SYNTHESIS AND PHOTOPOLYMERIZATION OF NEW PHOSPHORUS CONTAINING DENTAL MONOMERS

by

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To my husband…

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ABSTRACT

SYNTHESIS AND PHOTOPOLYMERIZATION OF NEW PHOSPHORUS CONTAINING DENTAL MONOMERS

Novel crosslinkers with phosphonate, phosphonic and carboxylic acid functions were prepared for use in dental materials. The crosslinkers were based on t-butyl α-bromomethacrylate (TBBr) and synthesized by two different methods.

The first method involved reaction of TBBr with Bisphenol A, followed by hydrolysis of t-butyl groups to acid chloride, and conversion to ester derivative using diethyl hydroxymethyl phosphonate.

In the second method, TBBr was reacted with tetraethyl 5,5'-(propane-2,2-diyl)bis (2-hydroxy-5,1-phenylene) diphosphonate and tetraethyl 2,5-dihydroxy-1,4-pheylene diphosphonate to give two new monomers. The selective hydrolysis of the carboxylate and phosphonate groups of the monomers using trifluoroacetic acid and trimethylsilyl bromide (TMSBr) gave carboxylic acid and phosphonic acid containing monomers.

A 1,6-heptadiene monomer with phosphonate functional groups was also synthesized from the reaction of TBBr and tetraethylmethylene diphosphonate.

The photopolymerization behaviors of the synthesized monomers with 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propyloxy) phenyl] propane (BisGMA), triethylene glycol dimethacrylate (TEGDMA) and glycerol dimethacrylate (GDMA) were investigated using Photo-Differential Scanning Calorimetry at 40 $^{\circ}$C using 2,2'-dimethoxy-2-phenyl acetophenone (DMPA) as photoinitiator.

ÖZET

YENİ FOSFOR İÇEREN ÇAPRAZ BAĞLAYICI DİŞÇİLİK MONOMERLERİNİN SENTEZİ VE IŞIKLA POLİMERİZASYONU

Diş malzemelerinde kullanılmak üzere fosfonat, fosfonik ve karboksilli asit grupları içeren yeni çapraz bağlayıcı monomerler hazırlandı. Monomerler t-bütil α-bromometil akrilat (TBBr)'den iki farklı metot kullanılarak sentezlendi.

İlk metot TBBr ile Bisfenol A'in reaksiyonunu, t-bütil gruplarının asit klorüre hidrolizini ve asit klorürün dietil hidroksimetil fosfonat ile ester oluşumunu içermektedir.

İkinci metotta TBBr'nin tetraetil 5,5'-(propan-2,2-dil)bis (2-hidroksi-5,1-fenilen) difosfonat ve tetraetil 2,5-dihidroksi-1,4-fenilen difosfonat ile reaksiyonlarından iki yeni monomer sentezlendi. Monomerlerdeki karboksilli asit ester ve fosfonat gruplarının trifloroasetik asit ve trimetilsilil bromür ile seçici hidrolizi ile karboksilik ve fosfonik asit içeren monomerler elde edildi.

Ayrıca fosfonat grupları içeren bir 1,6-heptadien monomeri TBBr'nin tetraetilmetilen difosfonat ile reaksiyonundan sentezlendi.

Sentezlenen monomerlerin fotopolimerizasyon davranışları 2-bis[4-(2-hidroksi-3-metakriloiloksi propiloksi fenil] propan (BisGMA), trietilen glikol dimetakrilat (TEGDMA) ve gliserol dimetakrilat (GDMA) ile 2,2'-dimetoksi-2-fenil asetofenon (DMPA) katalizörlüğünde 40 $^{\circ}$C de Foto Diferansiyel Taramalı Kalorimetri (Photo-DSC) metoduyla incelenmiştir.

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LIST OF SYMBOLS/ABBREVIATIONS

k_p	Propagation rate constant
R_p	Rate of polymerization
T_g	Glass transition temperature
CI	Co-initiator
CQ	Camphorquinone
DSC	Differential Scanning Calorimetry
NMR	Nuclear Magnetic Resonance Spectroscopy
PI	Photoinitiator
Poly(AA-*co*-IA)	Copolymer of acrylic acid and itaconic acid
FTIR	Fourier transform Infra Red Spectroscopy
TBBr	tert-Butyl-α-Bromomethyl Acrylate
TBHMA	tert-Butyl-α-Hydroxymethyl Acrylate
TEA	Triethyl amine
UV	Ultra Violet Spectroscopy

1. INTRODUCTION

1.1. Dental Materials

1.1.1. Anatomy of Tooth

A human tooth has three main parts:
The crown is the visible part of the tooth above the gum (gingiva),
The neck is the region of the tooth that is at the gum line, between the root and the crown,
The root is the anchor of the tooth that is below the gum (Figure 1.1.) [1]

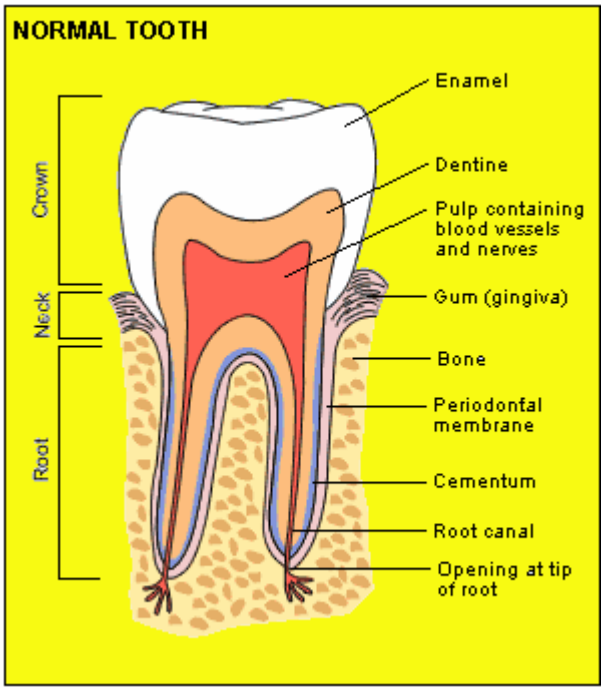


Figure 1.1. The anatomy of tooth

The *enamel*, tough, shiny, and white in color, is the hardest calcified tissue in the human body covering the outer surface of the crown. Directly beneath the enamel is the most sensitive part of the tooth, namely, *dentin*, which is yellow in color [1].

Dentin and enamel are composed of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ and collagen (Table 1). The collagen of the dentin provides hydroxyl, carboxyl and amino groups which can be utilized in bonding to this structure [2-4].

Table 1.1. Approximate composition of enamel and dentin

	Enamel	Dentin
Mineral phase (hydroxyapatite)	97 %	69 %
Organic phase (mainly collagen)	1 %	20 %
Water	2 %	11 %

Within the dentin, at the center of the crown and the root is the pulp, which contains the nerves and the blood vessels. The roots are embedded in the bone. The thin layers of bone like tissue called cementum covers the roots. The roots are connected to the jaw bone by a thin layer of soft tissue called periodontal membrane. It has elastic property and stretches between the cementum and bone around the tooth [5].

1.1.2. Characteristics of Ideal Dental Materials

Dental materials used in the dental profession are indeed many, varied and complex [6]. Requirements for some materials differ from those for others, depending on their uses; however, a list of ideal characteristics can be generated for the materials to be used within the mouth to repair or replace oral tissues (Table 1.2) [7].

Table 1.2. Characteristics of ideal dental material

Biocompatible	nontoxic, nonirritating, nonallergenic
Mechanically Stable and Durable	strong; fracture resistant; stiff
Resistant to Corrosion or Chemicals	does not deteriorate over time
Dimensionally Stable	minimally affected by temperature or solvents
Minimally Conductive Both Thermally and Electrically	insulators
Esthetic	oral tissue- like appearance
Easy to Manipulate	placement and finishing with reasonable time and effort
Adherent to Tissues	provide durable, tight union for retention and sealing
Tasteless and Odorless	not irritating or unpleasant
Cleanable/Repairable	can be maintained or fixed
Cost Effective	within the patient's budget

Dental personnel have appropriate materials for the many different situations that present, but no one material simultaneously meets all of the requirements. In other words there is no universal restorative material [7].

1.1.3. Dental Restorative Materials

Dental restorations can be classified into two types: Direct restorations and indirect restorations (Table 1.3) [8].

Table 1.3. Dental restoration materials

Direct Restorative	**Indirect Restorative**
Amalgams	Porcelain
Composite resins	Porcelain + Metals
Glass ionomer cements	Gold Alloy
Hybrid Materials	Base Metal Alloys

Direct restorations are done by inserting filling material directly into the tooth. Indirect restorations are fabricated outside of the mouth [8].

1.1.3.1. Amalgams

Amalgams are the alloys that contain one of the metals as mercury. A dental amalgam is a combination of mercury with specially prepared silver alloy in the presence of tin, copper, and zinc [6,7]. Each elements composing amalgam imparts certain properties to the finished product (Table 1.4) [6].

Table 1.4. Effects on properties of an amalgam restoration imparted by ingredients

PROPERTY	INGREDIENT			
	Silver	Tin	Copper	Zinc
Strength	Increases			
Durability	Increases			
Hardness			Increases	
Expansion	Increases	Decreases	Increases	
Flow	Decreases	Increases	Decreases	
Color	Imparts			
Setting time	Decreases	Increases	Decreases	
Workability		Increases		Increases
Cleanliness				Increases

In preparing the alloy for dental amalgam, the components are melted together, usually under an inert atmosphere, and then are homogenized at 400 ºC for 6-24 hr. When the powdered amalgam alloy and mercury are freshly mixed, a paste-like material is obtained. The cavity is restored at this point and the chemical setting process, which can be described by the following reaction, takes place in the cavity [9].

$$Ag_3Sn + Hg \longrightarrow Ag_2Hg_3 + Sn_{7\text{-}8}Hg$$

For more than a century, dental amalgam has played an important role in restorative dentistry [10-12]. They have many advantages over than other materials as a restorative material. Amalgam is used more than any other material to restore carious teeth. It is easy to insert into cavity and adapts readily to cavity walls. In obtaining its initial set, or hardness, amalgam allows time for condensing and carving. It has an acceptable crushing strength and is recognized as having a long life as a restoration. As an

amalgam restoration ages in the oral cavity, corrosion products form along the restoration-tooth interface. These compounds act as a mechanical block to micro leakage and account for the excellent clinical results obtained with silver amalgam.

However, amalgam has also many disadvantages as a restorative material. Because amalgam's color does not match the color of the teeth (Figure 1.2), it is generally not used on the visible surfaces of anterior teeth. Amalgam will tarnish with time, no matter how well the amalgam restoration is prepared and inserted. To avoid or reduce tarnish, the restoration is smoothed and highly polished a day or two after its insertion. The restoration may be reshined later at any time with little effort. Amalgam will also conduct heat or cold readily (high thermal conductivity). If the amalgam is placed too close to the pulp, it may irritate the pulp. Therefore, an intermediate base that will not conduct heat or cold as readily (low thermal conductivity) is placed under the amalgam [6].

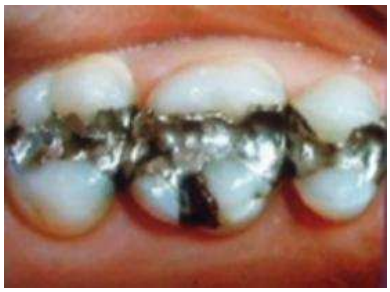


Figure 1.2. General appearance of amalgams [13]

1.1.3.2. Glass Ionomer Cements (GIC's)

Glass ionomer cements (GIC) have been extensively used in dentistry for over 30 years as an alternative to silver amalgams [14,15]. From a chemical view, cements are substances produced by an acid-base reaction [16,17].

The first glass ionomer cement product, **ASPA** (**A**lumino-**S**ilicate-**P**oly-**A**crylate), introduced in the 1970s, was formulated by adding polyacrylic acid as the liquid component to finely silicate powder. Today, glass ionomer cements are fabricated from a water–soluble polymeric acid, copolymers of acrylic and itaconic acids, acrylic and maleic

acids, acrylic and methacrylic acids (Figure 1.3) and a basic glass, typically a calcium fluoro-aluminosilicate (CaFAlSi) (at ratio of 2:1-3.5:1) [18,19].

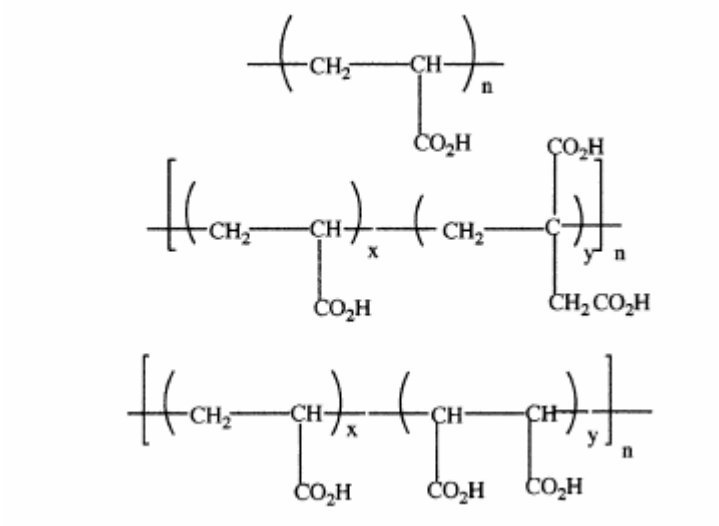


Figure 1.3. Some polyelectrolytes used in glass ionomer formulations

In setting mechanism the polymeric acid by releasing hydrogen ions [H+] in the presence of water, attack to the glass powder and lead to release of Ca^{2+} and Al^{3+} with F^- ions (Figure 1.4). Released cations form a silica gel area on the glass surface (Figure 1.5) [18,20,21].

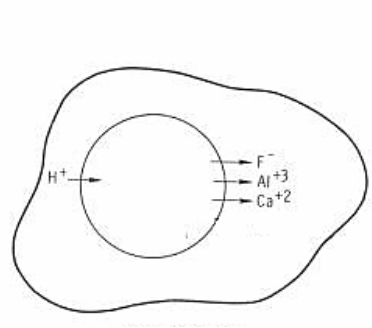


Figure 1.4. .Ion exchange

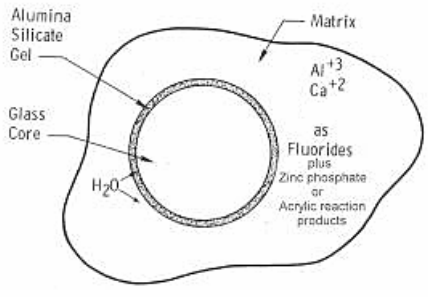


Figure 1.5. Silica gel (hydrogel)

Then, the rapid complexation of the Ca^{2+} ions with polycarboxylate anions (H^+ lost form), following by slower complexation of Al^{3+} species, gradually form a hard, ionically crosslinked , ceramic like matrix of the molecular structures as shown in Figure 1.6 [18].

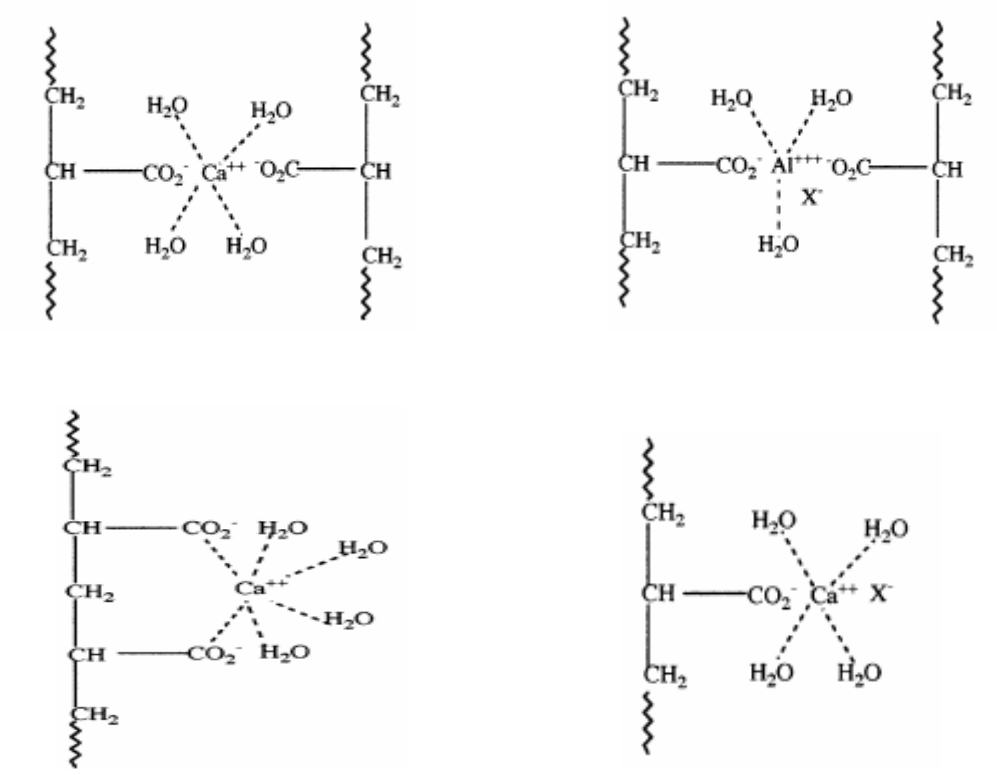


Figure 1.6. Possible Intra- and Intermolecular Ca^{2+} or Al^{3+} carboxylates (salt bridges or molecular structures) in cured GIC, where X represents OH^- or F^-

Glass ionomer cements have the useful property of inherent adhesion to both dentine and enamel, in general bond strengths are greater to enamel than to dentin (Table 1.5), leading to the conclusion that bonding occurs to the mineral phase of hydroxyapatite [19,22].

Table 1.5. Shear bond strengths of GIC to dentin and enamel

Substrate	Bond strength/ MPa
Dentin	1.5-4.5
Enamel	2.6-9.9

Furthermore glass ionomer cements release fluoride over a significant period, since fluoride as CaF_2 is a constituent of the glass. Fluoride release protects against decalcification of the surrounding tooth structure, decreases the dentin hypersensitivity

form exposed root surface and provide good antibacterial activity, and help reduce occurrence of secondary caries [18,23].

Also, they have aesthetic property because they have good translucency so they can be used in front teeth. In addition to these, glass ionomer cements have a number of important advantages [18] such as

a. They exhibit little to no exothermic reaction,
b. They exhibit little volume shrinkage because of contained glass,
c. They have coefficient of thermal expansion similar to tooth structure,
d. They have no free monomer present,
e. They are biocompatible [14].

A major disadvantage of glass ionomer cements is associated with early moisture sensitivity, which requires protection, immediately after placement with a varnish. Other disadvantages include the cement remaining vulnerable to desiccation, showing low resistance to wear and pressure, and exhibit lesser tensile and flexural strengths. Also acid hydrolysis causes disruption of the ionic cross-links (Figure 1.7) [18].

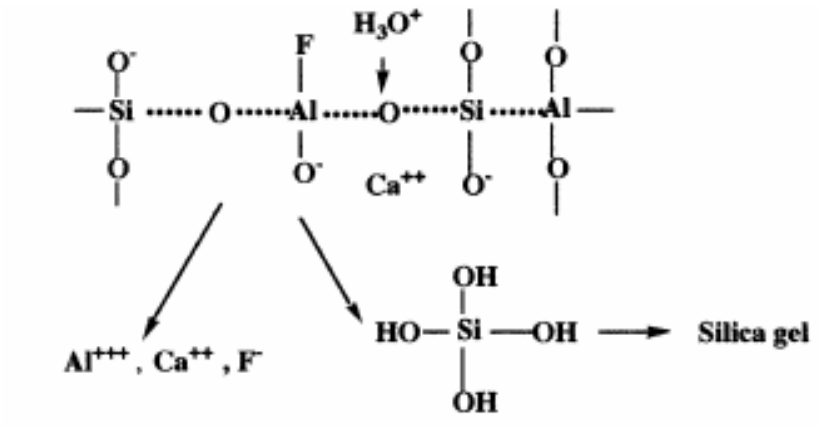


Figure 1.7. Acid hydrolysis or decomposition of glass powder

1.1.3.3. Composite Resins

The introduction of resin-based composite technology to restorative dentistry was one of the most significant contributions to dentistry in the last century. Composite resins are most widely used of the aesthetic repair materials [19]. By definition, a composite is a material that consists of two components. Typically, dental resin composites contain 15-20 wt % of free radically polymerizable organic resin matrix, 75-85 wt % of mixture of different inorganic filler (Table 1.6) [23].

Table 1.6. Typical composition of dental composites

Dental composites		
Inorganic filler	75-85 wt %	Barium alumino silica glass Quartz etc...
Organic filler	15-25 wt %	Polymerizable monomers Initiator system Stabilizer, pigments

Nowadays, in organic matrix, generally visible light-activated polymerizable resins are used as because of their aesthetic merit (Figure 1.8) and 'cure-on-command' feature [24-28]. There are variety of monomers within resin, but most are based on Bis-GMA (2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane) (Figure 1.9) [29], as patented by Bowen in 1959 as 'Bowen resin'. Other resins used in dental composites are Bis-EMA and UDMA (Figure 1.9). The selection of the monomers strongly influences the reactivity, viscosity, polymerization shrinkage and other physical properties.

