SYNTHESIS OF NOVEL ALKYL ALPHA-(HYDROXYMETHYL)ACRYLATE (RHMA) ETHER DIMER DERIVED POLYMERS AND THEIR POTENTIAL USE IN POWDER COATING

by

Erhan Özkal

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To My Family

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ABSTRACT

SYNTHESIS OF NOVEL ALKYL ALPHA-(HYDROXYMETHYL) ACRYLATE (RHMA) ETHER DIMER DERIVED POLYMERS AND THEIR POTENTIAL USE IN POWDER COATING

One of the newest and most effective technologies in coating industry is powder coating. Powder coating has been applied from wood to steel surfaces. Among many components, resin has the highest percentage in the mixture which determines the characteristics of a powder coating. Some of the significant characteristics are stability, reactivity and processability. One of the physical properties that affect the most the quality of a coating and also its manufacturing process is the T_g of the resin. The lowest T_g that is possible is around 55-60 ^{0}C for a powder coating that is to be cured at 120-150^{o}C. This T_g interval can be reached by aliphatic polyesters only at relatively high molecular weights (10,000-20,000 g/mol) which lowers the crosslink density. Decreasing molecular weight but keeping the high T_g can be achieved with aliphatic cyclopolymers. Previously in our research group, it has been shown that these T_g can be obtained at about 3000-6000 g/mol molecular weights using the cyclopolymers.

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. Solution polymerizations was performed in xylene using Cu(I)Br/PMDETA as the active catalyst complex. Since the T_g requirement has been successfully fulfilled previously in our research group, for the cylpolymers to be used in powder coating application reactive end groups must be introduced to the terminal positions of the polymer. To modify end groups, two strategies were chosen. First one was the addition of alcohol or acid functionality via the addition of alcohols and acids with terminal double bonds (non-polymerizable) under ATRP conditions. Second was to employ the click chemistry. The quantitative determination of the acid and alcohol end groups was challenging and new to the literature, and this quantitative analysis was crucial since the stoichiometric ratios of the polymers and cross-linkers have to be adjusted to obtain a good coating. Cross-linking and preliminary perspective were also investigated.

ÖZET

YENİ ALKİL ALFA-(HİDROKSİMETİL) AKRİLAT (RHMA) ETER DİMER TÜREVİ POLİMERLERİN SENTEZİ VE TOZ BOYACILIKTA POTENSİYEL KULLANIMI

Pudra (toz) boyacılık, kaplama sanayinin en yeni ve en etkili teknolojilerinden biridir. Son zamanlarda, ağaçtan çelik yüzeye kadar uygulanabilmektedir. İçinde pek çok kimyasal barındırsa da, polimer ana reçinesi en fazla yüzdeye sahip olup; toz boyanın karakteristiğini belirler. Bazı önemli özellikler, dayanıklılık, reaktiflik ve işlenebilirliktir. Kaplamanın kalitesini ve üretim verimini belirleyen en kesin fiziksel özelliklerden birisi T_g aralığıdır. Tüm gereksinimleri karşılayan en düşük T_g aralığı 55-60 ^{0}C civarındadır. Bu aralık ancak görece olarak yüksek moleküler ağırlıkta (10,000-20,000 gr/mol) alifatik poliesterler kullanılarak erişilse de , bu çapraz bağ yoğunluğu az olan kaplamalar vermektedir. Bu T_g değerleri daha düşük ağırlıklarda grubumuz tarafından halkalı polimerler kullanılarak 3000-5000 moleküler ağırlıklarinda elde edilebilmiştir.

T-bütil α-(hidroksimetil) eter dimerlerinden ATRP yöntemi ile üretilen alifatik halkalı polimerler pudra kaplama uygulamalarında potansiyel baz reçine olarak kullanılmak üzere sentezlenmiştir. Çözelti polimerleşmesi ksilen içinde, Cu(I)Br/PMDETA sistemini katalizör olarak kullanılmasıyla gerçekleştirilmiştir. Hedeflenen bölgedeki T_g ayarlaması araştırma grubumuz tarafından daha önce başarı ile yapılmıştır. Toz boyacılıkta kullanılmak üzere reaktif uç grupların polimerin uçlarına eklenmesi ve bunların analizi bu tezin ana konusu olmuştur. Uç grupları değiştirmek için, iki yöntem izlenmiştir. İlki, alkol ve asit gruplarının, kendi kendine polimerleşmeyen, ucu çift bağlı moleküllerin ATRP ortamında eklenmesi olmustur. İkincisi ise, bir başka uç grup değiştirme yöntemi olan klik kimyasının kullanılmasıdır. Uç grupların nicel olarak belirlenmesi zor ve literatür için de yeni bir yöntemdi, bilindiği gibi, polimerler ve çapraz bağlayıcılar arasındaki stokiyometrik oranın, kaplamanın niteliklerine doğrudan etkisi vardır. Çapraz bağlama ve ileriye dönük yeni fikirler de araştırılmaya başlanmıştır.

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ATRP	Atom Transfer Radical Polymerization
RHMA	Alkyl α-(hydroxymethyl)acrylate
TBHMA	Tert-butyl α-(hydroxymethyl)acrylate
PMDETA	*N*,*N*,*N*,*N'*,*N'*-pentamethyldiethylenetriamine
DABCO	1,4-Diazabicyclo[2.2.2]octane
TEG	Tetra-ethylene glycol di initiator
GPC	Gel Permation Chromatography
NMR	Nuclear Magnetic Resonans Spectroscopy
T_g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
UV	Ultra Violet

1. INTRODUCTION

1.1. Powder Coating

Conventional liquid technology (wet) has been used more than two centuries and starting from 1960s, powder coating (dry) started to find a way in the surface finishing market[1].

Powder coating is a dry process in which the coating material is applied to a surface by electrostatic or compressed air, or sometimes using a fluidized bed. Then the applied powder is heated (or cured) in an oven to its melting point, after it reaches to form a smooth film which give rise to a firm, durable finish resistant to scratches, cracking, peeling, UV rays[2].

Traditionally, powder coating has been considered as a volatile organic compound (VOC) free alternative to the conventional wet painting; thus, they are considered as a "green" technology where they compete with systems like waterborne coatings, radiation-cured coatings and high-solids solvent-based coatings [3]. Overall, the advantages and disadvantages of the powder coating can be briefly summarized (Table1.1):

Table 1.1. Advantages and disadvantages of powder coatings.

Advantages	Disadvantages
• Wide range of finishes • Ready to use • Ease of use • One-coat application • No effluent disposal • Solvent free • Reduced health hazards	• Contamination • Delicate when changing color • Powder adjustment on-site is not possible

1.2. Powder Coating Process

1.2.1. Powder Manufacturing

Powder coating is a mixture of polymers, pigments and other components (total number of components can be up to 15), each chosen to provide the properties required by the end user. The final powder coating material is subjected to several thermal and mechanical processes to achieve homogenized end product (Figure 1.1.)

The process starts with premixing prior to hot melt compounding where all raw materials are mixed because insufficient premixing affects the characteristic of the final product. Then, in an extruder, hot melt compounding is performed to melt all powders and to complete homogenization while pigment agglomerates are broken to be homogenously dispersed. Here the temperature is a key factor for the gloss property of a final product. After the completion of this hot melting, the product is cooled. The material is transported to grinding mills to transform it into a powdered form. The heat evolved by the mechanical action must be appropriately removed to operate below T_g and this is very critical for high molecular weight thermoplastic formulations since they are though, cryogenic treatment is the only method for proper grinding. Contemporary grinding devices are delivered with particle size classifying part which enables to downsize the particles to a reasonable dimension (10 mm to 75 µm). To reach the optimal size and homogeneity in the powder, further treatment may be done which may consist of cycloning, classifying, filtering or sieving [4].

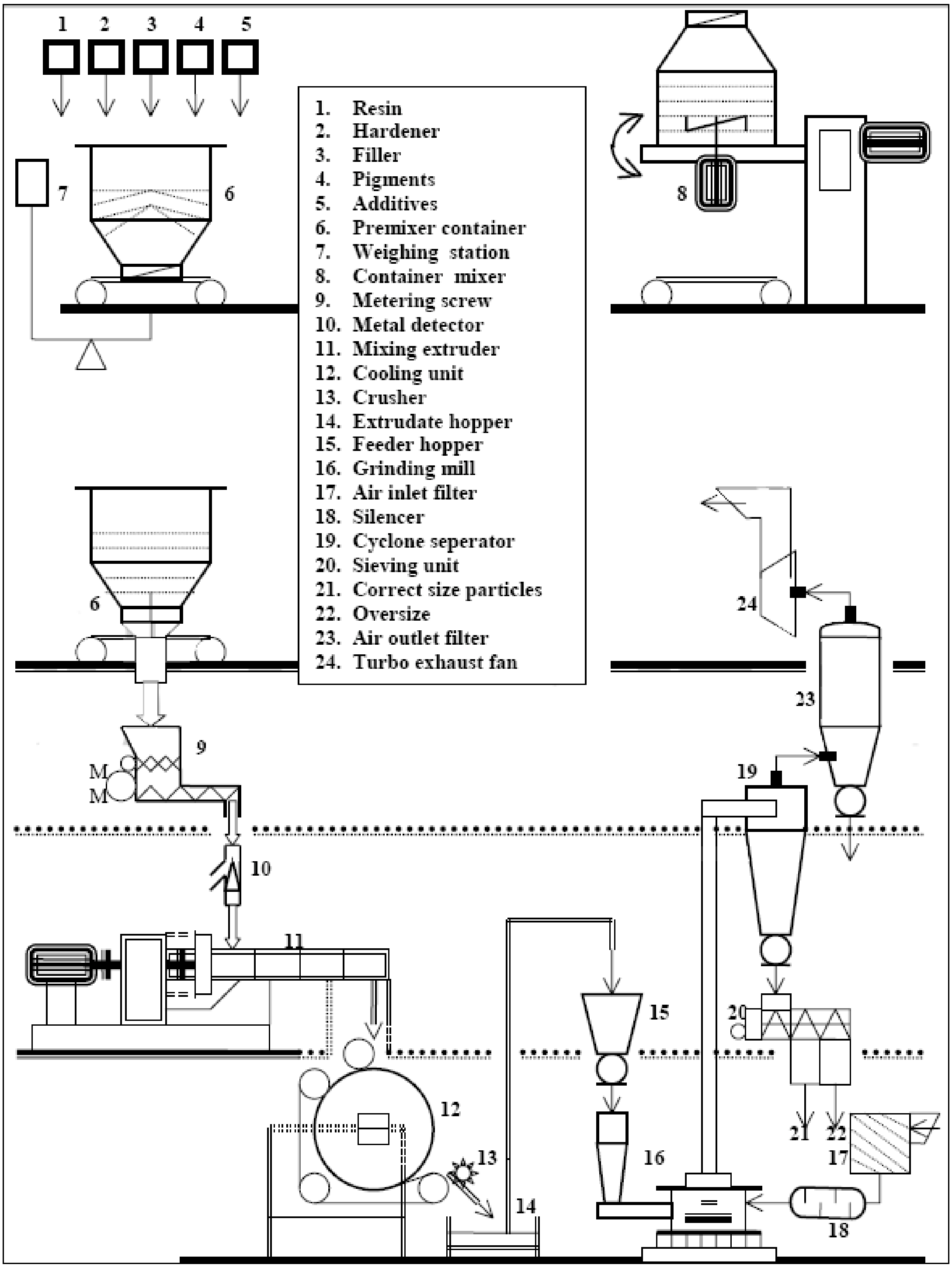


Figure 1.1. Schematic representation of powder coating process

1.2.2. Coating Application

The ready to use powder coating is then applicable to any surface that is stable at the curing temperature. Generally, the powder coating is applied to a surface by the aid of an electrostatic gun which positively charges the powders and spray them to the substrate surface which is electrically ground (Figure 1.2). When the surface is covered sufficiently, the ground is taken off and the covered surface is put into an oven to be cured at the temperature where the mixture cross-links.

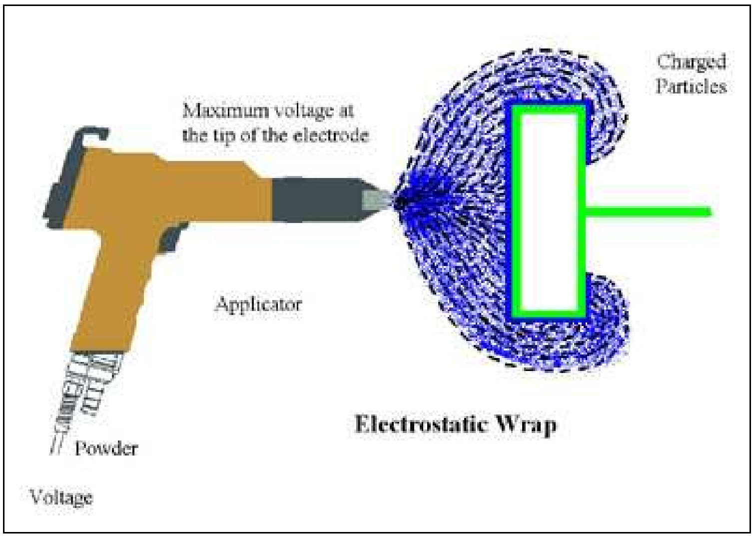


Figure 1.2. Electrostatic gun

The market for powder coatings are generally divided into two main parts as decorative and functional coatings (Table 1.2).

Table 1.2. The market for powder coatings [3].

Decorative coatings	Functional coatings
• Metal furniture • Household appliances • Automotive components • Clear automotive topcoats • Machinery and tools • Aluminum extrusions and sheet • General metal coating • Coil coating • Heat-sensitive substrates	• Thick films: - Pipes - Reinforcing bars for concrete - Valves and pipeline fittings • Thin films: - Building lintels - Cans and containers - Insulation for electronic parts

1.3. Material Requirements for Powder Coatings

There are several key factors for determining the right material for a specific powder coating application. Here in this section, the requirements for thermosetting powder coatings will be mostly discussed. The most crucial parameters are molecular weight, functionality, glass transition temperature, melt viscosity, and reactivity.

1.3.1. Molecular Weight

Like all polymeric materials, the resins are blends of molecules of different molecular weights. Therefore averaging of the molecular weights is necessary. Two of the well known equations for averaging molecular weights are most important: the number average molecular weight (M_n) and the weight of the average molecular weight (M_w) (Figure 1.3).

$$\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \qquad \bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

Figure 1.3. Number average molecular weight and weight of the average molecular weight.

Tensile strength and impact resistance are mainly dependent on the number average weight; while the weight average molecular weight governs mainly the melt viscosity of the resin [4]. Higher molecular weight resins give improved mechanical performances. They also make the system less sensitive to weighing errors, and differences in epoxy equivalent weight and acid value. However, higher molecular weights give higher melt viscosities, and these can affect the powder processing [3].

1.3.2. Functionality

Functionality can be defined as the average number of reactive groups per molecule. Generally, as the functionality increases the sensitivity of the formulation to the ratio of resin/curing agent decreases, which may improve chemical resistance but this may also cause poor flow-out of the coating since the coating’s melt viscosity increases faster during curing [3].

1.3.3. Glass Transition Temperature

Any polymer starts to flow above its T_g thus for powder coating, a sufficiently high T_g is a plus. The difference between T_g of a polymer and the ambient temperature directly affects the adhesion potential of the coating [3].

1.3.4. Melt Viscosity

As far as all parameters concerned, having the highest molecular weight and T_g for a polymer gives the best mechanical properties as a powder coating. However, these generally result in a dramatic increase of melt viscosity and this may result in some performance loss during manufacturing and application [4].

