown. The color did not change during polymerization. 4 mL samples were taken at regular intervals (20 min.) using a syringe purged with nitrogen. The resulting polymers were precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight.

2.2.8. ATRP of TBHMA Ether Dimer with TEG (Alcohol end group)

Experiment 1 TBHMA ether dimer (1.04 g, 3.6 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (12.3 mg, 0.086 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (20 μL, 0.068 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 7 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. At the second hour of reaction excess allyl alcohol (1g) added by syringe to the system. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.54 g, in a 54 per cent yield. Mw= 5763, PDI= 1,15.

Experiment 2 TBHMA ether dimer (1.34 g, 4.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (13.6 mg, 0.095 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (35 μL, 0.068 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 3 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. At the second hour of reaction excess allyl alcohol (1g) added by syringe to the system. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 1.00 g, in a 77 per cent yield. Mw= 7414, PDI= 1,24.

Experiment 3 TBHMA ether dimer (1.34 g, 4.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (14.1 mg, 0.098 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (40 μL, 0.068 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 3 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. At the second hour of reaction excess allyl

alcohol (1g) added by syringe to the system. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.9 g, in a 74 per cent yield. Mw= 5360, PDI= 1,24.

Experiment 4 TBHMA ether dimer (1.34 g, 4.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (13.6 mg, 0.095 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (30 μL, 0.068 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 3 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. At the second hour of reaction excess allyl alcohol (1g) added by syringe to the system. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 1.00 g, in a 70 per cent yield. Mw= 9307, PDI= 1,32.

Experiment 5 TBHMA ether dimer (1.34 g, 4.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (15.2 mg, 0.106 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (40 μL, 0.068 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 5 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. At the second hour of reaction excess allyl alcohol (1g) added by syringe to the system. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.85 g, in a 64 per cent yield. Mw= 5931, PDI= 1,37.

Experiment 6 TBHMA ether dimer (1.34 g, 4.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (13.8 mg, 0.096 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (40 μL, 0.068 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 5.5 hours. The CuBr solution was light

green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. At the second hour of reaction excess allyl alcohol (1g) added by syringe to the system. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.80 g, in a 59 per cent yield. Mw= 5462, PDI= 1,24.

Experiment 7 TBHMA ether dimer (1.34 g, 4.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (17.0 mg, 0.119 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (40 μL, 0.068 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 6 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. At the second hour of reaction excess allyl alcohol (1g) added by syringe to the system. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.95 g, in a 71 per cent yield. Mw= 5200, PDI= 1,25.

2.2.9. ATRP of TBHMA Ether Dimer with TEG (Acid end group)

Experiment 1 TBHMA ether dimer (1.34 g, 4.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (16.8 mg, 0.117 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (40 μL, 0.068 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 24 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. At the second hour of reaction excess 10-undecenoic acid (1g) added by syringe to the system. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.95 g, in a 70 per cent yield. Mw= 6571, PDI= 1,23.

Experiment 2 TBHMA ether dimer (1.34 g, 4.5 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (14.7 mg, 0.103 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (40 μL, 0.068 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 5.5 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. At the second hour of reaction excess 10-undecenoic acid (1g) added by syringe to the system. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.81 g, in a 61 per cent yield. Mw= 4994, PDI= 1,22.

Experiment 3 TBHMA ether dimer (1.14 g, 3.8 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (13.2 mg, 0.092 mmol) and PMDETA (16 μL, 0.076 mmol) catalyst system and TEG (30 μL, 0.051 mmol) initiator according to the given procedure. The polymerization was carried out at 80 ^{o}C for 5 hours. The CuBr solution was light green before transferring into the reaction flask. The reaction mixture was initially light green and clear and turned dirty green and deep green-brown with time. The reaction mixture was homogeneous during the polymerization. At the second hour of reaction excess 10-undecenoic acid(1g) added by syringe to the system. The resulting polymer was dissolved with 3 ml methylene chloride and precipitated into 50 mL methanol and 10 mL water and dried in a vacuum oven overnight. The obtained polymer was glasslike, soluble, 0.67 g, in a 58 per cent yield. Mw= 6947, PDI= 1,21.

3. RESULTS AND DISCUSSION

In the project, as mentioned before the aim was to get cyclic aliphatic polymers from acrylic acid ester ether dimers via atom transfer radical polymerization which can be used as powder coating base resins. Cyclopolymers that had been previously synthesized in our group had relatively high T_g's and were monofunctional. These polymers also needed to be functionalized at their end groups for the crosslinking reaction which is required for powder coating resins.

In the following section the results of the cyclopolymerization of t-butyl derivatives of RHMA ethers dimers by ATRP with optimized T_g and Mw will be presented. First, the synthesis and characterization of the monomers and the results from the cyclopolymerization studies will be presented. Then, functionalization of these polymers will be discussed.

3.1. Optimization study of Poly(TBHMA)

3.1.1. Synthesis of the TBHMA ether dimers

TBHMA ether dimers were synthesized by the extended Baylis-Hillman which is a tertiary amine-catalyzed coupling of an α,β-unsaturated carbonyl compound with an aldehyde[34]. Acrylates are one of the compounds which can undergo the Baylis-Hillman reaction. The reaction pathway that produces the TBHMA ether dimer is shown in Figure 3.1. The addition of formaldehyde to acrylate ester is catalyzed by 1,4-Diazabicyclo[2.2.2]octane (DABCO). Key step is the addition of the amine catalyst, DABCO, to α,β-unsaturated ester to form a stabilized nucleophilic anion. This *in situ* generated nucleophile then adds to the aldehyde and TBHMA product is obtained by the subsequent elimination of the amine. At higher temperatures, conversion of TBHMA to ether dimer which is shown in the Figure 3.1 is thermodynamically favorable. Conversion of TBHMA 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 TBHMA. Therefore, removal of the water from the reaction media leads to higher yields [35].

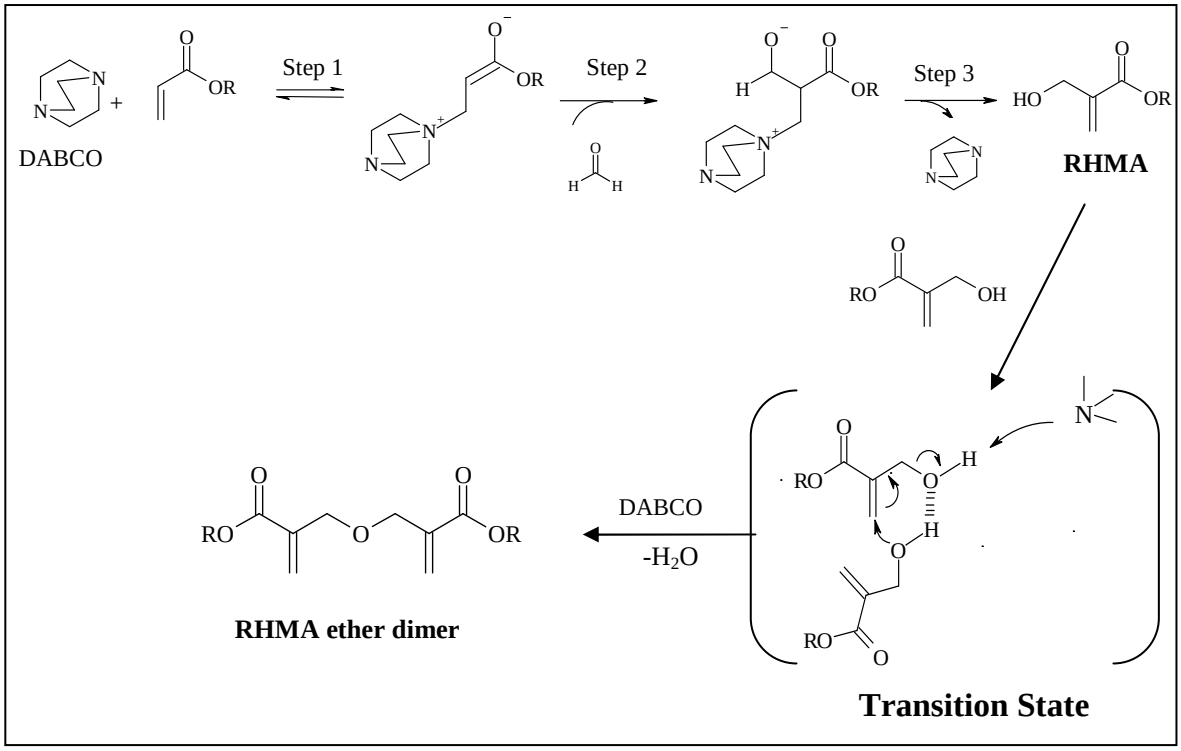

Figure 3.1. DABCO-catalyzed synthesis of TBHMA ether dimers.