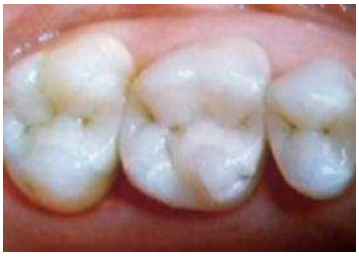
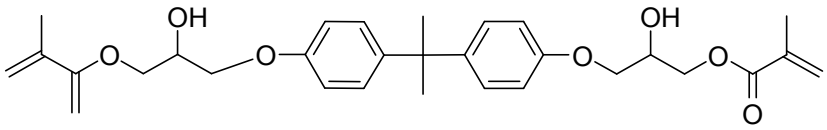
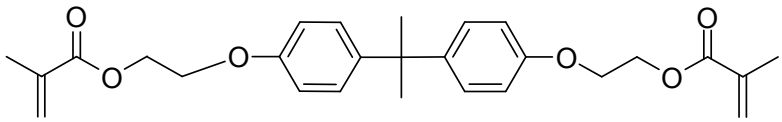


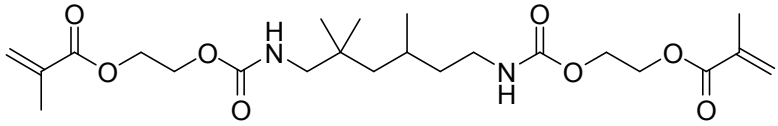
Figure 1.8. Composite resin in dental application



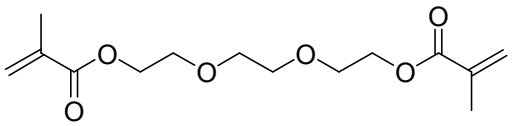
Bisphenol A glycolate dimethacrylate (Bis-GMA)



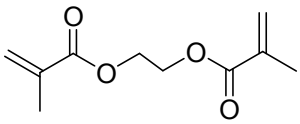
Bisphenol A ethoxylated dimethacrylate (Bis-EMA)



Urethane dimethacrylate (UDMA)



Triethyleneglycol dimethacrylate (TEGDMA)



Ethyleneglycol dimethacrylate (EGDMA)

Figure 1.9. Structures of frequently used base resins in dental composite filling material

The advantages of using Bis-GMA are its low volatility, and relatively low polymerization shrinkage and to give polymers with high modulus and glass transition temperature. However, the extremely high viscosity of Bis-GMA requires dilution with 20-35 wt per cent low viscosity monomer, such as triethyleneglycol dimethacrylate

(TEGDMA) or ethyleneglycol dimethacrylate (EGDMA). This also provides easier handling, higher filler loading and greater extent of polymerization. On the other hand, incorporation of these reactive diluents affects mechanical properties, volume shrinkage and water absorption [28-30]. By addition of particulate fillers which are harder than polymeric matrix, this drawbacks resulting from the addition of reactive diluents are being tried to overcome. Moreover, the system includes a photoinitiator (PI) or photoinitiating system [31]. Camphorquinone (CQ) is widely used photoinitiator in dental applications, in combination with tert-amines, such as ethyl-4-dimethylaminobenzoate (DMAB) as a co-initiator (CI) (Figure 1.10) [32]. The mixture is activated by visible light in the region of 450-480 nm [28].

camphorquinone (CQ) Ethyl-4-dimethylaminobenzoate (DMAB)

Figure 1.10. Structures of camphorquinone (CQ) and ethyl-4-dimethylaminobenzoate (DMAB)

Many approaches have been developed to improve properties of dental composites. The attempt is to overcome the disadvantages of diluent monomers; research has been done to produce low viscosity dimethacylate monomers requiring less diluent monomers. Tris[4-(2′-hydroxy-3′-methacryloyloxypropoxy)phenyl]methane (TTEMA) was found to a similar photopolymerization reactivity as the system containing Bis-GMA and TEGDMA and also less volume shrinkage than that system (Figure 1.11.) [33].

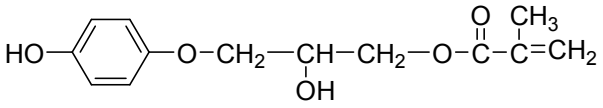


Figure 1.11. TTEMA

Davy et al., synthesized a monomer which exhibit low viscosity and low shrinkage (Figure 1.12) [34].

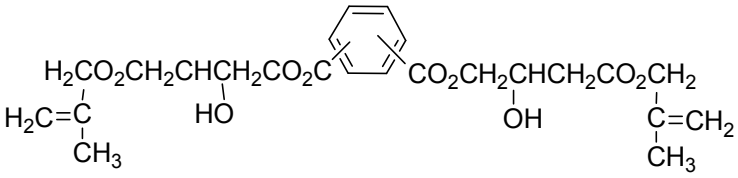


Figure 1.12. Modified dimethacrylate monomer (different isomerization possible)

In another study, Taylor et al. modified Bis-GMA structure as indicated in Figure 1.13 [35].

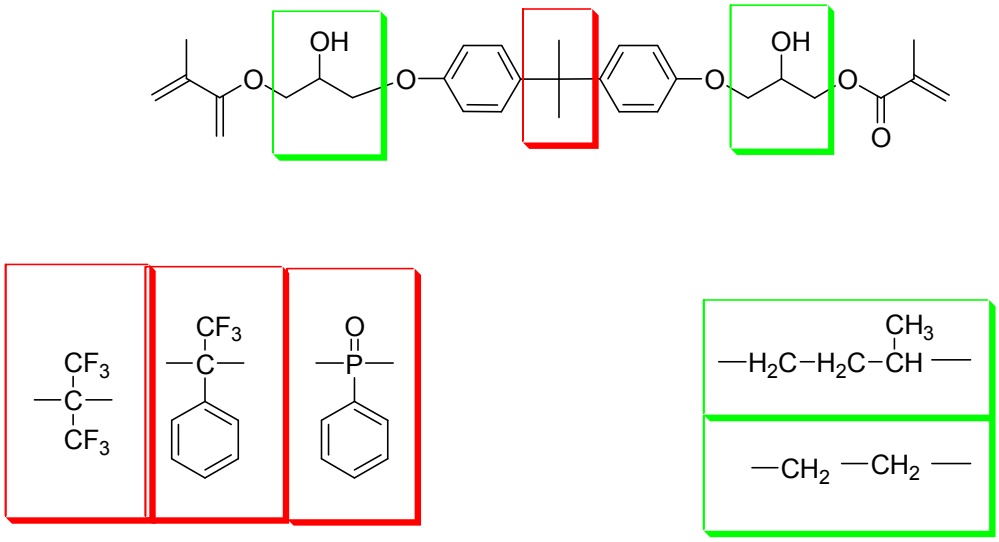


Figure 1.13. Modified Bis-GMA structure in some monomers

Also, other modifications were investigated by Stansbury et al. with incorporation of fluorine into monomer structure (Figure 1.14) [36].

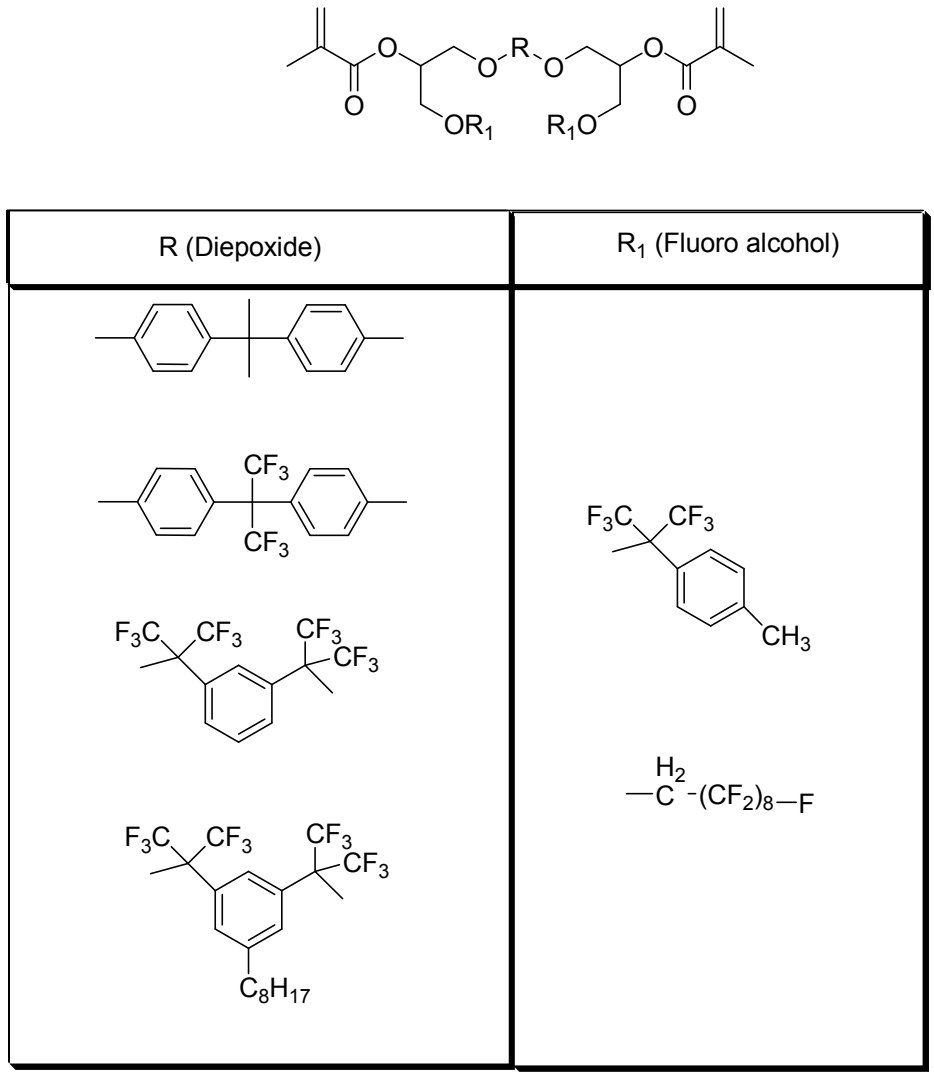


Figure 1.14. Fluorinated monomer structures

A new fluoride-releasing dimethacrylate monomer containing bis(imminodiacetic acid) chelating ligand and its complex with zirconium and fluoride were synthesized (Figure 1.15). It was shown that the experimental composite containing such a monomer has increased fluoride release [37].

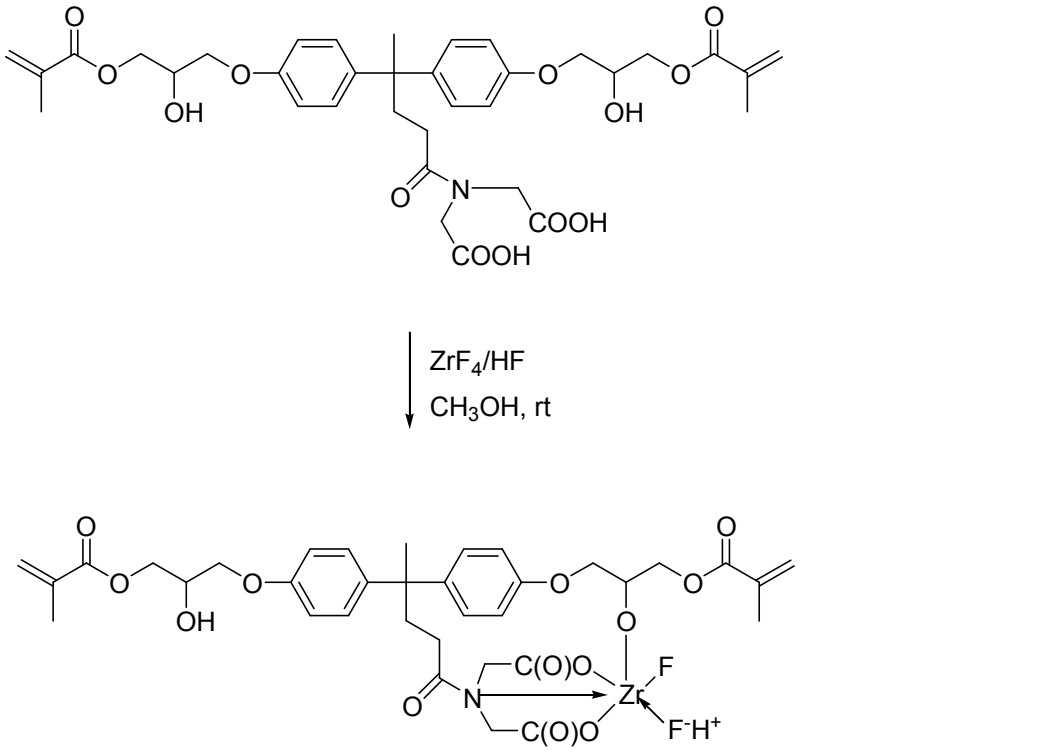


Figure 1.15. Synthesis of fluoride-releasing dimethacrylate monomer

Novel monomers with sulphur and phosphonate ester groups containing were also prepared by Pham et al. to increase binding of composite resin to tooth tissue (Figure 1.16) [38].

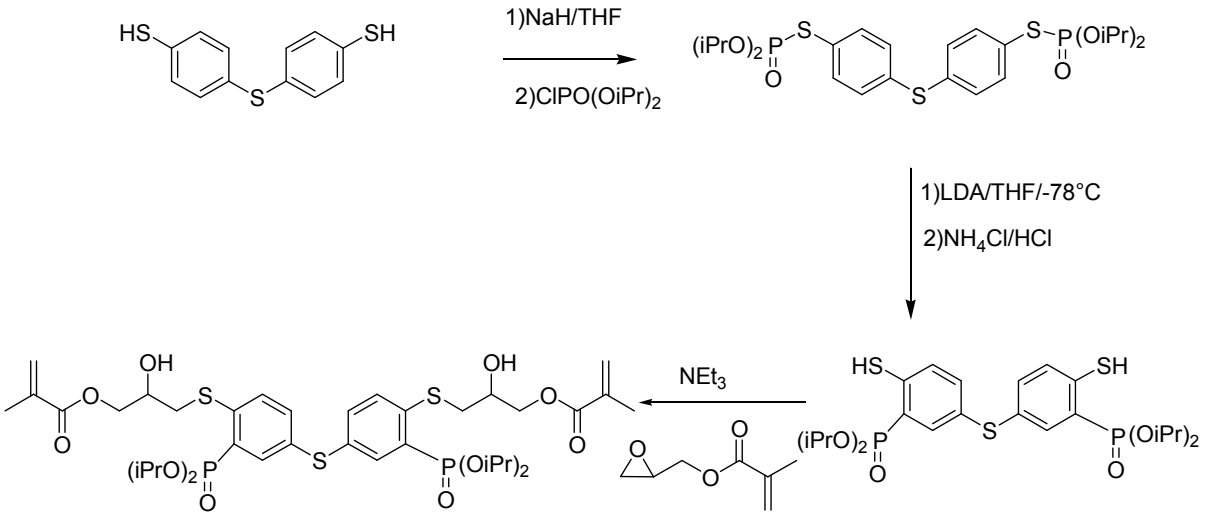


Figure 1.16. Phosphonated analogues of Bis-GMA

Although dental composite resin has superior in esthetic, mechanical properties and handling, the composite resin itself has no adhesive properties to teeth tissues. For this reason, in order that the dental composite resin is adhered to a tooth structure, it is considered to be necessary to use an exclusive adhesive having strong adhesive properties to a tooth structure [39].

1.1.3.4. Hybrid Materials

Hybrid materials that are also known as resin modified glass-ionomer cements are materials in which polymerizing resin is added to the glass ionomer matrix. They represent an attempt to overcome some of the problems with traditional glass ionomer cement and composite resins.

The setting mechanism of resin-modified glass-ionomers involves both the neutralization reaction (from the glass-ionomer phase) and photo-chemical process (from the organic phase). Figure 1.17 shows a hybrid system based on graft copolymer of polyacrylic and itaconic acid.

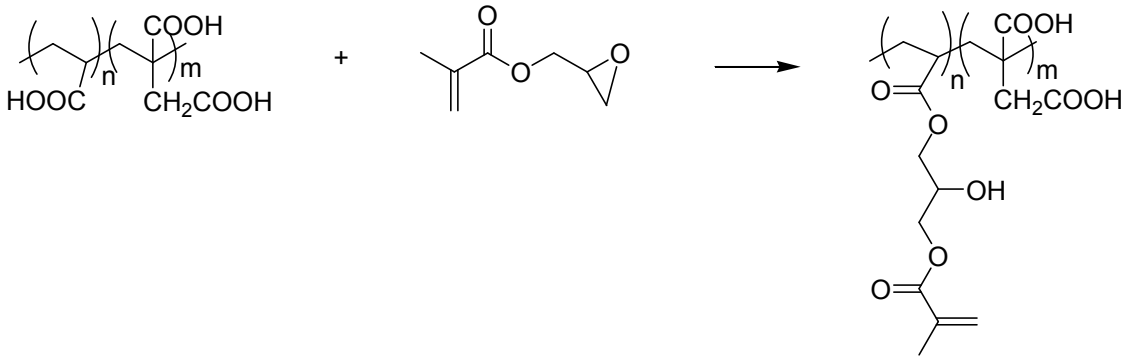


Figure 1.17. Poly(AA-co-IA) reaction with glycidyl methacrylate for producing a hybrid system [3]

The setting chemistry of resin-modified systems is complicated. As the acid base reaction progresses, the polymeric acid becomes more neutralized and phase separates from the organic phase. The product contains domains of different compositions.

These materials have improved initial esthetics, improved physical properties (such as tensile strength and fracture toughness), set on demand through light-curing, and have fewer desiccation and hydration problems. Since glass ionomer materials usually fail cohesively (the bond is stronger than the material), the stronger resin ionomers provide higher bond strength to tooth structure when application is proceed by conventional etching. In addition, resin can form a chemical bond with tooth structure [22].

Another approach to hybrid systems is the direct replacement of the carboxylic acid functionalized monomers or prepolymers. This method is called 'compomer' approach (Figure 1.18) [29]. They were marketed as a new class of dental materials that would provide the combined benefits of composites (the 'comp' of their name) and glass ionomers ('omer') [40].

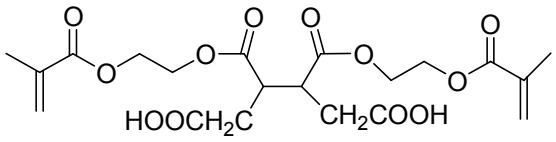


Figure 1.18. Aliphatic COOH containing dimethacrylates for compomers

Basically, these compomer monomers are able to react simultaneously with the methacrylate groups by free-radical polymerization and, in the presence of water from the environment, a limited acid-base reaction is observed. Since the more acidic group compomers contains the more hydrophilic and ionic the matrix becomes which results in greater the water absorption. Unlike resin modified glass ionomer cements when a compomer absorbs water its physical properties go down [22].

1.1.4. Adhesion in Dentistry

Today, the major problem of dental restorations is the lack of strong and permanent bonding between used synthetic material and the tooth.

Acid etching pretreatment of enamel with H_3PO_4 solutions was found clinical applications to bond enamel to restorative materials. But this technique was not successful to produce a bond between dentin and restorative materials. Also it required rinsing and drying steps. Nowadays, new generation bonding systems with proper bond to enamel and dentin are introduced to the market and called *self-etching adhesives* [41-44].

1.1.4.1. Self-Etching Adhesives/Primers

Self-etching adhesives/priming systems have been used in dentistry for bonding of composite resin to enamel and dentin for more than 10 years [47]. The commercial self-etching enamel-dentin adhesives consist of a mixture of self-etching adhesive monomers, crosslinkers, additional monofunctional co-monomers and additives (Figure 1.19) [45-49].

The self- etching primers, most likely due to their intrinsic acidity, have the ability to permeate dentin smears and impregnate the underlying dentin [46].

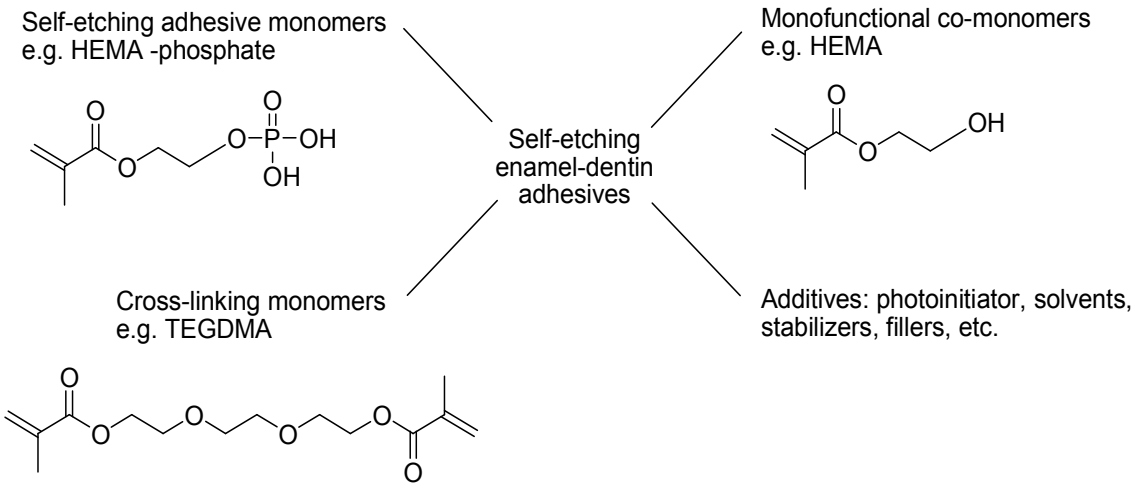


Figure 1.19. Components of currently available self-etching enamel-dentin primers/adhesives

In general, adhesive monomers are bifunctional molecules, containing a polymerizable group, for example, a methacrylate group, which can react both with the other monomers of the adhesive and the restorative material by copolymerization, an adhesive group AD, such as a strong acidic group capable of both etching the dental hard tissues and interacting with the tooth substance, and a spacer group R (Figure 1.20) [50,51].

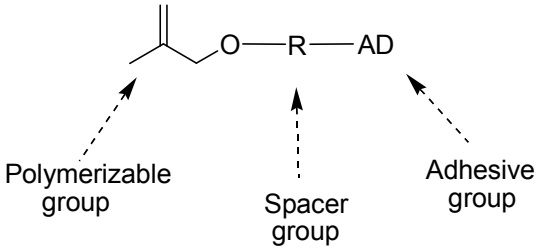


Figure 1.20. Design of an adhesive monomer

Spacer groups influence the solubility, flexibility and the wetting properties of the adhesive monomer. In Figure 1.21, common examples of spacer groups are indicated.

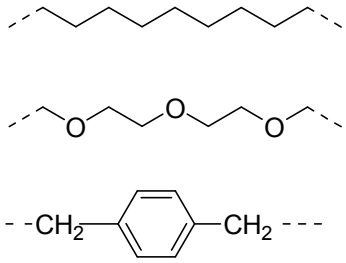


Figure 1.21. Examples of spacer groups, R

Suitable adhesive groups are acidic groups (Figure 1.22), in particular, phosphonic acids and mono-or dihydrogenphosphates, which are stronger acids than the carboxylic acids. The general potential of the acidic monomers to etch enamel largely depends on the acidity of the monomers that increases in the following order:

Carboxylic acids < phosphonic acids < acid phosphates < sulfonic acid

Acid groups can form ionic bonds by reacting with the inorganic part of dental hard tissue, which is hydroxyapatite. Chelating groups can form coordinative linkages with the calcium ions of enamel or dentin. Also, as dentinal collagen contains reactive groups such as amino or hydroxyl, the reaction of covalent coupling groups with the dentin can form covalent bonds with the collagen fibers if conditions are mild. Moreover, Van der Waals forces, London dispersion forces, hydrogen bonding or charge-transfer interactions may additionally contribute to the physical adhesion [48].