1.4. Chemistry of Powder Coatings

1.4.1. Curing Reactions Used in Powder Coatings

There are two types of coating methods used in powder coatings; first one is the one in which thermoplastic polymers are molten at the application temperature, and then they are solidified upon cooling, thus the coating material is subject to a physical change only (heating and cooling). Due its simplicity the method has a considerable market share.

Thermoplastic polymers do not have enough adhesion on metal surfaces. Thermosetting polymers can solve the problem by their ability of cross-linking which also enhances the molecular weight and thus give improved good mechanical properties. These cross-linkings give rise to a three-dimensional network. Network formation depends on the average functionality of the system. When the average functionality is around two, the full conversion will lead to a high molecular weight linear polymer without network formation. Generally, such kind of system does not have good solvent resistance. On the other hand having too much functionality can cause excessive cross-linking that can lead the formation of brittle films exhibiting unsatisfactory postforming properties and low impact resistance.

Several types of curing reactions are employed in thermosetting powder coatings. They can be classified into acid/epoxy, acid anhydride/epoxy, epoxy/amino, polyphenols/epoxy, polyetherification, isocyanate/hydroxyl, epoxy nucleophile catalyzed transesterification (encat), radiation curing. In this project, our focus is with the acid/epoxy curing reaction, where four possible reactions can occur when epoxy and acid groups are put together to react .

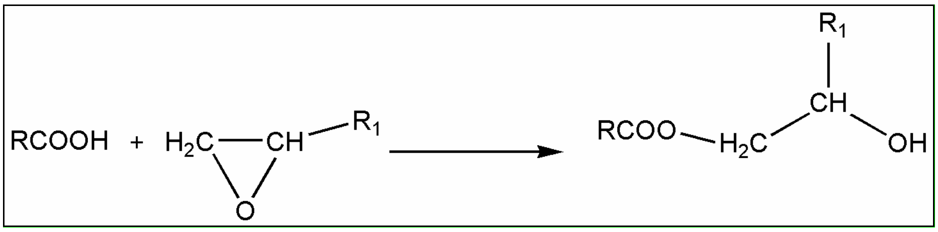


Figure 1.4. Reaction 1

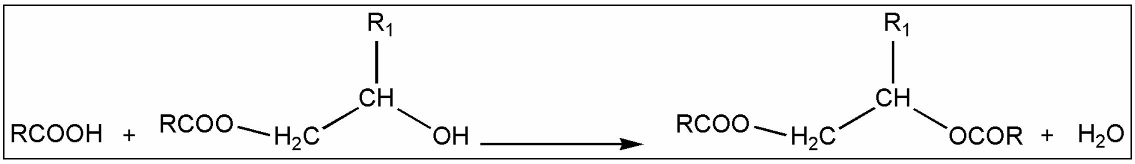


Figure 1.5. Reaction 2

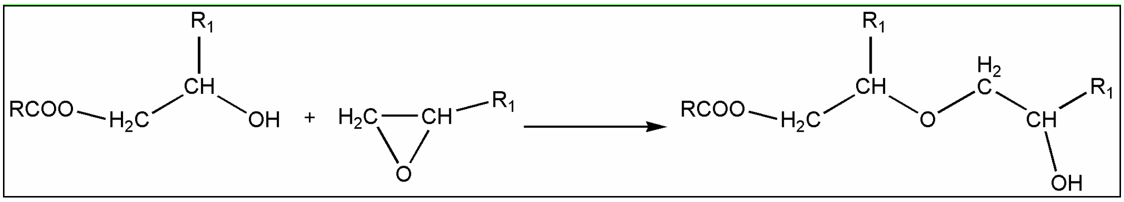


Figure 1.6. Reaction 3

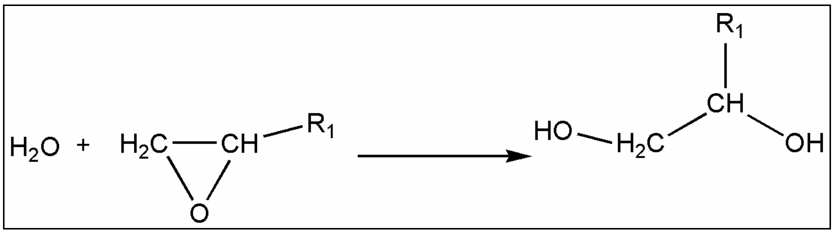
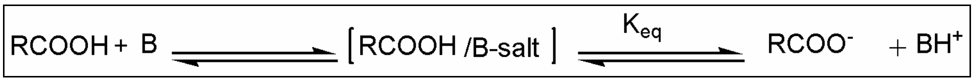


Figure 1.7. Reaction 4

Without any catalyst, the possibility of the first three reactions proceeds at the same rate [5]. Reaction 3 only occurs with in the presence of a strong acid; generally powder coating formulations are employed with basic catalysts, normally this reaction is not expected as a side reaction. However, when the stoichiometry of acid/epoxy functionality is 1:1 with a basic catalyst, the reaction 1 selectively occurs to give hydroxyl esters. In an excess of epoxy groups, and after a certain point where the acid group consumption is over, the etherification reaction proceeds as in the reaction 3.

As a whole, two reaction mechanisms are possible for a base catalyzed acid-epoxy reaction [45-48]. First one is the usage of tertiary amines as catalysts; the decomposition of acid-catalyst salt generates the active carboxylate anion (Figure 1.8-10):



$$\mathrm{RCOOH} + \mathrm{B} \rightleftharpoons [\mathrm{RCOOH}/\mathrm{B\text{-}salt}] \overset{K_{eq}}{\rightleftharpoons} \mathrm{RCOO^-} + \mathrm{BH^+}$$

Figure 1.8. The decomposition of acid-catalyst salt

Then the carboxylate anion attacks to the epoxy ring, resulting of an alkoxide anion.

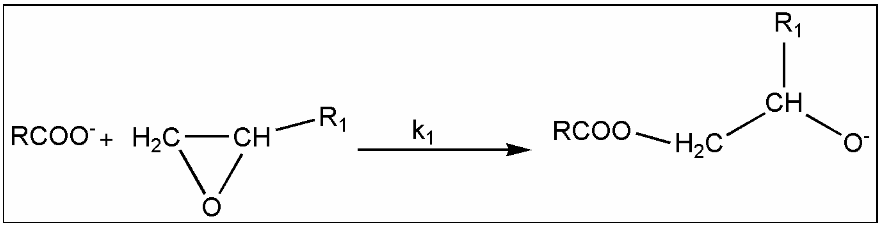


Figure 1.9. Resulting an alkoxide anion.

The alkoxide anion generates new carboxylate anions.

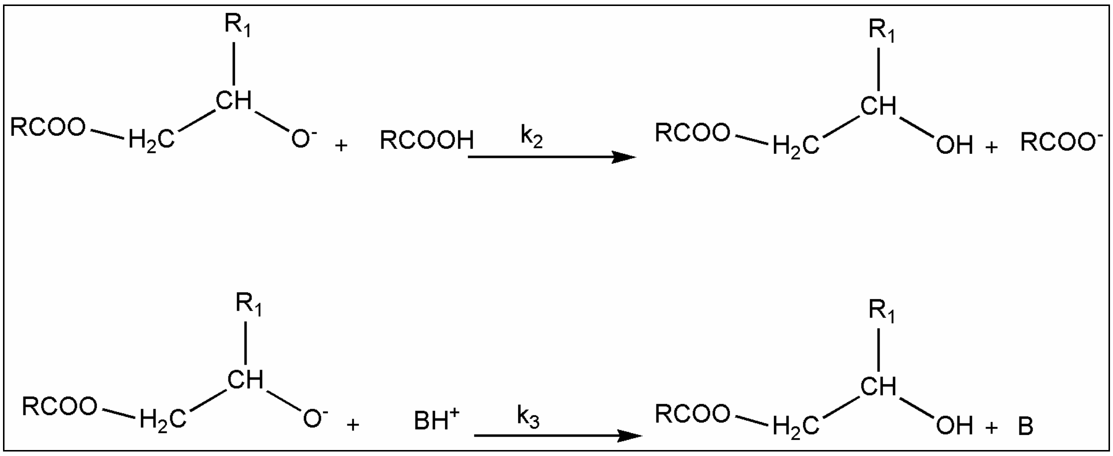


Figure 1.10. Generating new carboxylate anion.

Overall reaction rate is: $S_1 = k_1 [\mathrm{RCOO^-}] [\mathrm{epoxy}] = k_1 Keq [\mathrm{RCOO^-}] [\mathrm{epoxy}] [\mathrm{B}] / [\mathrm{BH^+}]$.

The rate is controlled by the concentration of the catalyst, the rate of decomposition of the acid-catalyst salt, or the value of the equilibrium constant K_{eq}.

The second possible mechanism works for the quaternary ammonium salts. The first reaction is the dissociation of the salt (Figure 1.11-14).

$$\boxed{AB \rightleftharpoons A^+ + B^-}$$

Figure 1.11. The dissociation of the salt.

Then the base directly attack to the epoxy generating alkoxide anion.

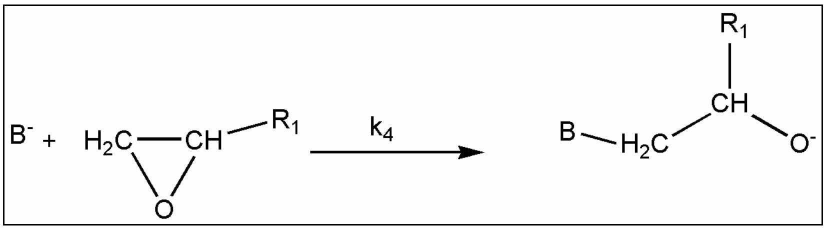


Figure 1.12. Generating alkoxide anion.

Carboxylate anion formation.

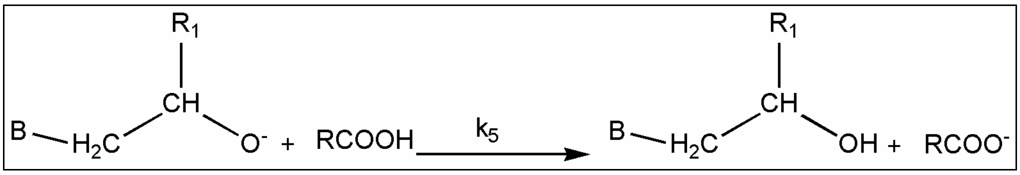


Figure 1.13. Carboxylate anion formation.

And again alkoxide and carboxylate anions in the next sequences.

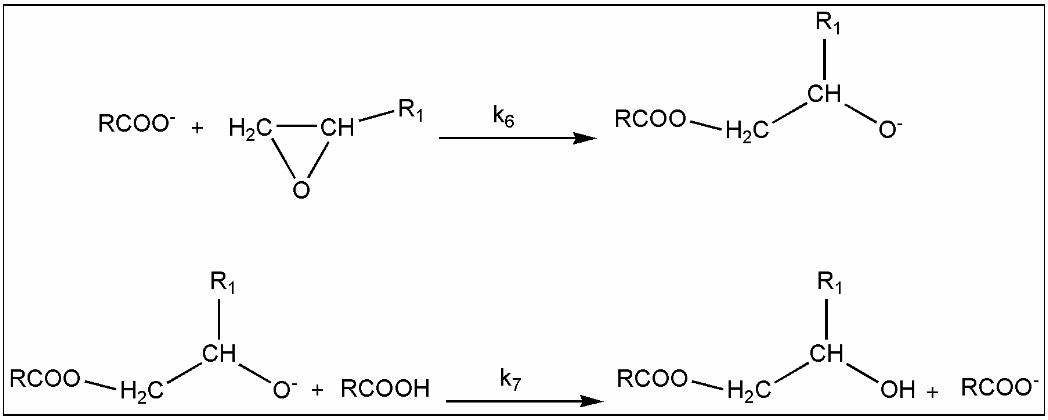


Figure 1.14. Alkoxide and carboxylate anions

For the reaction kinetics, 11 and 13 are considered as fast, no influence on rate of curing.

$S_4 = k_4$ [B] [epoxy]

$S_6 = k_6$ [$RCOO^-$] [epoxy]

Experimental reports obtained to support the above mechanisms [6,7].

1.4.2. Resins Used in Powder Coatings

There are several types of powder coatings in the market and they can be divided into five main groups (Table 1.3.) where the coating properties highly changes depending on the system used.

Table 1.3. Main properties of different types of thermoset powder coatings [8].

	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

The repeat unit in the backbone of the polymer is extremely important depending on whether it contains aromatic (Figure 1.16) or aliphatic (Figure 1.15) structure. Aromatic polymers are rigid in the structure and show good mechanical properties but due to their conjugation, they are prone to photodegradation. On the other hand, aliphatic polymers are resistant to sun light. To achieve desired mechanical properties, there is a great need of increasing the molecular weight.

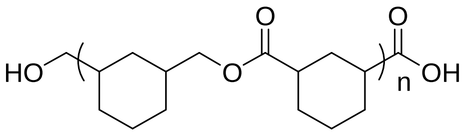


Figure 1.15. Aliphatic polyester.

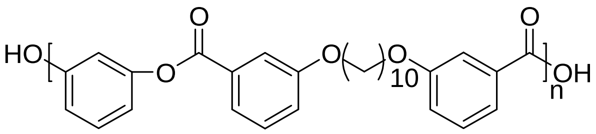


Figure 1.16. Aromatic polyester.

1.4.3. Formulations in Powder Coatings

Before starting any formulation, the end use should be well determined and it is the requirements of the end product that will give shape to the final formulation. General specifications can be classified as:

- The resin system
- The curing schedule
- The gloss level
- Color
- Type of finish
- Durability
- Other requirements

There are six basic types of chemicals used in the formulations:

1. Resins
2. Curing agents
3. Pigments
4. Flow and anti-cratering agents
5. Other additives
6. Fillers and extenders

In the formulations, the most important point is the stoichiometric balance deviations from it may result in poor mechanical and chemical performances. In formulations various additives are added to prevent defects and generate good leveling such as liquid flow additives (0.5 to 1.5%).

As the project is aimed for the synthesis of acid/epoxy type of powder coating, starting formulation of that kind stated below (Table 1.4):

Table 1.4. Polyester:TGIC mix ratio

Polyester resin		TGIC	Poylester:TGIC*	
Acid value	Equivalent weight	Equivalent weight	Calculated	Used
20	2805	108	96.3/3.7	96/4
33	1700	108	94.0/6.0	93/7
50	1122	108	91.2/8.8	90/10

* Weight ratio

First of all, the stoichiometric calculation is done but due to industrial background, rounding the calculated ratios increases the impact resistance of powder coating.

The use of higher acid value polymers increases the solvent and chemical resistance, but as the triglycidyl isocyanurate (TGIC) amount increases, the T_g decreases, that may cause some storage problems. Generally, in the industry 93/7 mix is a standard grade that gives good coating properties [3].

1.4.4. Cyclopolymers as Potential Resins for Powder Coatings

Cyclopolymers can be used as an alternative base resin. They are rigid enough to replace the aromatic resins. Also they do not have double bonds that photodegrade. Several cyclopolymers are reported in the literature. They are synthesized by conventional free radical methods. A great control is needed in molecular weight and end groups. Adjustment of the desired T_g and efficiency of cross-linking reactions are depended on them, respectively. Synthesis of cyclopolymers via controlled polymerization with the ability of reactive end groups should satistfy the desired properties. Therefore, atom transfer radical polymerization was investigated.

1.5. Atom Transfer Radical Polymerization (ATRP)

The most precise polymer synthesis is known as living polymerization, and the first example of which was discovered in the anionic polymerization of styrene with sodium naphthalenide in 1956 [9-10]. A drawback of the ionic techniques is their pronounced sensitivity to moisture, carbon dioxide, and numerous other acidic or basic compounds. Ionic polymerizations can only be applied to a limited range of monomers, and due to significant differences in the reactivity ratios of the monomers, copolymerization reactions are often challenging [11]. The exciting part of the controlled radical polymerization (CRP) is its being free of side reactions such as termination and can generate polymers of well-defined architectures and molecular weights [12].