3.1.2. Characterization of TBHMA ether dimers

The reaction progresses were screened by thin layer chromatography (TLC) using silica gel (SiO_2) plates and CH_2Cl_2 as the elution and dilution solvent. TLC screening of the reaction mixtures helped the actual time for the reaction completeness. Also it helped to screen the intermediates during the reaction progress. When reactants disappeared during the reactions, RHMA and its ether dimer appeared. The purification was carried out on basic Alox column. The ^{1}H-NMR and ^{13}C-NMR spectra of pure TBHMA ether dimer are shown in Figure 3.2 and Figure 3.3 respectively.

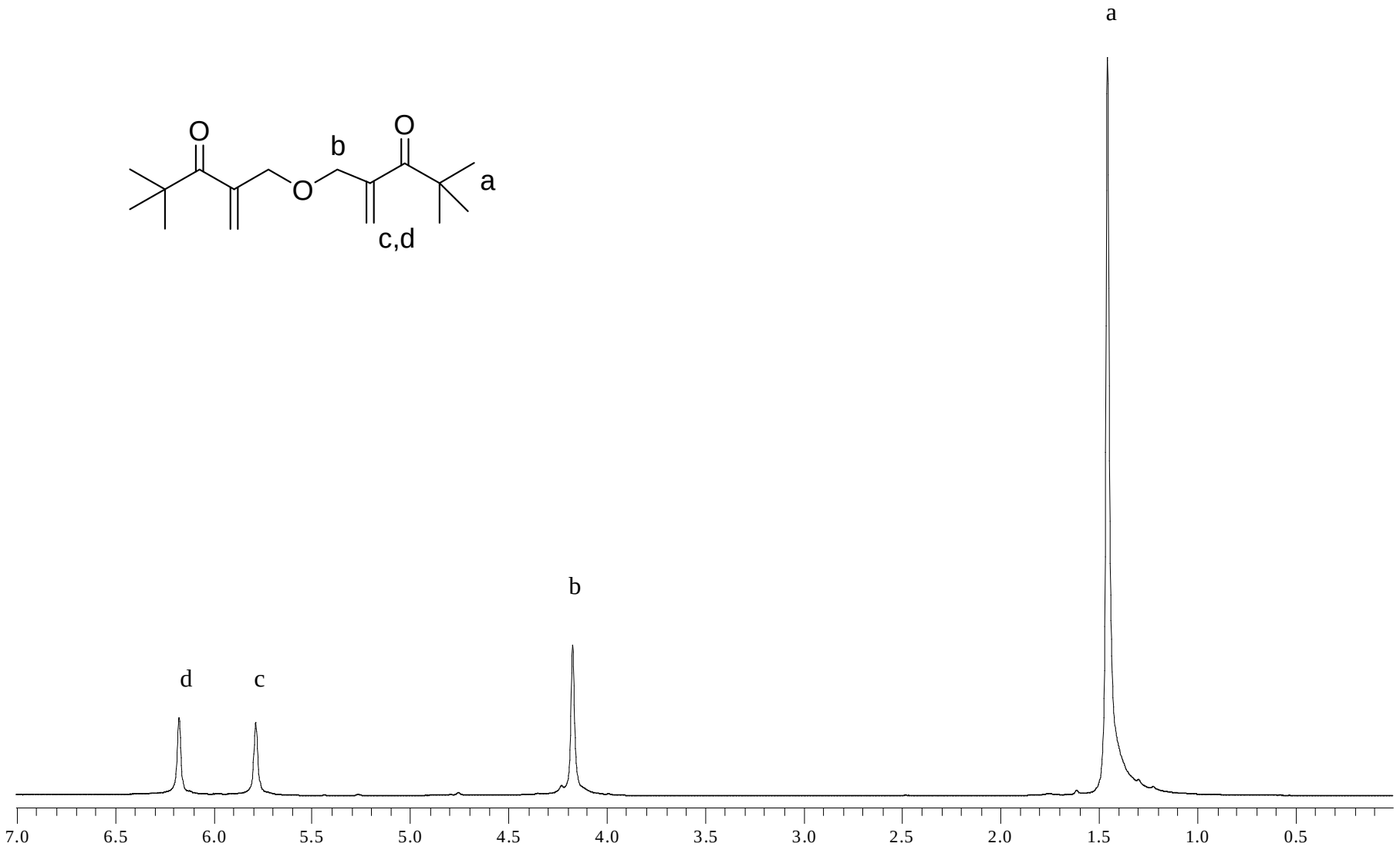

Figure 3.2. ^{1}H-NMR of TBHMA ether dimers.

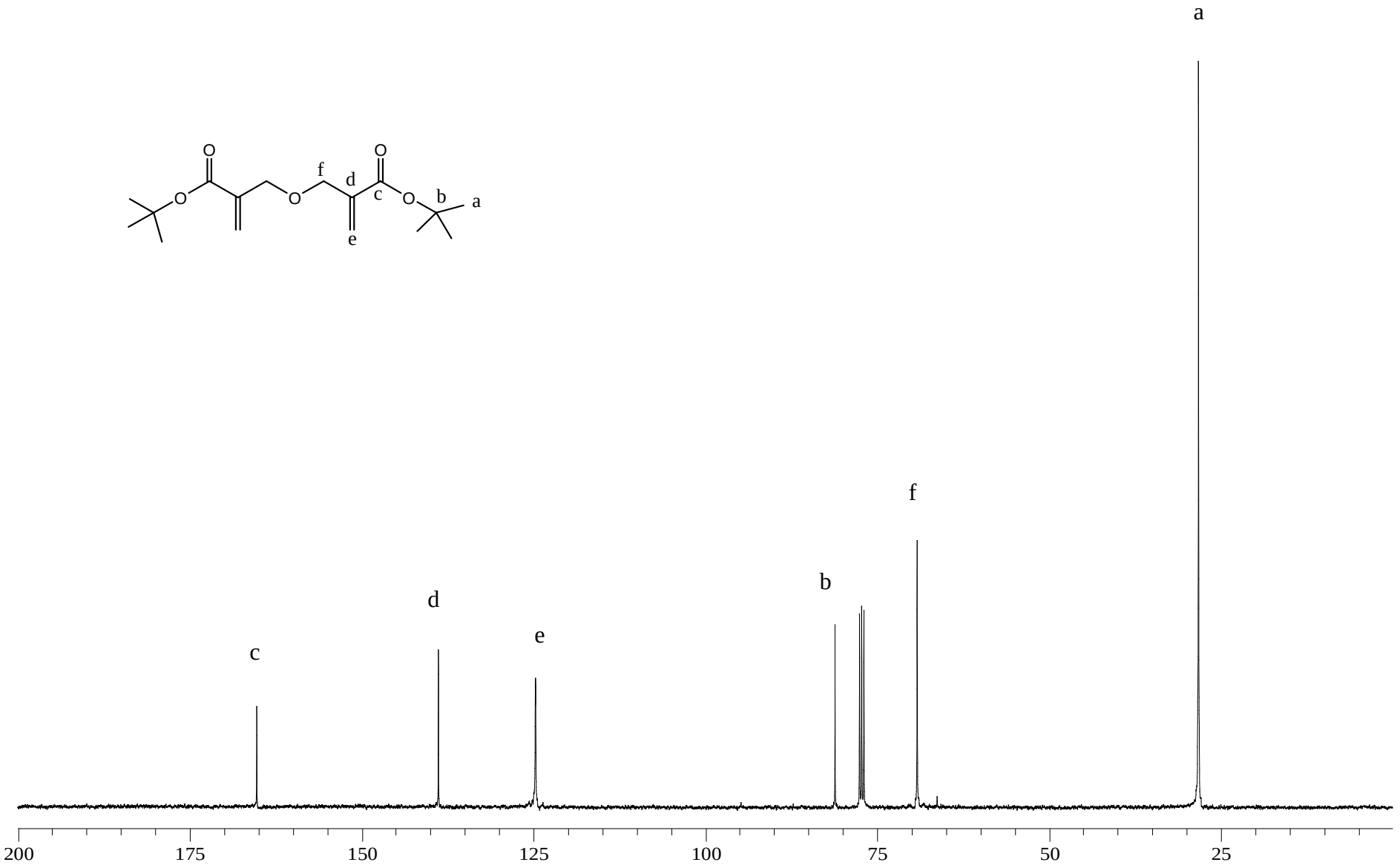

Figure 3.3. ^{13}C-NMR of TBHMA ether dimers.

3.1.3. Cyclopolymerization of TBHMA Ether Dimers by ATRP Using Soft Block Containing Di-initiators

The cyclopolymerization of TBHMA ether dimers were previously successfully carried out in our research group. For the new set of polymerizations, the same catalyst-ligand-solvent system (CuX/PMDETA, xylene) was used except the ratio of monomer to initiator was changed in order to tune the molecular weights and glass transition temperatures. The general cyclopolymerization scheme is shown in Figure 3.4.