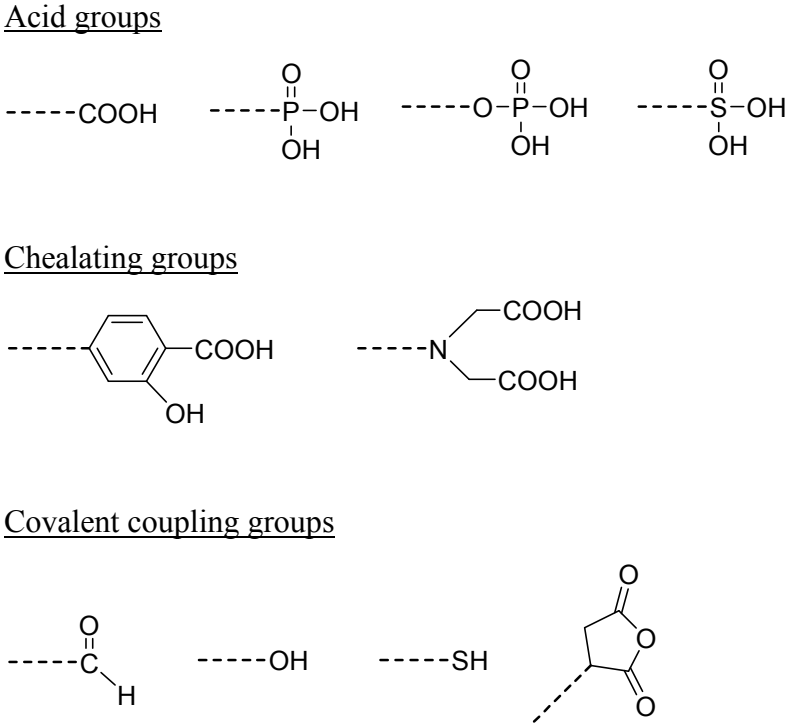


Figure 1.22. Examples of adhesive groups, A

In general, phosphorus-containing monomers are capable of etching enamel and dentin and promote monomer diffusion. Among the phosphorus-containing monomers, mainly polymerizable phosphonic acids or phosphoric acids are used.

Polymerizable Phosphoric Acids:

One of the first chemical compounds proposed to improve bonding to human dentin was the glycerol dimethacrylate ester of phosphoric acid (GDMP). Further

examples of commercially available acidic methacrylate phosphates applied to improve bonding on dentin are, methacryloyloxyethyl phenyl hydrogen phosphate (MEP-P), 10-methacryloyloxy methacrylate MDP, methacryloyloxyethyl dihydrogen phosphate (MEP, HEMA-phosphate), dipentaerythrolpentaacryloyl dihydrogen phosphate (PENTA-P) (Figure 1.23) [48].

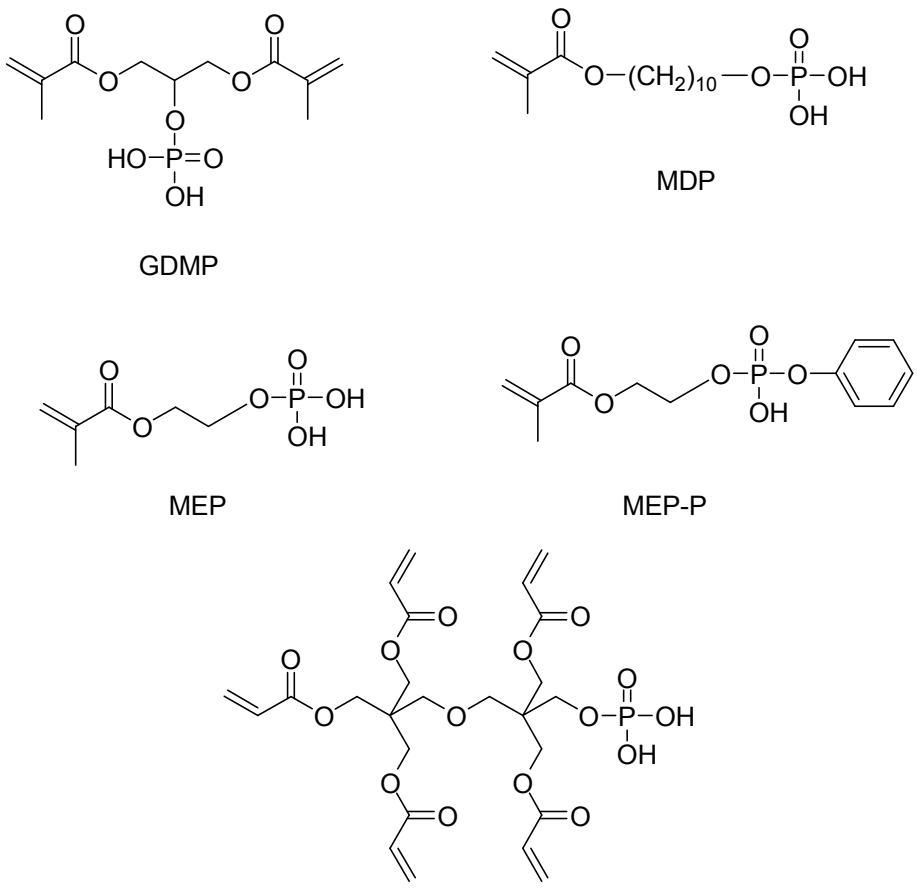


Figure 1.23. Examples of polymerizable acidic phosphates used in dentin adhesives

Some other examples of phosphoric acid containing monomers are shown below [53].

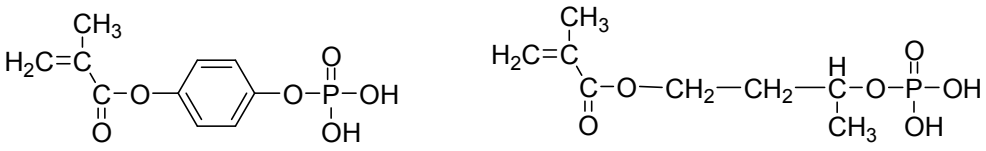


Figure 1.24. Example to adhesive monomers

Phosphoric acid esters are favorable as components of dentin adhesives because they are able to remove the smear layer on the dentin and achieve a strong bond between the restorative material and the tooth substance. However, the disadvantage of polymerizable phosphoric acids is their low hydrolytic stability [51,52].

In general, the hydrolytic stability of the phosphoric acid esters increases in the following order: dialkyl hydrogen phosphate < trialkyl phosphate < monoalkyl dihydrogen phosphate (Figure 1.25).

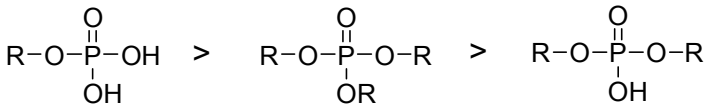


Figure 1.25. Order of hydrolytic stability of the phosphoric esters

In the case of acidic methacrylate phosphates, an additional hydrolytic instability results from the hydrolysis of the methacrylate ester bond. For MEP the hydrolysis of both the methacrylate and phosphate ester bonds resulted in the formation of methacrylic acid and HEMA (Figure 1.26) [48].

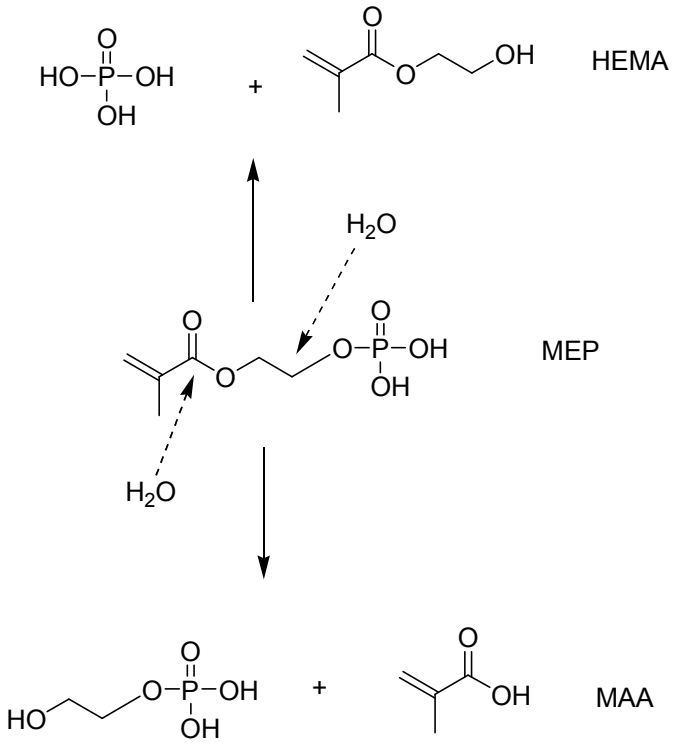
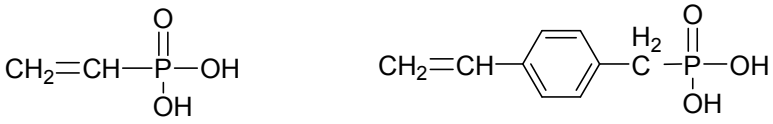


Figure 1.26. Hydrolysis of MEP in the presence of water

Polymerizable Phosphonic Acids:

Hydrolytic instability of the methacrylate phosphates can be solved by using monomers that contain more hydrolytically stable bonds between the polymerizable group and the strongly acidic phosphorus group.

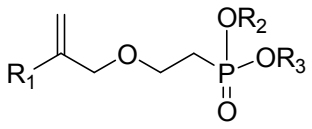
A first evaluation of polymerizable phosphonates for dental adhesives was achieved by use of vinyl phosphonic acid (VPA) and 4-vinylbenzyl phosphonic acid (VBPA). It has shown that they can improve the adhesion of the filling composites on etched enamel. Unfortunately, VPA and VBPA are less reactive than methacrylates in radical polymerization [48].



VPA VBPA

Figure 1.27. Structure of monomeric phosphonic acids VPA and VBPA

To overcome the instability of phosphoric acid, Moszner et al. synthesized new monomers containing more hydrolytically stable bonds between the polymerizable methacrylic group and the strong acidic phosphorus group Figure 1.28 [51].



R_1 : COOH, $COOC_2H_5$, CN, $CON(C_2H_5)_2$
$R_{2,3}$: H, CH_3

Figure 1.28. Example of phosphonic acid monomers

Among the synthesized monomers, 2-[4-(dihydroxyphosphoryl)-2-oxa butyl] acrylate (EAEPA) and 2,4,6-trimethylphenyl 2-[4-(dihydroxyphosphoryl)-2-oxabutyl] acrylate (MAEPA) show the best dentin adhesive properties, whereas the carboxylic acid and nitrile derivatives, 2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylic acid (CAEPA) and 2-[4-(dihydroxyphosphoryl) -2-oxabutyl]acrylonitrile (NAEPA), exhibited less adhesive action. The monomers CAEPA, NAEPA and MAEPA are hydrolytically stable in aqueous solutions at room temperature (Figure 1.29). The synthesized phosphonic acids dissolve well in water, acetone or ethanol [48].

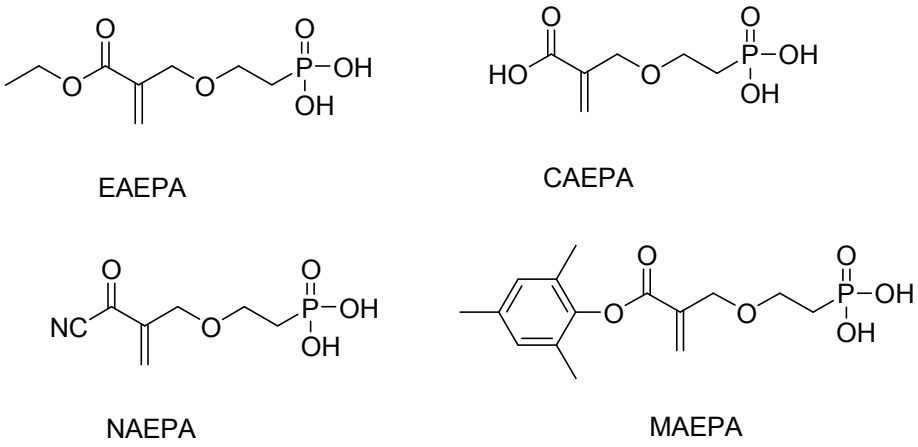
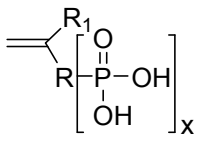


Figure 1.29. Examples of polymerizable phosphonates

Moreover, in another study, it is possible to find dental materials with high resistance to hydrolysis and good adhesive properties. These dental materials comprise phosphonic acid with structure given below [54].



R : alkyl group with at least 6 atoms or aryl group etc…

R_1: H, methyl, ethyl, isopropyl or butyl etc…

x : 1 or 2

Figure 1.30. General structure of invention

Some examples of this study indicated in Figure 1.31.

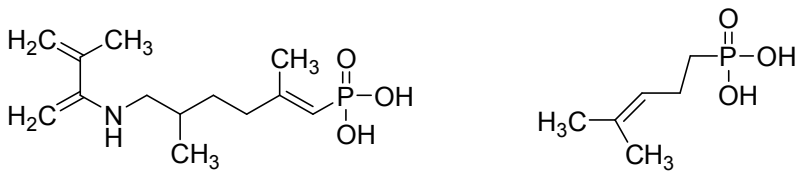


Figure 1.31. Some examples to dental phosphonic acids

Phosphonic acid-containing monomers with high degree of hydrolytic stability were synthesized for the preparation or as components of polymers, adhesives or other materials and in particular of dental materials (Figure 1.32) [55].

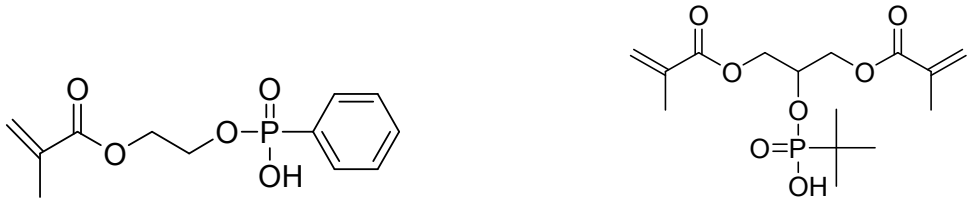


Figure 1.32. Examples of dental phosphonic acids

Polymerizable Carboxylic Acids:

Only a few polymerizable carboxylic acids are used commercially as a self-etching adhesive. Examples are 4-methacryloyloxyethyl trimellitic acid (4-MET), 10-methacryloyloxydecyl malonic acid (MAC-10) (Figure 1.33). Aqueous solutions of these acids show a pH value below 2.0 and enable to etch both the dentin and enamel [48].

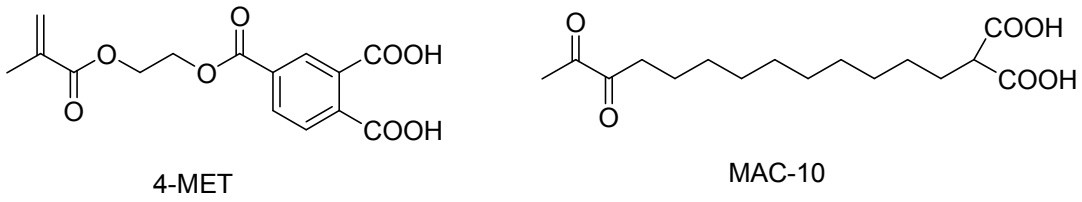


Figure 1.33. Examples of COOH-containing adhesive monomers

Monofunctional Co-Monomers in Adhesives:

The currently used self-etching systems contain mono functional non-acidic methacrylates, which are effective in some main properties such as, miscibility, viscosity, etc…

HEMA is a water soluble, low viscosity monomer that improves the miscibility and solubility of the polar and nonpolar adhesive components and the wetting behavior of the liquid adhesive on the dental hard tissue (Figure 1.34)

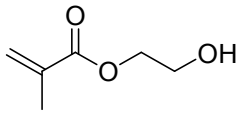


Figure 1.34. Structure of HEMA

Also, different substitutes of HEMA, N-(2-hydroxyethyl)-methacrylamide (HEMAM) and N-methyl-N-(2-hydroxyethyl)-acrylamide (MHEAM) were synthesized as they have improved hydrolytic stability and very low cytotoxicity (Figure 1.35) [48].

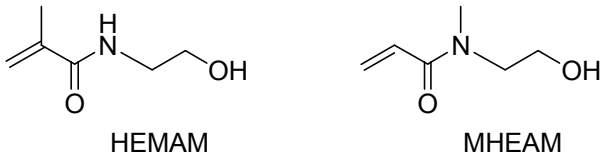


Figure 1.35. Structure of HEMA substitutes with improved hydrolytic stability

1.2. Introduction to Photopolymerization

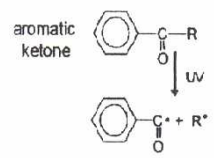
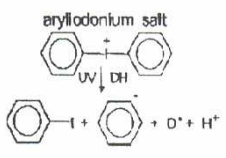
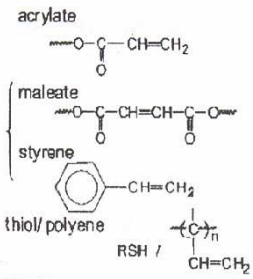
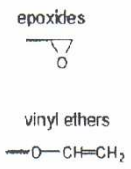
Dental curing process must fulfill a basic requirement. It must be a fast process at room temperature. Because photopolymerization satisfies this requirement, it is widely used in polymerizable dental systems.

Dental polymerizable systems are usually made of three main components [56].

a. A photoinitiator that effectively absorbs the incident light and generates radicals or ions,
b. Functionalized monomer or oligomer that will polymerize
c. A reactive diluent to adjust viscosity.

Photopolymerization is mainly classified into two groups, depending whether on the reaction proceeds by cationic type or radical type mechanism (Table 1.7). In photoinduced radical polymerization, aromatic ketones are used as initiators which decompose to generate free radical. The produced radicals initiate the polymerization of vinyl monomers by a chain growth addition mechanism. On the other hand, in photoinduced cationic polymerization, a protonic acid is generated by photolysis of triarylsulfonium (TAS) or diaryliodonium salts to initiate the polymerization of epoxides or vinyl ethers [56].

Table 1.7. Different types of photo-curable resins

Mechanism	RADICAL	CATIONIC
Photoinitiator		
Monomers and functionalized polymers		

Radical polymerization type of curing is the most popular and most widely applied [57].

1.2.1. Photoinitiators

Photoinitiators govern the rate of initiation and penetration of light into the sample, and therefore control the depth of the cure. It is essential to select the initiator showing the highest initiation efficiency and undergoing a fast photobleaching upon UV exposure in order to achieve a deep-through cure [56].

Classification of photoinitiators is based on the type of polymerization system they initiate, i.e. free radical or cationic. There are also a few cases of initiators (e.g. iodonium and sulphonium salts, arene complexes), which are able to initiate polymerizations via both cationic and radical processes.

Radical photoinitiating systems are commonly classified according to the nature of the mechanism that produces the free-radical intermediates upon irradiation of the initiators [58]. The mechanisms characterizing the classes of photoinitiators are:

Photofragmentation that generates radical pairs through a highly efficient α-cleavage process (type-I) and the H abstraction process from donor molecules (type-II).

Type-I class includes aromatic carbonyl compounds that are known to undergo a homolytic C-C bond scission upon UV exposure (Figure 1.36):

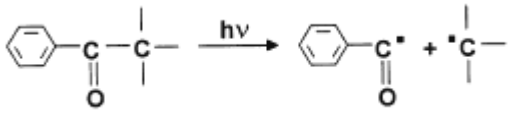


Figure 1.36. Example to type-I photoinitiator

The benzoyl radical is the major initiating species, while the other fragment may, in some cases, also contribute to the initiation. The most efficient photointiators include

benzoin ether derivatives, benzyl, ketals, hydroxyalkylpheneones, α-aminoketones, and acylphosphine oxides.

Type-II systems usually consist of two components: An aromatic ketone with a H-donor molecule. Aromatic ketones, when promoted to their excited states by irradiation, do not undergo a fragmentation but rather abstract a H atom from a H-donor molecule to generate a ketyl radical and a donor radical. The donor radical initiates polymerization. In Figure 1.37 there is a typical example, benzophenone.

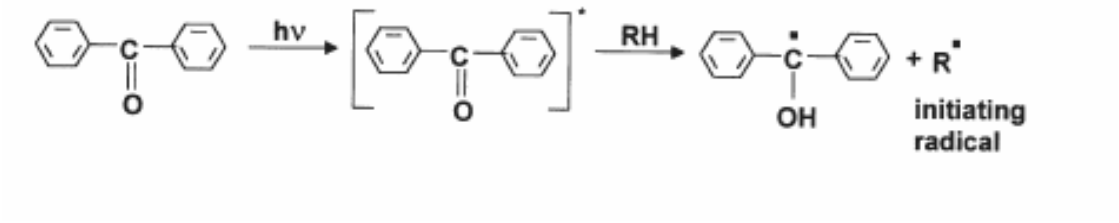


Figure 1.37. Example to type-II photoinitiator

Other examples includes; xanhones and thioxanthones, aromatic diketones, phenyl glyoxalates, 3-ketocoumarins, camporquinone, etc.

Figure 1.38 gives the structures of some photoinitiators which are commonly used in both dentistry and other applications [56].

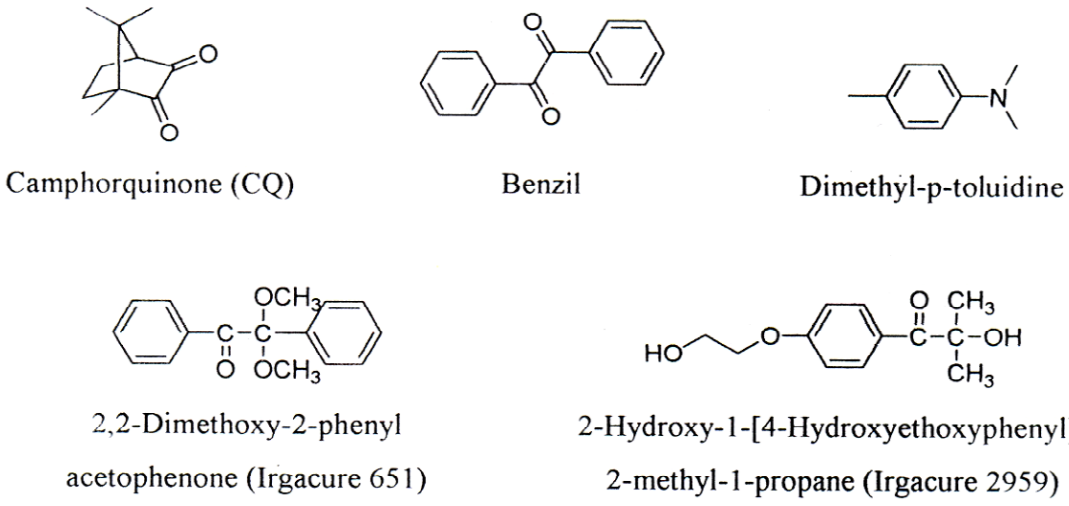
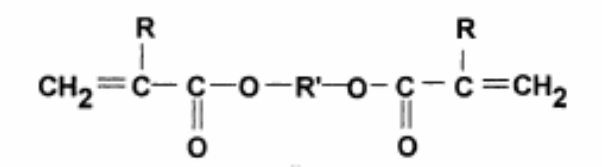


Figure 1.38. Commonly used photoinitiators

1.2.2. Monomers

The most widely used monomers in photopolymerization are multifunctional acrylates and methacrylates due to their high reactivity and moderate to low volatility [59].

Figure 1.39 shows the general structure of the commonly used acrylate/methacrylate based resin systems [57].



R = H, CH_3

R^1 = polyether, polyester, polymethane

Figure 1.39. Commonly used (meth)acrylate monomers for light curable systems

The polymerization of dimethacrylate monomer, initiated by UV- generated benzoyl radicals, is assumed to develop according to following scheme (Figure 1.40).