One of the most developed controlled / living polymerization (CLP) technique is the atom transfer radical polymerization (ATRP). It has gained the attention of the academy and industry, due to the fact that, ATRP has mild reaction conditions and is applicable to wide range of initiators and monomers. ATRP synthesized polymers are capable of chain end-functionalized and can be further used in post-polymerization modifications [13] and serve as macroinitiators in the synthesis of block copolymers [14]. Thanks to its mechanism (Figure 1.17), the radicals, or the active species, are generated through a reversible redox process catalyzed by a transition metal complex [15].

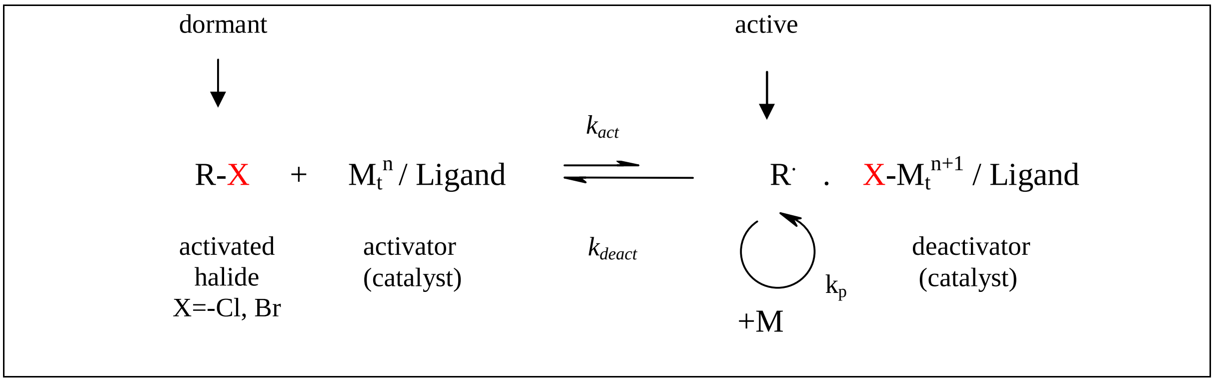


Figure 1.17. The mechanism of ATRP.

ATRP is multi-component reaction which is very dependent on the right balance among them. Every monomer has its own atom transfer equilibrium constant for its active and dormant species. The polymerization rate is determined by the magnitude of the equilibrium constant ($K\text{eq} = k_{\text{act}} / k_{\text{deact}}$), there is only radical termination by coupling or disproportionation which can affect the rate. Too small equilibrium rate will not work or slowly work for ATRP. Each monomer also possesses its own intrinsic radical propagation rate.

The number of growing chains can be controlled by the initiators. . If initiation is fast and transfer and termination negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator in a living polymerization.

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

The rate of polymerization is first order with respect to concentration of the initiator, typically activated alkyl halides (RX). X must move between transition metal complex and the growing chain in order to get well-defined polymers. Hence, the best known halides are bromine and chlorine. R group carbon being as carbonyl, aryl, or allyl can preferably be used as ATRP initiators.

The key component in ATRP is the catalyst. There are prerequisites for an effective transition metal catalyst. First, two readily accessible oxidation states separated by one electron is a must for the metal center. Second, an affinity toward a halogen is needed. Third, coordination sphere around the metal should have the ability of an expansion upon oxidation where accommodate a halogen. Fourth, the ligand and metal complex should be strong.

Bulk and in solution or heterogeneous system are okay for ATRP. Chain transfer to solvent must be as much as little. Solvent and the catalytic system interactions must be kept in the consideration. Poisoning of the catalyst by the solvent (e.g., phosphine or carboxylic acids in copperbased ATRP) [16] and solvent-assisted side reactions, which is more pronounced in a polar solvent [17], should be minimized.

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

The potential of the aliphatic cyclopolymers in terms of the material requirements of a powder coating resin has been mentioned above. ATRP technique has been chosen to achieve cyclopolymers with living end groups, and low polydispersities (Figure 1.18). Previously in our research, ATRP was successfully tuned for the controlled cyclopolymerization by tuning the ATRP components but further studies are needed to turn these cyclopolymers into a powder coating resin which include chain end functionalization, quantitative determination of end groups and finally cross-linking of these end groups with curing agents.

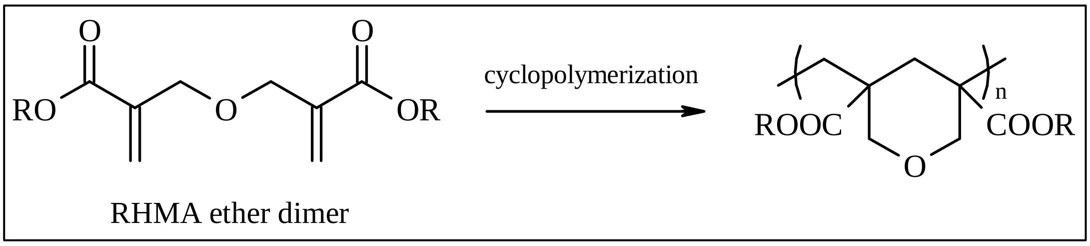


Figure 1.18. Cyclopolymerization of RHMA ether dimers.

In our research group, three types of alkyl α-(hydroxymethyl)acrylate ether dimers (ethyl, n-butyl and t-butyl) have been previously studied. The results showed that the bulkier the R groups, the more efficient is the cyclization [18]. These results are consistent with the results obtained from the conventional free radical polymerization [19, 20].

Finally, cyclopolymers within the desired T_g range were synthesized by using soft block containing di-initiator. A linear correlation between molecular weight and T_g was observed, in the targeted moleular weight range (Figure 1.19).

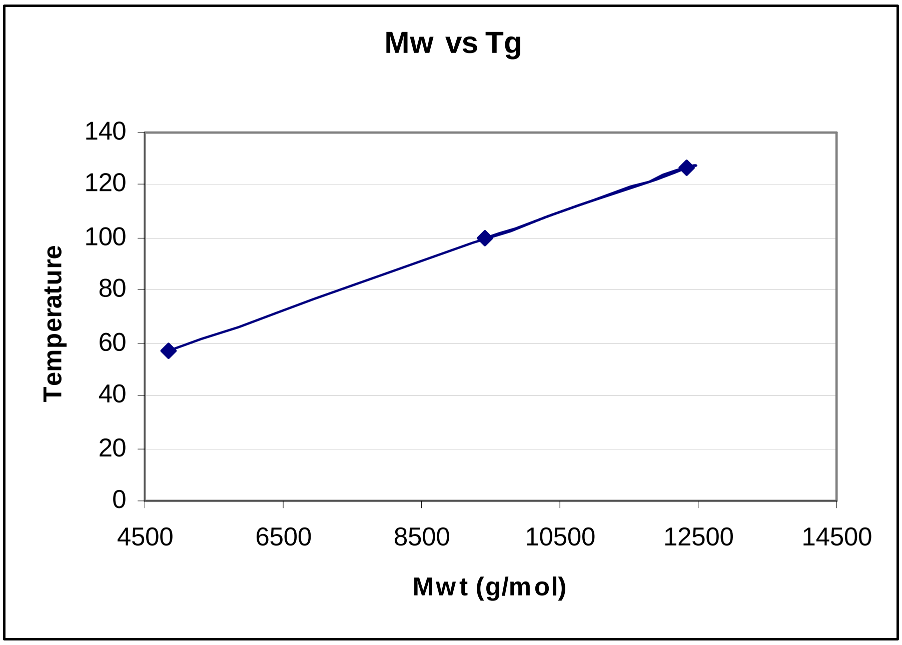


Figure 1.19. Mw and T_g Relationship of TBHMA derived polymers [21].

1.7. End Group Functionality of Polymers

1.7.1. Telechelic Approach

To achieve end groups with desired functionality via ATRP, there are two main ways. First, the usage of an initiator with one side bearing desired end group and the other is a halogen; to yield a polymer with a mono-functionality. The halogen end group can be easily turned into the needed functionality by simple organic reactions (Figure 1.20). Second, the synthesis of a di-functional initiator with two halogen end groups which will lead to a polymer whose both end groups are halogen bearing. Those halogens can be reacted to get desired functionality.

Recently, there is a dramatic increase in the use of one simple organic reaction which is click chemistry. Click chemistry as it is named by Sharpless gained the attention of the scientists since it enables high specificity, quantitative yields in the presence of most functional groups and the absence of side products other than simple molecules such as water, carbon dioxide [22]. The most termed reaction as click chemistry is the copper-catalyzed Huisgen dipolar cycloaddition (Figure 1.21) reaction between an azide and an alkyne leading to 1,2,3-triazole.[23-25].

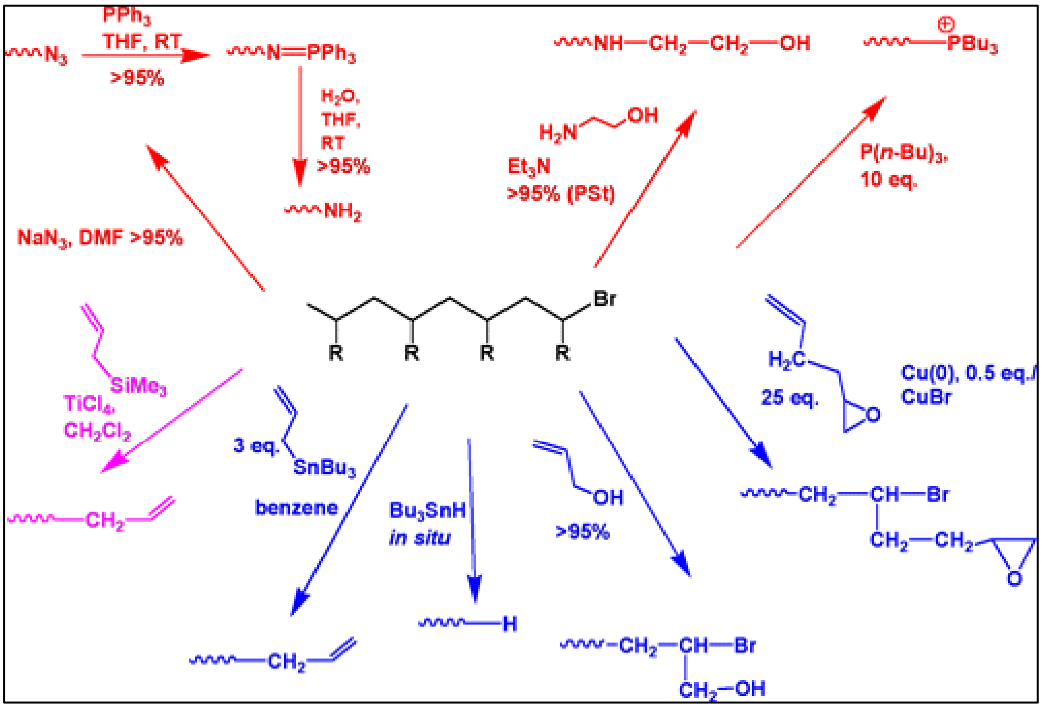


Figure 1.20. End group modifications [15].

There are several applications in the field of polymer chemistry, and it has already been employed successfully in material science [26]. The synthesis of a excess of telechelic [27-31] or backbone- functionalized [32, 33] polymers as well as more complex structures such as cross-linked nanoparticles and micelles, [34, 35] dendrimers, [36, 37]segmented copolymers, [38, 39] cyclic polymers, [40] star [41-43] and brush [44, 45] copolymers, networks, [46] and many others has been demonstrated.

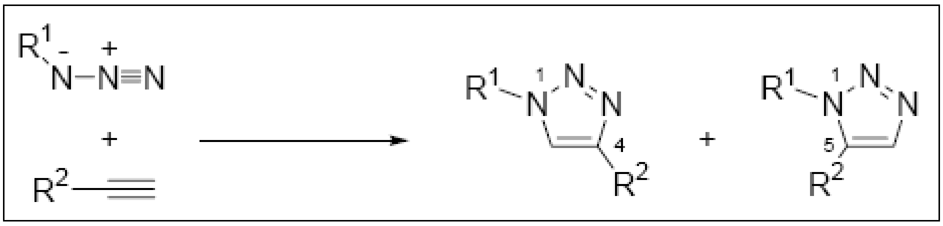


Figure 1.21. Huisgen dipolar cycloaddition reaction.

2. OBJECTIVE

ATRP of TBHMA ether dimers, the tuning of the glass transition temperature by changing the molecular weight and the backbone structure and some preliminary end group studies have been performed in our research group. What remains challenging is the achievement of the curing reactions, efficiently, quantitative determination of the end groups and to have a final curable powder coating mixture.

By combining previous works on TBHMA derived polymers, the ultimate goal was to synthesize the first known example of a powder coating containing living cyclic polymers with low polydispersities and well-defined molecular weights (Mw 5000-7000) that is able to achieve T_g (60-80 ^{o}C) for low-temperature cured powder coatings. Hence, a considerable amount of effort was spent to get reactive end groups for the curing reactions.

3. EXPERIMENTS

3.1.Monomer Synthesis

3.1.1. 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%), 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, tetrahydrofuran (THF) were all obtained from Merck and used as received.

3.1.2. Apparatus

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

3.1.3. 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 the desired product. The pure product 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-($\mathit{C}H_3$)$_3$], 124.69 (C=CH_2), 138.83 ($\mathit{C}H_2$=C), 165.26 (C=O) ppm.

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

3.1.4. Synthesis of Tetra Ethylene Glycol di Initiator (TEG-DI)

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 120 mL with distilled water. The organic layer was separated and evaporated under reduced pressure to give the desired product. Evaporation of the solvent gave the pure TEG-DI initiator as a light brown liquid in around 80 per cent yield [21].

^{13}C-NMR ($CDCl_3$): δ= 30.89 (CH_3), 55.88 (C-($\mathit{C}H_3$)$_2$), 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.

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

Ethylene glycol 20 fold excess (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 a 100 mL three-necked round-bottom flask fitted with a condenser and a magnetic stirrer. Using ice bath for cooling, 4.8245 g (0.021 mol) of 2-Bromo-2- methylpropionyl bromide and 20 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 250 mL methylene chloride, extracted firstly three times with 75 mL of 0.5 N HCl, then six 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 initiator as a light brown liquid in around 60 per cent yield.

^{1}H-NMR ($CDCl_3$): δ= 1.92 (s, 6H, CH_3), 3.71 (t, 2H, OCH_2), 4.27 (t, 2H, OCH_2), 5.27 (t, 1H, OH) ppm.

3.2. Polymer Synthesis

3.2.1. Materials

Copper (I) bromide (CuBr) (Aldrich, 99.999%), and pentamethyldiethylene triamine (PMDETA) (Aldrich, 99%) were used as received without purification. The synthesized initiators (TEG-DI and HEBIB) 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.

3.2.2. 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°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.

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

All glassware, needles and stirring bars were dried overnight in an oven at 120 °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 TBHMA 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.

3.2.4. The Procedure for the Purification of the Resulting Polymers

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

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

TBHMA ether dimer (1.35 g, 4.5 mmol) was polymerized in 7 mL xylene (0.64 M) by using CuBr (16.5 mg, 0.115 mmol) and PMDETA (24 μL, 0.115 mmol) catalyst system and TEG-DI (40 μL, 0.15 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. 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, 0.71 g, in a 53 per cent yield.