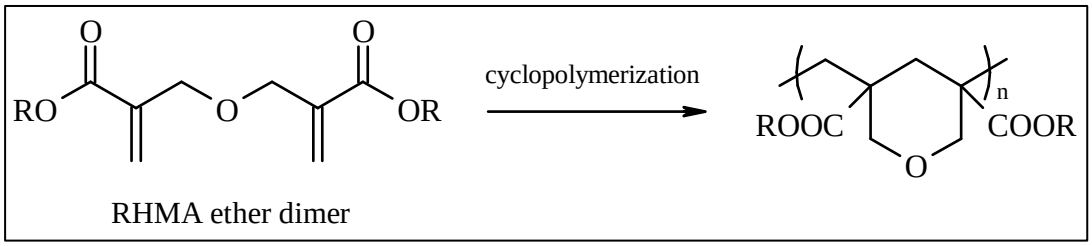

Figure 3.4. Cyclopolymerization of RHMA ether dimers.

Initially, ATRP was carried out with mono functional initiator EBiB and polymers with desired molecular weights and low polydispersities were obtained (Table 3.1, entries 1 and 2).

Table 3.1. The results from ATRP of TBHMA Ether Dimers at 80^0C.

Entry	Initiator	Conv [a]	$M_{n,cal}$	$M_{n,sec}$	M_w/M_n	T_g
1	EBiB	63	9400	5800	1,17	129
2	EBiB	36	10700	10900	1,19	149
3	DEG	38	9120	8400	1,14	106
4	DEG	47	22560	19000	1,20	137
5	TEG	54	3240	4840	1,16	57
6	TEG	75	9000	12342	1,26	127
7	TEG	67	8040	9408	1,26	100

[a] Measured by gravimetric methods

The T_g of the cyclopolymers obtained were measured. The results indicated that in the molecular weight range chosen the T_g depended on molecular weight. The T_g's were high even at relatively low molecular weights (Table 3.1). Since the target of the project was to obtain powder coating resins that could be cured at low temperatures, the T_g of

the polymers had to be decreased to about 55-75 ^{o}C. In addition, these preliminary trials were done using monofunctional initiators, and therefore, the end groups of the polymers obtained were only monofunctional. We needed to use a difunctional initiator to get a crosslinkable *difunctional* cyclopolymer. To solve both of the issues together, we decided to synthesize difunctional initiators that could decrease the T_g of the cyclopolymers. To achieve this, di- and tetra-ethylene glycol were incorporated into the di-initiator structure as soft blocks (Figure 3.5). The incorporation was achieved through di-esterification of the glycols with 2-bromo-2- methylpropionyl bromide.

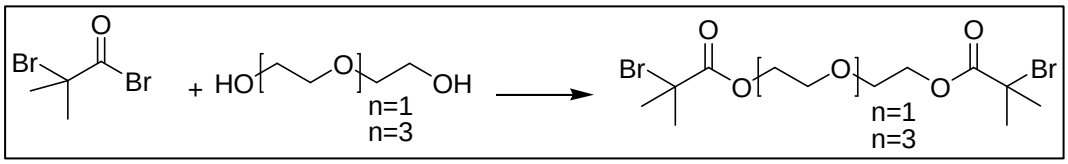

Figure 3.5. Synthesis of initiators using di- and tetra-ethylene glycol.

The NMR data of the synthesized di-initiators are shown in Figures 3.6, 3.7, 3.8 and 3.9.

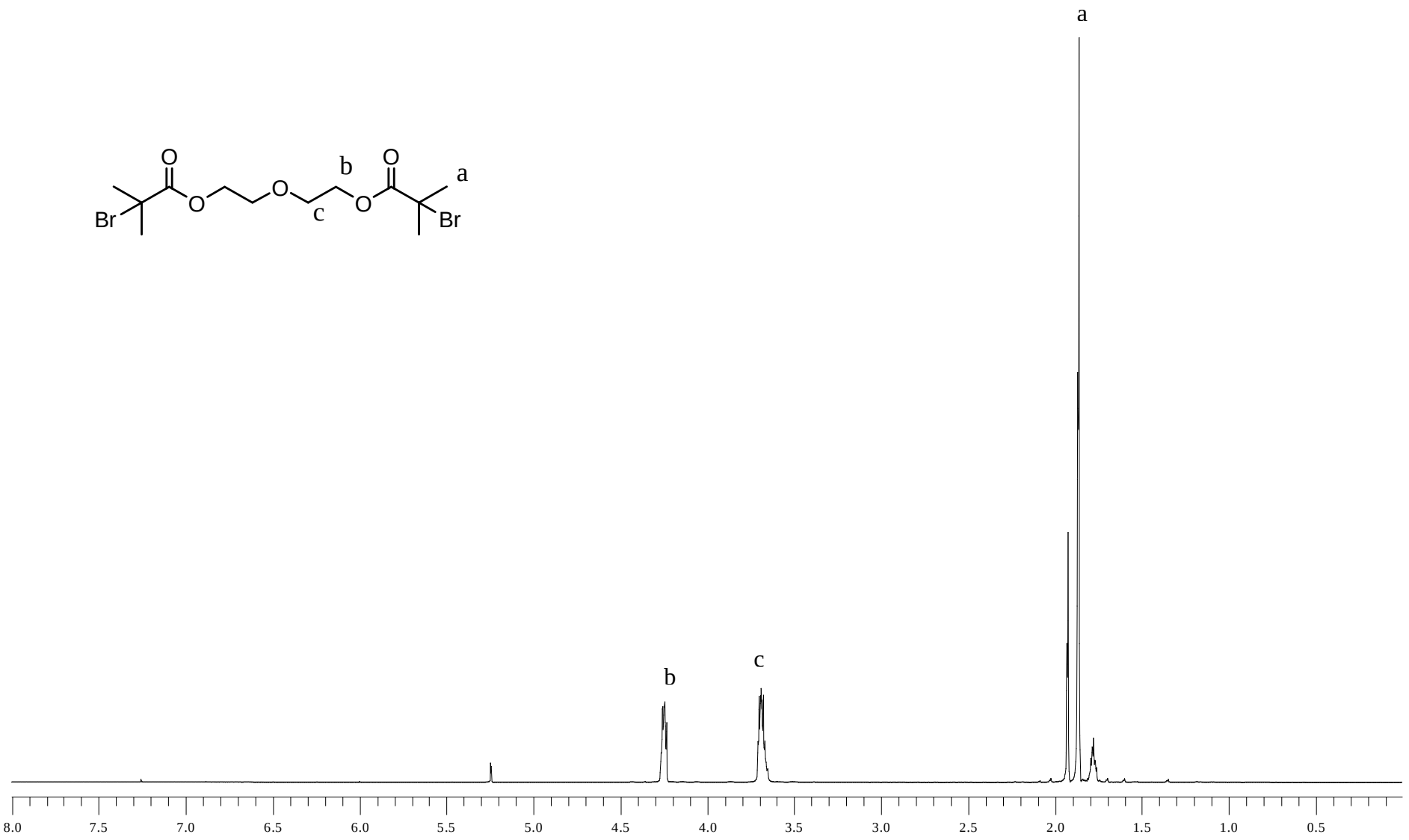

Figure 3.6. ^{1}H-NMR of Di-ethylene glycol di-initiator.