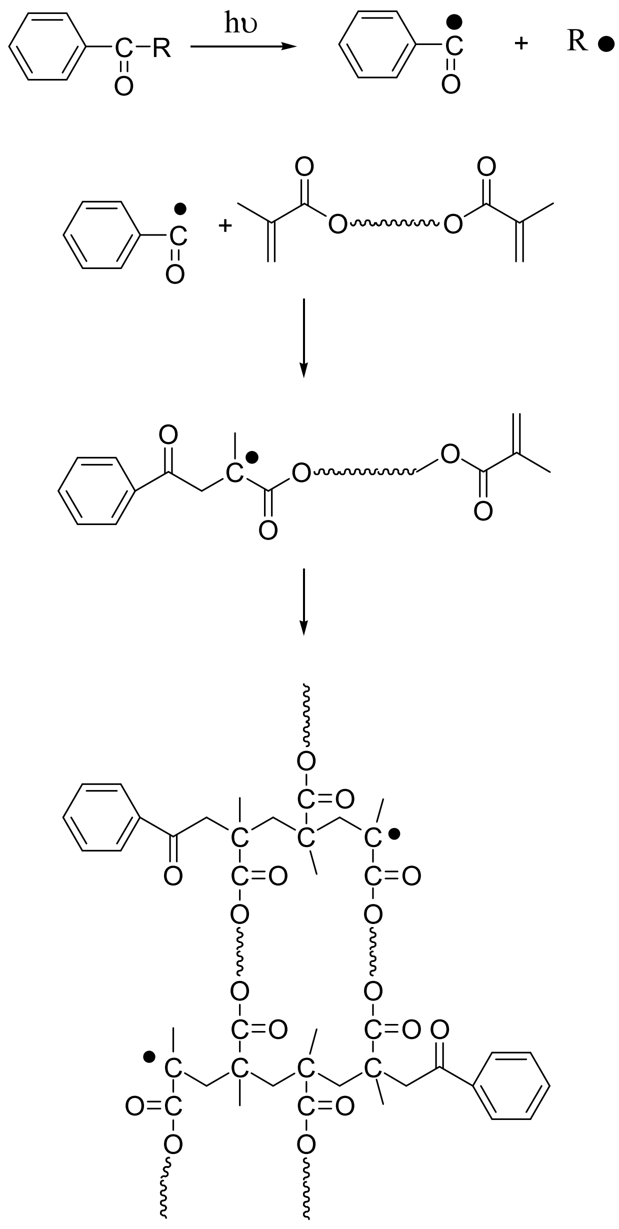


Figure 1.40. Mechanism of the photopolymerization of a dimethacrylate monomer

The rate of polymerization initially depends on the reactivity of the functional group, its concentration and the viscosity of the resin. The chemical structure, distance and flexibility between the functional groups, and the functionality of both monomer and/or oligomer are also important. These factors determine the final degree of polymerization, as well as the physical and chemical characteristics of the UV-cured polymer [60].

For instance, monomers capable of hydrogen bonding generally shows higher rate of polymerization (R_p) compared to their non-hydrogen bonding analogues. A plausible explanation for this enhanced polymerization rate is that hydrogen bonding results in preorganization in the monomers, by forcing the double bonds in close to each other. As a consequence, the propagation rate constant (k_p) will be enhanced [61]. Furthermore, hydrogen bonding will increase the overall viscosity of the bulk monomer solution, thus hindering radical termination and causing an increase in radical concentration. This will increase polymerization rate [62]. However, there is a critical distance between double bond and the hydrogen bonding moiety (alkyl bridge length) beyond which there is no effect on R_p in the case of the preorganization theory. This is because conformational mobility of the skeletal bonds between the hydrogen-bonding moiety, the double bond will reach a level whereby the double bond can be regarded as isolated from the hydrogen-bonding moiety [61,62].

The monomer type and structure have a dramatic effect on the behavior of dental materials. Currently, the most commonly used monomer systems for dental composites are Bis-GMA and TEGDMA mixtures. To improve the physical and mechanical properties of dental materials, new monomer formulations should show an increase in the reaction rate and double bond conversion while maintaining other desirable properties of current resin formulations. Resins that undergo a greater degree of conversion exhibit enhanced properties and contain a lower amount of leachable components, thereby improving the biocompatibility of the dental restoration.

Coinitiators are secondary components in the photopolymerization systems. The amines used as coinitiator are both toxic and mutagenic, but they are a necessary component of the camphorquinone visible light photoinitiating system. Though work has been done to improve the amine coinitiator, the major purpose has been to decrease the toxicity and improve the polymerization process. Generally, a commercial amine without a methacrylate group has been used as the coinitiator. To enhance the biocompatibility of the coinitiator further, some studies involve the synthesis of monomers which contains two methacrylate groups and two amine groups that could be polymerized to form a more biocompatible polymer system (Figure 1.41) [63].

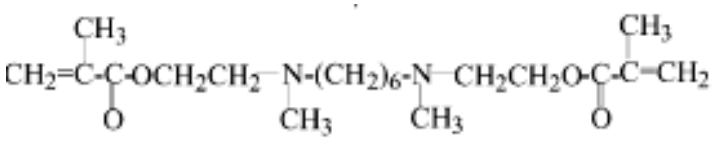


Figure 1.41. N,N'-dimethyl,-N,N'-di(methacryloxyethyl)-1,6-hexanediamine (NDMH)

The monomer in Figure 1.41 has two different kinds of functional groups: methacrylates, which can be free radically polymerized, linking the NDMH to the crosslinked polymer chain; and the amines which serve as coinitiators for hydrogen abstraction.

There is a major drawback of the photocurable composites; the fact that they undergo volumetric shrinkage of 2-5% during polymerization is [64]. This polymerization shrinkage during a direct composite restorative procedure creates a detrimental strong stress at the interface between the cavity wall and the composite restoratives, which often cause adhesion failure or micro cracking of the enamel margin. Consequently, the micro gap induced by the setting stress of composites between the restorative and the cavity wall may give rise to postoperative hypersensitivity, secondary caries and pulpits. These are the main causes of the failure of composite restorations [65]. Therefore, polymerization shrinkage is a very important factor in selecting restorative materials in clinics.

Polymerization shrinkage is caused mainly by changing from the distance between the free monomer molecules loosely bonded by weak van der Waals force to the distance between the monomers tightly linked by a covalent bond in a polymer. Many manufacturers have endeavored to reduce the polymerization shrinkage of composites by synthesizing of novel monomers or blends of fillers. In addition, many researchers have developed various clinical restorative techniques such as incremental filling, slow start polymerization and delayed curing to reduce or eliminate polymerization shrinkage during the restorative procedure [65]. However, this problem has not been solved.

1.2.3. Light Sources

Another significant factor in the photo-curing process is the light source because the initiation rate can be varied by changing the light intensity. Simply, increase in light intensity will lead to increase in polymerization rate. In general, two major light sources are used.

a. Arc light
b. Laser light

An **arc lamp** is the general term for a class of lamps that produce light by an electric arc (or voltaic arc). The lamp consists of two electrodes typically made of tungsten which are seperated by a gas. The type of lamp is often named by the gas contained in the bulb; including neon, argon, xenon, sodium, metal halide, and mercury. The gas pressure can be low (10-3 torr), medium (1-2 atm), or high (> 2 atm). The medium-pressure mercury lamp is the most important light source used in the photo- or UV-curing industry [66] The common flourescent lamp is actually a low-pressure mercury arc lamp where the inside of the bulb is coated with a light-emitting phosphour. Lightning could be thought of as a type of natural arc lamp, or at least a flash lamp.

The word 'LASER' is an acronym standing for 'Light Amplification by Stimulated Emission of Radiation' [67]. Lasers offer the prospect of an excitation source of exceedingly high intensity compared to classical light sources. The output of a laser can be pulsed or a continuous beam; visible, IR, or UV; with power ranging from less than a milliwatt to millions of watts. Some lasers offer fixed wavelength, whereas some others offer tunable wavelengths [66].

In dentistry, 420-500 nm light in visible region is used [68].

1.2.4. Photopolymerization Kinetics of Monomers

Photopolymerization kinetics can be studied in various methods such as differential scanning calorimetry, dilatometry, fluorescence spectroscopy, and RT-FTIR spectroscopy.

By these techniques, heat evolved, volume shrinkage, increase in viscosity or disappearance of the reactive groups are monitored.

By using differential scanning calorimetry technique, the rate of polymerization, propagation, and termination rate constants can be calculated from heat flow during polymerization according to the following equations (Figure 1.42):

$$R_p = \frac{(Q/s)\ M}{n\ \Delta H_p\ m} \qquad \frac{k_p}{k_t^{1/2}} = \frac{R_p}{[M]\ (\Theta I_0 \varepsilon [A])^{1/2}}$$

(Q/s) : heat flow per second during reaction
M : molar mass of the monomer
n : number of double bonds per monomer molecule
ΔH_p : heat released per mol of double bonds reacted
m : the mass of the monomer in the sample
Θ : the initiator efficiency
[M] : molar concentration of the double bonds
I_0 : incident light intensity
ε : extinction coefficient of the initiator
[A] : initiator concentration

Figure 1.42. Equation of the rate of polymerization

At the very beginning of the irradiation autoacceleration occurs because of the rapid increase in viscosity until the reaction reaches its maximum rate value. It is followed by a period where the polymerization develops, the time after which autodeceleration starts taking place when propagation becomes diffusion controlled. Ultimately, vitrification leads to a complete stop of the curing process through the end of the polymerization. A certain amount of unreacted acrylic double bonds remains in the crosslinked polymer, which may ultimately affect the long term properties of the UV-cured material [66] (Figure 1.43).

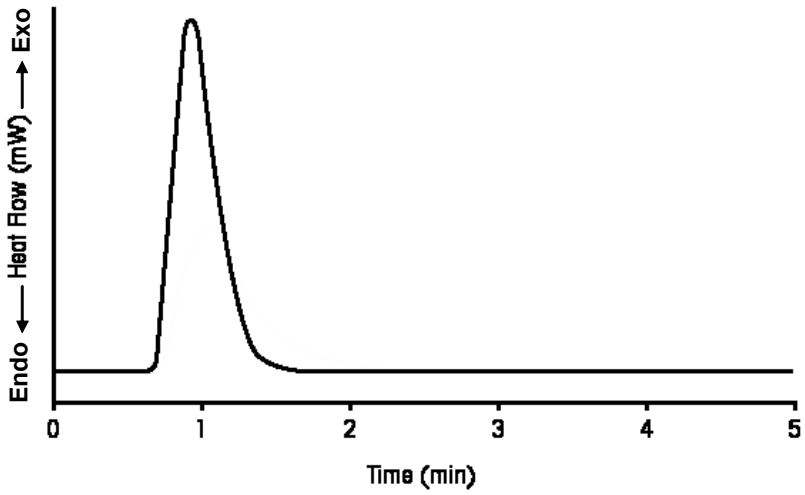


Figure 1.43. Representative heat flow versus time plot obtained from differential scanning calorimetry technique

1.2.5. Other Applications of Photopolymerizing Systems

Photocuring technology has found a variety of industrial applications due to the unique properties, such as high speed, solvent-free formulations, low energy consumption, ambient temperature operations, and tailor-made properties of the photocured polymers.

Besides its wide use in dental restorative filling systems, photopolymerization has also found applications in coating industry, for instance fast-drying varnishes, paints or printing inks, quick-setting adhesives, sealants; and also optical disks, microcircuits, and contact lenses are some of the other areas which photocuring technology is used [56,69,70].

2. OBJECTIVES

The major problem encountered in dentistry is dental caries. Synthesis of dental repair materials capable of binding to tooth tissue is very important for long term stability of these materials.

The purpose of the present study is to develop new phosphorus-containing dental monomers with

a. ability to form bonds with dental tissues
b. high rate of polymerization and copolymerization with common monomers used in dentistry
c. biocompatibility
d. hydrolytic and storage stability
e. solubility in water and ethanol
f. good mechanical properties in polymeric form
g. low volume of shrinkage in polymeric form

For this purpose, novel phosphonate ester, phosphonic acid and carboxylic acid containing monomers based on alkyl α-hydroxy methyl acrylates were synthesized and characterized. The polymerization reactivity of the monomers was determined.

3. EXPERIMENTAL

3.1. Materials and Apparatus

3.1.1. Materials

Chemicals used in this study were as follows:

Tert-butyl acrylate (Aldrich), paraformaldehyde (Merck), 1.4-diizobicyclo [2.2.2] octane (DABCO) (Aldrich), anhydrous $CaCl_2$ (Merck), anhydrous Na_2SO_4 (Merck), $CuCl_2$ (Merck), diisopropylamine (Merck), diethylphosphite (Aldrich), triethylamine (Aldrich), n-butyllithium (Merck), ammonium chloride (Merck), K_2CO_3 (Merck), 2,2 Bis-(4-hydroxy)-propane (Bisphenol A) (Aldrich), hydroquinone (Aldrich), thionyl chloride (Acros), PBr_3 (Aldrich), NaCl (Merck), 2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]-propane (Bis-GMA) (Aldrich), tri(ethyleneglycol)dimethacrylate (TEGDMA) (Aldrich), diethylhydroxymethyl phosphonate (Aldrich), TMSBr (Aldrich), trifluoro acetic acid (Aldrich) were used as received.

The photoinitiator, 2,2'-dimethoxy-2-phenylacetophenone (Irgacure 651 or DMPA from Ciba-Geigy), was recrystallized from hexane before use. The solvents; ether, hexane, carbon tetrachloride, methylene chloride, acetone, methanol, dimethylsulfoxide (DMSO), hydrochloric acid (HCl) were all purchased from Merck and used as received.

Solvents for chromatography (CH_2Cl_2 and ethyl acetate) were received from Akkimya and distilled before use. Tetrahydrofuran (THF) was obtained from JT Baker and dried over Na and freshly distilled before use.

3.1.2. Apparatus

^{1}H-NMR and ^{13}C-NMR spectra were recorded using Varian Gemini 400 MHz spectrometer. Fourier transform infrared (FT-IR) analyses were performed by FT-IR Perkin Elmer using NaCl windows. Photopolymerizations and kinetic investigations were

carried out by TA Instruments differential photocalorimeter (DPC) (Q100) containing a high pressure mercury lamp.

3.2. Synthesis of Starting Materials

3.2.1. Synthesis of tert-Butyl-α-Hydroxymethyl Acrylate (TBHMA)

tert-Butyl acrylate (128.12 g, 1 mol), paraformaldehyde (30 g, 1 mol), 1,4-diazobicyclo [2.2.2] octane (DABCO) (14 g, 0.125 mol), dimethylsulfoxide (227ml) and water (85 ml) were added to a 1000 ml round bottom flask and placed in a oil bath at 70 °C. After the reaction mixture was heated at 90 °C for 30 min, it was cooled and aqueous phase was separated. The organic phase was washed with 1 wt per cent HCl (2x100 ml), dried with anhydrous $CaCl_2$ and filtered. The solution was then distilled under reduced pressure in the presence of a free radical inhibitor, $CuCl_2$, and pure TBHMA was collected as a colorless liquid in 30-40 per cent yield.

^{13}C NMR ($CDCl_3$): δ= 27.9 (CH_3), 62.4 (CH_2-O), 81.2 [*C*-$(CH_3)_3$], 124.4 (*C*H_2=C), 140.6 (*C*=CH_2), 165.4 (C=O) ppm.

^{1}H NMR ($CDCl_3$): δ= 1.5 (s, 9H, CH_3), 2.7 (s, 1H, O-H), 4.2 (s, 2H, CH_2-O), 5.7, 6.1 (d, 2H, CH_2=C) ppm.

FT-IR (NaCl): 3420 (OH), 2978-2934 (C-H), 1709 (C=O), 1639 (C=C), 1159-1054 (C-O) cm^{-1}.

3.2.2. Synthesis of tert-Butyl-α-Bromomethyl Acrylate (TBBr)

To a solution of TBHMA (21.24 g, 134.4 mmol) in 130 ml of ether, PBr_3 (6 ml, 63 mmol) was added dropwise in an ice bath, under nitrogen. The mixture was stirred at room temperature for 3 hours. Then H_2O (69 ml) was added dropwise to this solution in an ice bath and the aqueous phase was separated. The aqueous phase was extracted with hexane (3×23 ml). The organic phases were combined, washed with saturated NaCl solution (2×23 ml) and dried with anhydrous $CaCl_2$. After the removal of ether by rotary

evaporator, distillation was done under reduced pressure to obtain pure product in 81 per cent yield.

^{13}C NMR ($CDCl_3$): δ= 27.9 (CH_3), 29.7 (CH_2-Br), 81.5 [*C*-$(CH_3)_3$], 127.8 (*C*H_2=C), 138.8 (*C*=CH_2), 164.1 (C=O) ppm.

^{1}H NMR ($CDCl_3$): δ= 1.5 (s, 9H, CH_3), 4.1 (s, 2H, CH_2-Br), 5.8, 6.2 (d, 2H, CH_2=C) ppm.

FTIR (NaCl): 2978-2934 (C-H), 1718 (C=O), 1621 (C=C), 1226-1158 (C-O), 720 (C-Br) cm^{-1}

3.3. Synthesis of A Phosphonic Acid Monomer from TBBr-Bisphenol A

3.3.1. Synthesis of di-tert-Butyl 2,2′-(4-4′-(Propane-2,2-diyl)bis(4,1-Phenylene)) bis(Methylene) Diacrylate (Monomer A)

TBBr (6.2 g, 28.0 mmol) was added dropwise to a mixture of Bisphenol A (3.2 g, 14.0 mmol) and triethylamine (5.4 g, 53.4 mmol) in THF (15 ml) in ice bath under nitrogen atmosphere. After the reflux of the mixture for 1 day, THF was evaporated and the residue was diluted with 15 ml of dichloromethane. Then 1-2 ml of 1 wt per cent NaOH was added in an ice-bath and the solution was washed with water (3×12 ml). The organic layer was dried over anhydrous $CaCl_2$. After removal of dichloromethane, the pure product was obtained by precipitation into methanol in 64 per cent yield.

^{13}C NMR ($CDCl_3$): δ= 28.4 [(*C*H_3)$_3$-C], 31.3 [(*C*H_3)$_2$-C], 41.9 [*C*-$(CH_3)_2$], 66.5 (CH_2-O), 81.5 [*C*-$(CH_3)_3$], 114.4 [C (Ar)-H], 125.5 (*C*H_2=C), 128.3 [C (Ar)-H], 137.8 [*C* (Ar)-C], 143.7 (*C*=CH_2), 156.5 [C (Ar)-O], 165.1 (C=O) ppm.

^{1}H NMR ($CDCl_3$): δ= 1.4 [s, 18H, (*C*H_3)$_3$-C], 1.5 (s, 6H, CH_3-C-Ar), 4.6 (s, 4H, CH_2-O), 5.8 (d, 2H, CH=C), 6.2 (d, 2H, CH=C), 6.7 [d, 4H, C (Ar)-H], 7.0 [d, 4H, C (Ar)-H] ppm.

FTIR (NaCl):2972-2862 (C-H), 1712 (C=O), 1636 (C=C), 1150 (C-O) cm^{-1}.

3.3.2. Synthesis of 2,2′-(4-4′-(Propane-2,2-diyl)bis(4,1-Phenylene)) bis(Methylene) Diacryloyl Chloride (Monomer B)

Thionyl chloride (4ml) was added dropwise to TBBr-Bisphenol A diester monomer (monomer A) in an ice bath, under nitrogen purge. After complete addition, the solution was stirred at room temperature for 24 hours under nitrogen. The excess thionyl chloride was removed.

^{13}C NMR ($CDCl_3$): δ= 31.2 [(CH_3)$_2$-C], 41.8 [C-(CH_3)$_2$], 66.0 (CH_2-O), 114.4 [C (Ar)-H], 128.1 [C (Ar)-H], 134.8 (CH_2=C), 140.8 [C (Ar)-C], 144.4 (C=CH_2), 155.9 [C (Ar)-O], 167.7 (C=O) ppm.

^{1}H NMR ($CDCl_3$): δ= 1.6 [s, 6H, (CH_3)$_2$-C], 4.7 (s, 4H, CH_2-O), 6.5 (d, 4H, CH_2=C), 6.8 [d, 4H, C (Ar)-H], 7.2 [d, 4H, C (Ar)-H] ppm.

FTIR (NaCl): 2965 (C-H), 1736 (C=O), 1636 (C=C), 1172 (C-O) cm^{-1}.

3.3.3. Synthesis of 2-[4-(1-{4-[2-(Ethoxy-Ethyl-Phosphinoyl Methoxycarbonyl)-Allyloxy] -Phenyl}-1-Methyl-Ethyl)-Phenoxymethyl]-Acrylic Acid Diethoxy-Phosphoryl Methyl Ester (Monomer 1)

To a mixture of diethyl hydroxymethyl phosphonate (0.86 g, 5.1 mmol) and triethylamine (0.52 g, 5.1 mmol) in 4 ml of dry THF, monomer B (1.0 g, 2.3 mmol) was added dropwise in an ice bath under nitrogen. After the mixture was stirred at room temperature for 1 day, it was diluted with 12 ml dichloromethane and then extracted with water (3×5 ml). The organic layer was dried with anhydrous Na_2SO_4. The pure product was obtained as a light yellow viscous liquid after column chromatography (silica gel 0.063-0.200 mm) using ethylacetate-methanol (100:5) eluent in 43 per cent yield.

^{13}C NMR ($CDCl_3$): δ= 16.7 (CH_3-CH_2), 31.3 [(CH_3)$_2$-C], 42.0 [C-(CH_3)$_2$], 56.6, 58.3 (d, CH_2-P), 63.2 (CH_2-O), 66.2 [CH_2-O-C (Ar)], 114.4 [C (Ar)-H], 127.7 (CH_2=C), 128.0 [C (Ar)-H], 135.4 [C (Ar)-C], 143.9 (C=CH_2), 156.3 [C (Ar)-O], 164.8 (C=O) ppm.

^{1}H NMR ($CDCl_3$): δ= 1.3 [s, 12H, $(CH_3)_3$-C], 1.6 (s, 6H, CH_3-C-tert), 4.2 (q, 8H, C*H*$_2$-CH_3), 4.5 (m, 4H, CH_2-P), 4.7 (4H, m, CH_2-O), 6.1 (d, 2H, CH=C), 6.4 (d, 2H, CH=C), 6.8 [d, 4H, C (Ar)-H], 7.0 [d, 4H, C (Ar)-H] ppm.

FTIR (NaCl): 2976-2950 (C-H), 1730 (C=O), 1638 (C=C), 1153 (C-O), 1238 (P=O), 1023 (P-O-Et) cm^{-1}.