3.2.6. ATRP of TBHMA Ether Dimer with TEG-DI (Alcohol end group)

TBHMA ether dimer (1.51 g, 5.1 mmol) was polymerized in 7 mL xylene (0.73 M) by using CuBr (7.1 mg, 0.050 mmol) and PMDETA (11 μL, 0.050 mmol) catalyst system and TEG-DI (17 μL, 0.058 mmol). The polymerization was carried out at 80 ^{o}C for 2.5 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 and a half of the 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, 0.67 g, in a 45 per cent yield.

3.2.7. ATRP of TBHMA Ether Dimer with TEG-DI (Acid end group)

TBHMA ether dimer (2.00 g, 6.7 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (30.8 mg, 0.215 mmol) and PMDETA (45 μL, 0.215 mmol) catalyst system and TEG-DI (40 μL, 0.068 mmol). 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.

3.2.8. ATRP of TBHMA Ether Dimer with HEBIB (mono hydroxyl end group)

TBHMA ether dimer (2.00 g, 6.7 mmol) was polymerized in 7 mL xylene (0.96 M) by using CuBr (30.8 mg, 0.215 mmol) and PMDETA (45 μL, 0.215 mmol) catalyst system and HEBIB (44 mg, 0.208 mmol). The polymerization was carried out at 70 ^{o}C for 0.5 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.

3.3. Click Chemistry

3.3.1. Materials

Copper (I) bromide (CuBr) (Aldrich, 99.999%), pentamethyldiethylene triamine (PMDETA) (Aldrich, 99%), sodium azide (Merck, 99%), 4-pentynoic acid (Aldrich, 95%) were used as received without purification. The solvents; tetrahydrofuran (THF), methylene chloride (DCM) and methanol were obtained from Merck, dimethyl formamide (DMF) from Fluka (99% GC Grade) and were used as received.

3.3.2. 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^oC/min. All polymer samples were purified by passing via neutral aluminum oxide columns to remove the copper catalyst followed by one reprecipitations before NMR, GPC, DSC and TGA analyses.

3.3.3. The Procedure for the Preparation of Azide End-Functionalized TBHMA Polymer

The preparation of azide end-functionalized TBHMA polymer was conducted in a three-necked round bottom flask using DMF as the solvent. The polymer was dissolved in 15 mL DMF. Then sodium azide was added to the solution. The reaction mixture was stirred for 48 h at room temperature. The resulting reaction mixture was evaporated under reduced pressure (never to complete dryness) and the obtained azide was precipitated into methanol / H_2O; this mixture was vacuum filtered and dried in a vacuum oven (not above 35 ^0C), over night. Then, the azide functionalized polymer was dissolved in a minimum amount of THF or DCM and reprecipitated into methanol / H_2O (5/1) and vacuum filtered and dried in a vacuum overnight (not above 35 ^0C).

The characterization of the azide formation has been carried out by Infrared (IR). 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.

3.3.4. The Preparation of Azide End-Functionalized TBHMA Polymer

Polymers previously prepared by the procedure described in section 3.2.5. (1.64 g, 0.209 mmol) were dissolved in 15 mL DMF and 20 fold excess of sodium azide added (0.272 g, 4.18 mmol) to the solution. The reaction mixture was stirred for 48 h at room temperature. The resulting reaction mixture was evaporated under reduced pressure (never to complete dryness) and the obtained azide was precipitated into 150 mL methanol / 30 mL H_2O; this mixture was vacuum filtered in a buchner funnel and dried in a vacuum oven (not above 35 ^{0}C), preferably over night. After that, azide end grouped polymer was dissolved in a minimum amount of THF or DCM and precipitated into 150 mL methanol / 30 mL distilled H_2O and preferably was vacuum filtered in a buchner funnel and dried in a vacuum oven or after removing the solution dried in a vacuum oven over night (not above 35 ^{0}C). The obtained polymer was white powder, soluble, 1.4 g, in a 85 per cent yield.

3.3.5. The Procedure for the Click Chemistry of Azide End-Functionalized TBHMA Polymer

Azide end-functionalized TBHMA polymer prepared by the procedure 3.3.3. was dissolved in 5 mL DMF and then 4 fold excess of 4-pentynoic acid, 2 fold excess of PMDETA, 2 fold excess of CuBr (0.129 g, 0.902 mmol), 3 mL DMF was added. After that, three times freeze-thaw cycle is applied to the reaction mixture and the mixture was stirred at least 24 h at room temperature.

3.3.6. The Procedure for the Purification of the Resulting Polymers

To remove the catalyst, all polymers were passed through a neutral aluminum oxide column prepared with THF / methanol (300 mL) solvent, collecting the only fraction that eluted and evaporated under reduced pressure only DMF remains. Polymers were reprecipitated into methanol / water and were vacuum filtered in a buchner funnel; dried in a vacuum oven overnight. The pure polymers were dissolved in THF and analyzed by GPC and NMR.

3.3.7. Click Chemistry of Azide End-Functionalized TBHMA Polymer (Acid end group)

Azide end-functionalized TBHMA polymer prepared by the procedure 3.2.8. (1.72 g, 0.451 mmol) was dissolved in 5 mL DMF and then 4 fold excess of 4-pentynoic acid (0.177 g, 1.806 mmol), 2 fold excess of PMDETA (0.188 mL, 0.902 mmol), 2 fold excess of CuBr (0.129 g, 0.902 mmol), again 3 mL DMF was added. After that, three times freeze-thaw cycle is applied to the reaction mixture and the mixture was stirred at 70 h at room temperature.

The resulting polymer was passed through a neutral aluminum oxide column to remove the catalyst, prepared with 10 THF / 1 methanol (300 mL) solvent, collecting the only fraction that eluted and evaporated under reduced pressure only DMF present. Polymers were reprecipitated into 5 methanol / 1 water (120 mL) and was vacuum filtered in a buchner funnel; dried in a vacuum oven overnight. The obtained polymer was white powder, soluble, 1.4 g, in an 81 per cent yield.

3.4. Chain Extension with Isophorone Diisocyanate

3.4.1. Materials

Isophorone diisocyanate (IPDI) (Fluka, 95%), pyridine (Acros, 99+%). The synthesized polymer samples were purified by passing via basic aluminum oxide columns to remove the copper catalyst followed by two reprecipitations before. The solvents; methylene chloride and methanol were obtained from Merck and used as received. Xylene (mixture of isomers) was purified by distillation over Na metal and benzophenone.

3.4.2. Apparatus

GPC analyses were done using a Viscotek GPCmax VE-2001Analysis System. PL Gel 5 µm MIXED-C Column was calibrated against polystyrene standards.

3.4.3. The Procedure for the Preparation of Chain Extension with IPDI

All glassware, needles and stirring bars were dried overnight in an oven at 120 ^{o}C and purged with nitrogen gas before use. The preparation of chain extension reaction for TBHMA ether dimer derived telechelic dihydroxyl functional polymers (TBHMA-OH) was conducted in a round bottom flask using xylene as the solvent. The polymer was dissolved in 2 mL xylene into the reaction flask. The solution was stirred and purged with nitrogen for 20 min. IPDI was added to the solution by syringe. Then, the solution was immersed into a preheated oil bath. The catalyst, pyridine was introduced into the reaction flask by syringe. Chain extension reactions 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.

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.

3.4.4. The Preparation of Chain Extension with IPDI

TBHMA-OH (205.5 mg, 0.037 mmol) chain extension reaction was performed in 2 mL xylene by using IPDI (8.3 mg, 0.037 mmol) and pyridine (10 mg, 0.13 mmol) catalyst. The reaction was carried out at 110 ^{o}C for 2 hours. The reaction mixture was homogeneous during the reaction. 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, 0.203 g, in a 99 per cent yield.

3.5. Cross-linking (Curing) Reactions

3.5.1. Cross-linking with Castor Oil Glycidyl Ether

3.5.1.1. Materials

1,4-diazabicyclo[2.2.2]octane (DABCO) (Aldrich, 98%), Benzyl trimethyl ammonium chloride (BTMAC) (Merck, 98%), Castor oil glycidyl ether (Castor-E) and BYK A550 (air release agent) taken from the Research Group of S.H. Kusefoglu were used as received without purification. The solvent; methylene chloride (DCM) were obtained from Merck and used as received.

3.5.1.2. Apparatus

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

3.5.1.3. The Procedure for the Preparation of Polymer Cross-linking with Castor Oil Glycidyl Ether in a Sealed Vial

Bifunctional carboxylic acid end group TBHMA polymers (TBHMA-COOH) were dried under vacuum at around 60 ^{0}C for at least one day. Tri-epoxy functional castor oil derivative (castor-E) was pre-heated in an oil bath, under nitrogen medium in a sealed vial, at 70 ^{0}C for 20 mins. The reactions were performed in a tightly sealed vial in a pre-heated oil bath at 180 ^{0}C, under nitrogen medium. The Castor-E was weighted into a vial and then the reactive polymer was added on. They were dissolved in DCM. Immediately, DABCO was added to the solution and the vial was sealed and DCM was evaporated in a pre-heated 70 ^{0}C oil bath under nitrogen flow. Then, the vial was put in a pre-heated 180 ^{0}C oil bath, still on-going nitrogen flow. Finally, the vial was opened and cooled to the room temperature and after an over night period, by addition of again DCM, the resistance against DCM was tested. The reaction products were analyzed by Infrared (IR) and TGA scans were performed under nitrogen flow using a TA Q50 at a heating rate of 10^{o}C/min.

3.5.1.4. The Preparation of Polymer Cross-linking with Castor Oil Glycidyl Ether in a Sealed Vial

Experiment 1. Cross-linking with castor oil glycidyl ether was performed with TBHMA-COOH (151.1 mg, 0.035 mmol) in 4 mL DCM by using Castor-E (26.3 mg, 0.022 mmol) and BTMAC (1-2 crystals) catalyst. The reaction was carried out at 180 ^{o}C for 3 hours. The resulting polymer was tested for its resistance against DCM.

Experiment 2. Cross-linking with castor oil glycidyl ether was performed with TBHMA-COOH (155.3 mg, 0.023 mmol) in 4 mL DCM by using Castor-E (19.9 mg, 0.017 mmol) and DABCO (1-2 crystals) catalyst. The reaction was carried out at 180 ^{o}C for 3 hours. The resulting polymer was tested for its resistance against DCM.

3.5.2. Cross-linking with TGIC

3.5.2.1. Materials

Benzyl trimethyl ammonium chloride (BTMAC) (Merck, 98%), triglycidyl isocyanurate (TGIC) taken from the Pulver Termoset Powder Coating, was used as received without purification. BYK A550 (air release agent) taken from the Research Group of S.H. Kusefoglu was used as received without purification. The solvent; methylene chloride (DCM) and methanol were obtained from Merck and used as received.

3.5.2.2. Apparatus

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

3.5.2.3. The Procedure for the Preparation of Crosslinked Polymer with TGIC

Bifunctional carboxylic acid end grouped TBHMA polymers (TBHMA-COOH) were dried under vacuum at around 60 ^{0}C for at least one day. The reactions were performed in a tightly sealed vial in a pre-heated oil bath at 180 ^{0}C, under nitrogen medium. The polymer was weighted into a reaction flask and then TGIC and BTMAC was added on. They were dissolved in DCM-methanol mixture. Solvent was evaporated under vacuum to become a viscous homogenized liquid. The reactive mixture was poured on a surface and waited overnight for complete dryness. Next day, homogenized dry mixture was placed in a pre-heated oven at 70 ^{0}C for one hour. Then, it was placed into a pre-heated 180 ^{0}C oven for 2 hours. Finally, and the sample was cooled to the room temperature and after an over night period, by addition of DCM, the resistance against DCM was tested. The reaction products were analyzed by Infrared (IR) and TGA scans (under nitrogen flow using a TA Q50 at a heating rate of 10^{o}C/min).

3.5.2.4. The Preparation of Polymer Cross-linking with TGIC

Cross-linking with TGIC was performed with TBHMA-COOH (150.2 mg, 0.025 mmol) in 5 drops of methanol – 5 mL DCM by using TGIC (mg, 0.016 mmol), BYK A550 (1 drop from 14 mg / 6 mL DCM stock solution) and BTMAC (1.56 mg, 0.0084 mmol) catalyst. The reaction was carried out at 180 ^{o}C for 2 hours. The resulting polymer was tested for its resistance against DCM.

3.6. Copolymerization with Acid Terminated Polymers (Undecenoic Acid Derived)

3.6.1. Materials

Copper (I) bromide (CuBr) (Aldrich, 99.999%), and pentamethyldiethylene triamine (PMDETA) (Aldrich, 99%) were used as received without purification. The synthesized initiators (TEG-DI and HEBIB) 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.

3.6.2. Apparatus

GPC analyses were done using a Viscotek GPCmax VE-2001Analysis System. PL Gel 5 µm MIXED-C Column was calibrated against polystyrene standards. 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.

3.6.3. The Procedure for the Preparation of Copolymerization with Acid Terminated Polymers

All liquid chemicals were purged with nitrogen for at least 20 minutes prior to use. The copolymerization was conducted in a three-necked round bottom flask. The solid macroinitiator acid terminated poly(TBHMA ether dimer) was added to a reaction flask fitted with a stirring bar and which had been sealed with rubber septa and purged with nitrogen for 15 minutes. *n*-BA was added to the reaction flask by syringe. The resulting mixture was stirred and degassed until the macroinitiator dissolved. Then, the solution was degassed for an additional 20 minutes and immersed into a preheated oil bath at 80 ^{o}C. CuBr was put in a separate vial sealed with a rubber septum and 2 mL of *n*-BA was added to the CuBr and purged with nitrogen for 20 minutes. PMDETA was added to the vial and the resulting mixture was stirred and heated until the CuBr dissolved. The resulting solution was then transferred into the reaction flask by syringe. Polymerization was carried out under nitrogen at 80 ^{o}C for 6 h. The final polymer was precipitated into methanol/water (5/1) and dried in a vacuum oven overnight.

The 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.

3.6.4. The Preparation of Copolymerization with Acid Terminated Polymers

Acid terminated poly(TBHMA ether dimer) (0.16 g, 0.017 mmol) was copolymerized in bulk, n-butyl acrylate (5.34 g, 0.04 mol) by using CuBr (10 mg, 0.07 mmol) and PMDETA (15 μL, 0.072 mmol) catalyst system 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, 0.77 g, in a 14 per cent yield.

4. RESULTS AND DISCUSSION

4.1. Optimization study of Poly(TBHMA)

4.1.1. Synthesis of the TBHMA ether dimers

Extended Baylis-Hillman reaction enables the synthesis of TBHMA ether dimers since its mechanism is a tertiary amine-catalyzed coupling of an α,β-unsaturated carbonyl compound with an aldehyde [47] and the mechanistic pathway to the TBHMA ether dimer is shown in Figure 4.1. Here, the addition of the amine catalyst, 1,4-Diazabicyclo[2.2.2]octane (DABCO), to α,β-unsaturated ester to form a stabilized nucleophilic anion is the most important step. This generated nucleophile attacks to the aldehyde and TBHMA starts to be produced by the elimination of the amine moiety. As the temperature increases, the conversion of TBHMA to its ether dimer is thermodynamically favorable. However, this conversion is very sensitive to water. In the formation of TBHMA ether dimer, water is formed and its presence cleaves the etheric bonds back to TBHMA. Thus, to achieve higher yields, the removal of the water must be preferred.