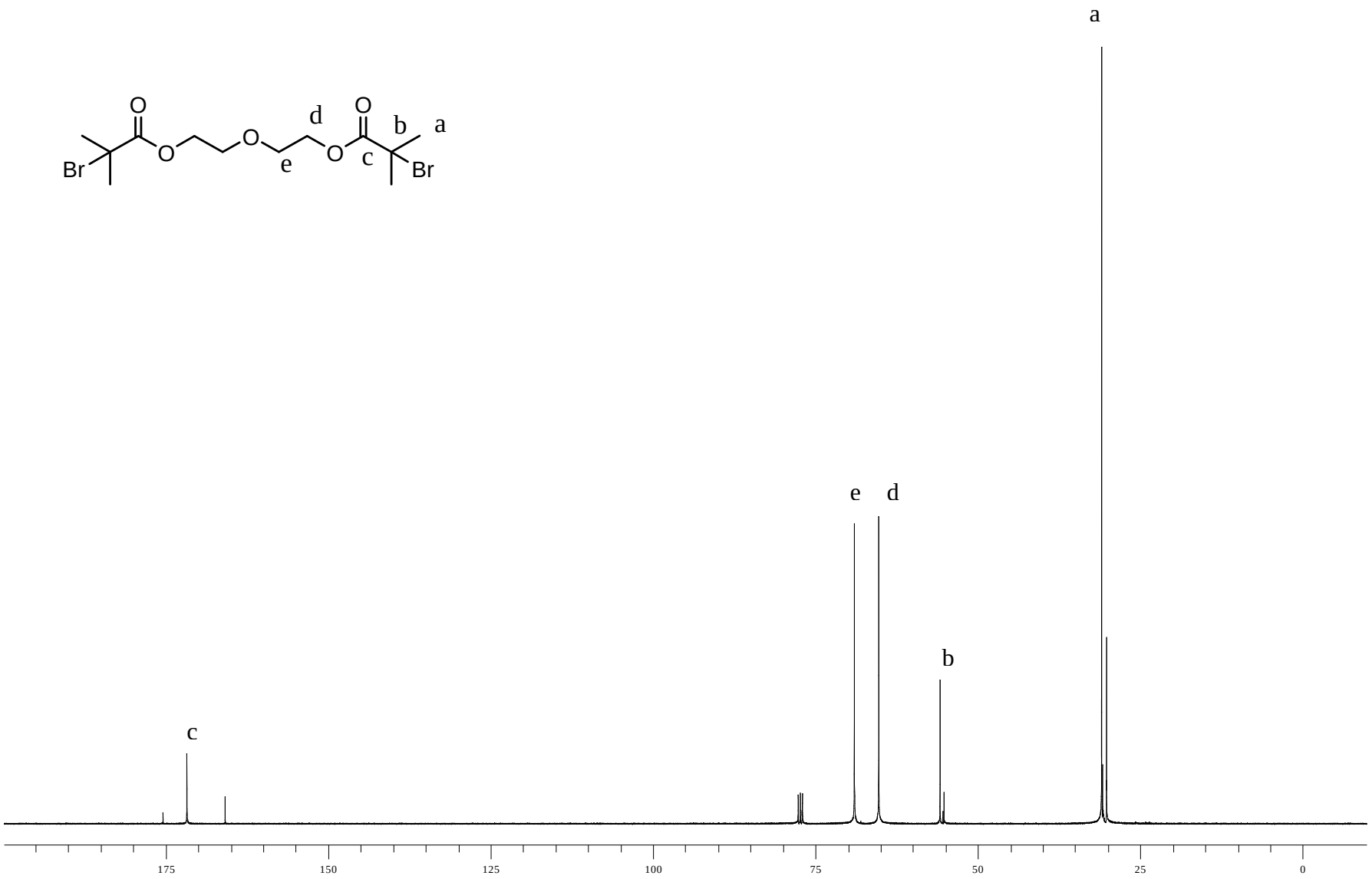

Figure 3.7. ^{13}C-NMR of Di-ethylene glycol di-initiator.

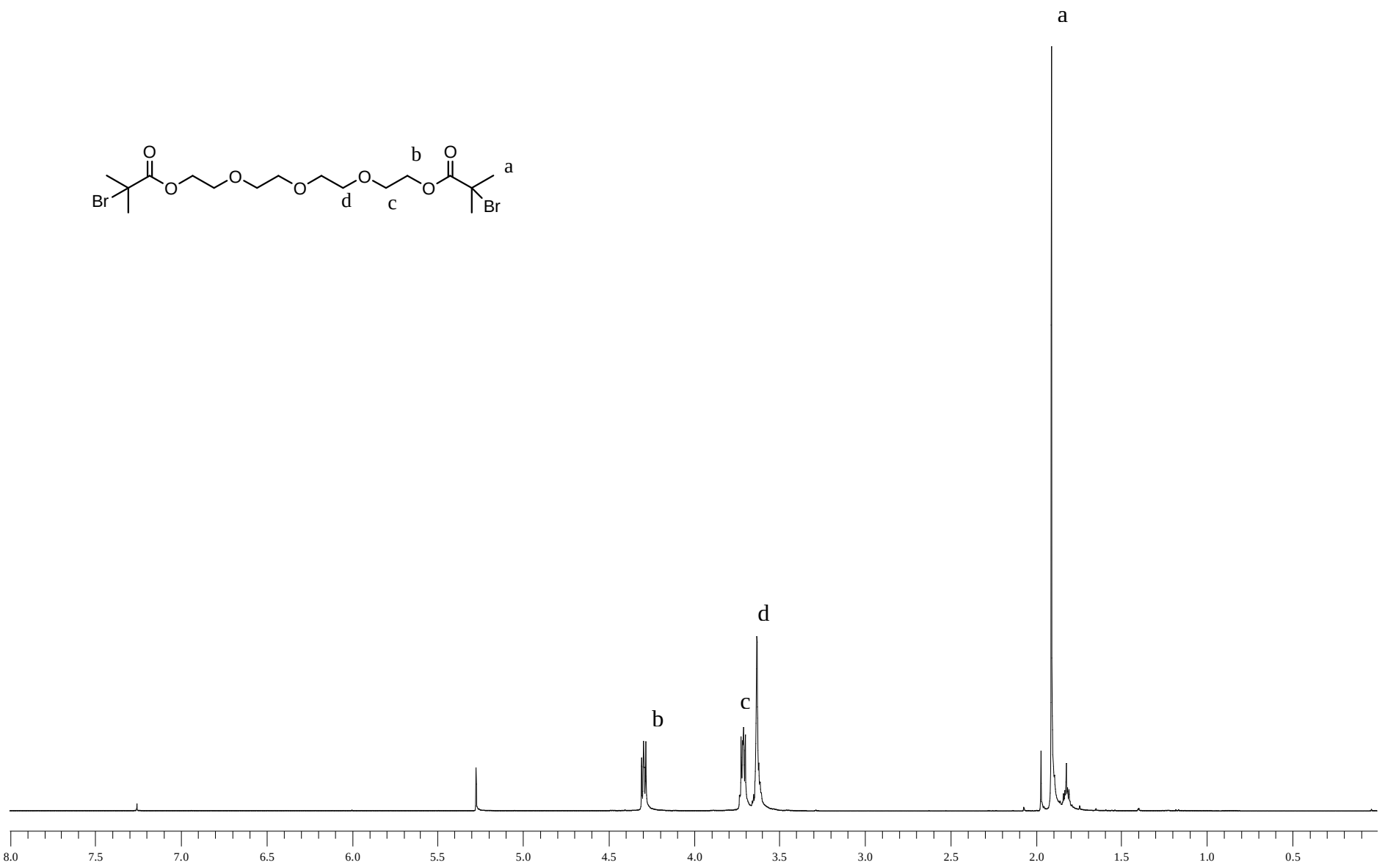

Figure 3.8. ^{1}H-NMR of Tetra-ethylene glycol di-initiator.

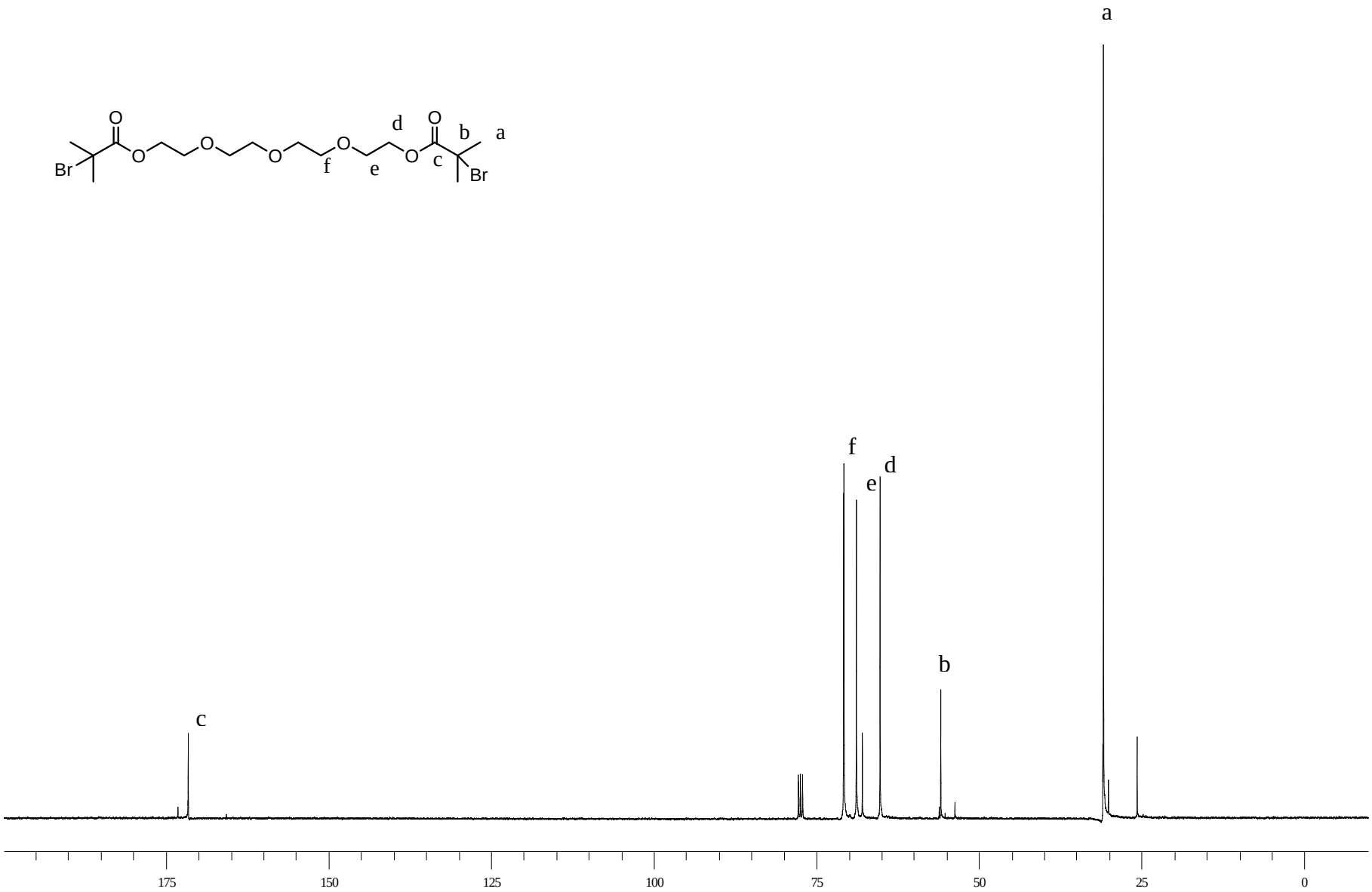

Figure 3.9. ^{13}C-NMR of Tetra-ethylene glycol di-initiator.