3.3.4. Synthesis of 2-(4-{1-Methyl-1-[4-(2-Phosphonomethhoxycarbonyl-Allyloxy)-Phenyl]-Ethyl}-Phenoxymethyl)-Acrylic Acid Phosphonomethyl Ester (Monomer 2)

TMSBr (3.75 g, 24.5 mmol) was added dropwise to a solution of monomer **1** (1.9 g, 2.7 mmol) in 1.9 ml of dry CH_2Cl_2 under nitrogen in an ice bath.and then the solution was stirred at room temperature for 18 hours. After the evaporation of the solvent, 5 ml of MeOH was added and the mixture was allowed to stir at room temperature overnight. The solvent was evaporated, and the product was obtained as a yellowish brown viscous liquid in 88 per cent yield.

To purify the compound: 2 ml H_20 added to the viscous compound, a suspension formed. Na_2CO_3 was added slowly to neutralize compound. Then, all bubbling stopped and one phase yellow solution obtained. The solution was washed with ethyl acetate (3 x 1 ml), chloroform (3 x 1 ml), then the aqueous phase acidified with concentrated HCl to pH = 1, the formed suspension was washed with ethyl acetate. Ethyl acetate was dried with Na_2SO_4 and evaporated, the product obtained as a light yellow paste in 42 per cent yield.

^{13}C NMR ($CDCl_3$): δ= 31.8 [(*C*H_3)$_2$-C], 42.9 [*C*-$(CH_3)_2$], 59.0, 60.6 (d, CH_2-P), 61.8 (CH_2-O), 67. 5 [*C*H_2-O-C (Ar)], 115.6 [C (Ar)-H], 129.1 (*C*H_2=C), 137.6 [C (Ar)-H], 145.2 [*C* (Ar)-C], 157.8 (*C*=CH_2), 166.4 [C (Ar)-O], 173.3 (C=O) ppm.

FTIR (NaCl): 3500-2000 (OH), 2963 (C-H), 1712 (C=O), 1610 (C=C), 1232 (P=O) cm^{-1}.

3.4. Synthesis of Phosphonic Acid Monomers from o-Hydroxyaryl Phosphonates

3.4.1. Synthesis of Tetraethyl 4,4'-(Propane-2,2-diyl)bis (4,1-Phenylene) Diphosphate

To a mixture of Bisphenol A (5.49 g, 24.0 mmol) and diethylphosphite (8.30 g, 60.1 mmol) in carbon tetrachloride (25 ml), triethylamine (6.12 g, 60.5 mmol) was added dropwise. The reaction mixture was stirred 2 days at room temperature. Then, it was extracted with water (3×4 ml) and the obtained organic layer was dried with anhydrous Na_2SO_4. Removal of solvent gave a yellow viscous liquid in 36 per cent yield.

^{13}C NMR ($CDCl_3$): δ= 15.5 (CH_3-CH_2), 30.2 [(CH_3)$_2$-C], 41.6 [C-(CH_3)$_2$], 63.9 (CH_2-O), 118.8 [C (Ar)-H], 127.4 [C (Ar)-H], 146.4 [C (Ar)-C], 148.1 [C (Ar)-O] ppm.

^{1}H NMR ($CDCl_3$): δ= 1.3 (t, 12H, CH_2-CH_3), 1.6 [s, 6H, C-(CH_3)$_2$], 4.1 (q, 8H, CH_2-CH_3), 7-7.3 [m, 8H, H (Ar)] ppm.

3.4.2. Synthesis of Tetraethyl 5,5'-(Propane-2,2-diyl)bis (2-Hydroxy-5,1-Phenylene) Diphosphonate

To 5.3 g (52.4 mmol) of diisopropylamine in THF (25 ml) under nitrogen at -78 °C was added n-butyl lithium (4.5 ml of 10 M solution). The mixture was stirred at -78 °C for 30 min and then a solution of 4,4' – Bis(phosphate) from Bisphenol A (5.10 g, 10.2 mmol) in 15 ml THF was slowly added. The mixture was stirred for 1 hour longer at -78 °C and 3 hours at room temperature yielding red slurry. The reaction was next poured over a mixture of 60 ml of aqueous ammonium chloride and 60 ml of dichloromethane. The organic layer was separated and dried over Na_2SO_4. After removal of solvents a reddish viscous liquid was obtained in 91 per cent yield.

^{13}C NMR ($CDCl_3$): δ= 16.1 (CH_3-CH_2), 30.7 [(CH_3)$_2$-C], 41.9 [C-(CH_3)$_2$], 62.8 (CH_2-O), 106.9, 109.4 [C (Ar)-P], 117.4 [C (Ar)-H], 128.9 [C (Ar)-H], 134.0 [C (Ar)-H], 141.4 [C (Ar)-C], 160.1 [C (Ar)-O] ppm.

^{1}H NMR ($CDCl_3$): δ= 1.2 (t, 12H, CH_2-CH_3), 1.6 (s, 6H, C-$(CH_3)_2$), 4.1 (q, 8H, CH_2-CH_3), 7-7.3 [m, 6H, H (Ar)] ppm.

3.4.3. Synthesis of di-tert-2,2′-(4,4′-(Propane-2,2-diyl)bis(2-(Diethoxyphosphoryl)-4,1-Phenylene))bis(oxy)bis(Methylene) Diacrylate (Monomer 3)

To a mixture of 4,4' – Bis(phosphonate) from Bisphenol A (2.1 g, 4.20 mmol) and K_2CO_3 (11.6 g, 83.9 mmol) in 10 ml acetone, TBBr (2.3 g, 10.5 mmol) was added dropwise. The reaction mixture was refluxed for 2 days. Then, acetone was evaporated and the residue was diluted with dichloromethane (15 ml) and extracted with water (3×5ml). The organic phase was dried over anhydrous Na_2SO_4. Removal of solvent on a rotoevaporator left thick reddish paste. The pure product was obtained as a light yellow viscous liquid after column chromatography (silica gel 0.063-0.200 mm, ethylacetate-methanol (100:4) eluent) in 65 per cent yield.

^{13}C NMR ($CDCl_3$): δ= 16.2 (CH$_3$-CH_2), 28.0[(CH$_3$)$_3$-C], 30.7 [(CH$_3$)$_2$-C], 41.8 [C-$(CH_3)_2$], 61.9 (CH_2-O), 66.2 (CH_2-O), 81.3 [C-$(CH_3)_3$], 111.8 [C (Ar)-H], 114.5 [d, C (Ar)-P], 125.3 (CH$_2$=C), 133.1 [C (Ar)-H], 136.5 [C (Ar)-C], 142.4 (C=CH_2), 157.9 [C (Ar)-O], 164.5 (C=O) ppm.

^{1}H NMR ($CDCl_3$): δ= 1.2 (t, 12H, CH_3-CH_2), 1.5 (s, 18H, CH_3-C), 1.6 (s, 6H, CH_3-C), 4.0 (q, 8H, CH_2-O), 5.2 (s, 4H, CH_2-O), 6.2 (s, 2H, CH=C), 6.3 (s, 2H, CH=C),6.8 (d, 2H, CH=CH), 7.2(m, 2H, CH=CH), 7.7 (m,2H, CH=C) ppm.

FTIR (NaCl): 2976 (C-H), 1715 (C=O), 1646 (C=C), 1146 (C-O), 1261 (P=O), 1030 (P-O-Et) cm^{-1}.

3.4.4. Synthesis of 2,2′-(4,4′-(Propane-2,2-diyl)bis(2-(Diethoxyphosphoryl)-4,1-Phenylene))bis(oxy)bis(Methylene) Diacrylic Acid (Monomer 4)

CF_3COOH (1.28 g, 11.26 mmol) was added dropwise to TBBr-Bisphenol A monomer (1.1 g, 1.4 mmol) under nitrogen in an ice bath. The mixture was stirred at room

temperature for 24 h. The CF_3COOH was evaporated with nitrogen bubbling. Then the pure product was precipitated in acetone as white crystals, 0.3 g (32 per cent yields).

^{13}C NMR (MeOD): δ= 16.7 (CH_3-CH_2), 31.2 [(CH_3)$_2$-C], 43.1 [C-(CH_3)$_2$], 63.8 (CH_2-O), 67.9 (CH_2-O), 113.5 [C (Ar)-H], 115.4, 117.3 [d, C (Ar)-P], 127.3 (CH_2=C), 134.4 [C (Ar)-H], 137.6 [C (Ar)-C], 144.3 (C=CH_2), 159.7 [C (Ar)-O], 168.4 (C=O) ppm.

^{1}H NMR (MeOD): δ= 1.2 (t, 12H, CH_3-CH_2), 1.6 (s, 6H, CH_3-C), 4.0 (q, 8H, CH_2-O), 4.8 (s, 4H, CH_2-O), 6.2 (s, 2H, CH=C), 6.4 (s, 2H, CH=C),7.0 (d, 2H, CH=CH), 7.5(m, 2H, CH=CH), 7.6 (m,2H, CH=C) ppm.

FTIR (NaCl): 3500-2500 (OH), 2982 (C-H), 1707 (C=O), 1631 (C=C), 1260 (P=O), 1015 (P-O-Et) cm^{-1}.

3.4.5. Synthesis of 2,2′-(4,4′-(Propane-2,2-diyl)bis(2-Phosphono-4,1-Phenylene)) bis(oxy) bis(Methylene) Diacrylic Acid (Monomer 5)

TMSBr (1.76 g, 11.5 mmol) was added dropwise to a solution of monomer (1 g, 1.3 mmol) in 0.75 ml of dry CH_2Cl_2 under nitrogen in an ice bath and then the solution was stirred at room temperature for 18 hours. After the evaporation of the solvent, 5 ml of MeOH was added and the mixture was allowed to stir at room temperature overnight. The solvent was evaporated, and the product was obtained as a reddish brown viscous liquid. Purification of this monomer was not successful.

^{13} C NMR (MeOD): δ= 30.9 [(CH_3)$_2$-C], 42.2 [C-(CH_3)$_2$], 68.5 (CH_2-O), 114.1 [C (Ar)-H], 116.4, 118.8 [d, C (Ar)-P], 128.2 (CH_2=C), 132.4 [C (Ar)-H], 134.6 [C (Ar)-H], 138.4 [C (Ar)-C], 142.6 (C=CH_2), 159.3 [C (Ar)-O], 168.6 (C=O) ppm.

3.4.6. Synthesis of 1,4-Phenylene Tetraethyl Diphosphate

To a mixture of hydroquinone (1.32 g, 12.0 mmol), diethylphosphite (3.46 g, 25.1 mmol) in 7.2 ml carbon tetrachloride, triethylamine (2.52 g, 25.0 mmol) was added dropwise in ice bath under nitrogen atmosphere. The mixture was stirred overnight at

room temperature, then 8 ml water was added and organic layer was extracted with water (2×5 ml). The obtained organic layer was dried over anhydrous $CaCl_2$. Removal of solvent on rotary evaporator left tetraethyl (1,4-phenylene) bis phosphonate as a colorless liquid, 3.3 g (72 per cent).

^{13}C NMR ($CDCl_3$): δ= 14.8 (*C*H_3-CH_2), 63.4 (CH_2-O), 119.9 (*C*H=CH), 146.3 (C-O) ppm.

^{1}H NMR ($CDCl_3$): δ= 1.3 (t, 12H, C*H*$_3$-CH_2), 3.9-4.2 (m, 8H, CH_3-C*H*$_2$), 7.2 [s, 4H, C (Ar)-H] ppm.

3.4.7. Synthesis of Tetraethyl 2,5-Dihydroxy-1,4-Phenylene Diphosphonate

To 6.52 g (64.4 mmol) of diisopropylamine in THF (20 ml) under nitrogen at -78 ºC was added n-butyllithium (5.7 ml of 10 M solution). The mixture was stirred for 30 min and then tetraethyl (1, 4-phenylene) diphosphonate (4.90 g, 12.8 mmol) dissolved in 15 ml of THF was syringed into the reaction mixture. After the reaction mixture was stirred at -78 ºC for 1 hour; dry-ice acetone bath was removed and stirring was continued for an additional 3 hours. It was next poured over a mixture of 60 ml of aqueous ammonium chloride and 60 ml of dichloromethane. Aqueous layer was separated and extracted with dichloromethane-ether mixture (3×15 ml). The combined organic layers were dried over anhydrous Na_2SO_4 Removal of solvents left the product as a reddish crystal, 4.20 g in 86 per cent yield.

^{13}C NMR ($CDCl_3$): δ= 15.2 (*C*H_3-CH_2), 62.2 (CH_2-O), 114.5 (d, C-P), 118.4 (*C*H=C), 152.5 (C-OH) ppm.

^{1}H NMR ($CDCl_3$): δ= 1.3 (t, 12H, C*H*$_3$-CH_2), 4.2 (q, 8H, CH_3-C*H*$_2$), 7.0 [m, 2H, CH (Ar)], 9.6 (s, 2H, O-H) ppm.

3.4.8. Synthesis of di-tert-Butyl 2,2′-(2,5-bis(Diethoxyphosphoryl)-1,4-Phenylene)bis (oxy)bis(Methylene) Diacrylate (Monomer 6)

TBBr (1.92 g, 8.7 mmol) was added dropwise to a mixture of tetraethyl (2,5-dihydroxy-1,4-phenylene) bisphosphonate (1.33 g, 3.5 mmol), acetone (8 ml), and K_2CO_3 (9.65 g, 69.8 mmol). The reaction mixture was refluxed at 60 °C for 2 days. At the end of reflux the acetone was evaporated and dichloromethane was added (15 ml). Then the reaction mixture was extracted with water (3×5 ml). The organic layer was separated and dried with Na_2SO_4. Evaporation of CH_2Cl_2 gave the product as a reddish viscous liquid in 92 per cent yield.

^{13}C NMR ($CDCl_3$): δ= 16.0 (CH_3-CH_2), 27.7 [(CH_3)$_3$-C], 62.1 (CH_3-CH_2), 67.1 (CH_2-O), 81.0 [C-(CH_3)$_3$], 118.7 [C (Ar)-C], 121.4, 123.2 [d, C (Ar)-P], 125.2 (CH_2=C), 136.4 (CH_2=C), 153.3 [C(Ar)-O], 164.1 (C=O) ppm.

^{1}H NMR ($CDCl_3$): δ= 1.3 (t, 12H, CH_3-CH_2), 1.5 [s, 18H, (CH_3)$_3$-C], 4.13 (q, 8H, CH_3-CH_2), 4.76 (CH_2-O), 6.2 (s, 2H, CH=C), 6.3 (s, 2H, CH=C), 7.4-7.5 [m, 2H, CH (Ar)] ppm.

FTIR (NaCl): 2973 (C-H), 1700 (C=O), 1636 (C=C), 1231 (P=O) and 1025 (P-OEt) cm^{-1}.

3.4.9. Synthesis of 2,2′-(2,5-bis(Diethoxyphosphoryl)-1,4-Phenylene)bis(oxy)bis (Methylene) Diacrylic Acid (Monomer 7)

CF_3COOH (0.56 g, 49.1 mmol) was added dropwise to monomer (0.55g, 8.3 mmol) on ice, under nitrogen. After mixing at room temperature for 24 hours, excess CF_3COOH was removed by direct nitrogen bubbling. Then the product was precipitated into cold MeOH.

^{13}C NMR (DMSO): δ= 16.0 (CH_3-CH_2), 62.3 (CH_3-CH_2), 67.2 (CH_2-O), 118.6 [C (Ar)-C], 121.6, 123.4 [d, C (Ar)-P], 126.2 (CH_2=C), 136.4 (CH_2=C), 153.1 [C (Ar)-O], 166.5 (C=O) ppm.

^{1}H NMR (DMSO): δ= 1.2 (t, 12H, C*H*$_3$-CH$_2$), 3.2 (s, 2H, O-H), 4.1 (q, 8H, CH$_3$-C*H*$_2$), 4.8 (CH$_2$-O), 6.1 (s, 2H, CH=C), 6.3 (s, 2H, CH=C), 7.3 [m, 2H, CH (Ar)] ppm.

FTIR (NaCl): 3500-2500 (OH), 2889 (C-H), 1691 (C=O), 1639 (C=C), 1210 (P=O), 1019 (P-O-Et) cm^{-1}.

3.4.10. Synthesis of 2,2′-(2,5-Diphoshono-1,4-Phenylene)bis(oxy)bis (Methylene) Diacrylic Acid (Monomer 8)

TMSBr (0.46 g, 30.3 mmol) was added dropwise to a solution of monomer (0.50 g, 7.6 mmol) in 2 ml of dry CH_2Cl_2 under nitrogen and then the solution was refluxed for 1 hour. After the evaporation of the solvent, 3 ml of MeOH was added and the mixture was allowed to stir at room temperature overnight. The solvent was evaporated, and the product was precipitated into CH_2Cl_2 as a white solid. Purification of this monomer was not successful.

^{13}C NMR (MeOD):= 67.9 (CH$_2$-O), 118.5 [*C* (Ar)-C], 125.1, 126.9 [d, C (Ar)-P], 127.2 (*C*H$_2$=C), 136.5 (CH$_2$=*C*), 154.4 [C (Ar)-O], 166.9 (C=O) ppm.

3.5. Synthesis of 2,6-bis(t-Butoxycarbonyl)-Tetraethyl Phosphonate Dimer (Monomer 9)

To a suspension of sodium hydride (1.11 g, 55 per cent dispersion in oil) in dry THF (20 ml), tetraethyl methylenediphosphonate (2.45 g, 8.5 mmol) was added and allowed to stir at room temperature for 1 hour. Then TBBr (4.68 g, 21.2 mmol) was added dropwise. The reaction mixture was left to reflux for two days. After quenching the mixture with aq. NH_4Cl (60 ml), it was extracted ethyl acetate (3×20 ml). The organic phase was then washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure give yellow viscous liquid, the pure product was obtained as a colorless liquid after column chromatography (silica gel (0.0063-0.200mm), ethylacetate-methanol (100:4) eluent) in 60 per cent yield.

^{13}C NMR ($CDCl_3$): δ= 15.3 (CH_3-CH_2), 27.0 [C-(CH_3)$_3$], 31.0 (CH_2), 45.6, 46.9, 48.2 (t, C-P), 61.6 (CH_2-OP), 79.2 [C-(CH_3)$_3$], 127.4 (CH_2=C), 136.8 (C=CH_2), 165.8 (C=O) ppm.

^{1}H NMR ($CDCl_3$): δ= 1.2 (t, 12H, CH_2-CH_3), 1.4 (s, 18H, C-(CH_3)$_3$), 2.9 (t, 4H, allylic-CH_2), 4.1 (m, 8H, O-CH_2), 5.8 (s, 2H, CH_2=C), 6.1 (s, 2H, CH_2=C) ppm.

FTIR (NaCl): 2978 (C-H), 1715 (C=O), 1627(C=C), 1246 (P=O), 1028 (P-O-Et) cm^{-1}.

3.6 Photopolymerizations

3.6.1. Sample Preparation

All the synthesized monomers were mixed with three different commercially used dental materials (TEGDMA, BisGMA and GDMA) with the molar ratio of 95:5 (TEGDMA: monomer), 80:20 (TEGDMA: monomer), 50:45:5 (Bis-GMA: TEGDMA: monomer) and 95:5 or 90:10 (GDMA: monomer). Also, the homopolymerization of the monomers were carried out for the suitable monomers.

3.6.2. Polymerization Procedure

All the photopolymerizations were carried out by TA Instruments Q 100 Photo-DSC using 2,2-dimethoxy-2-phenyl acetophenone (Irgacure 651) as the photoinitiator. The initiator (4-5 mg) was first dissolved in methylene chloride (1-2 ml). Approximately 4 mg of sample (nearly 250 nm thickness) was carefully placed in an uncovered aluminum DSC pan. Then, the photoinitiator disolved in CH_2Cl_2 was added with a micro-syringe to give a final concentration in the monomer of 2.0 mol per cent after evaporation of the solvent. After placing the sample and reference pans, the DSC chamber was purged with nitrogen for 10 min to remove air and CH_2Cl_2 before polymerization and purging was continued during polymerization. The samples were irradiated for 10 minutes at 40 °C.

Monochromatic 365 nm ultraviolet light with an incident light intensity of 15 mW/cm^2 was used for all photopolymerizations. The heat flux as a function of time was monitored using DSC under isothermal conditions and both the rates of polymerization

(R_p) and conversions were calculated as a function of time. The theoretical heat evolved for methacrylate and methacrylic acid double bonds were used as the heat of reaction value, ΔH_p= 55 and 64.5 kcal/mol. The rates of polymerizations (**R_P**) were calculated according to the following formula:

$$R_p = \frac{(Q/s)M}{n\Delta H_p m}$$

Figure 3.1. Equation of rate of polymerization

Where **Q/s** is the heat flow per second during reaction, **M** is the molar mass of the monomer, **n** is the number of double bonds per monomer molecule, **ΔH_p** is the heat released per mole of double bonds reacted and **m** is the mass of the monomer in the sample.

4. RESULTS AND DISCUSSION

Novel monomers aiming for desired properties for use in dental materials have been synthesized. These are crosslinkers with phosphonate, phosphonic and carboxylic acid functions, based on t-butyl α-hydroxymethyl acrylate (TBHMA), synthesized by two different methods. Incorporation of phosphonic acid functionality into monomer structures will increase biocompatibility and adhesion to tooth material. Also, rigid aromatic groups in the monomer structures will improve mechanical properties.

4.1. Synthesis of Starting Materials

4.1.1. Synthesis of tert-butyl-α-hydroxymethyl acrylate (TBHMA)

The Baylis-Hillman reaction, the coupling of α,β-unsaturated carbonyl compounds with aldehydes catalyzed by tert-amine or phosphine, is an important carbon-carbon bond forming reaction [1-3]. TBHMA was synthesized from the Baylis-Hillman reaction between tert-butyl acrylate and paraformaldehyde in the presence of 1.4-diazobicyclo [2.2.2] octane (DABCO) as catalyst (Figure 4.1) using literature procedures [71,72] with the mechanism indicated in Figure 4.2.