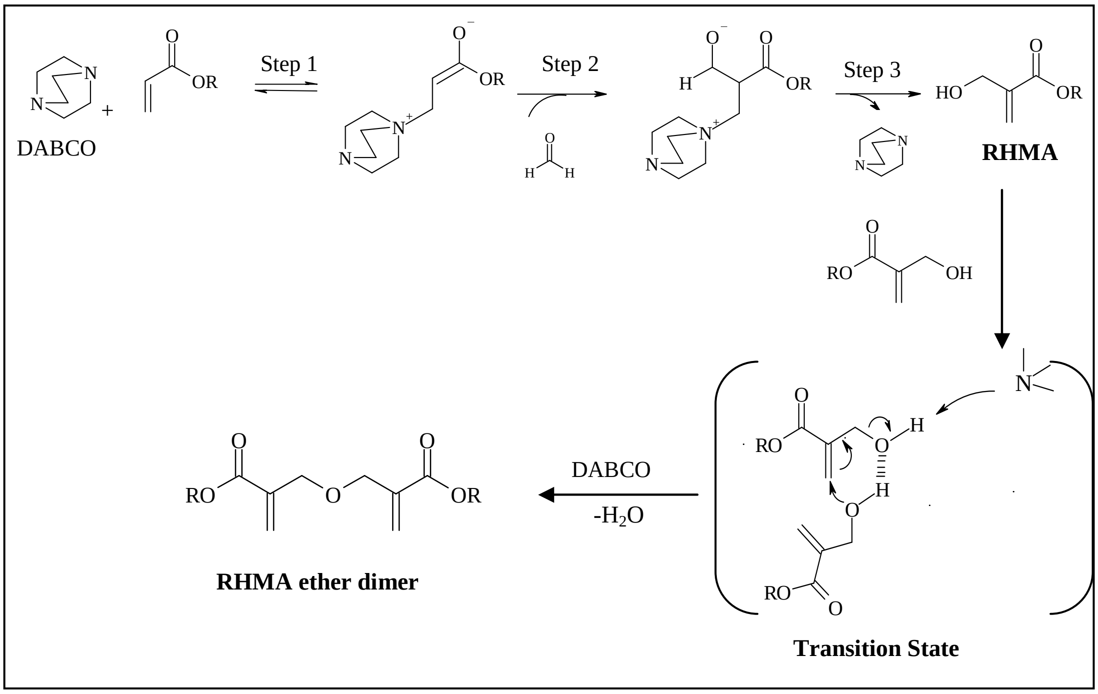


Figure 4.1. Synthesis of TBHMA ether dimer monomer.

For the screening of the reaction medium, thin layer chromatography (TLC) was used via silica gel (SiO_2) plates and CH_2Cl_2 as the elution and dilution solvent. It helped to screen reaction intermediates and the actual time for the reaction completeness. When reactants disappeared during the reactions, TBHMA and its ether dimer appeared. TBHMA acetal derivative were also observed as by-products.

In the synthesis of TBHMA ether dimer, good purity was obtained when acid extraction of the crude reaction mixture dissolved in CH_2Cl_2 was followed by vacuum distillation. The further purification was carried out on basic Alox column.

4.1.2. Cyclopolymerization of TBHMA Ether Dimers by ATRP Using TEG-DI

The cyclopolymerization of TBHMA ether dimers by ATRP using soft block containing di-initiators were previously successfully carried out in our research group. The general cyclopolymerization scheme is shown in Figure 4.2. 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 60-80 ^{o}C.

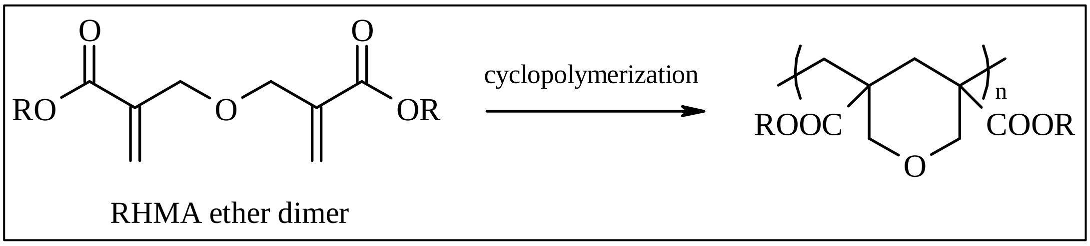


Figure 4.2. Cyclopolymerization of RHMA ether dimers.

To achieve this, tetra-ethylene glycol was incorporated into the di-initiator structure as soft block (Figure 4.3). The incorporation was achieved through di-esterification of the glycol with 2-bromo-2- methylpropionyl bromide.

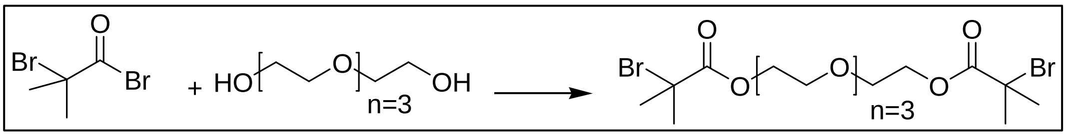


Figure 4.3. Synthesis of initiators using tetra-ethylene glycol.

Then, cyclopolymerizations were carried out using this di-initiator (Figure 4.4).

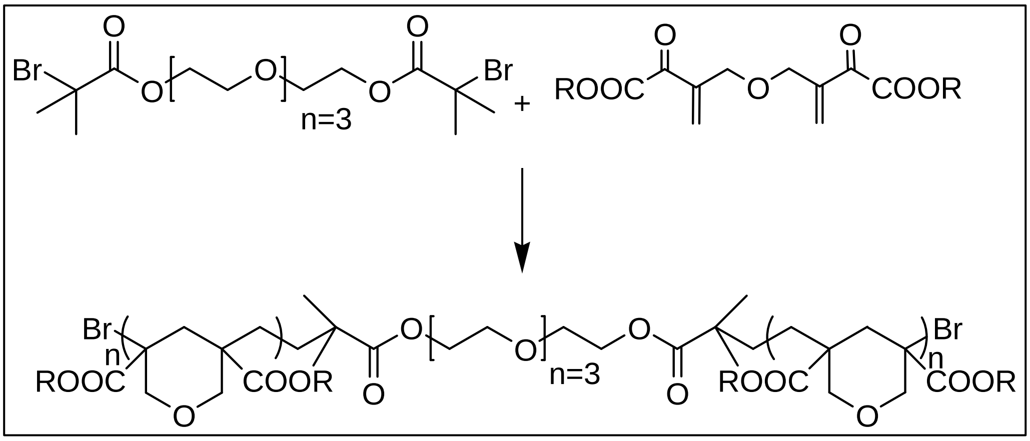


Figure 4.4. Polymerization of TBHMA ether dimer via ATRP.

Unless stated otherwise all the polymers mentioned in the coming sections were synthesized using the soft block containing di-initiators.

4.2. Functionalization of Cyclopolymers

Functionalization studies upon end groups were carried out using two main approaches:

- The first approach was the post functionalization of halogen terminated polymers by using ATRP. For end the functionalization, allyl alcohol and undecenoic acid were reacted with the end groups under ATRP conditions to give alcohol and acid end groups respectively. This approach leads to end-functional/crosslinkable polymers. The reason for 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, the reaction should stop after the first addition of the double bond.

- The second approach was the synthesis of functional polymers using click chemistry. In this approach, TBHMA ether dimer derived polymers were reacted with sodium azide and then with 4-pentynoic acid. This approach, in principle, should lead to polymers with cross-linkable end groups, too.

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

For the end functionalization, hydroxyl and carboxylic acid end groups were targeted (Figure 4.5). Allyl alcohol and undecenoic 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 [^{1}5]. Undecenoic 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.

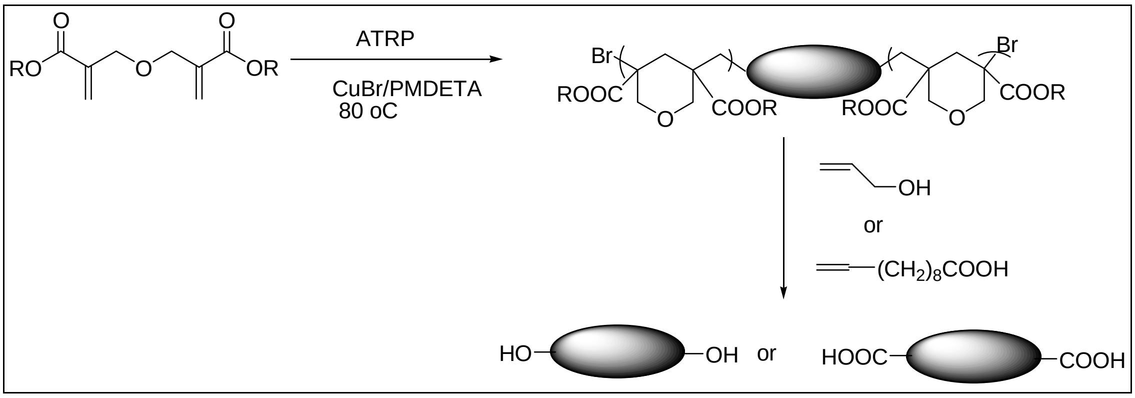


Figure 4.5. Representation of end-functional polymer synthesis.

These two reagents were added at 150 minutes after initiation. Since the addition of these reagents stops the polymerizations, the desired molecular weight can be obtained. Both allyl alcohol and undeconoic acid were used in excess amounts for the completeness of the reactions.

As the Table 4.1 shows, polymers with different molecular weights where acid and alcohol end group functionalities were targeted were synthesized. The addition of allyl alcohol and undecenoic acid were previously reported in the literature, however a quantitative analysis of the end groups has never been carried out. Thus, we carried out ^{31}P-NMR for the determination of the end groups. This novel method which has not been published yet due to its Proprietary Nature (GE Global Research Center has the intellectual Property Rights) has been tested on reference polymers with known end group concentrations where excellent results were obtained (See section 4.2.4. A set of data was collected from the ^{31}P-NMR spectra of the reference polymers which consist of monohydroxyl functional polymers obtained by employing a hydroxyl containing initiator hydroxyl-ethyl bromoisobutyrate (HEBIB)).

Table 4.1. Results of poly(TBHMA) polymers with hydroxyl and carboxyl end groups[a].

Entry	End-Group	$[M]_o$:$[I]_o$:$[Cat]_o$	Time (h)	Conv[b] (%)	$M_{n,cal}$ (10^3 g/mol)	$M_{n,sec}$ (10^3 g/mol)	M_w/M_n
1	COOH	31:1:1	2.5	45	4185	3606	1.24
2	COOH	31:1:1	3	42	3900	3800	1.20
3	COOH	31:1:1	3.5	31	2880	3097	1.22
4	COOH	32:1:1	2.5	37	3450	3509	1.24
5	COOH	48:1:1	3	64	8960	5976	1.24
6	COOH	89:1:1	2.5	39	10530	7685	1.25
7	COOH	110:1:1	3	36	11520	9632	1.28
8	COOH	31:1:1	3.5	46	4280	4571	1.23
9	OH	31:1:1	2.5	42	3900	3332	1.22
10	OH	47:1:1	2.5	47	6580	5644	1.22
11	OH	34:1:1	2.5	60	6050	6371	1.26
12	OH	110:1:1	3.5	45	14400	7886	1.26
13	OH	31:1:1	2.5	67	6235	6259	1.25

[a] Polymerizations were carried out in xylene at 80°C. The concentrations of monomers in xylene were in between 0.65-0.97 M.

[b] Measured by gravimetric methods.

The measured concentrations of both acid and hydroxyl groups were much lower than expected (Table 4.4). In some cases these groups were completely absent. The expected addition of allyl alcohol and undecenoic acid to the cyclopolymer end groups under ATRP conditions seemed not so efficient. We believe that the tertiary bromo-end groups and thus the generated tertiary radicals seem to be too stable (or energetically too low) to react with the double bonds of the allyl alcohol or undecenoic acid. At this point, we also suspected that the low conversions could be the result of irreversible termination reactions which are known to occur at high conversions during the initial synthesis of the cyclopolymer by the ATRP process. Therefore, we synthesized a new set of polymers where the conversions were kept low. The analysis of these polymers by again ^{31}P-NMR showed that keeping the conversions low did not make any significant change in the conversion of the end groups to the corresponding alcohols or acids.

As a result, we believe that the reactivity of the tertiary end groups of the cyclopolymers is low to react with the allyl alcohol and undecenoic acid. It is also possible that in the ATRP conditions, the poisoning of the CuBr by allyl alcohol or undecenoic acid is also responsible for the low efficiency of the conversions, especially in the case of the carboxylic acid.

4.2.2. Synthesis of End functional Polymers via Click Chemistry

As widely used in the recent literature, click chemistry was also applied to get carboxyl end groups on TBHMA ether dimer derived polymers. Azidation of tertiary bromide end groups were targeted by using sodium azide [43]. After monitoring with IR; 4-pentynoic acid in the presence of catalyst, Cu(I)Br; was reacted to obtain di-carboxyl TBHMA ether dimer derived polymers (Table 4.2 and Figure 4.6). ^{1}H-NMR (Figure 4.7) and IR (Figure 4.8 - 4.10) confirmed the qualitative conversion of the bromo end groups to acidic end groups. For quantitative analysis of the end groups, which is very important for cross-linking reactions, ^{31}P-NMR spectra were taken (Figure 4.12).

Table 4.2. Results of poly(TBHMA) polymers with carboxyl end groups via click chemistry

Entry	End Group	$M_{n,sec}$ (10^3 g/mol)	M_w/M_n
1	COOH	7309	1.11
2	COOH	7909	1.08
3	COOH	11434	1.23
4	COOH	8503	1.16

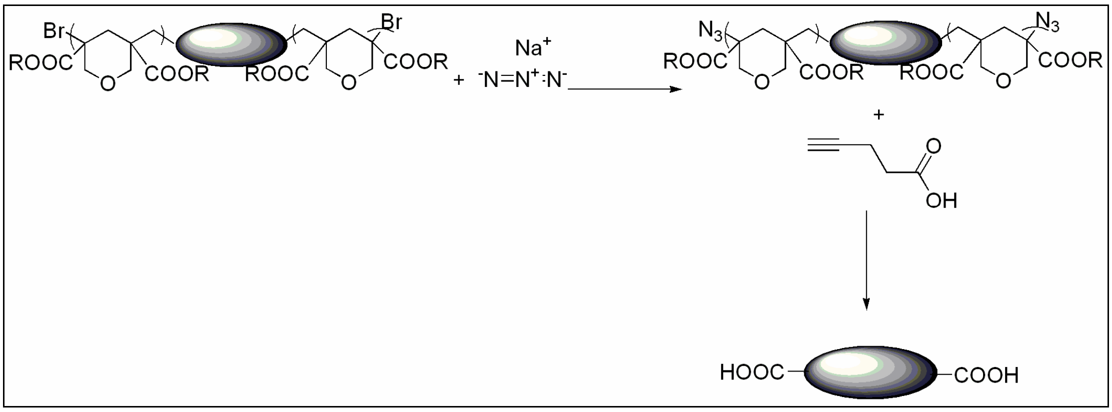


Figure 4.6. Representation of end-functional polymer synthesis via click chemistry.

According to the ^{31}P-NMR results (Table 4.4.) with click chemistry the end group conversion to carboxylic acid was more successful than the previous method employed; however conversions were not high enough to achieve high cross-linking. For click chemistry, having only used high conversion ATRP derived polymers (over 50%) could affect the efficiency of the click reactions. Therefore, similar experiments were carried out with low conversion polymers, but even employing these did not improve the results much in the undecenoic acid case.

As a result it is possible that the low conversion of the end groups is an outcome of the low reactivity of the tertiary bromides and the cyclic structure which increases the steric crowding. Although the literature contains examples of click chemistry on tertiary bromides we believe that this reaction should not be very efficient on tertiary carbons where the reaction is expected to follow an SN_1 pathway rather than SN_2. The low concentration of acid end groups as observed by NMR may also be experimental due to the interaction of the reagents used in the ^{31}P-NMR with the polymer end groups. We did not check such interactions yet, therefore, the ^{31}P-NMR results of the click chemistry needs to be studied in details in the future.