Then cyclopolymerizations were carried out using these di-initiators (Figure 3.5). In these trials, again, monomer to initiator ratio was altered to control the molecular weights of the cyclopolymers obtained. As the results indicate the cyclopolymers containing soft blocks in their backbone had much lower T_g's (Table 3.1). For example, comparison of entry 3 and 7 with entry 1, shows that T_g of soft block containing polymers are lower than entry 1 despite their higher molecular weights.

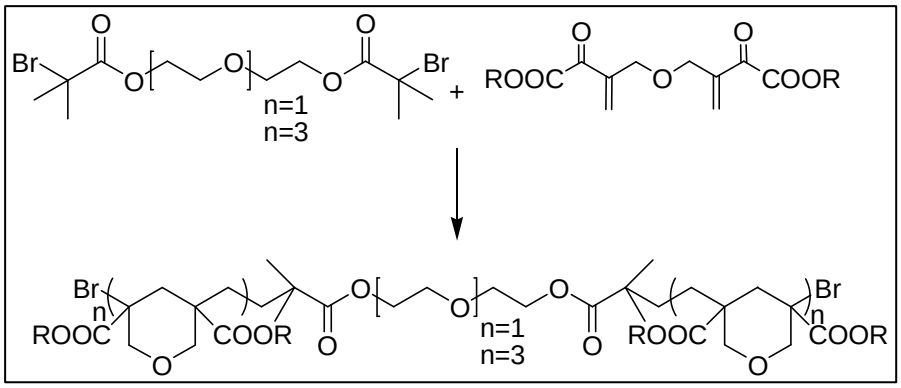

Figure 3.10. Polymerization of TBHMA Ether Dimer via ATRP.

The targeted T_g values were obtained with the cyclopolymers containing TEG soft block whose molecular weights were around 5000 (entry 5). As expected the effect of TEG was much more pronounced than DEG (Compare entry 3 with entry 7).

The correlation between molecular weight (Mn) and glass transition temperature, showed a linear behavior (Figure 3.11) in the molecular weight range worked.

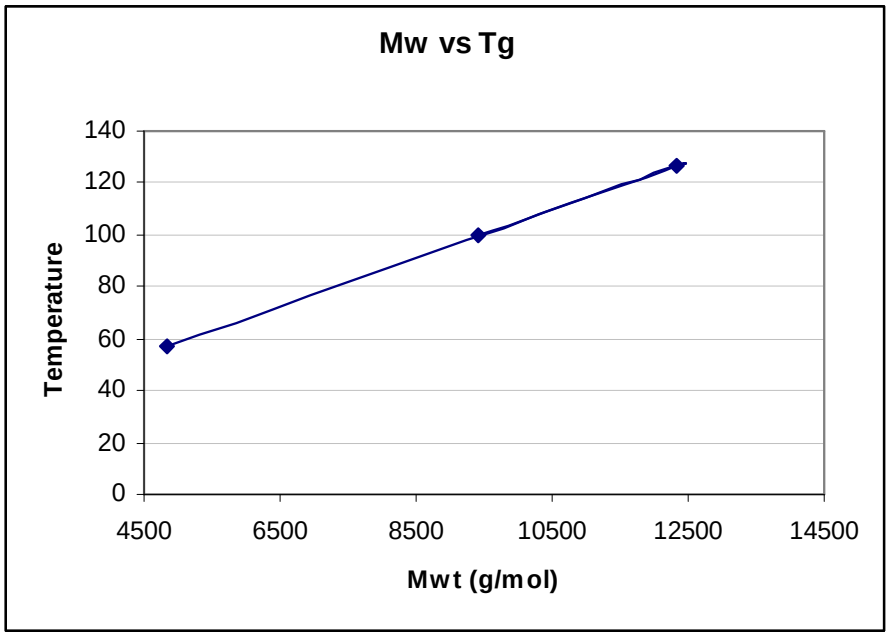

Figure 3.11. Mw and T_g Relationship with TEG initiator.

As a result, cyclopolymers with desired T_g values were obtained by using soft block containing di-initiators successfully.

3.1.4. Kinetic study of ATRP of TBHMA ether dimer

The result of the kinetic study of cyclopolymerization of TBHMA ether dimers at 80^0C is shown in Table 3.2 and Figures 3.12-13. The data indicates that molecular weights increased with the conversion linearly. Molecular weight distribution was low and increased only slightly with time and conversion.

Table 3.2. Results from kinetic study of ATRP of TBHMA ether dimer at 80^oC[a].

Entry	Monomer	Time (min)	Conversion[b] (%)	$M_{n,sec}$ (g/mol)	PDI
1	TBHMA	20	54	2954	1.23
2	TBHMA	40	65	3680	1.19
3	TBHMA	60	75	4387	1.19
4	TBHMA	80	79	4791	1.18
5	TBHMA	100	82	4833	1.21

[a] Polymerizations were carried out with [M]:[TEG]:[CuBr]:[Ligand]=25:1:1:1 ratios in xylene at 80^oC.The concentrations of monomers in xylene were in between 0.91-0.97 M.

[b] Measured by gravimetric methods.

A linear plot of ln ($[M]_o/[M]$) versus time was observed for the ATRP of TBHMA ether dimer, which indicates that the number active species (k_p [P$^{\cdot}$]) remained essentially constant throughout the course of the cyclopolymerization (Figure 3.12) Also linear evolution of molecular weight with conversion showed that although polydispersity increased, polymerization was still under control (Figure 3.13). From these results it can be said that the polymerization progress has a controlled path which means that there were negligible amount of termination reactions and therefore all the chain ends can be assumed to be living/active. These groups, in principle, should allow further functionalization, thus the synthesis of telechelic polymers.

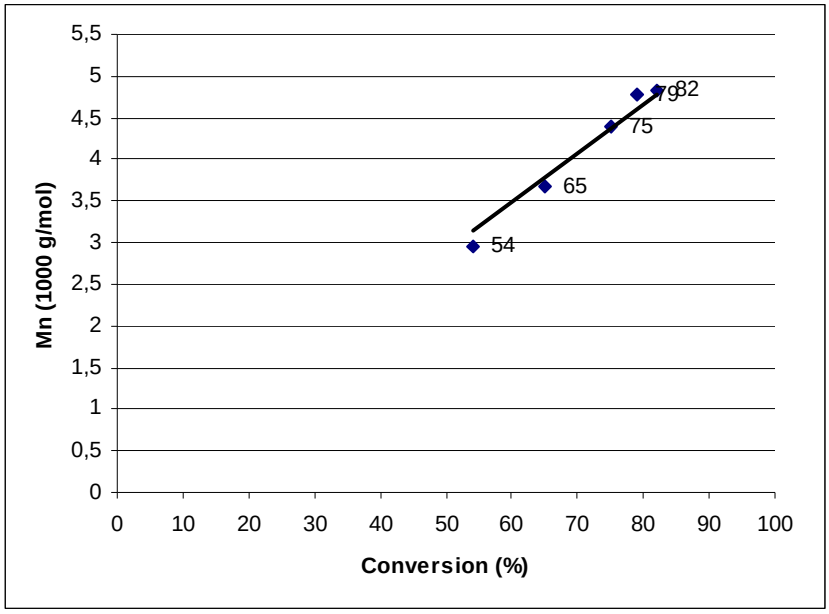

Figure 3.12. Plot of M_n versus conversion for TBHMA ether dimer polymerization via ATRP. Conditions: 80^{o}C; [M] =0.96M; $[M]_o$:[I]:[Cu]:[L]=25:1:1:1.