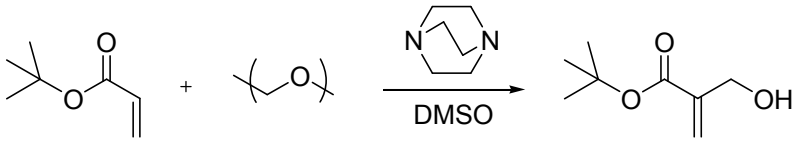


Figure 4.1. Synthesis of TBHMA

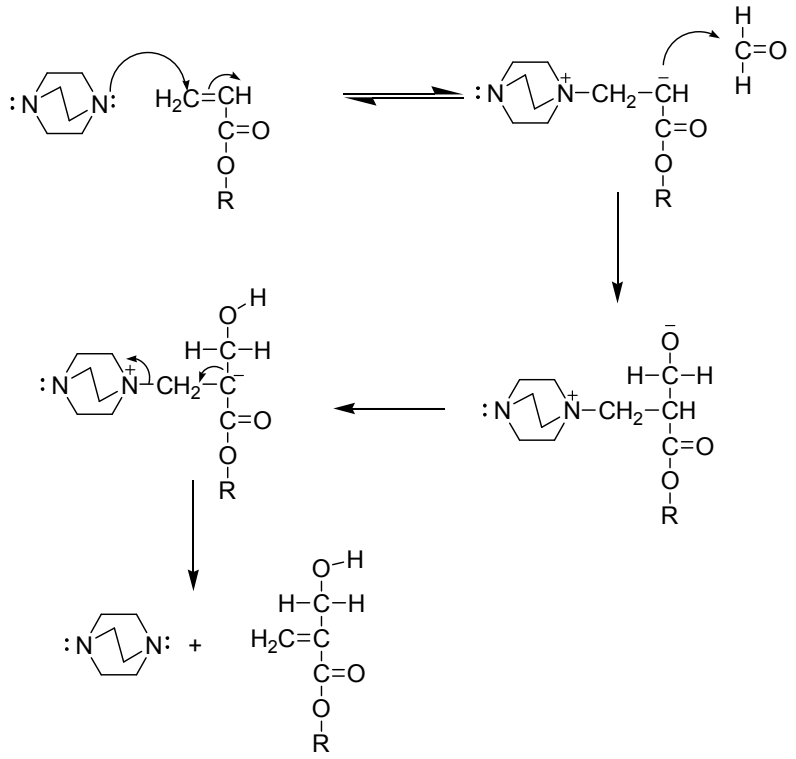


Figure 4.2. Mechanism of Baylis-Hillman reaction

The ^{13}C-NMR spectrum of TBHMA (Figure 4.3) was characterized by tert-butyl carbons at 28.1 and 81.2 ppm, methylene carbon attached to hydroxyl at 62.4 ppm, double bond carbons at 124.4 and 140.6 ppm, and carbonyl carbon peak at 165.4 ppm.

The ^{1}H-NMR spectrum of TBHMA (Figure 4.4) showed tert-butyl hydrogens at 1.49 ppm, methylene hydrogens at 4.25 ppm, hydroxyl hydrogen at 2.68 ppm, and double bond hydrogens at 5.72 and 6.12 ppm.

The advantages offered by this monomer are giving polymers with high glass transition temperatures (T_g) and capability of functionalization before or after polymer formation, through either the alcohol or ester group.

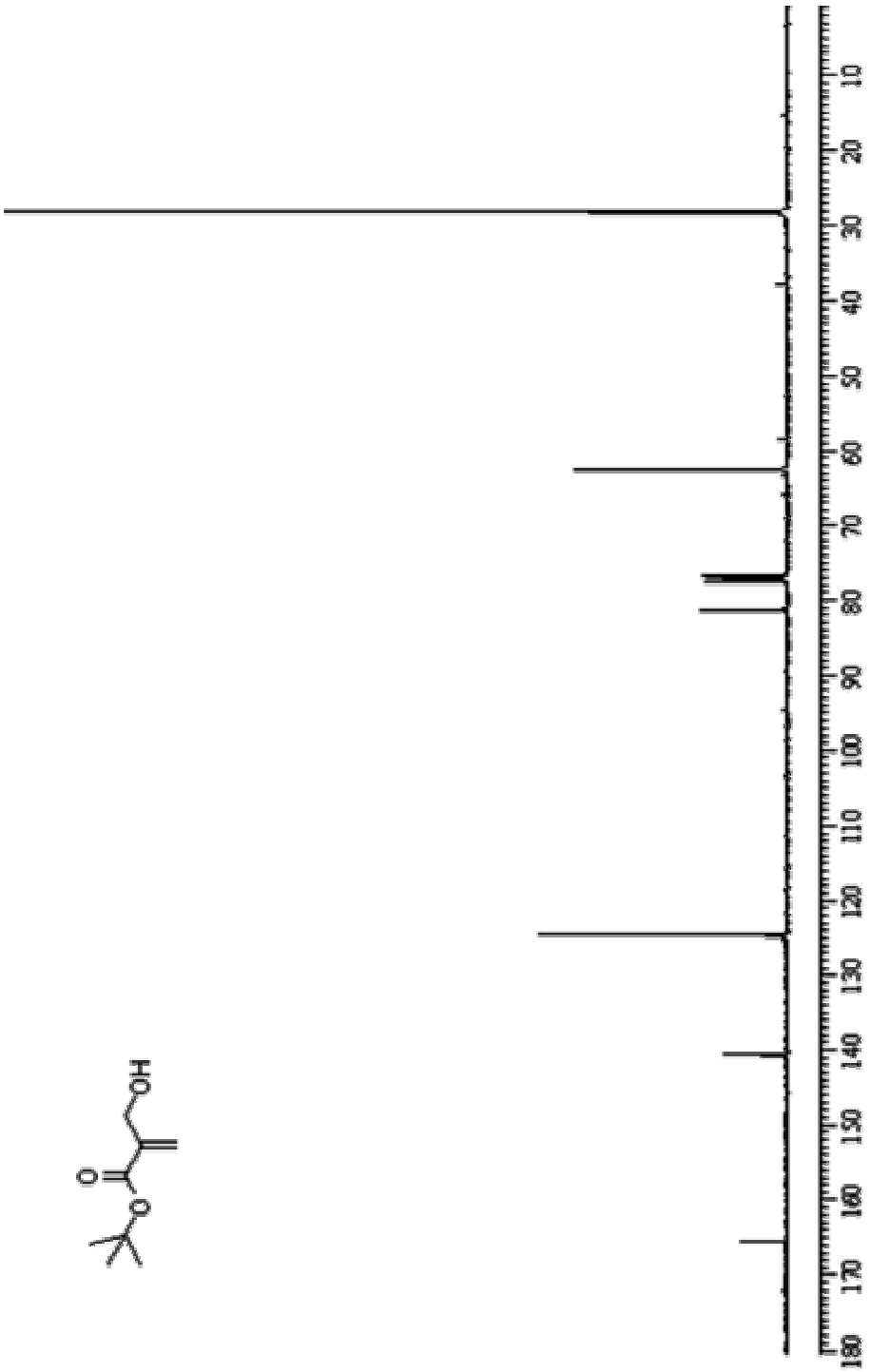


Figure 4.3. ^{13}C-NMR spectrum of TBHMA

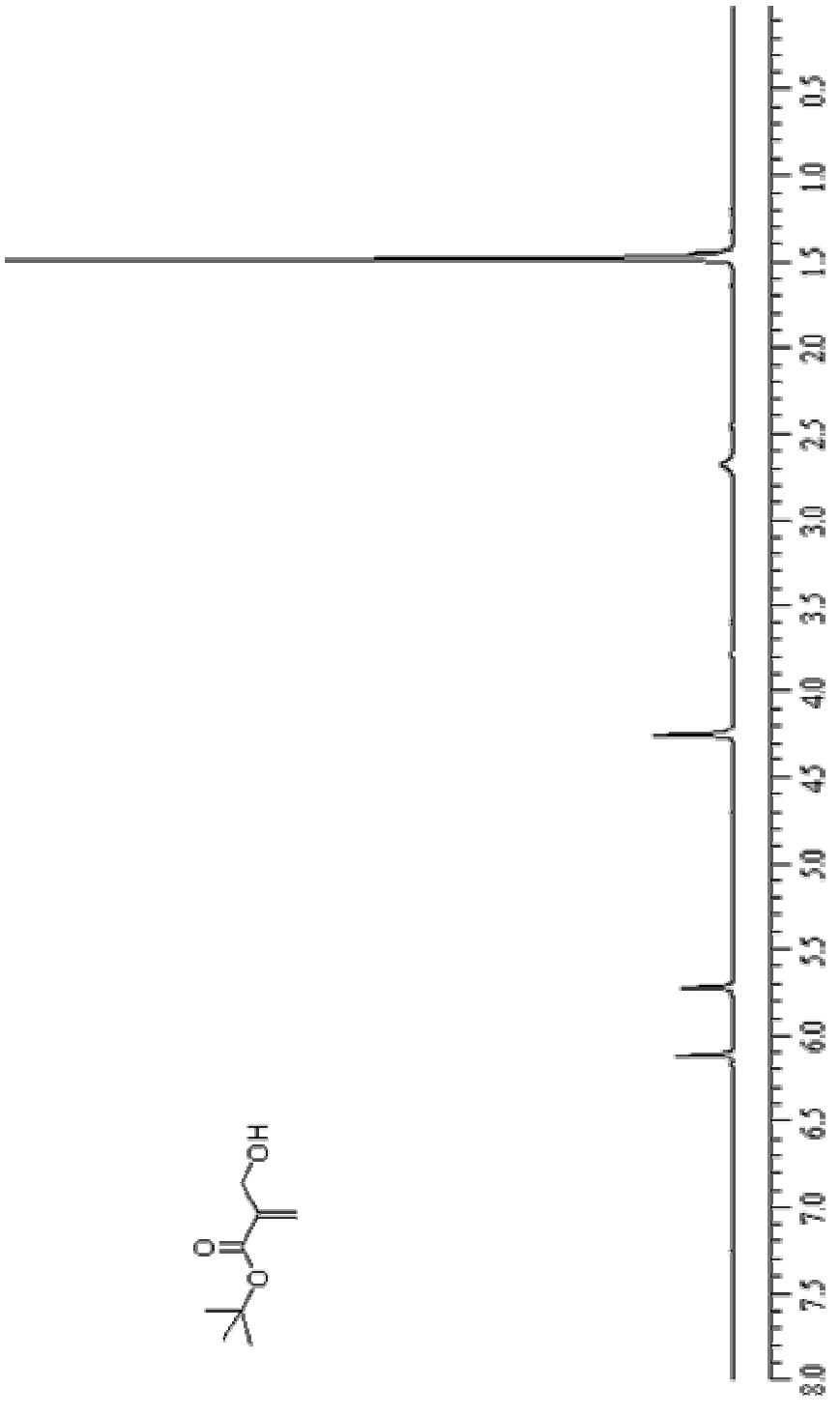


Figure 4.4. ^{1}H-NMR spectrum of TBHMA

4.1.2. Synthesis of tert-butyl-α-bromomethyl acrylate (TBBr)

Reaction of TBHMA with excess PBr_3 in ether gave TBBr as a colorless liquid after 3 hours of mixing at room temperature (Figure 4.5). The reaction should be carried under nitrogen purge to remove HBr gas evolved during the reaction. Otherwise, HBr evolution may lead to the formation of side-products or may inhibit the expected product formation.

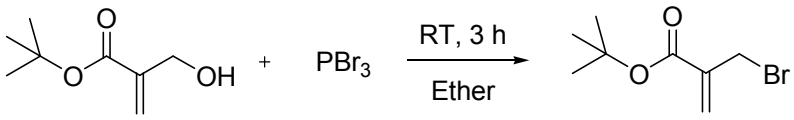


Figure 4.5. Synthesis of TBBr

The ^{13}C-NMR spectrum of TBBr (Figure 4.6) showed the disappearance of the methylene peak attached to hydroxyl at 62.4 ppm and appearance of a new peak at 29.7 ppm corresponding to the methylene carbon attached to Br.

The ^{1}H-NMR spectrum (Figure 4.7) showed complete disappearance of hydroxyl proton peak at 2.68 ppm. Also, in the IR spectrum, hydroxyl absorption peak at 3420 cm^{-1} was not observed.

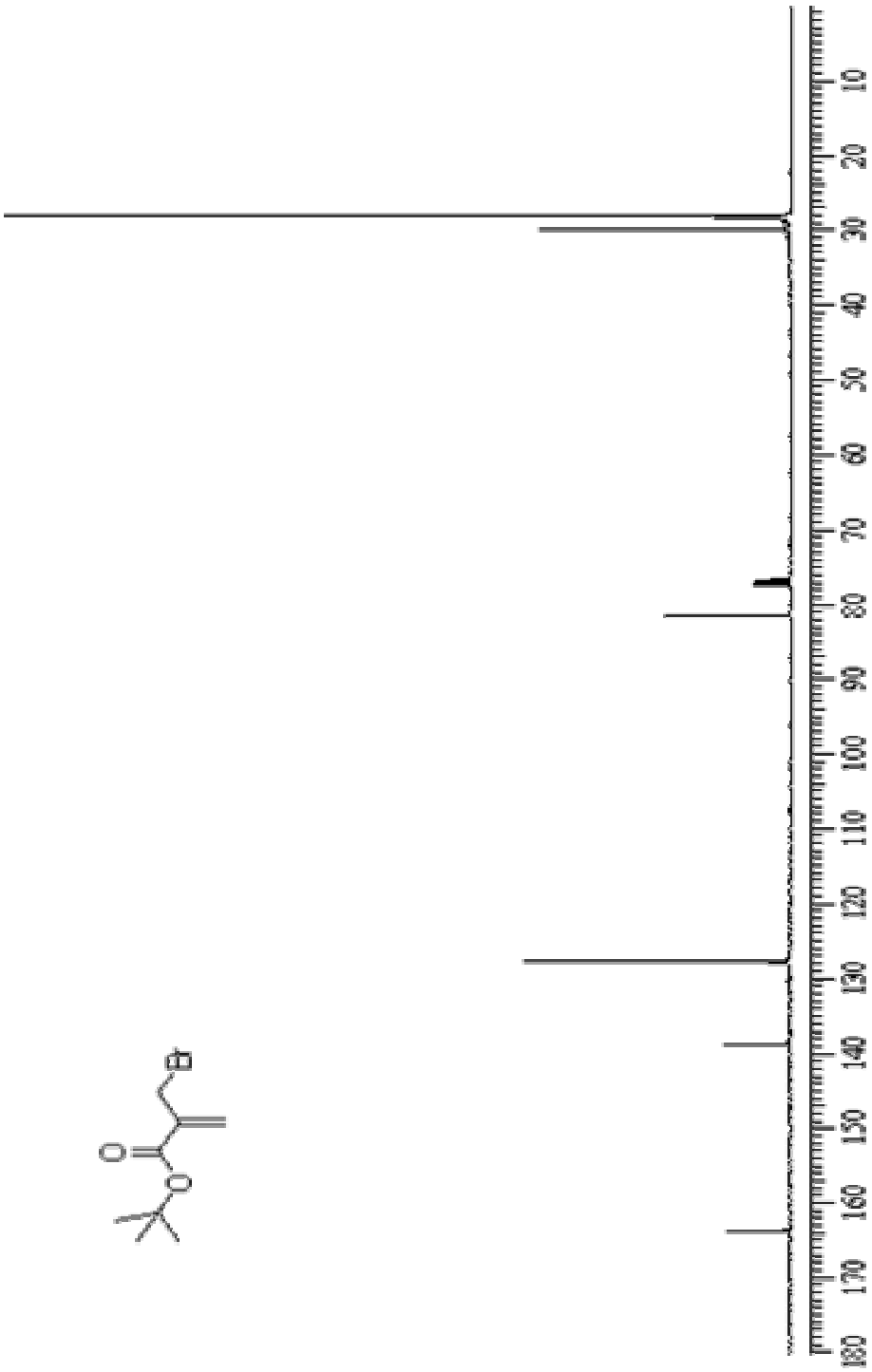


Figure 4.6 ^{13}C-NMR spectrum of TBBr

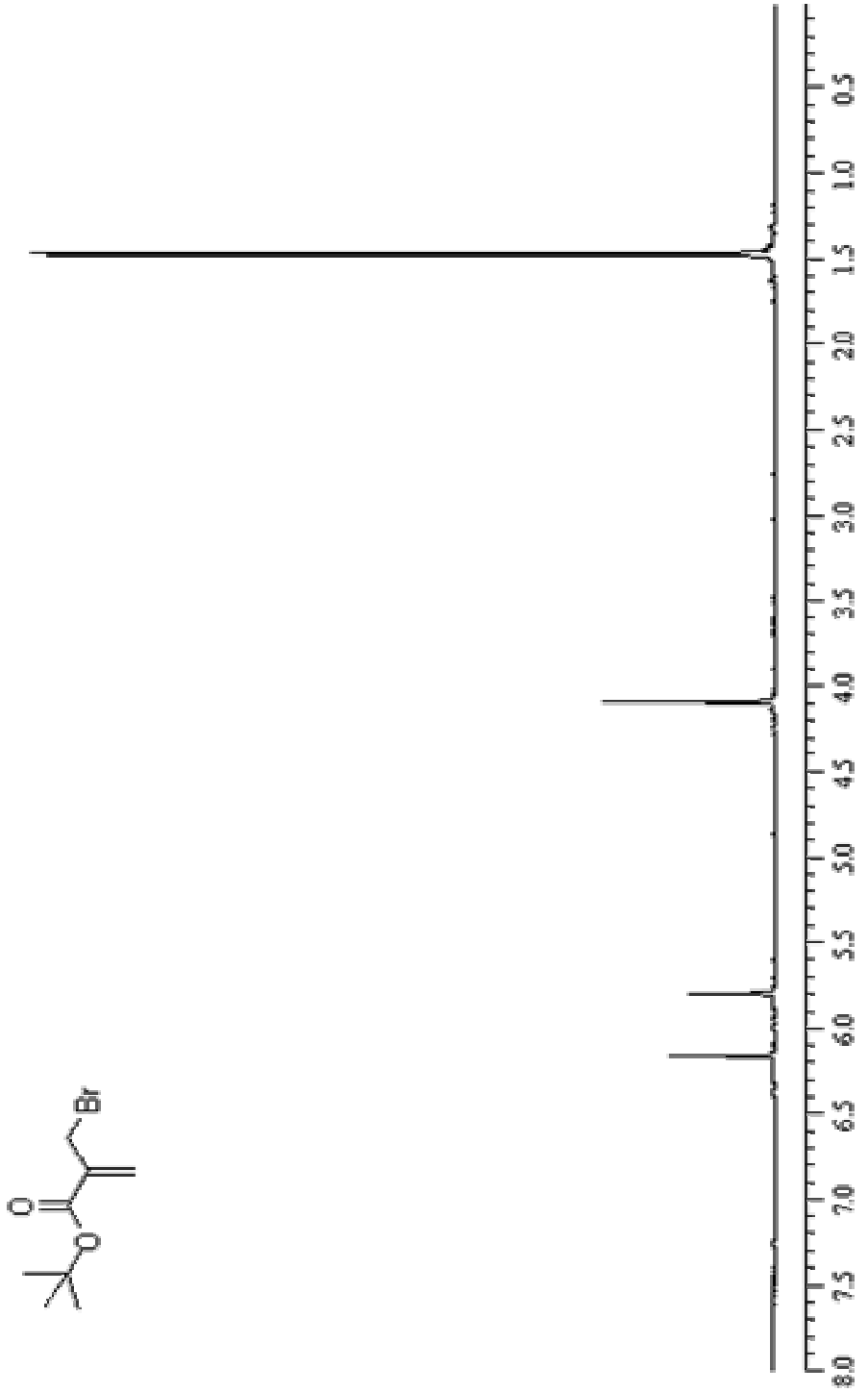


Figure 4.7. ^{1}H-NMR spectrum of TBBr

4.2. Synthesis of a Phosphonic Acid Monomer from TBBr-Bisphenol A

The first method for the synthesis of a novel crosslinker with phosphonic acid functions involved four steps (Figure 4.8)

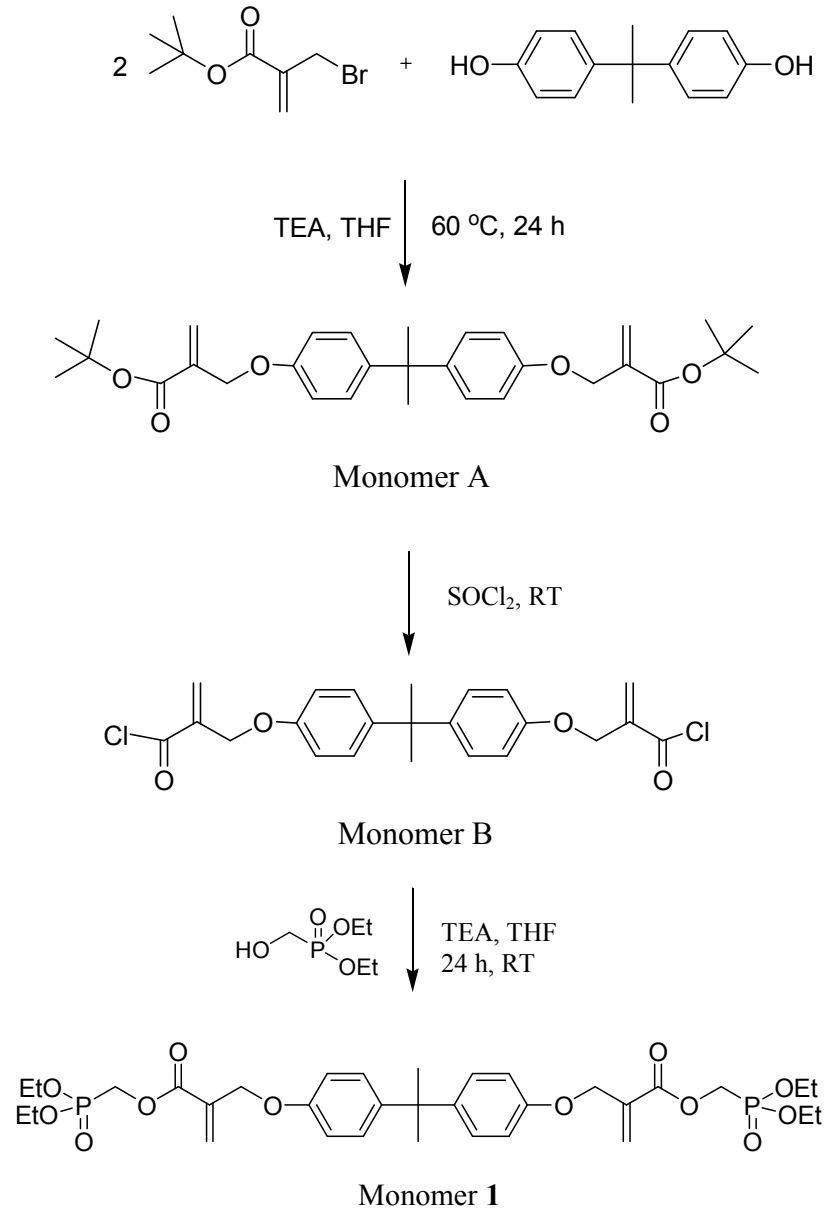


Figure 4.8. Synthesis of monomer **A**, **B** and **1**

In the first step, TBBr was directly reacted with Bisphenol A using TEA as catalyst in THF to give monomer **A**. The second role of TEA is to trap HBr gas evolved during the

reaction. The pure product was obtained in 64 per cent yield as a white solid with the melting point of 66-67 ^{o}C.

The ^{13}C-NMR spectrum of monomer **A** (Figure 4.9) showed characteristic peaks for t-butyl group at 28.4 and 81.5 ppm, methyl carbons of Bisphenol A at 31.3 ppm, a quaternary carbon at 41.9 ppm, methylene carbon at 66.5 ppm, double bond carbons at 125.5 and 143.7 ppm, aromatic carbons at 114.4, 128.6, 137.8, 156.5 ppm and carbonyl carbon peak at 165.1 ppm.

The ^{1}H-NMR spectrum of this monomer (Figure 4.10) showed t-butyl hydrogens at 1.4 ppm, methyl hydrogens of Bisphenol A at 1.5 ppm, methylene hydrogens at 4.6 ppm, double bond hydrogens at 5.8 and 6.2 ppm, and aromatic hydrogens at 6.7, 7.0 ppm.