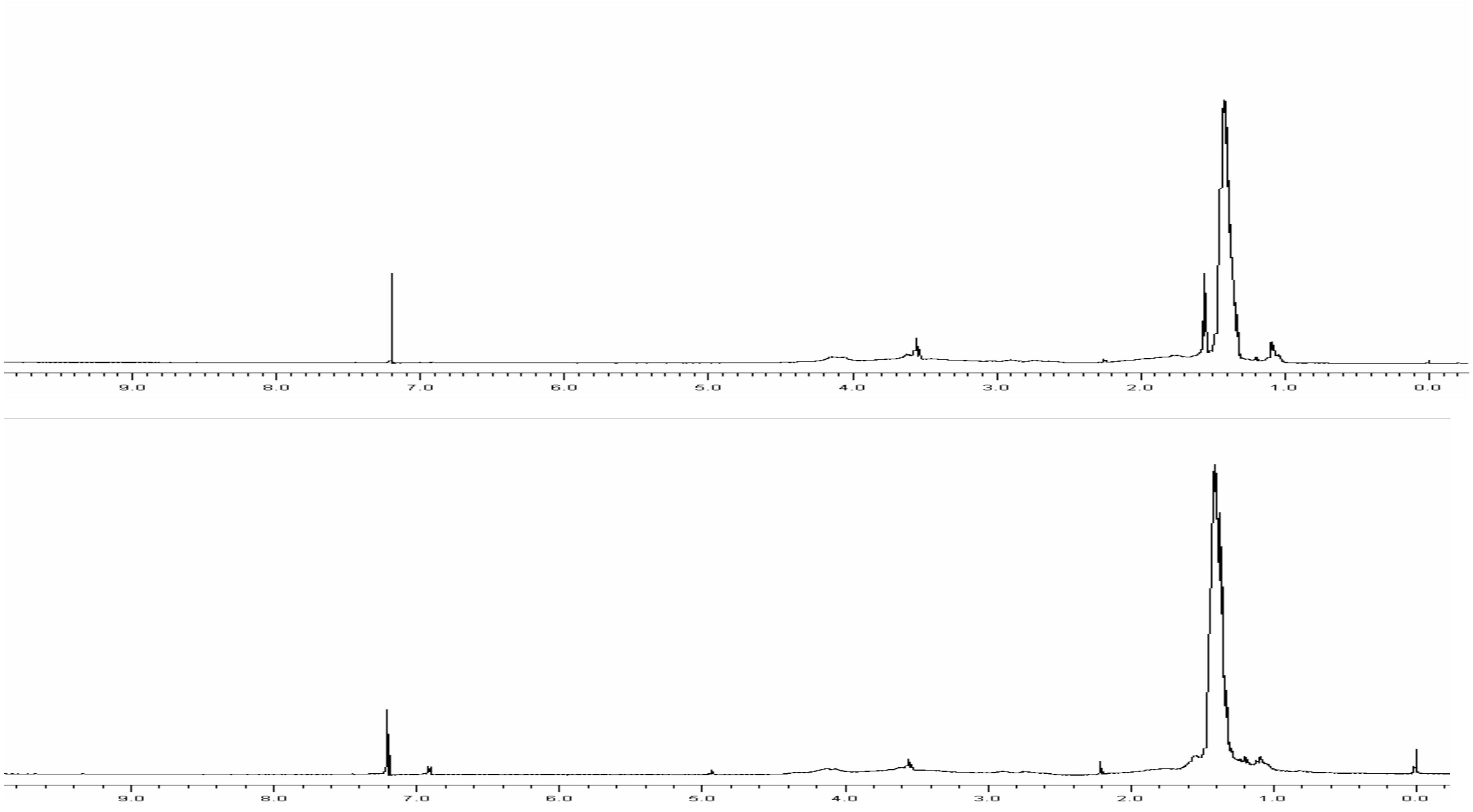


Figure 4.7. ^{1}H-NMR spectra of the TBHMA ether dimer derived polymer before and after click chemistry.

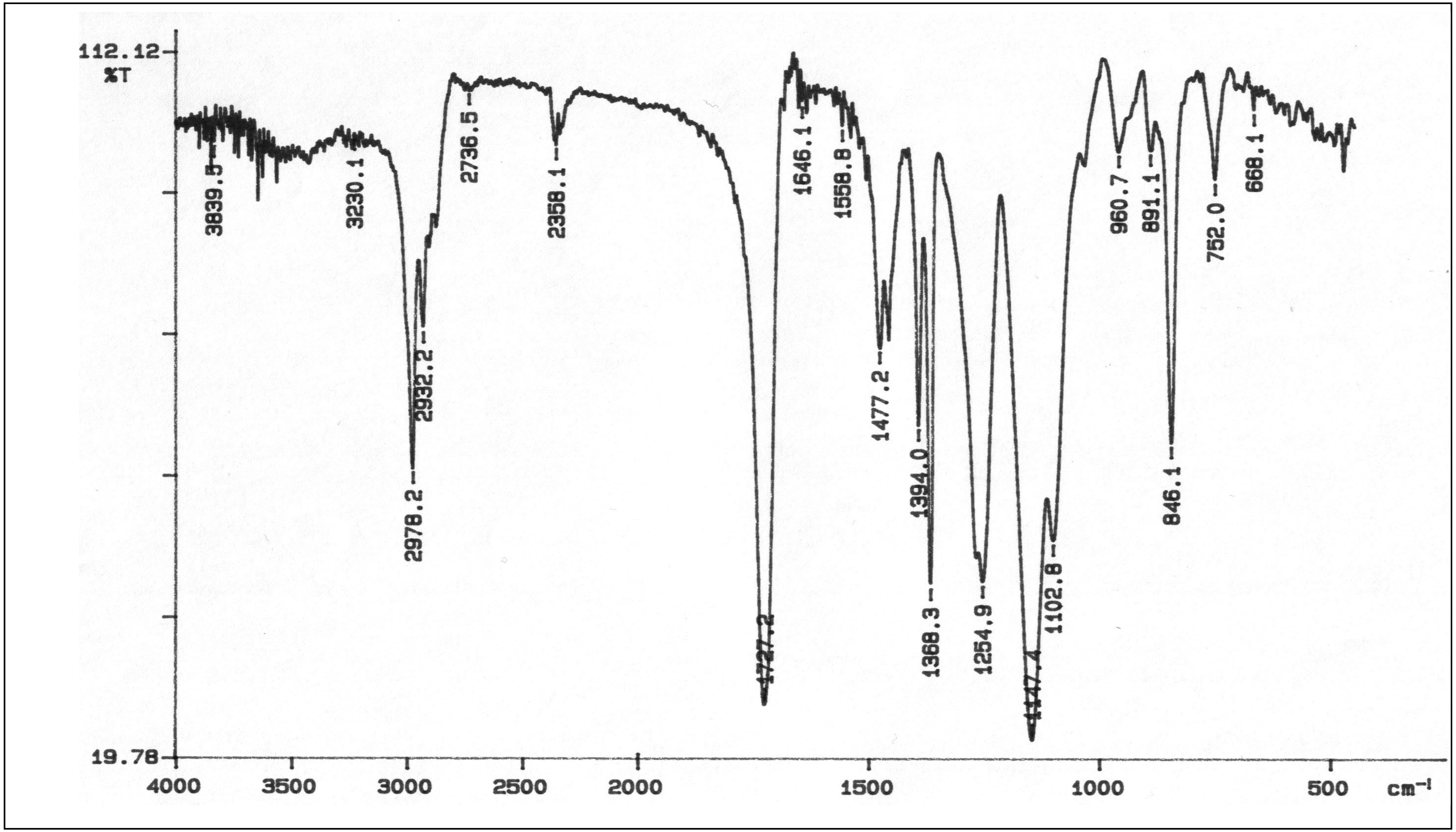


Figure 4.8. IR spectrum of the TBHMA ether dimer derived polymer before click chemistry.

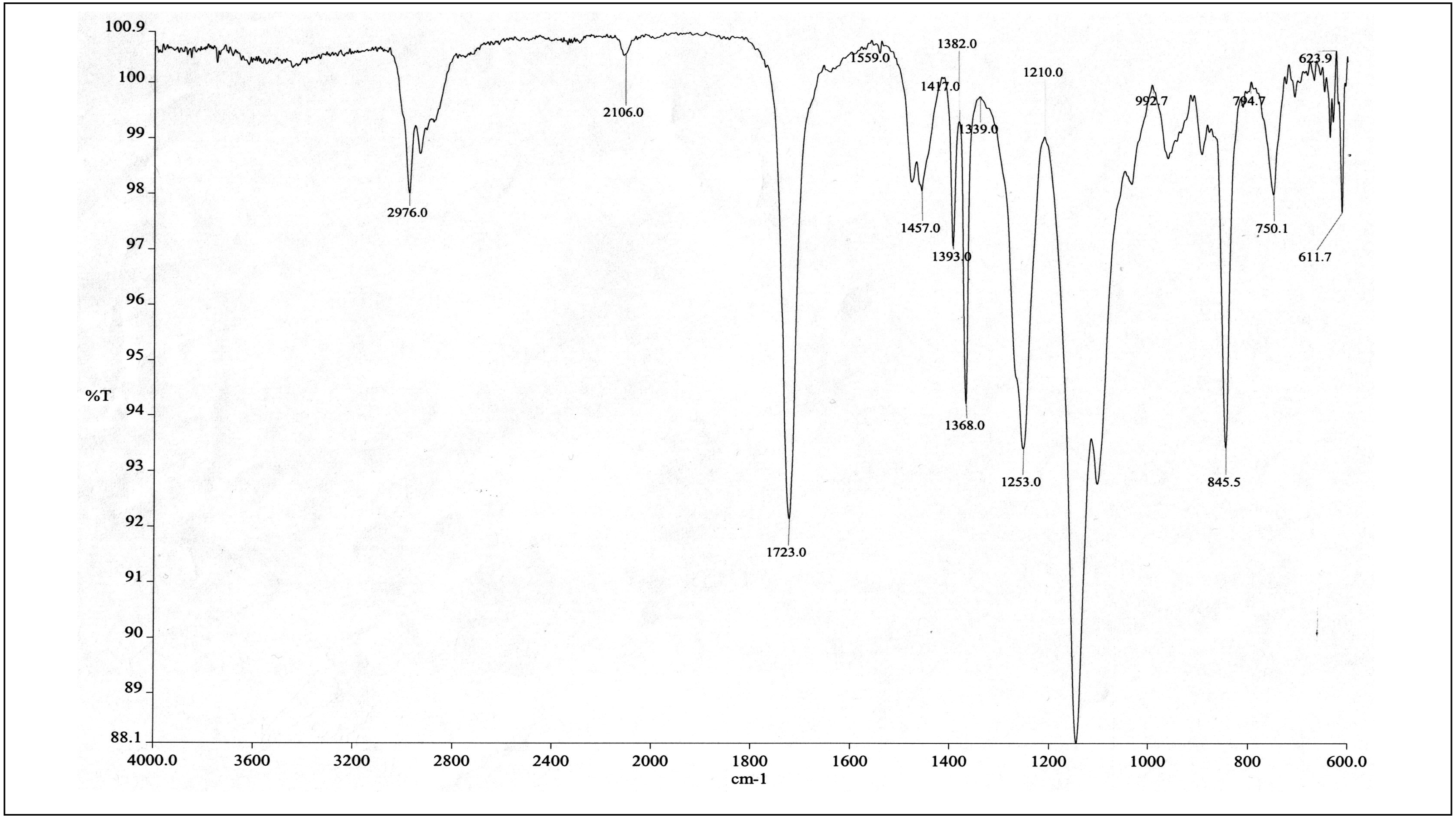


Figure 4.9. IR spectrum of the TBHMA ether dimer derived polymer after azidation.

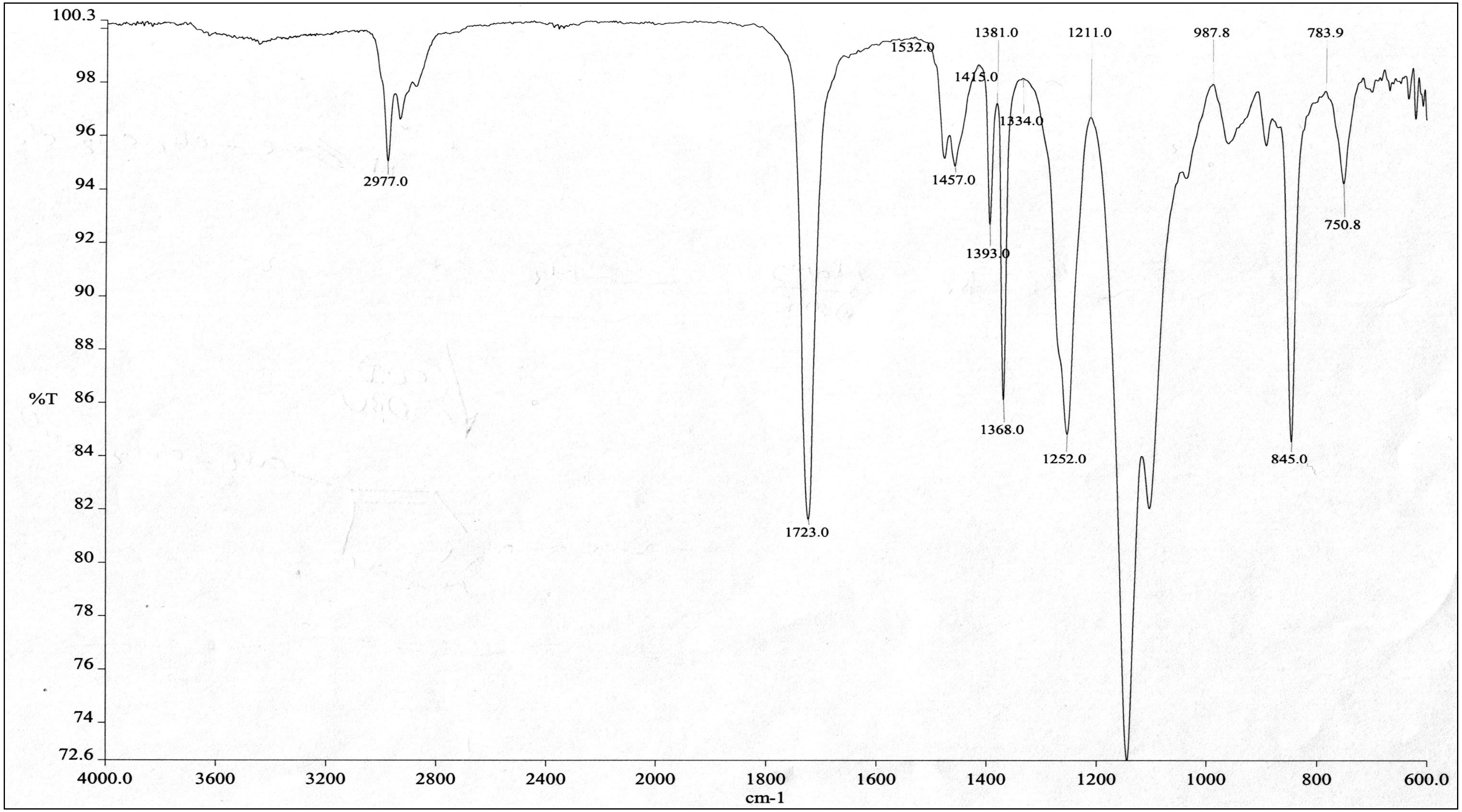


Figure 4.10. IR spectrum of the TBHMA ether dimer derived polymer after click chemistry.

4.2.3. Synthesis of End functional Polymers via HEBIB Initiation

For the mono-end functionalization, hydroxyl end group was targeted (Figure 4.11). Hydroxyl containing HEBIB initiator was used to introduce hydroxyl end groups [49]. Here, it is important to mention that as the hydroxyl group is on the initiator, high yield of that functionality is expected in the final polymers (Table 4.3).