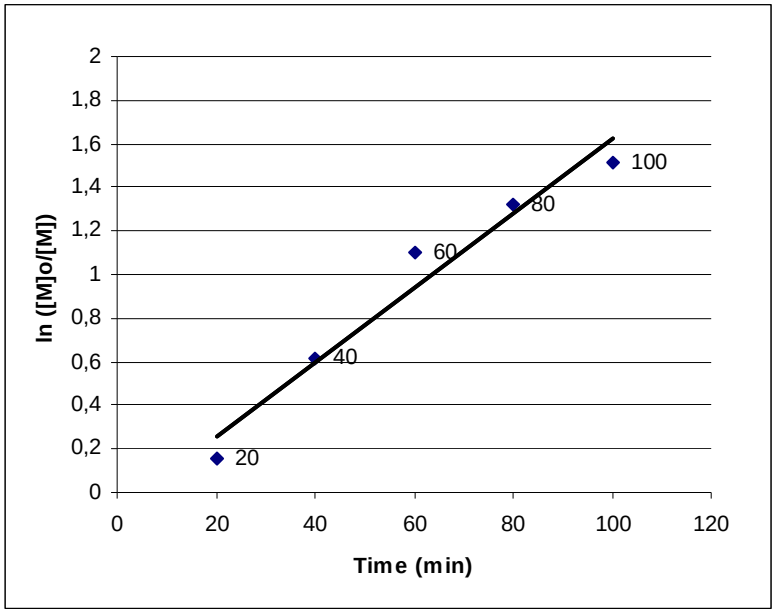

Figure 3.13. Plot of ln ($[M]_o/[M]$) versus time for TBHMA ether dimer polymerization via ATRP. Conditions: 80°C; [M]=0.96M; [M]o:[I]:[Cu]:[L]=25:1:1:1.

3.2. Functionalization of Cyclopolymers

Functionalization studies were carried out using two main approaches:

- The first approach was the direct synthesis of functional polymers using functional monomers. For this purpose, glycidyl acrylate ether dimer was synthesized. This approach, in principle, should lead to polymers with pendant functional/crosslinkable groups.
- The second approach was the post functionalization of halogen terminated polymers by using ATRP. For end functionalization allyl alcohol and undeconoic acid were reacted with the end groups under ATRP conditions to give alcohol and acid end groups respectively. This approach should lead to end-functional/crosslinkable polymers. The reason of using these specific compounds is that they both have double bonds which can be reacted under ATRP conditions but since these double bonds are not polymerizable ones, the reaction should stop after the first addition of the double bond.

3.2.1. Pendant Group Approach

3.2.1.1. Synthesis of the Glycidyl α-(Hydroxymethyl)acrylate GHMA ether dimers

Two different approaches were taken to synthesize the GHMA ether dimer. The first approach was to synthesize glycidyl acrylate first and then use the Baylis-Hillman reaction to get to the desired dimer (Figure 3.14 and 3.16).

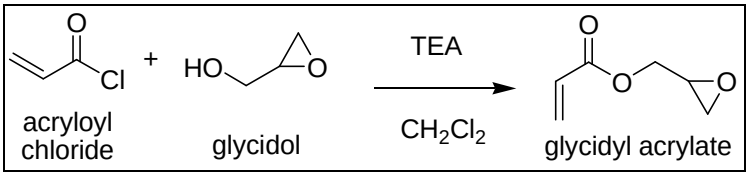

Figure 3.14. First synthetic route for GA monomer.

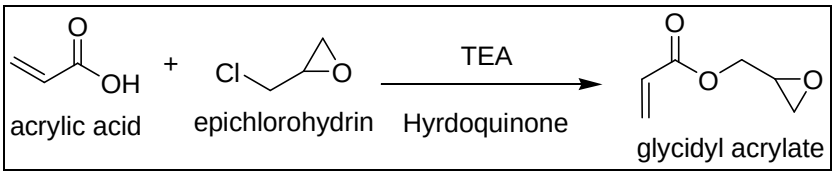

Figure 3.15. Second synthetic route for GA monomer.

The glycidyl acrylate could be synthesized either by the reaction of acryloyl chloride and glycidol (Figure 3.14) or by the reaction of acrylic acid and epichlorohydrin (Figure 3.15). Both reactions gave high yields. The second root was employed first because of the availability of the reagents. Once the glycidyl acrylate was obtained it was reacted with DABCO and paraformaldeyhde at 95 ^{o}C. However under these reaction conditions the epoxy groups opened and the hydroxyl peak appeared.

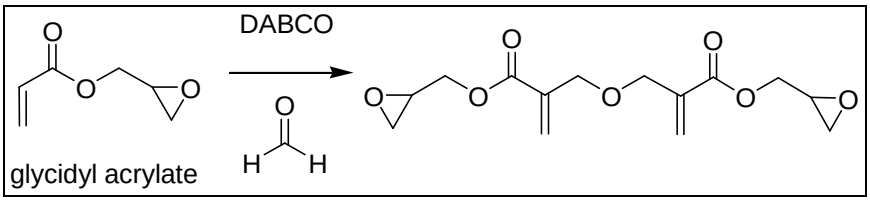

Figure 3.16. First synthetic route for GHMA ether dimer monomer.

Instead of optimizing the reaction conditions, we decided to try the second approach for the dimer synthesis which changed the synthetic route totally. In this approach, the THBMA dimer was taken as the starting material and it was reacted with $SOCl_2$ to obtain the corresponding acid chloride (Figure 3.17).

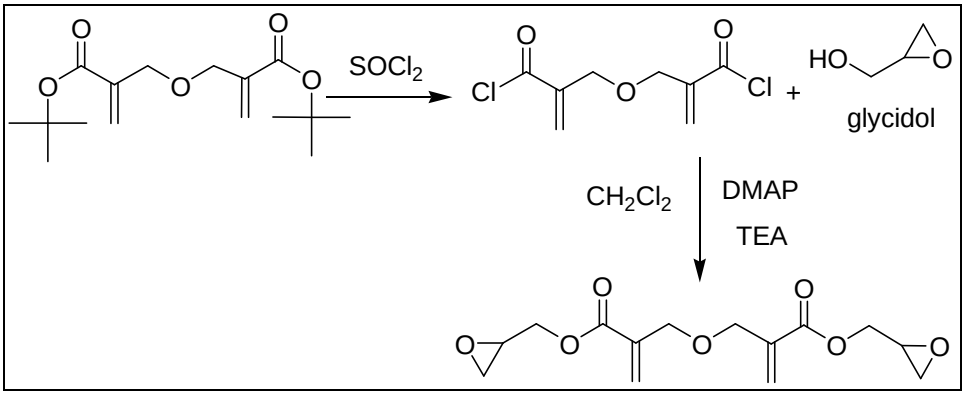

Figure 3.17. Second synthetic route for GHMA ether dimer monomer.

The acid chloride then was reacted with glycidol in the presence of TEA, DMAP as catalyst to obtain the desired glycidyl-dimer. The reaction yield was low and the reaction mixture contained many impurities. However the desired dimer was isolated after column chromatography (Figure 3.18, 3.19). The ether-dimer approach was abandoned due to low yield of reaction and toxicity concerns during its synthesis. Therefore, instead of the glycidyl acrylate ether dimer, we decided to employ the commercially available glycidyl acrylate and methacrylate to produce pendant crosslinkable epoxies.