The FT-IR spectrum of monomer **A** (Figure 4.11) showed characteristic absorbtions of C-H, C=O, C=C, C-O groups at 2972, 1712, 1636, 1150 cm^{-1}.

Addition of excess thionyl chloride to monomer **A** gave TBBr-Bisphenol A diacid chloride intermediate (monomer **B**) after mixing for 24 hours at RT (Figure 4.8). The excess $SOCl_2$ was removed by direct nitrogen bubbling into the solution.

The ^{13}C-NMR spectrum (Figure 4.9) of the diacid chloride showed the disappearance of t-butyl carbon peaks of monomer A at 28.4 and 81.5 ppm.

The ^{1}H-NMR spectrum (Figure 4.10) also confirmed the disappearance of t- butyl peaks.

The FT-IR spectrum of the product (Figure 4.12) showed characteristic absorptions of C-H, C=O, C=C and C-O and groups at 2965, 1736, 1636 and 1172 cm^{-1}.

The third step involved the reaction of the diacid chloride intermediate (monomer **B**) with diethylhydroxymethyl phosphonate in presence of TEA in dry THF to give monomer **1** with phosphonate groups (Figure 4.8). The pure product was obtained as a

light yellow viscous liquid after column chromatography (silica gel 0.063-0.200 mm) using ethylacetate-methanol (100:5) eluent in 43 per cent yield.

This monomer was soluble in THF, acetone, MeOH, CH_2Cl_2, but insoluble in hexane, petroleum ether and diethylether.

The ^{13}C-NMR spectrum of monomer **1** (Figure 4.9) showed characteristic peaks for ethyl carbons at 16.7 and 63.2 ppm, and methylene carbon attached to phosphorus at 56.6 and 58.3 ppm (doublet).

The ^{1}H-NMR spectrum of this monomer (Figure 4.10) also showed ethyl hydrogens at 1.3 and 4.2 ppm plus methylene hydrogens at 4.6 ppm.

The FT-IR spectrum of the product (Figure 4.13) showed characteristic absorptions of C-H, C=O, C=C, P=O, C-O and P-OEt groups at 2980, 1730, 1638, 1238, 1153 and 1023 cm^{-1}.

The advantageous property of this monomer is capability of improving thermal and mechanical properties of the ultimate material, due to the rigidity of the monomer itself and the bulky end groups. Also, it contains dimethacrylate functionality which increase rate of polymerization. Therefore, this monomer can be used in dental composite formulations.

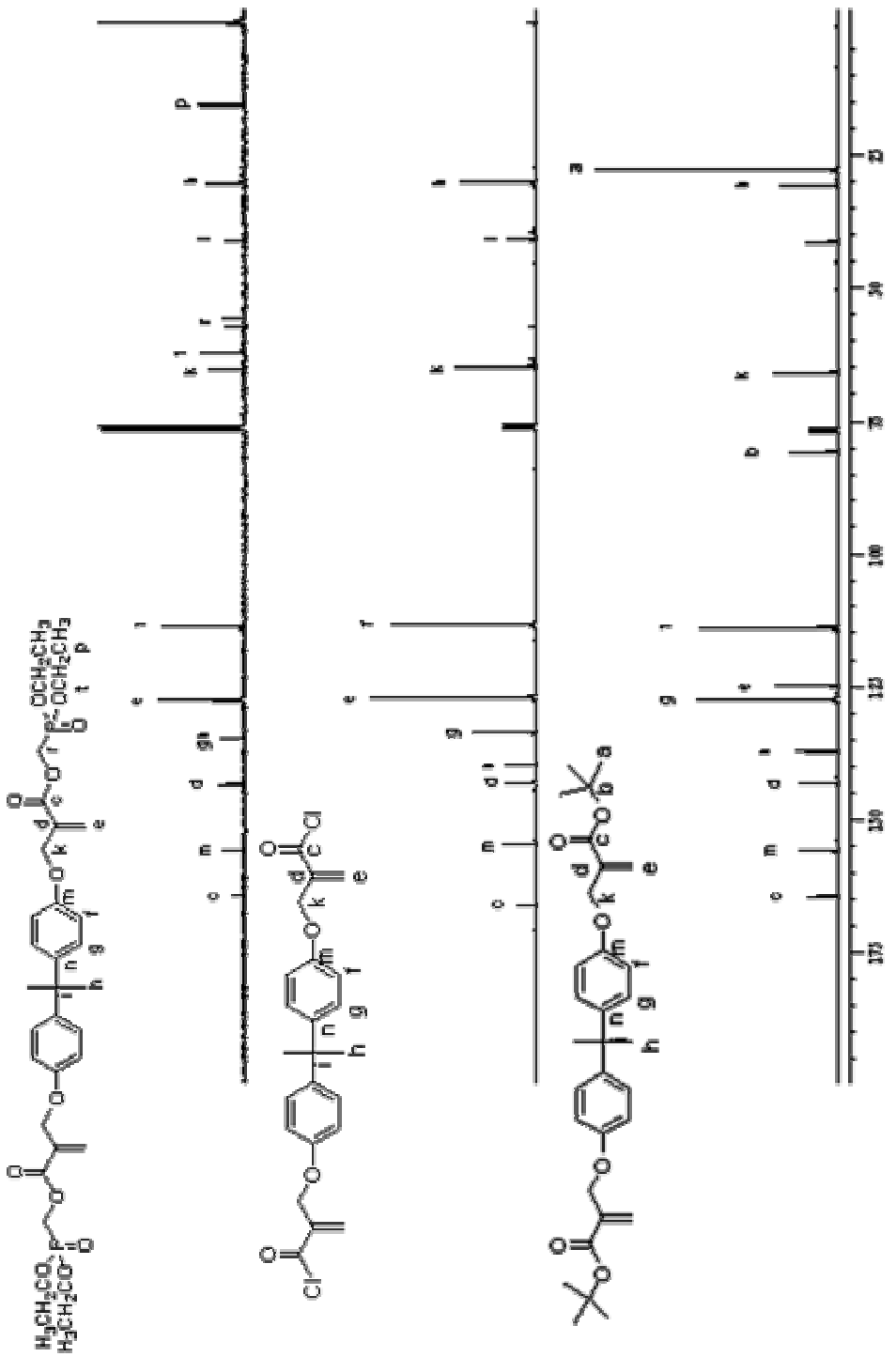


Figure 4.9. ^{13}C NMR spectra of monomer A, B and 1

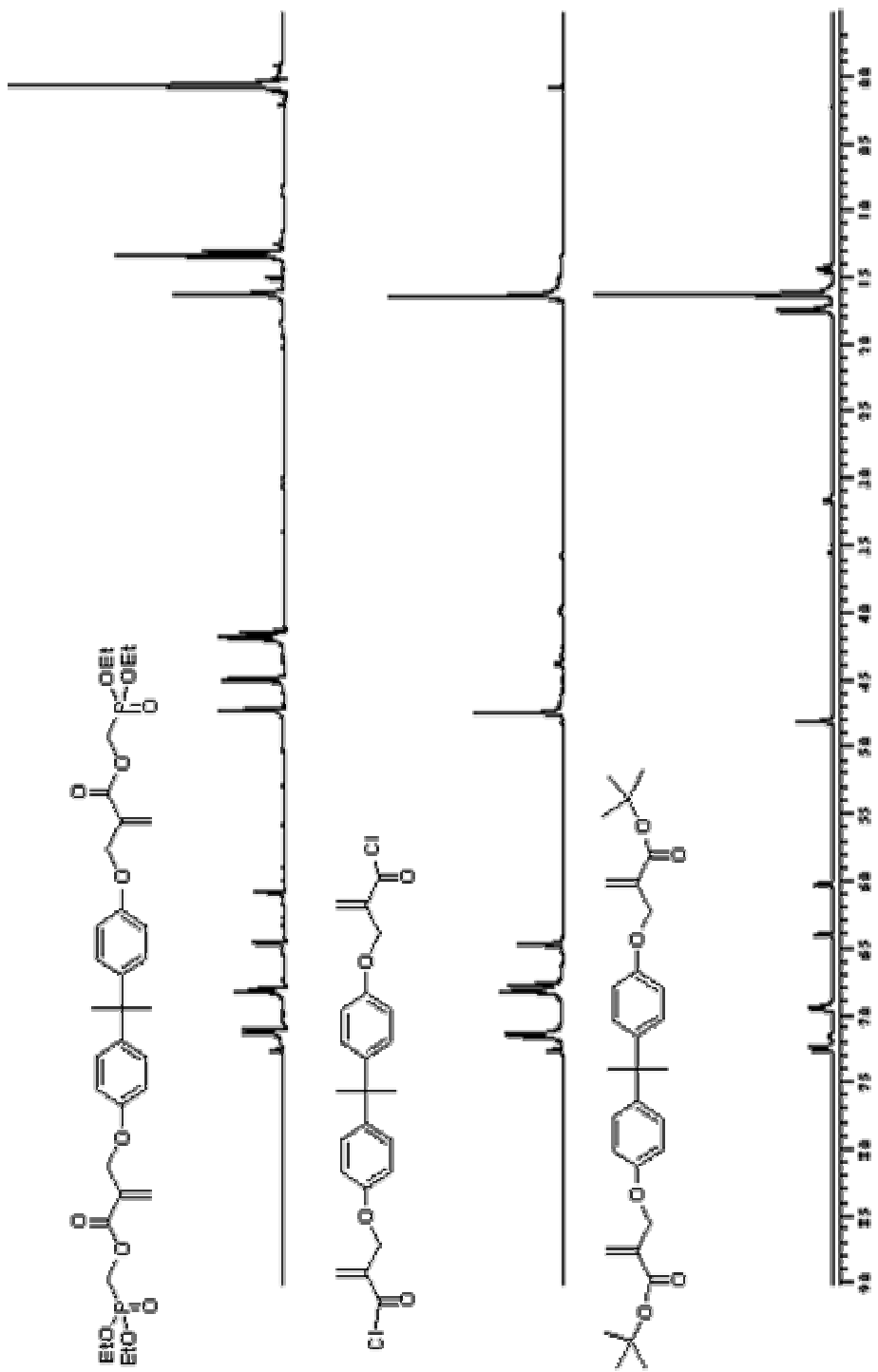


Figure 4.10. ^{1}H NMR spectra of monomer A, B and 1

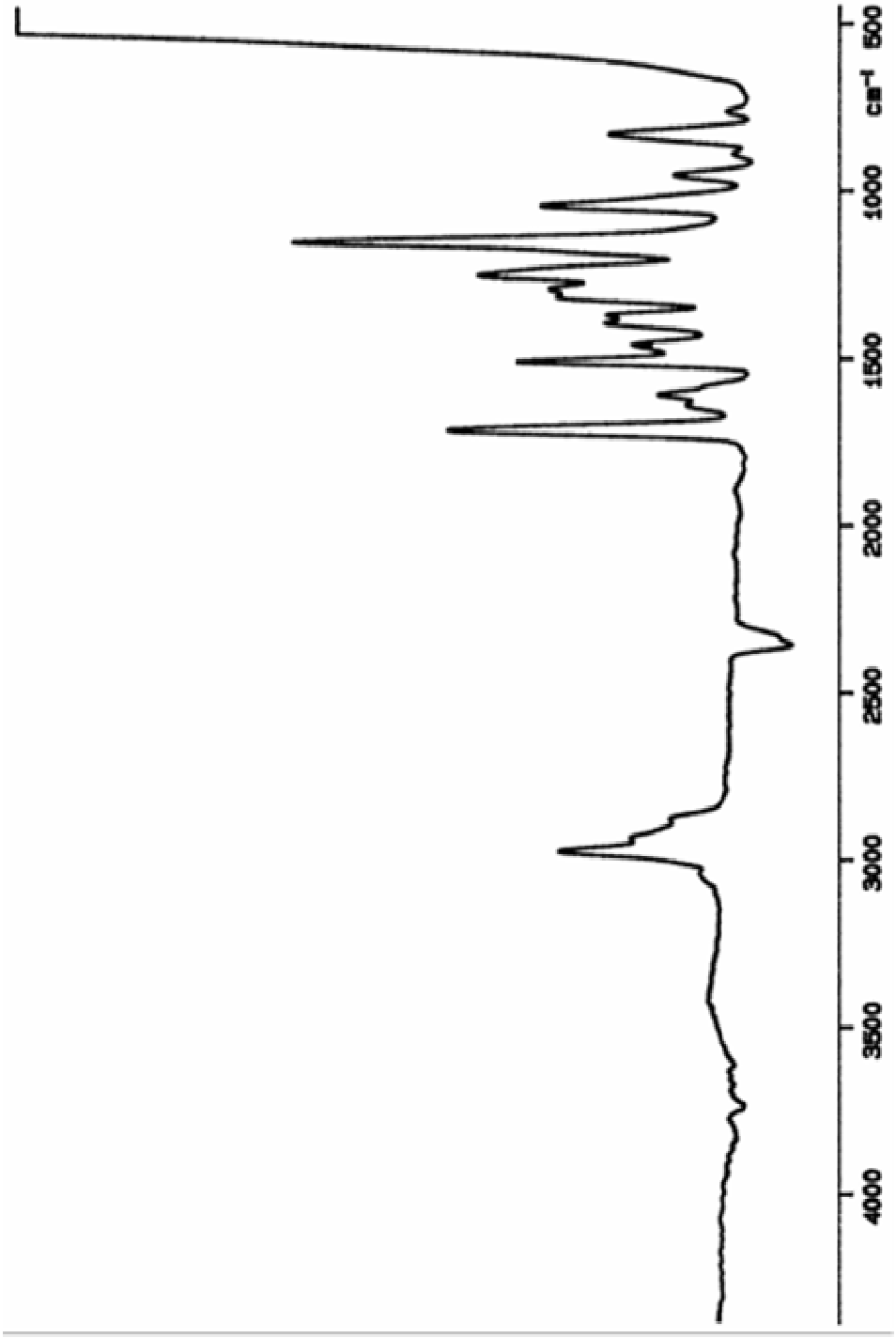


Figure 4.11. IR Spectrum of monomer A

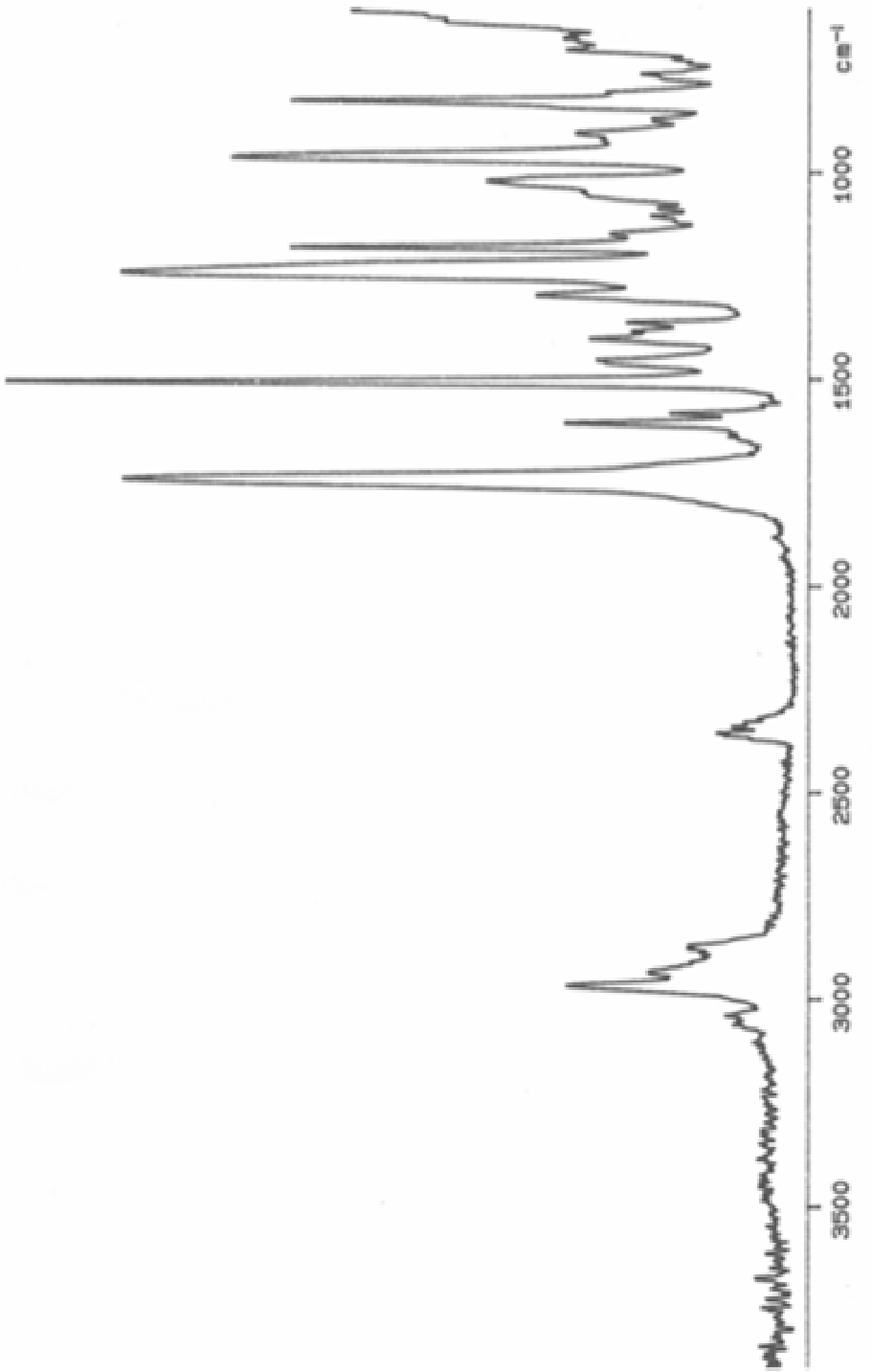


Figure 4.12. IR Spectrum of monomer B

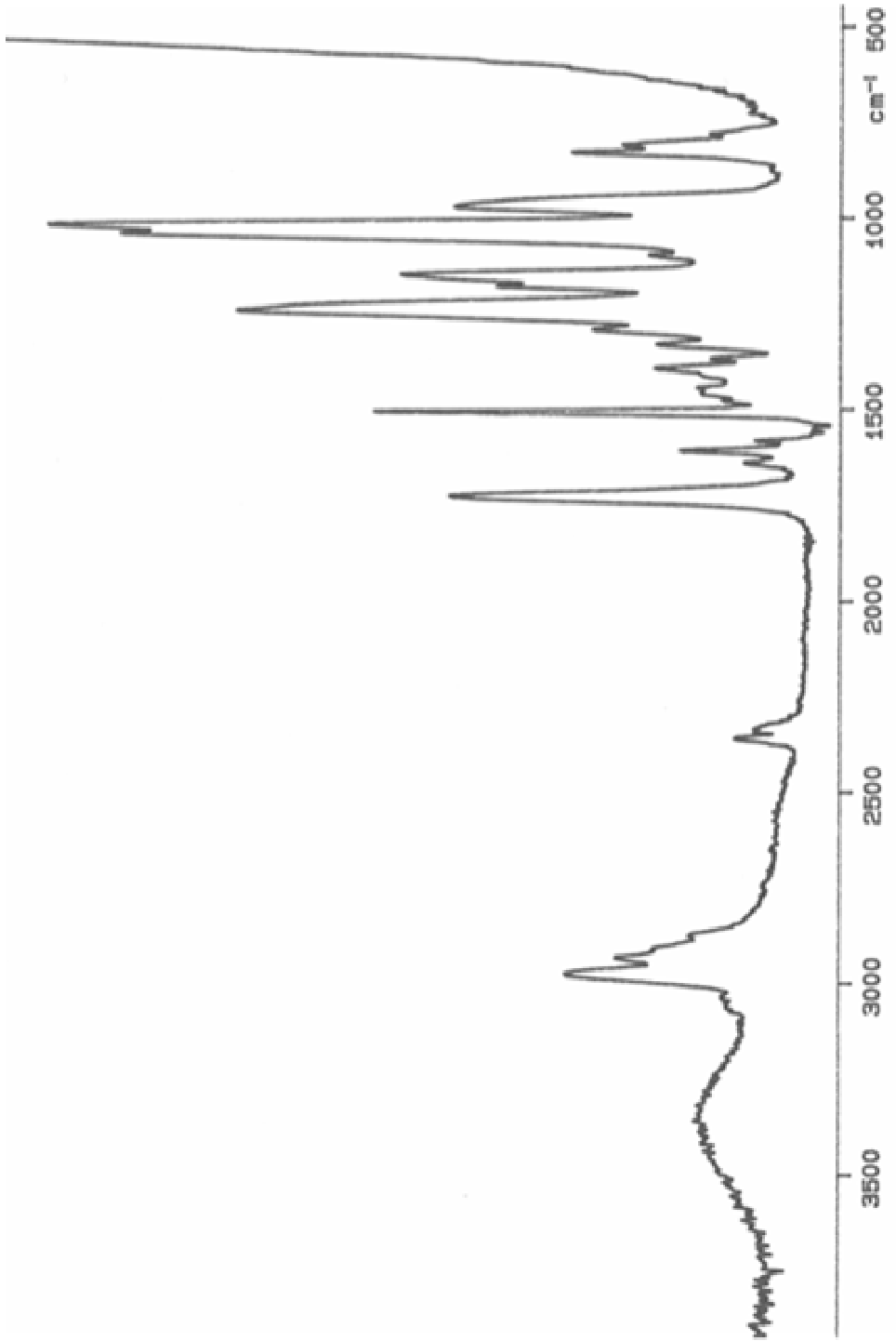


Figure 4.13. IR Spectrum of monomer 1

At the last step, monomer **1** was hydrolyzed selectively under mild conditions. The silylation of monomer **1** with TMSBr in dry CH_2Cl_2 followed by methanolysis of the silyl ester gave monomer **2** (Figure 4.14). Then, it formed a suspension with small amount of water and converted into its salt by using Na_2CO_3 so that it became soluble in water and the solution was washed with CH_2Cl_2. pH of the aqueous solution was set to 1 with concentrated HCl. Extraction of aqueous phase with CH_2Cl_2 gave pure product as a yellow viscous liquid in 42 per cent yield.

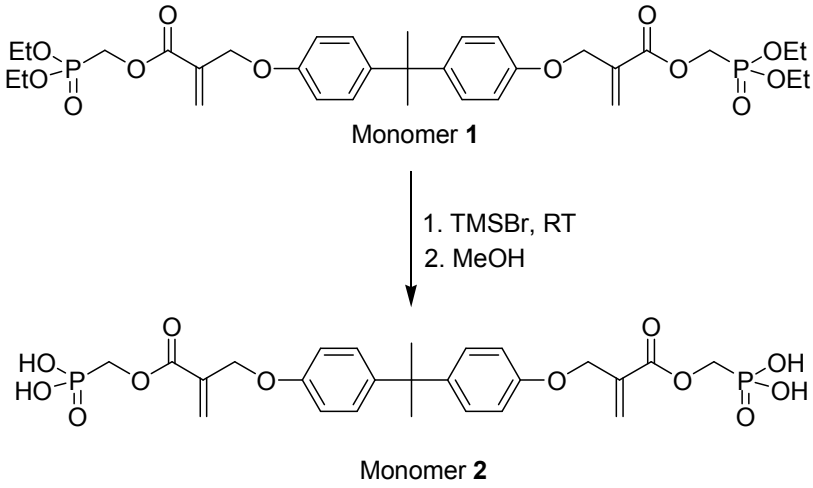


Figure 4.14. Synthesis of monomer **2**

The ^{13}C-NMR (Figure 4.15) spectrum of this monomer showed the disappearance of the ethyl ester peaks of monomer **1**, confirming the complete reaction.