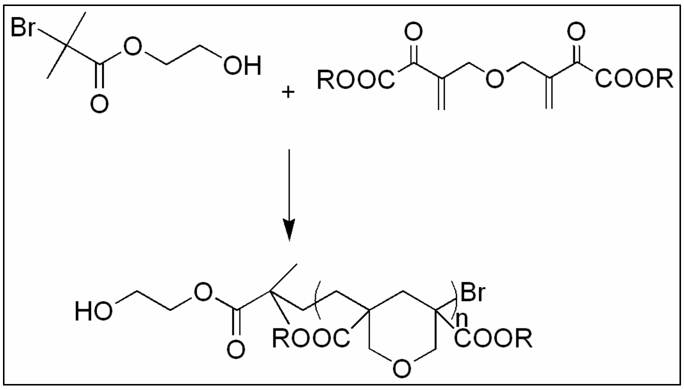


Figure 4.11. Representation of end-functional polymer synthesis by HEBIB initiator.

Table 4.3. Results of poly(TBHMA) polymers with alcohol eng group by HEBIB initiator[a].

Entry	End Group	$[M]_o$:$[I]_o$:$[Cat]_o$	Time (h)	Temp (^{0}C)	Conv[b] (%)	$M_{n,cal}$ (10^3 g/mol)	$M_{n,sec}$ (10^3 g/mol)	M_w/M_n
1	m-OH	31:1:1	3	80	70	6510	9536	1.49
2	m-OH	31:1:1	2	80	76	7068	9712	1.33
3	m-OH	53:1:1	2	80	70	11200	10003	1.46
4	m-OH	31:1:1	1	70	80	7440	8186	1.21
5	m-OH	31:1:1	1	60	65	6045	8015	1.30
6	m-OH	31:1:1	0.5	70	65	6045	6885	1.23

[a] Polymerizations were carried out in xylene. The concentrations of monomers in xylene were in 0.97 M.

[b] Measured by gravimetric methods.

4.2.4. Characterization of the End Groups

For the identification of the end groups, initially ^{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.

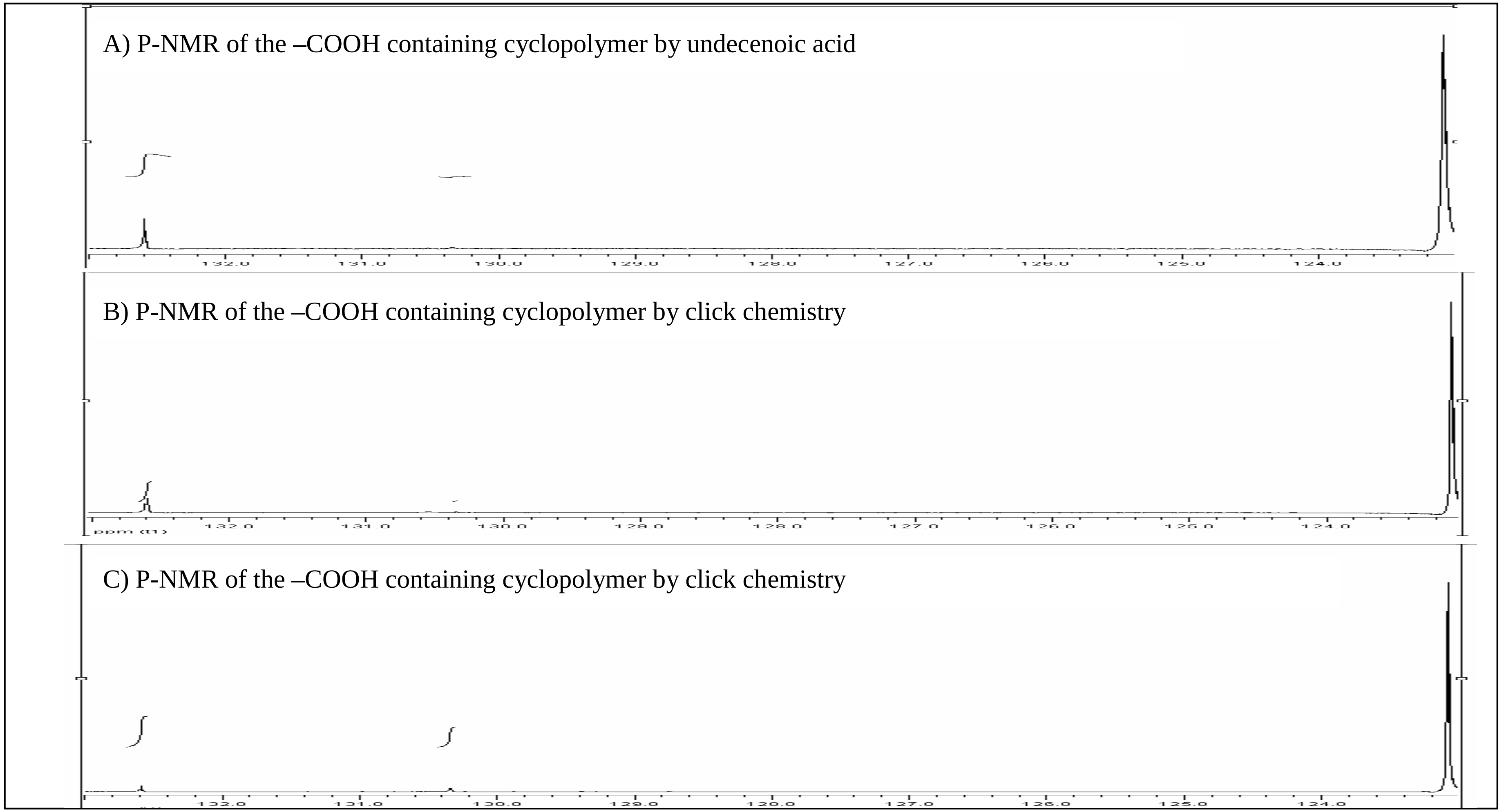
The end groups were finally identified (Table 4.4) using ^{31}P-NMR techniques [48]. After finding the derivatization procedure, a set of ^{31}P-NMR data were taken. This technique does not only help the identification of the end groups but also allows the quantification of the end groups in ppm levels (min 20 ppm). Thus, from the NMR data the observed OH and COOH concentrations were calculated in ppm, and these were compared with the theoretical values predicted based on GPC measurements. The ratio of these two measurements gave an idea about the relative concentration of the end groups (Figure 4.12-4.13).

Table 4.4. Results of. ^{31}P-NMR study.

Entry	End Group	Conv (%)	$M_{n,cal}$ (10^3 g/mol)	$M_{n,sec}$ (10^3 g/mol)	Exp (ppm)	Theo^a (ppm)	Yield ppm (%)
1	BR^b	51	5150	5790	0	0	0
2	COOH^c	36	11520	9632	25	9344	0.27
3	COOH^c	30	2790	3097	279	29060	0.96
4	COOH^c	37	3450	3509	261	25648	1.02
5	COOH^d	84	4620	3810	617	23622	2.61
6	COOH^d	64	9390	7838	3922	11483	34.15
7	m-OH^e	63	10080	10003	1336	1699	78.63
8	m-OH^e	65	6045	8015	1864	2121	87.87
9	m-OH^e	65	6045	6885	2322	2469	94.05
10	m-OH^e	76	7068	9712	1750	1750	99.96
11	OH^f	46	7360	5644	164	5689	2.89
12	OH^f	55	6235	6235	567	2727	20.78

[a] ppm by weight. [b]ATRP without end group modification. [c] End group modification via undecenoic acid addition. [d] End group modification via click chemistry. [e] ATRP using HEBIB initiator. [f] End group modification via allyl alcohol addition.

Entries 7-10 correspond to the polymers synthesized by the monohydroxyl containing initiators. As can be seen from Table 4.4 the NMR results correlate well to the expected values. Deviation from the theoretical value (100%) may be an indication of transesterification reactions due to the hydroxyl end groups. These results served as proof for the validity of the ^{31}P-NMR technique that has been used later for the identification and quantification of acid and hydroxyl end groups. Indeed, as expected, with the bromo terminated polymer (entry 1) no acid or alcohol functionality was observed in the NMR.

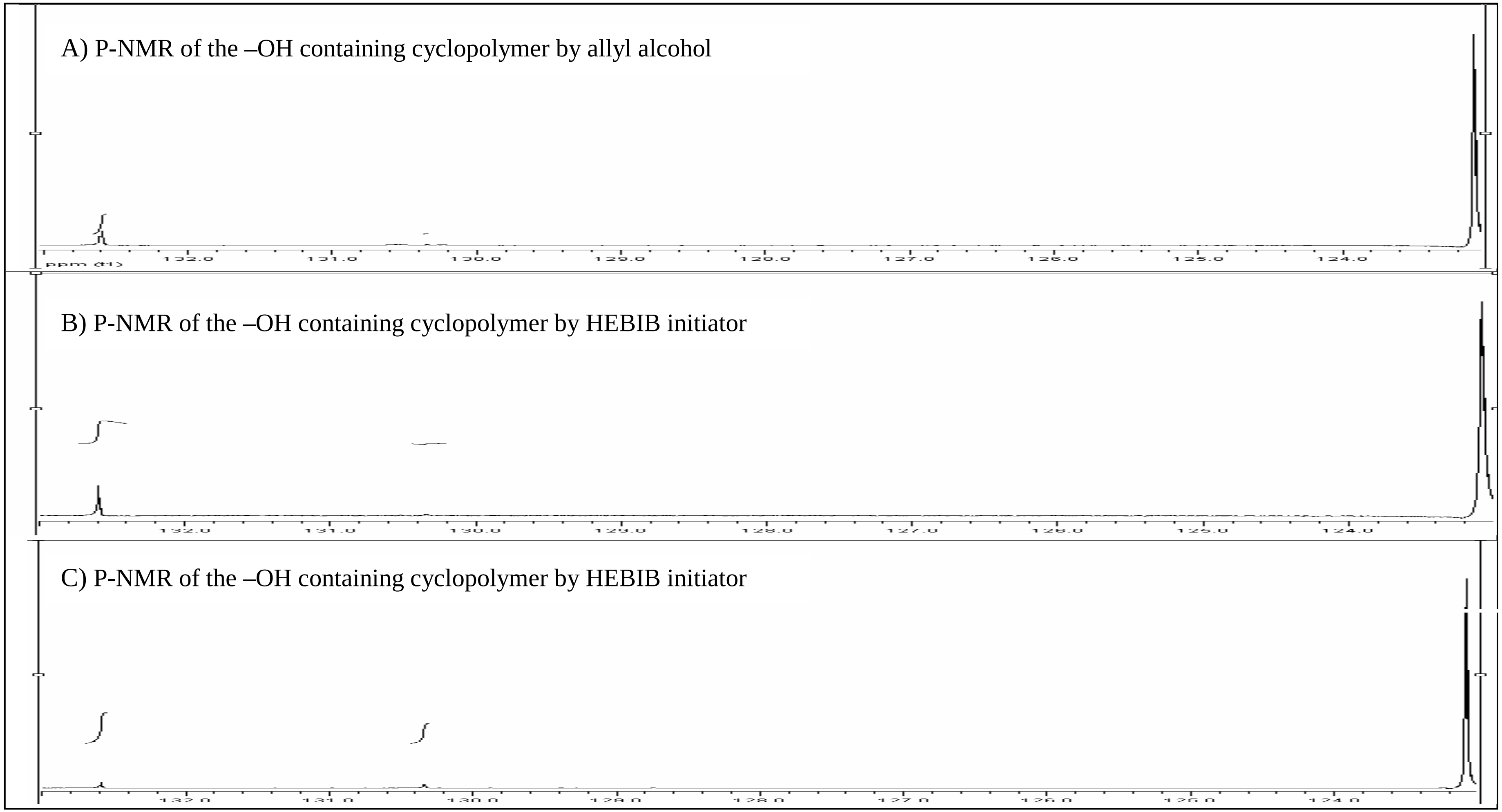


A) P-NMR of the –COOH containing cyclopolymer by undecenoic acid

B) P-NMR of the –COOH containing cyclopolymer by click chemistry

C) P-NMR of the –COOH containing cyclopolymer by click chemistry

Figure 4.12. ^{31}P-NMR Results of the – COOH end functionalized cyclopolymers.



A) P-NMR of the –OH containing cyclopolymer by allyl alcohol

B) P-NMR of the –OH containing cyclopolymer by HEBIB initiator

C) P-NMR of the –OH containing cyclopolymer by HEBIB initiator

Figure 4.13. ^{31}P-NMR Results of the –OH end functionalized cyclopolymers

4.5. End Group Reactivity

In this section chain extension reactions and curing reactions were carried out to investigate the reactivity of the end-groups. It is important to mention that these experiments were carried out before the ^{31}P-NMR technique became available to our research group. Therefore, the reactions that will be presented in this section were mostly carried out to show the presence or the absence of the hydroxyl or acid end groups. Unless stated otherwise, the experiments were carried out with allyl alcohol and undecenoic acid added cyclopolymers.

4.6. Chain Extension Reactions with IPDI

To prove the presence of the alcohol modified end groups, chain extension reactions with difunctional isophorone diisocynate (IPDI) were performed (Figure 4.14). It was expected that if the polymers were functionalized fully at their end groups, the reaction with IPDI would result in a considerable increase in molecular weight.

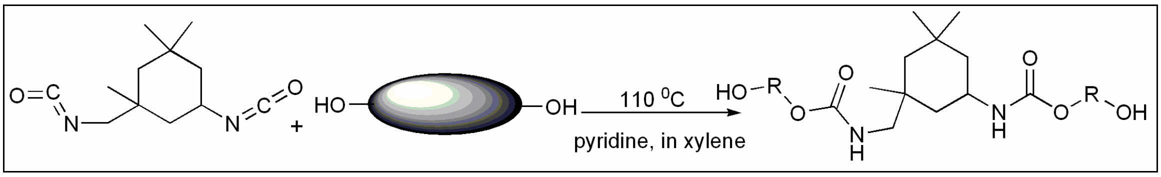


Figure 4.14. Representation of chain extension reactions with IPDI.

When the extension reactions were carried out, only slight increases in molecular weights were observed (Table 4.5). The stagnation of the molecular weights can be explained by the absence of the reactive end groups. But this the can also be the result of the unoptimized reactions conditions, since even if the reactions were performed under nitrogen, any water present in the reaction medium could result in the the loss of the isocyanate functionality which would make the chain extension reactions impossible. In addition, it is known that; tertiary amines are not the best catalysts for these reactions, for example, dibutylin dilauryl mercaptide derivatives are better catalysts than tertiarty amines [50].

Table 4.5. Results of chain extension reactions with IPDI[a]

Entry	Group	Mn,sec (10^3 g/mol)	Time (h)	Temp. (^{0}C)	Conv %	Group	Mn,sec (10^3 g/mol)	Mw/Mn	Δ Mn
1	OH[b]	5200	1.1	100	~99	OH	6343	1.20	1143
2	OH[c]	5462	1.1	100	~99	OH	6291	1.21	829
3	OH[d]	5931	2	110	~99	OH	7385	1.21	1454
4	PEG[e]	2720	1.3	110	~99	OH	3432	1.34	712

[a] IPDI and the synthesized polymers were used in 1:1 molar ratio based on end group concentrations. [b] 13.16×10^{-5} mol (end groups) [c] 7.52×10^{-5} mol [d] 13.64×10^{-5} mol [e] PEG-3000

4.5. Cross-linking (Curing) Reactions

4.5.1. Cross-linking with Castor Oil Glycidyl Ether

In order to get a cross-linked network, tri-functional castor oil glycidyl ether (castor-E) was also used as a cross-linker (Figure 4.15).