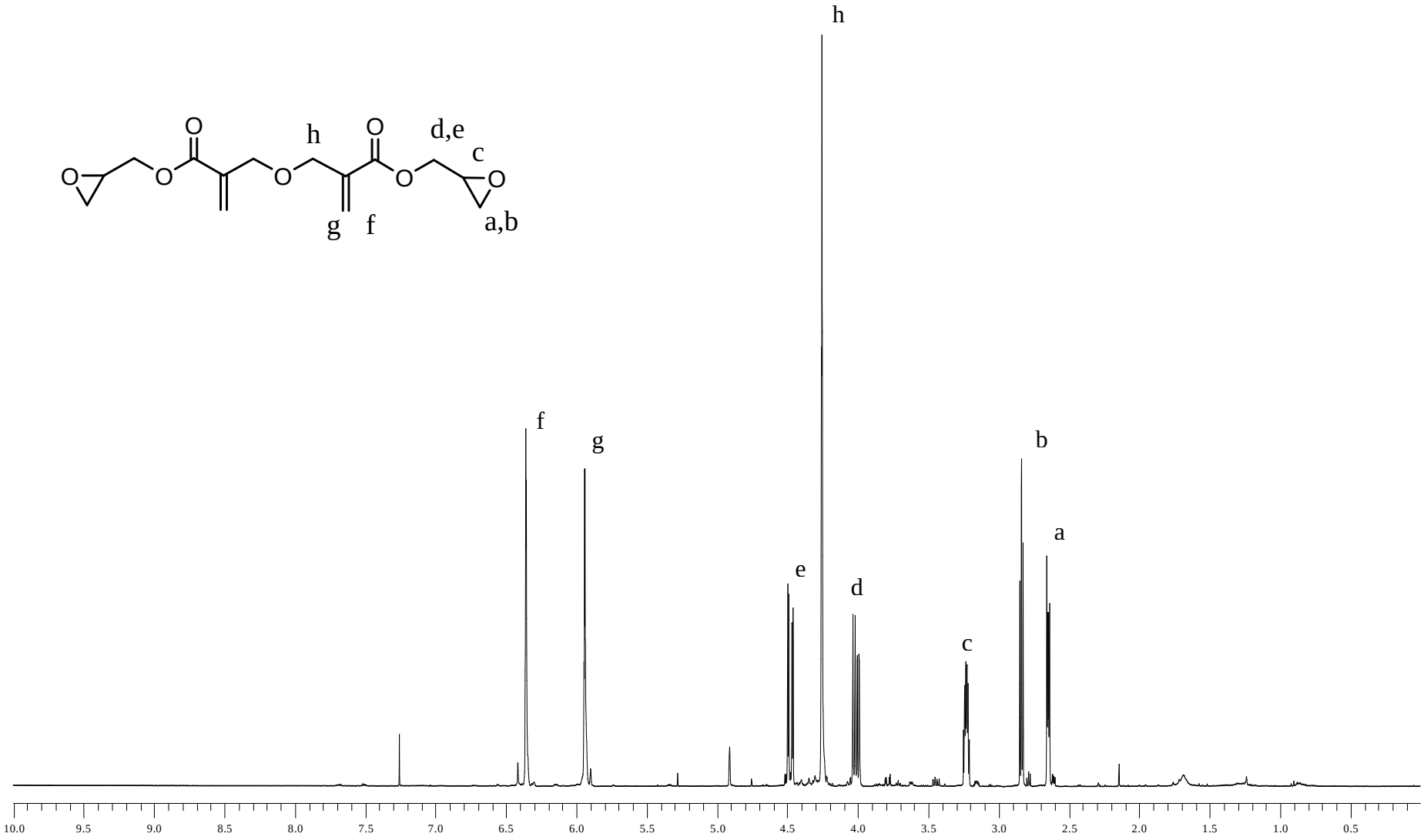

Figure 3.18. ^{1}H-NMR of GHMA ether dimer monomer.

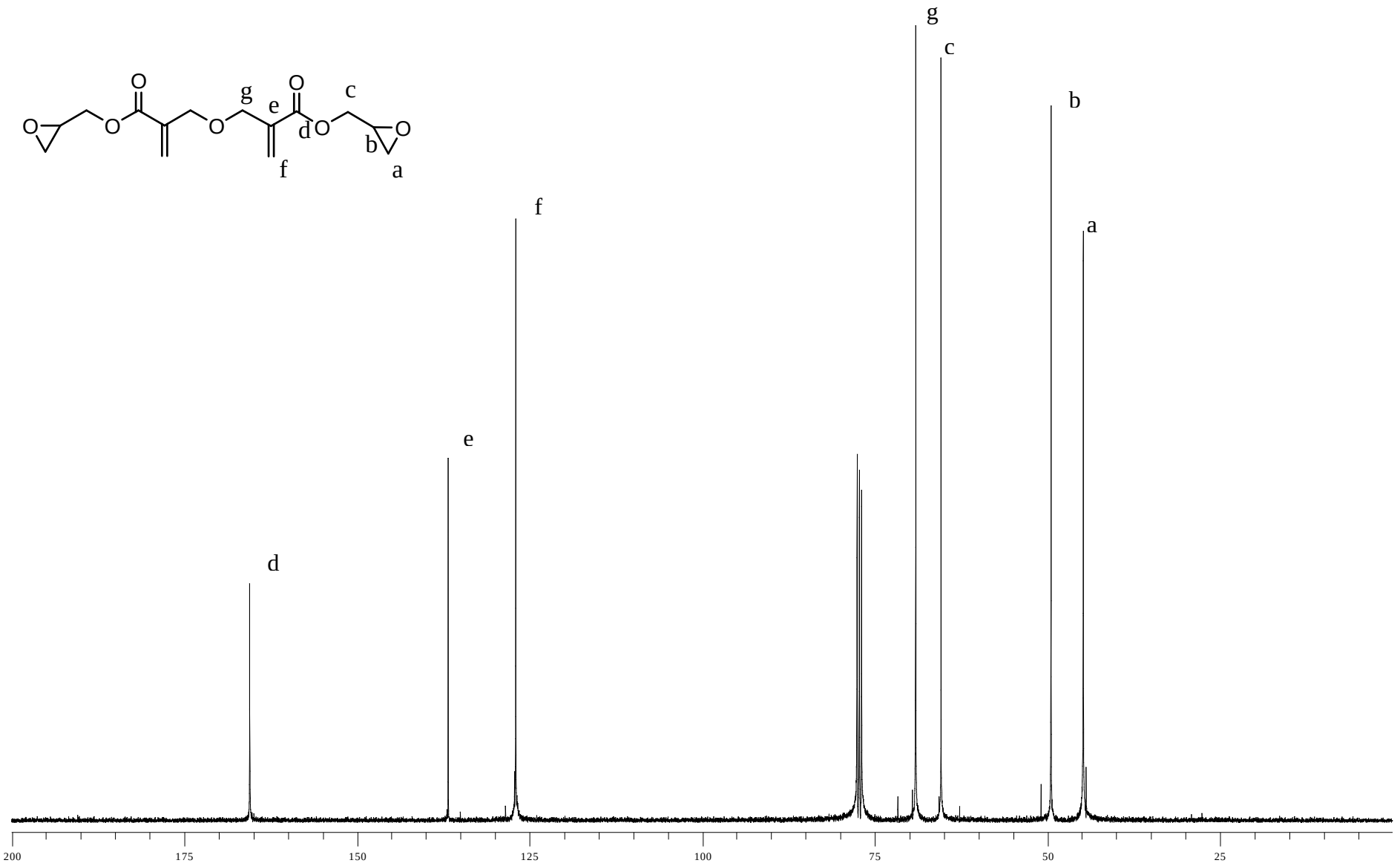

Figure 3.19. ^{13}C-NMR of GHMA ether dimer monomer**.**

3.2.1.2. Synthesis of Glycidyl Acrylate or Glycidyl Methacrylate Incorporated Copolymers

In this approach, the incorporation of epoxy units to the polymer backbone was achieved via glycidyl acrylate or glycidyl methacrylate copolymerization with TBHMA. In the copolymerization studies glycidyl acrylate or glycidyl methacrylate monomers were added into the polymerization of TBHMA ether dimer at different time intervals (30-60-90 minutes). By this way, different polymer architectures were targeted (Figure 3.20).

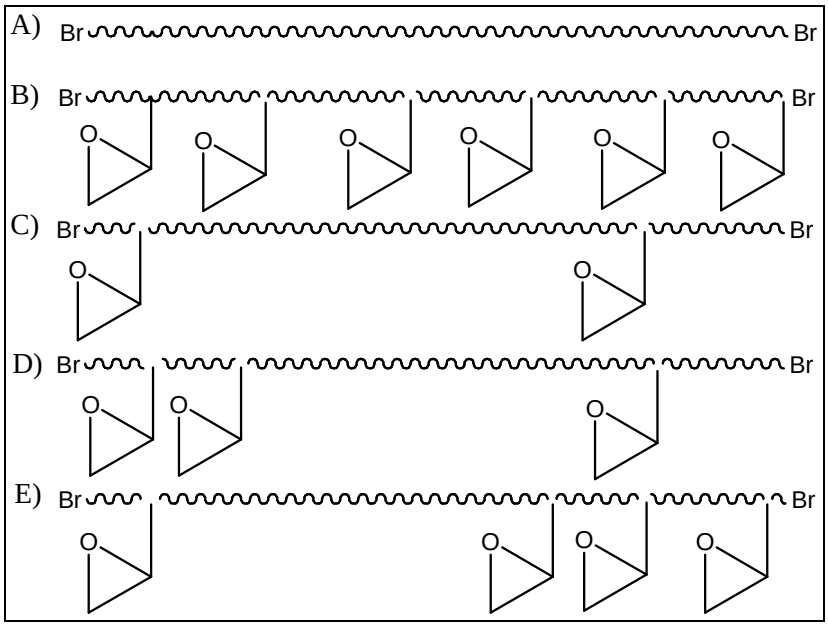

Figure 3.20. Representation of architectures of copolymers with the comparison of poly(TBHMA) (A), poly(GHMA) (B) and some possible copolymers (C), (D),(E).

Table 3.3. The comparison of poly(TBHMA) polymers with synthesized copolymers.

Entry	Monomer	Conv [a]	$M_{n,sec}$	M_w/M_n	T_g
1	TBHMA	54	4840	1,16	57
2	TBHMA	75	12342	1,26	127
3	TBHMA	67	9408	1,26	100
4	GA+ TBHMA	82	12621	1,24	97
5	GMA+ TBHMA	76	8971	1,29	110
6	GMA+ TBHMA	N/A	7747	1,23	113

[a] Measured by gravimetric methods.

In all of these cases, polymerization results were satisfactory in terms of conversion, molecular weight, polydispersity and T_g. The copolymers containing the glycidyl acrylates showed lower T_g values than the homopolymers at similar molecular weights (compare entry 4 with entry 3 from table 3.3). But the problem rises from the impossible identification of epoxy groups directly from NMR or IR results, which are the only characterization techniques that are used in this study.

3.2.2. End Group Approach

3.2.2.1. Synthesis of End functional Polymers via Allyl Alcohol and Undeconoic Acid Addition.

For the end functionalization, hydroxyl and carboxylic acid end groups were targeted. Allyl alcohol and undeconoic acid were chosen for the functionalizations. Allyl alcohol is the simplest alcohol which has a double bond in its structure and also it is the most available and most used alcohol for the end group functionalization [35]. Undecanoic acid is used for the characterization ease in NMR investigations. It is important to mention that both compounds react with a radical but do not lead to polymerization.