Experiments showed that with castor-E, curing reactions occurred at higher temperatures than the targeted values (120 - 140 ^{o}C). The cross-linked material did not dissolve in organic solvents which showed that cross-linking was efficient. However, the cross-linked material was very brittle (Table 4.6).

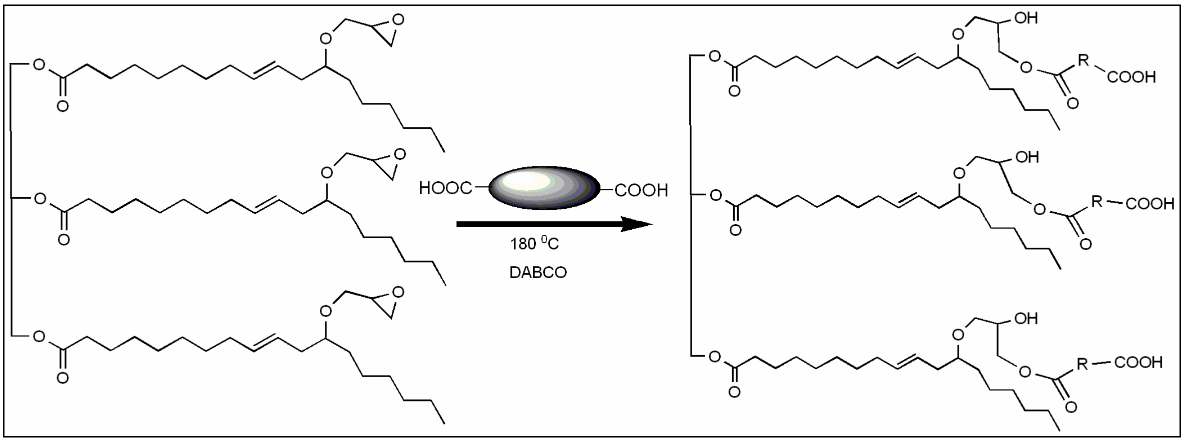


Figure 4.15. Representation of cross-linking with epoxidized castor oil

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Table 4.6. Results of. cross-linking with castor oil glycidyl ether[a]

Entry	Group	Time (h)	Temperature (^{o}C)	Resistance to DCM
1	COOH[b]	3	160	Not Resistant
2	COOH[c]	0.5	180	Not Resistant
3	Blank	0.5	180	Not Resistant
4	COOH[d]	1	180	Not Resistant
5	COOH[e]	3	180	Resistant
6	COOH[f]	2	180	Partially
7	Blank	3	180	Not Resistant

[a] In calculations, the Castor oil glycidyl ether epoxy functionality was taken as 3.5 and molecular weight was taken as 1200 g/mol (Later, it was found out that the epoxy functionality is 1.2) TBHMA polymers were used 0.9 equivalent w.r.t. gycidyl ether [b] 4.66 x10^{-5} mol. [c] 8 x10^{-5} mol. [d] 7.76 x10^{-5} mol. [e] 7.60 x10^{-5} mol. [f] 6.66 x10^{-5} mol.

The TGA analysis of TBHMA derived polymers showed an initial weight loss at 189 ^{o}C which corresponds to the degradation of esteric t-butyl groups to carboxylic acids by a heat induced process. The formation of carboxylic acid functionality by such a process may be the reason why curing, as observed by the solubility test, was observed with these samples. Actually the isothermal analysis of the TBHMA cyclopolymers in TGA for 30 min at 180 ^{0}C showed that some degradation occurred even at the curing temperature (Figure 4.17).

4.5.2. Cross-linking with TGIC

To achieve successful powder coating, TGIC was used (Figure 4.16). TGIC is the number one choice of industry as a cross-linker with acid functional polymers. The mixing of the cyclopolymer, TGIC and the catalyst, benzyl trimethyl ammonium chloride, was achieved with the addition of methanol to the system. Methanol was then evaporated prior to the curing. The curing did not give good solvent resistance, it is at his point that we became suspecious about the presence of the acid end groups (Table 4.7).

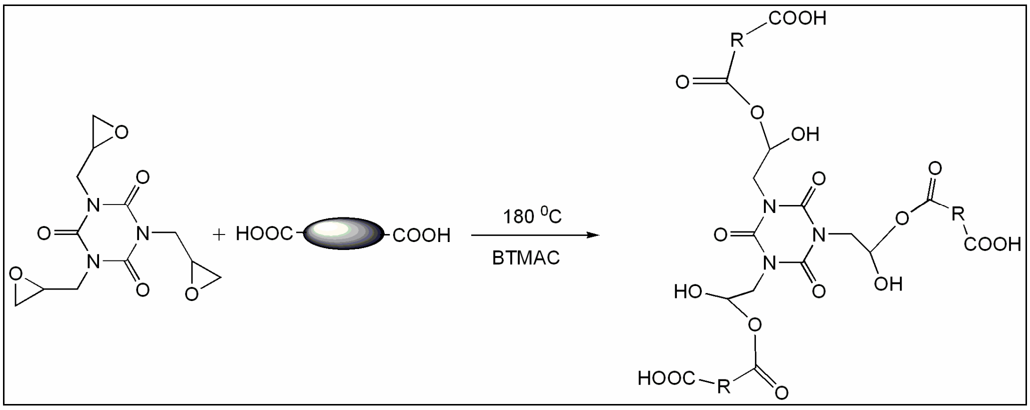

Figure 4.16. Representation of Cross-linking with TGIC

After these results we became interested to a new method for synthesizing telechelic polymers: the click chemistry. Thus as mentioned above polymers with the expected carboxylic and groups were synthesized. Preliminary results from the curing reactions showed good solvent resistance even though, the results of ^{31}P-NMR state that the end group modification via click chemistry was not quantitative. Here, having tertiary living end groups probably limits the efficiency of the click chemistry.

Table 4.7. Results of. cross-linking with TGIC[a].

Entry	Group	Time (h)	Temperature (^{o}C)	Resistance to DCM
1	COOH[b]	1	180	Not Resistant
2	COOH[c]	1.5	180	Not Resistant
3	COOH[d]	2	180	Resistant
4	COOH[e,f]	2	180	Resistant

[a] TGIC has triepoxy groups and TBHMA derived polymers have difunctionality. Equimolar acid and epoxy end groups were reacted [b] 8.32x10^{-5} mol (end groups). [c] 7.96 x10^{-5} mol. [d] 5.02 x10^{-5} mol. [e] 3.82 x10^{-5} mol. [f] Synthesized via click chemistry.

4.6. Copolymerization with Acid Terminated Polymers (Undecenoic Acid Derived)

To ensure that the low addition of undecenoic acid to the bromo ends of the polymers, copolymerization reactions were performed. The so-called undecenoic acid terminated TBHMA ether dimer derived polymers were used as macro initiators. We believed that If the molecular weight would shift to the higher values in a controlled manner then it would be obvious that living end groups, in this case activated bromo end groups, should still be present. As suspected the copolymers had very narrow molecular weight distributions, and in the GPC traces, the peaks corresponding to the macroinitiators were completely absent indicating that almost all the polymer end groups were bromo terminated and not acid terminated (Table 4.8).

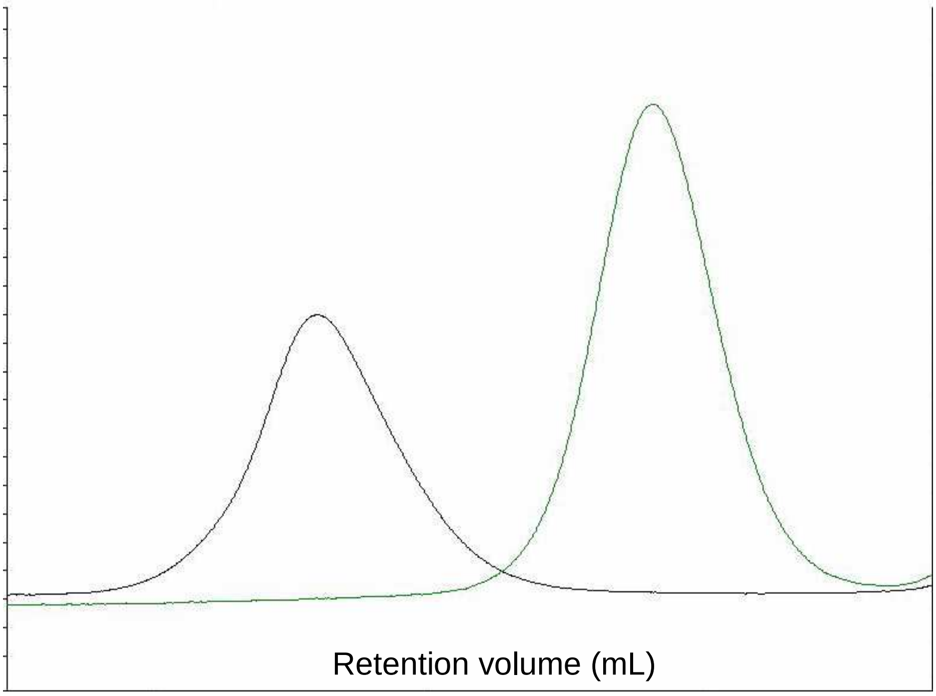

Figure 4.17. Overlay of GPC traces - macroinitiator and block copolymer

Table 4.8. Results of. Copolymerization

Entry	Group	Ppm %[a]	Macroinitiator		Block Copolymer			
			$M_{n,sec}$ (10^3 g/mol)	M_w/M_n	Mononer	Time (h)	$M_{n,sec}$ (10^3 g/mol)	M_w/M_n
1	COOH	1.02	3509	1.24	*n*-BA	6	48534	1.26
2	COOH	0.27	9632	1.28	*n*-BA	6	48922	1.22

[a] The presence of the end groups determined by ^{31}P-NMR.

Therefore, this result supports our thoughts in the low efficiency of the addition reactions.

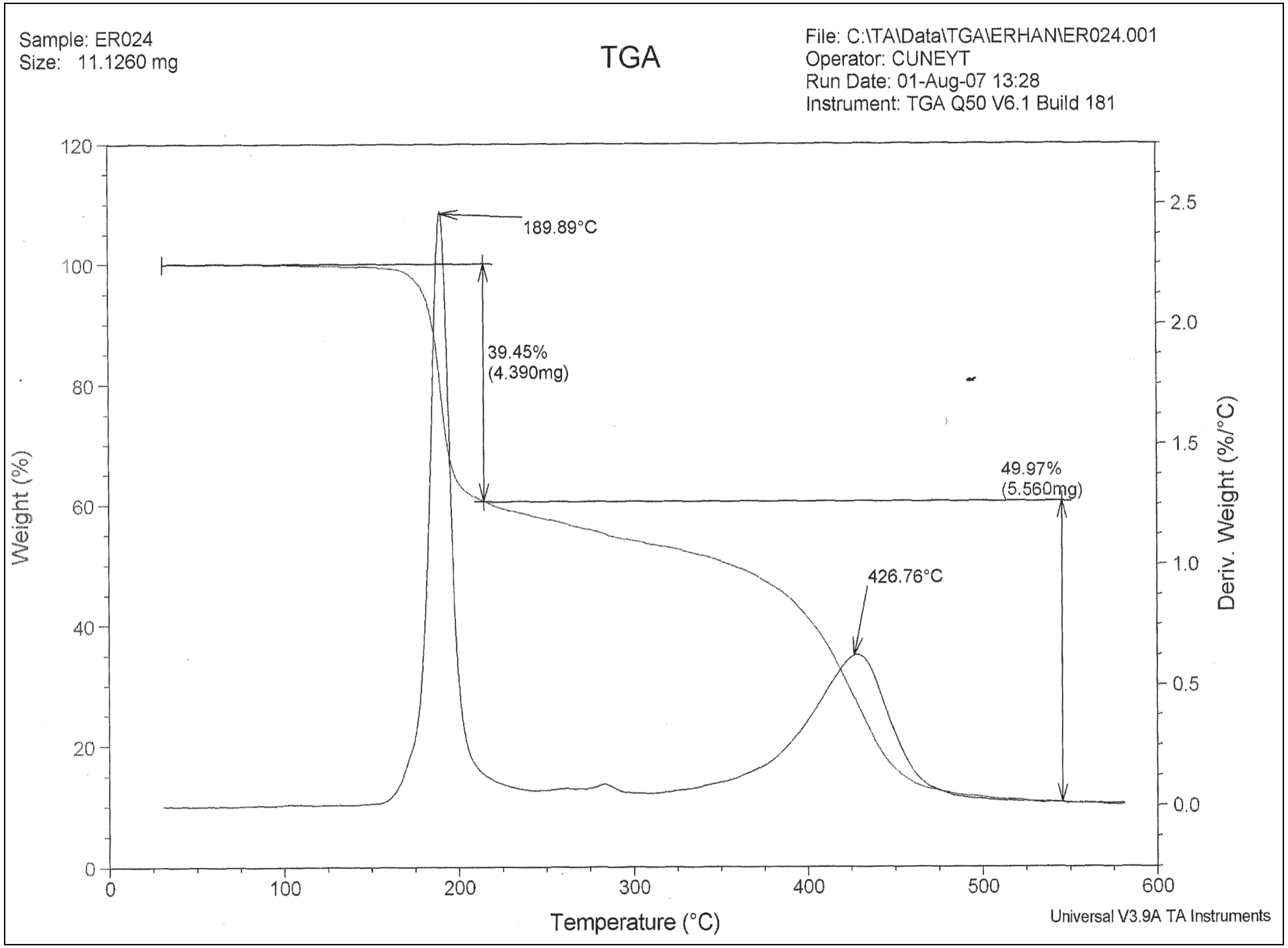

Figure 4.18. TGA analysis of undecenoic acid derived polymer.

5. CONCLUSION

The potential of cyclopolymers derived from the ATRP cyclopolymerization of TBHMA ether dimer was investigated for powder coatings. Post-polymerization techniques were employed to get desired reactive end groups for the powder coating applications. Allyl alcohol and undecenoic acid were used under the ATRP conditions according to the recent the literature to get telechelic polymers with alcohol and carboxylic acid end groups, respectively. Our experiments show that the addition of allyl alcohol and undecenoic acid was not an efficient way to get these telechelic polymers. At least, in our case, generated end groups with bromine were tertiary and also hindered. The radicals that formed at the both ends were relatively stable to react with the double bonds of the allyl alcohol and undecenoic acid. The low conversions of the end groups to alcohol and acid functionality was shown by both crosslinking and ^{31}P-NMR data. In addition, when modified polymers generated by the addition of the allyl alcohol and undecenoic acid were used as ATRP macro initiators they copolymerized perfectly, which showed that these end groups still served as initiators. These results prove that the allyl alcohol or undecenoic acid addition was not efficient since the addition of these should result in polymers with dead end groups.

To increase the efficiency of the end group modification, click chemistry and HEBIB initiator was used. The click chemistry derived polymers have promising results but not satisfactory and HEBIB initiated polymers have results from good to perfect but give rise to polymers with monofunctional end groups.

To achieve satisfactory cross-linking reactions further investigation on click chemistry and its optimum reaction medium studies must be done.

6. PERSPECTIVE

Several experiments can be carried out to get fully functionalized en groups. First and the most significant way could be generation of secondary bromine end groups by adding small amount of acrylate monomers at the end of ATRP cyclopolymerization. Then, the addition of allyl alcohol, undecenoic acid or the azide could be easier. As a second method, a co-monomer at the end of ATRP (or as a post-polymerization reagent) such as maleic anhydride can be employed . A Third method can be the use of HEBIB derived polymers in combination with click chemistry but then, the T_g adjustment must be done, since polymers with higher T_g results in the formation of a brittle network. To overcome this problem, for instance, using long alkyl groups in place of esteric t-butyl groups may decrease the T_g to the desired interval (60 – 80 ^{0}C).

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