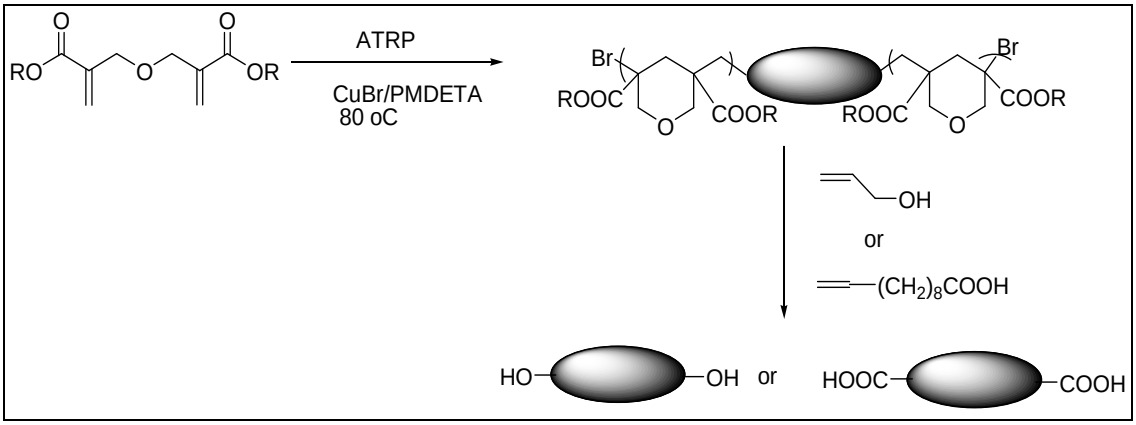

Figure 3.21. Representation of end-functional polymer synthesis.

The addition times of these two reagents were done at different time intervals (30, 60, 90 and 120 minutes). Since the addition of these reagents stops the polymerizations,

when added at different times different molecular weights should be obtained. Both allyl alcohol and undeconoic acid were used in excess amounts for the completeness of the reactions.

Table 3.4. Results of poly(TBHMA) polymers with hydroxyl and carboxyl end groups[a].

Entry	Group	Conv[b]	$M_{n,cal}$	$M_{n,sec}$	M_w/M_n	T_g
1	OH	54	6504	5763	1,15	98
2	OH	77	5457	7414	1,24	101
3	OH	74	4594	5360	1,24	93
4	OH	71	4407	5200	1,25	129
5	OH	70	5787	9307	1,32	116
6	OH	64	3973	5931	1,37	N/A
7	OH	59	3662	5462	1,24	125
8	COOH	70	4345	6571	1,23	86
9	COOH	58	4049	6947	1,21	125
10	COOH	61	3786	4994	1,22	N/A

[a] Polymerizations were carried out with [M]:[TEG]:[CuBr]:[Ligand]=25:1:1:1 ratios in xylene at 80°C. The concentrations of monomers in xylene were in between 0.91-0.97 M.

[b] Measured by gravimetric methods.

As the table 3.4 shows, polymers with different molecular weights and end group functionalities were obtained successfully. It can be concluded from the T_g value of entry 8 and entry 1, 3, 4 that having undecanoic acid functionality lowers T_g value with respect to allyl alcohol functionality due to its long aliphatic CH_2 units which may act as a plasticizer.

3.2.2.2. Characterization of the End Groups.

For the identification of the end groups, first ^{1}H-NMR, ^{13}C-NMR and IR techniques were employed. However due to the very low end group concentrations the peaks corresponding to the end group carbons or hydrogens could not be detected.

The end groups were finally identified using ^{31}P-NMR techniques [32]. After finding the derivatization procedure, a set of ^{31}P-NMR data were taken. From the

information correlation studies were done in order to correlate the molecular weights to the peak integrals (Figure 3.22).

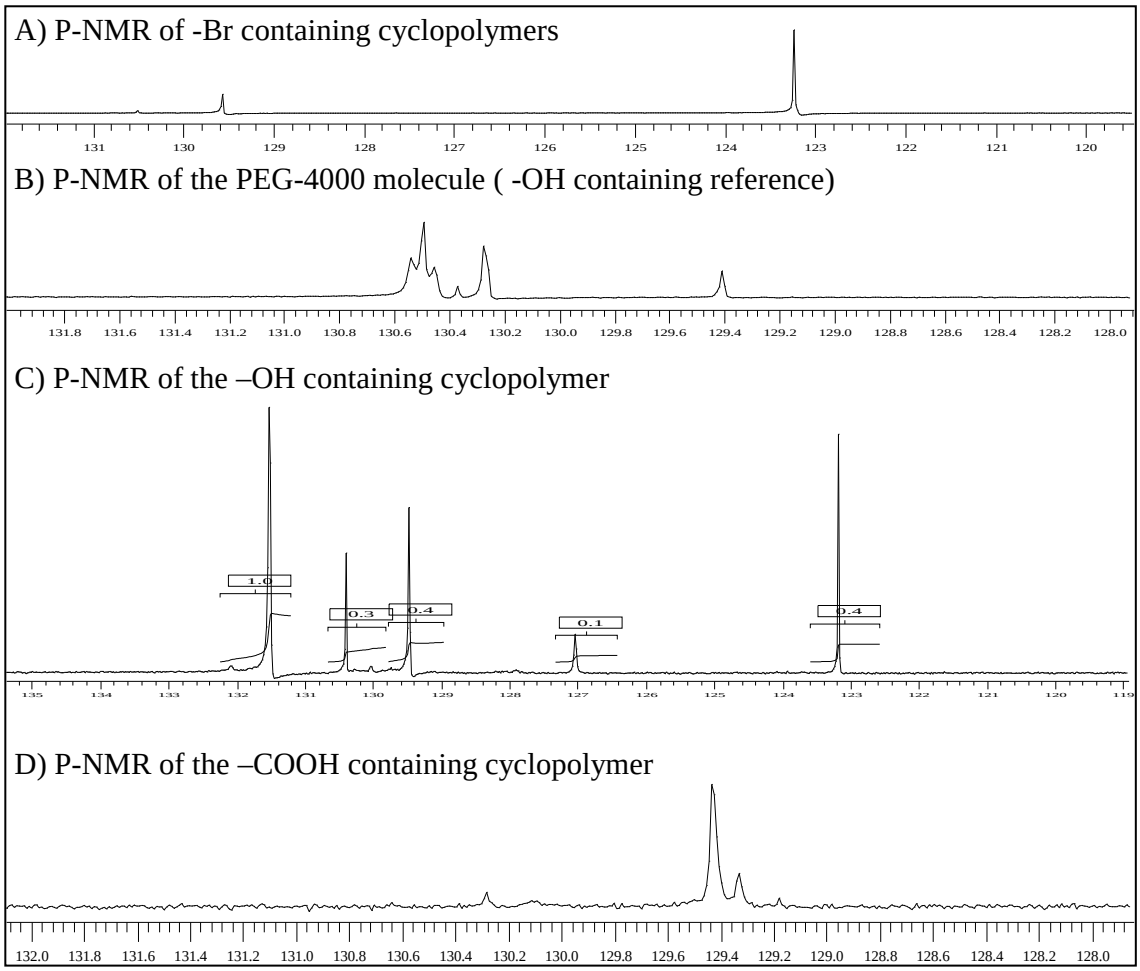

Figure 3.22. ^{31}P-NMR Results of the End-Functionalized Cyclopolymers.
A) Br- containing polymer, B) PEG-4000 reference polymer, C) –OH containing polymer,
D) –COOH containing polymer

From the ^{31}P-NMR results, it can be said that the appearance of new peaks which correspond to the polymer phosphorus derivatized acid or alcohol end groups prove that the targeted alcohol or acid end groups are present. Unfortunately, the molecular weights obtained by the integration of ^{31}P-NMR, did not fit to the GPC results. More experiments are needed to correlate the molecular weights of the polymers measured by GPC with those obtained from ^{31}P-NMR results.

4. CONCLUSION

As a summary, the potential of cyclopolymers derived from the t-butyl derivatives of RHMA ethers dimers by ATRP for the powder coating application was investigated. To achieve the goal, cyclopolymers with optimized T_g and Mw and living end groups were targeted. The desired T_g values for powder coating applications were achieved by using TEG di-initiator and at molecular weights between 4000 to 5000. Functionalization studies were also carried out. The cyclopolymer end groups were reacted with allyl alcohol and undecanoic acid under ATRP conditions to give alcohol and acid end groups, respectively. The presence of such end groups were proven by 31P-NMR, however, more studies are needed to analyze quantitatively the end-groups which is necessary for preparing a powder coating formulation. Polymers with pendent epoxy groups were also synthesized by copolymerization of glycidyl acrylate and the TBHMA dimer. These polymers need to be analyzed further, so that they can be used as crosslinking agents in powder coating formulations. Such studies involve miscibility studies, quantitative analyses of epoxy pendent groups.

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