The FT-IR spectrum of monomer **2** (Figure 4.16) showed a broad peak between 3500-2000 cm^{-1} due to the phosphonic acid group. The spectrum also showed C-H peak at 2963 cm^{-1}, carbonyl peak at 1712 cm^{-1}, C=C peak at 1610 cm^{-1} and P=O peak at 1232 cm^{-1}.

This acidic monomer is soluble in water, which is a very important property for self-etching adhesive monomers. It may enable to etch enamel and dentin. However, the phosphonic acid groups of this monomer are attached to the double bond through an ester linkage. Therefore this monomer will not be hydrolytically stable in aqueous solution.

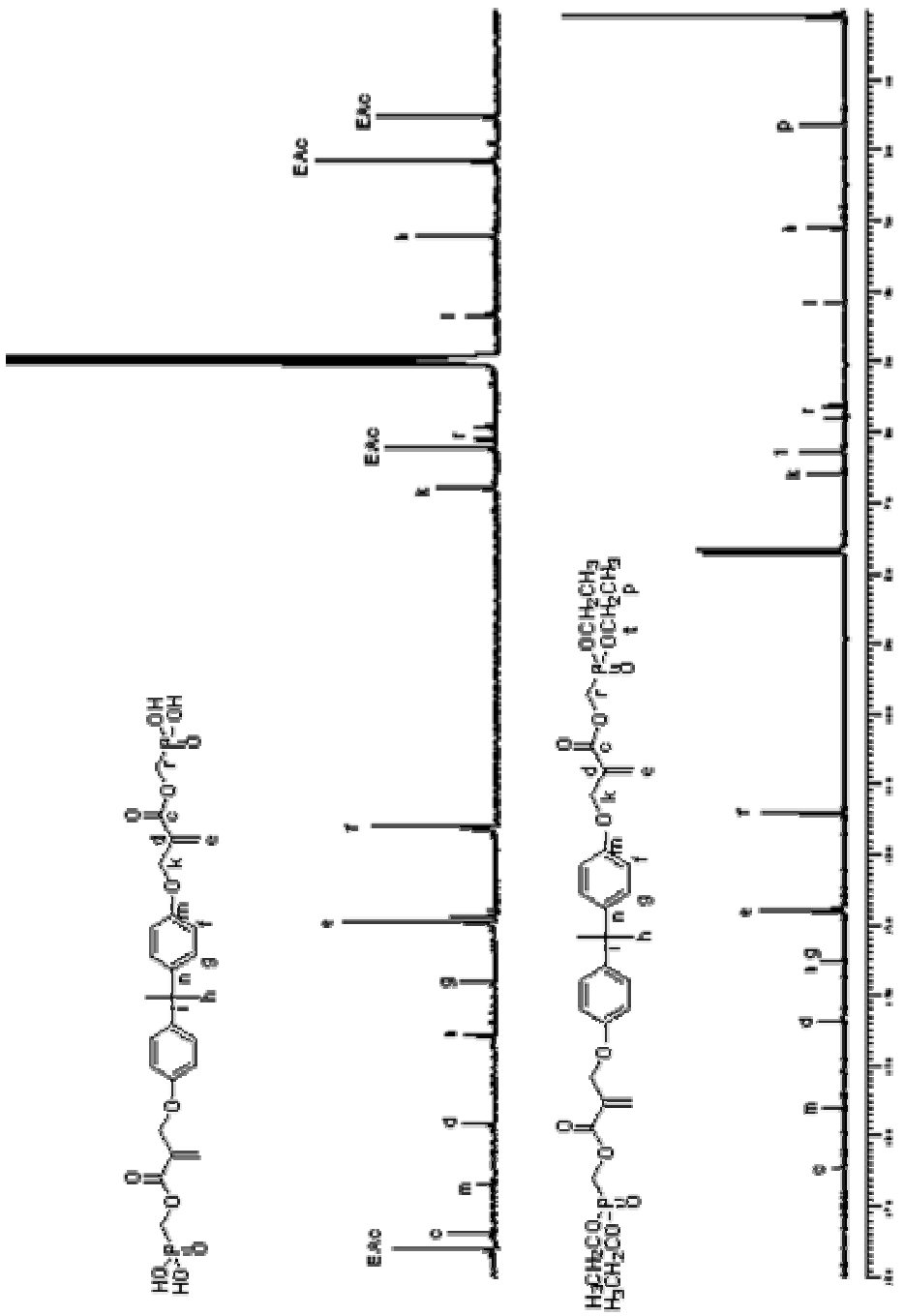


Figure 4.15. ^{13}C NMR spectra of monomer **1** and **2**

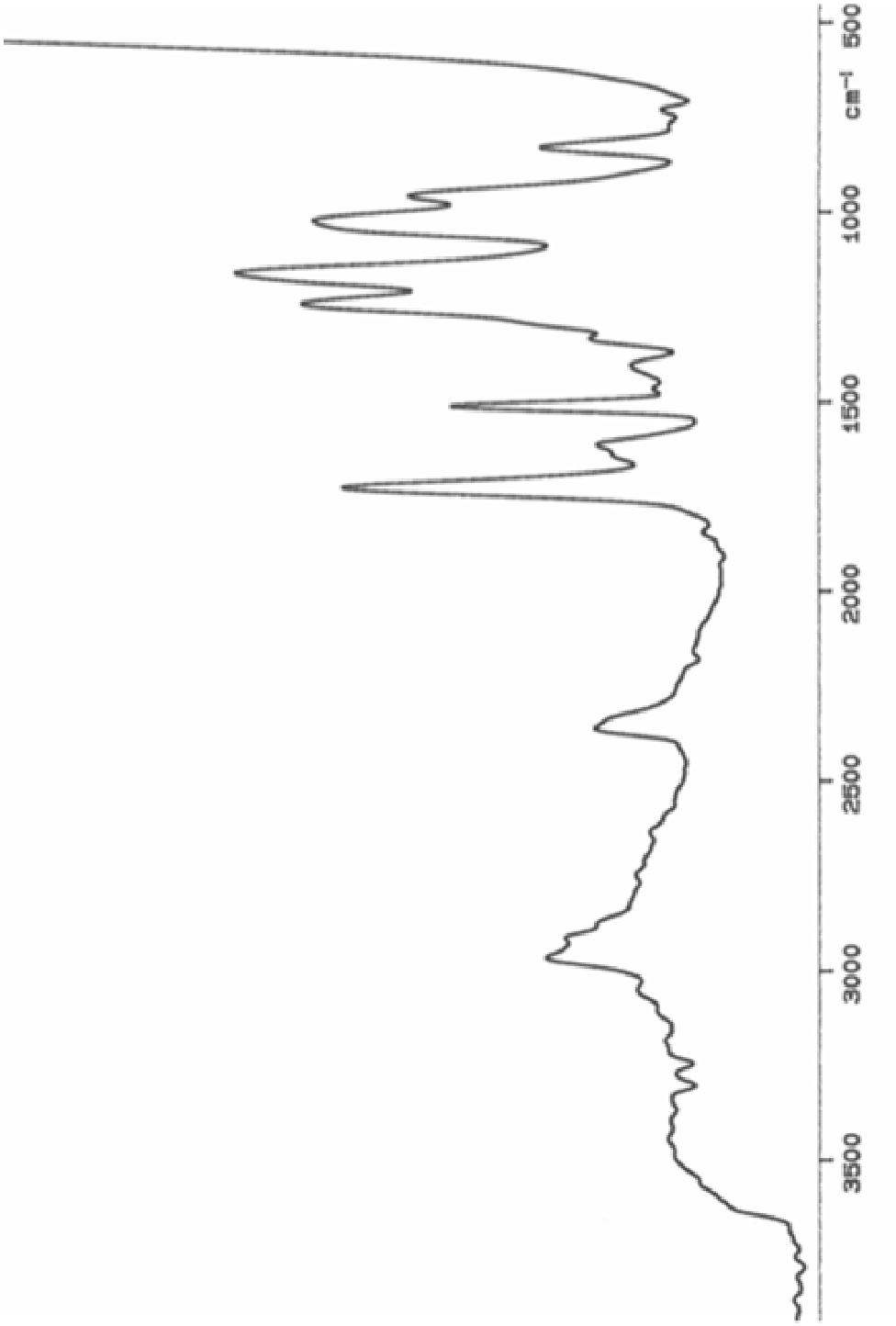


Figure 4.16. IR Spectrum of monomer **2**

4.3. Synthesis of Phosphonic Acid Monomers from o-Hydroxyaryl Phosphonates

The second method for the synthesis of novel crosslinkers with carboxylic and phosphonic acid functions for use in dental materials is based on the reaction of TBBr and o-hydroxyaryl phosphonates.

4.3.1. Synthesis of Monomers 3, 4 and 5 from Bisphenol A

A novel phosphonic acid monomer was prepared by the base catalyzed rearrangement of diethyl phosphate derivative of Bisphenol A. Synthesis of monomer involved four steps (Figure 4.17).

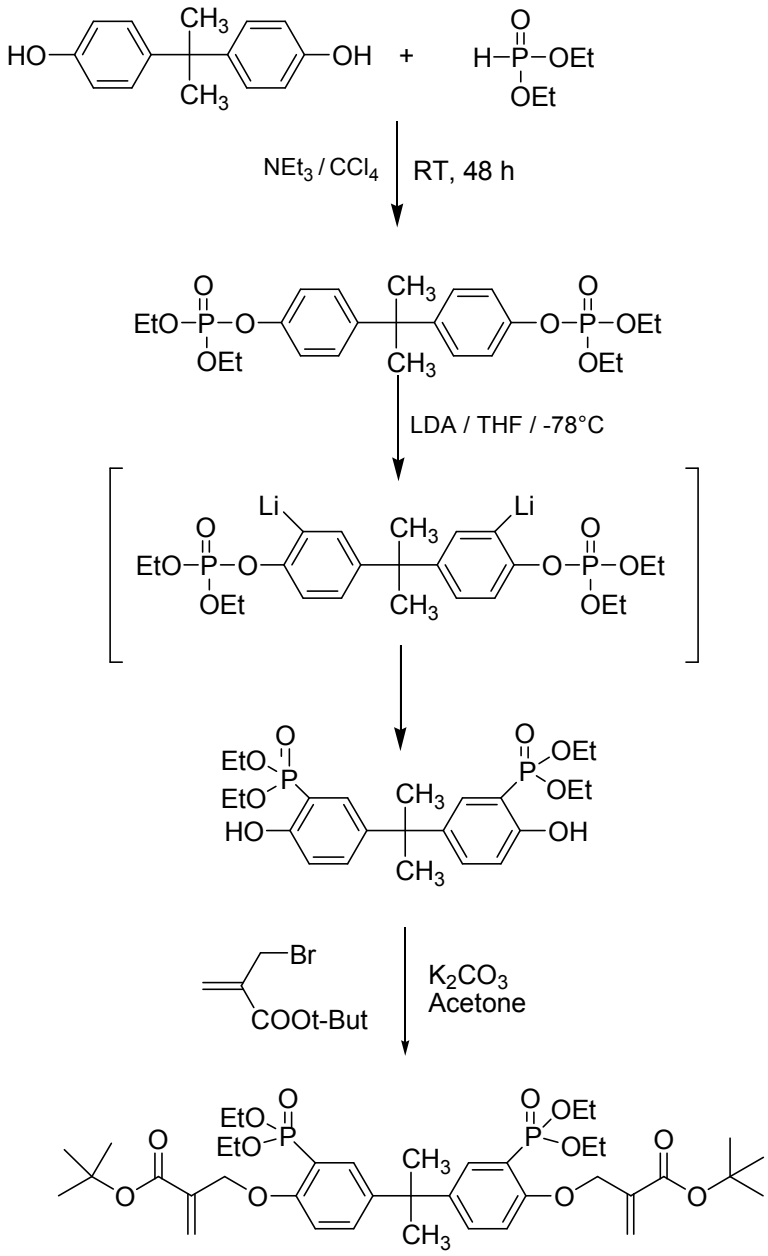


Figure 4.17. Synthesis of monomer **3**

At the first step, phosphate ester of Bisphenol A was obtained by the reaction of Bisphenol A with diethylphosphite in presence of triethylamine. The product was obtained as a yellow viscous liquid in 36 % yield.

The ^{13}C-NMR spectrum of the product (Figure 4.18) showed ethyl peaks of phosphate at 15.5 ppm and 63.9 ppm, methyl and quaternary carbon peaks of Bisphenol A group at 30.2 and 41.6 ppm and aromatic carbons at 118.8, 127.4, 146.4, and 148.1 ppm.

It is important to dry well the formed viscous product for the next step.

Treatment of the phosphate with butyllithiumdiisopropylamide at –78 ºC resulted in the rearrangement to the aryl phosphate ester (Figure 4.17). The rearrangement involves the lithiation of phosphate esters followed by collapse of the lithiated species with the migration of phosphorus from O → C. The use of well-dried THF is crucial for this reaction.

The ^{13}C-NMR spectrum (Figure 4.18) of the phosphonate showed a doublet at 106.9 and 109.4 ppm due to aromatic carbon attached to phosphorus. The carbon attached to the OH appeared at 160.1 ppm.

The FT-IR spectrum of the phosphonate (Figure 4.19) showed O-H, C-H, C=C, P=O and P-OEt absorbtions at 3734, 2971, 1605, 1169 and 1023 cm^{-1}.

At the third step, TBBr was reacted with the phosphonate compound in the presence of K_2CO_3 as catalyst in acetone. After 2 days of reflux, the product was obtained as a red paste. Purification by column chromatography using ethylacetate-methanol (100:4) eluent gave the pure product (monomer **3**) as light yellowed colored viscous liquid in 65 per cent yield (Figure 4.17).

This monomer was soluble in acetone, dichloromethane, methanol, THF, but it was insoluble in hexane and petroleum ether. It was partially soluble in ether.

The ^{13}C-NMR spectrum of monomer **3** (Figure 4.18) is characterized by t-butyl carbons at 28.0 and 81.3 ppm, methyl carbons of Bisphenol A at 30.7 ppm, a quaternary carbon at 41.8 ppm, ethyl ester peaks at 16.2 and 61.9 ppm, methylene carbons adjacent to double bond at 66.2 ppm, double bond carbons at 125.3 and 142.4 ppm, aromatic carbons at 111.8, 114.5, 133.1, 136.5, 157.9 and carbonyl carbon at 164.5 ppm.

The FT-IR spectrum of this monomer (Figure 4.20) showed the C-H, C=O, C=C, P=O, C-O and P-OEt peaks at 2970, 1715, 1646, 1261, 1146 and 1030 cm^{-1}.

Monomer **3** due to its rigid structure and two double bonds will give crosslinked polymers with good mechanical and thermal properties. The incorporation of two methacrylate functionality makes it capable of radical polymerization. Furthermore, the phosphonate groups (on the aromatic rings) are connected to the double bonds through hydrolytically stable ether links. In water this monomer may tend to undergo further hydrolysis due to the remaining –COOt-butyl and –POOEt groups. But this will not reduce the adhesive properties. This monomer has two sides to be hydrolyzed, carboxylate and phosphonate groups.

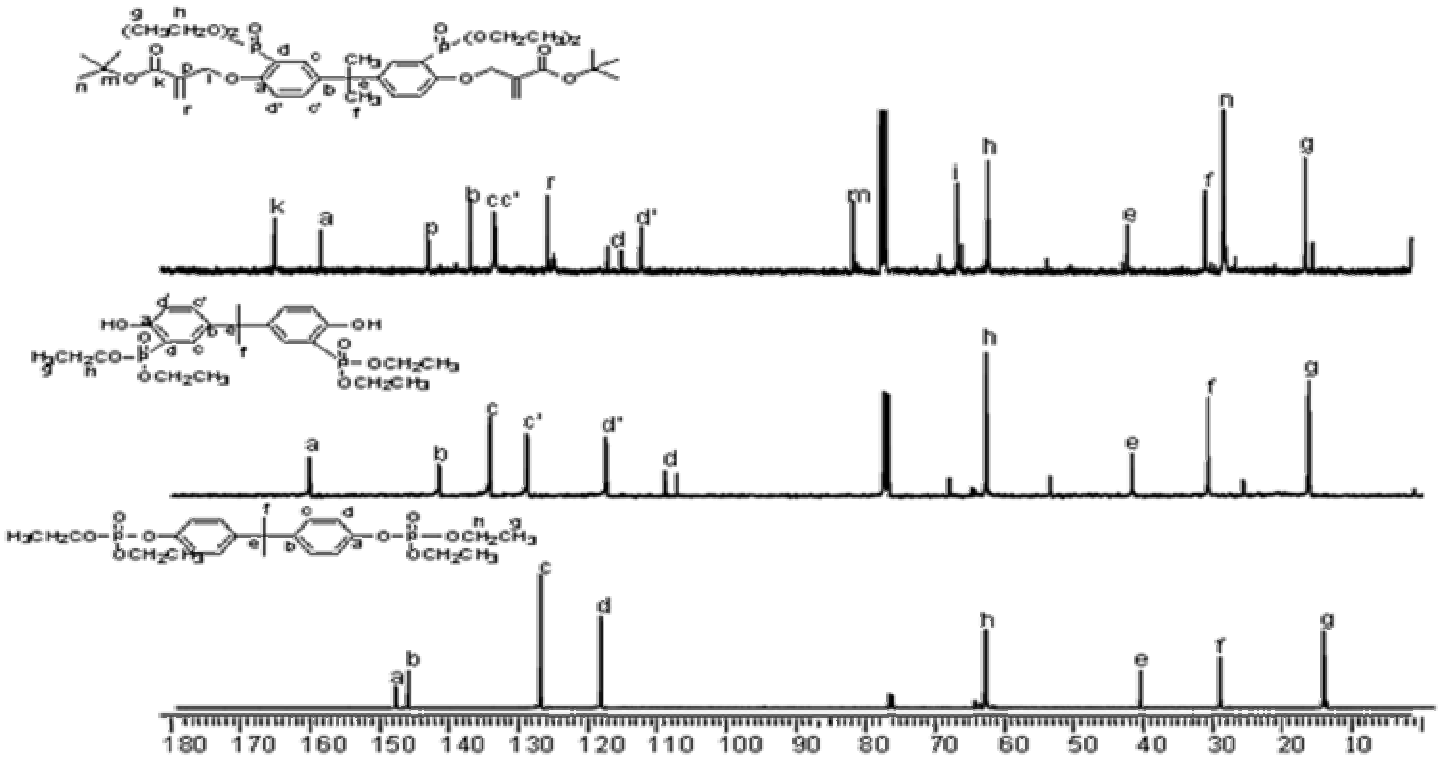


Figure 4.18. ^{13}C NMR spectra of phosphated Bisphenol A, phosphonated Bisphenol A and monomer **3**

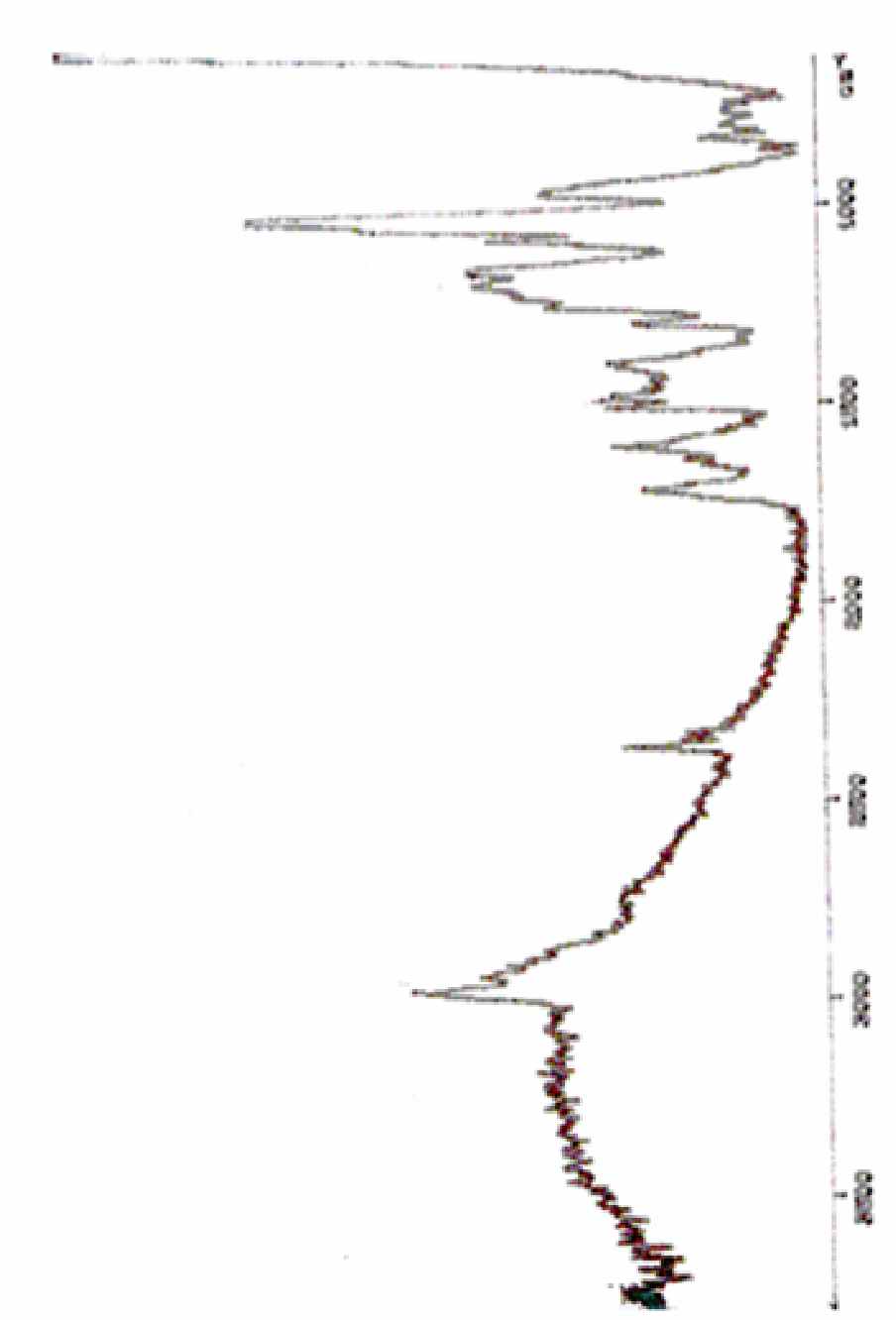


Figure 4.19. IR Spectrum of phosphonated Bisphenol A

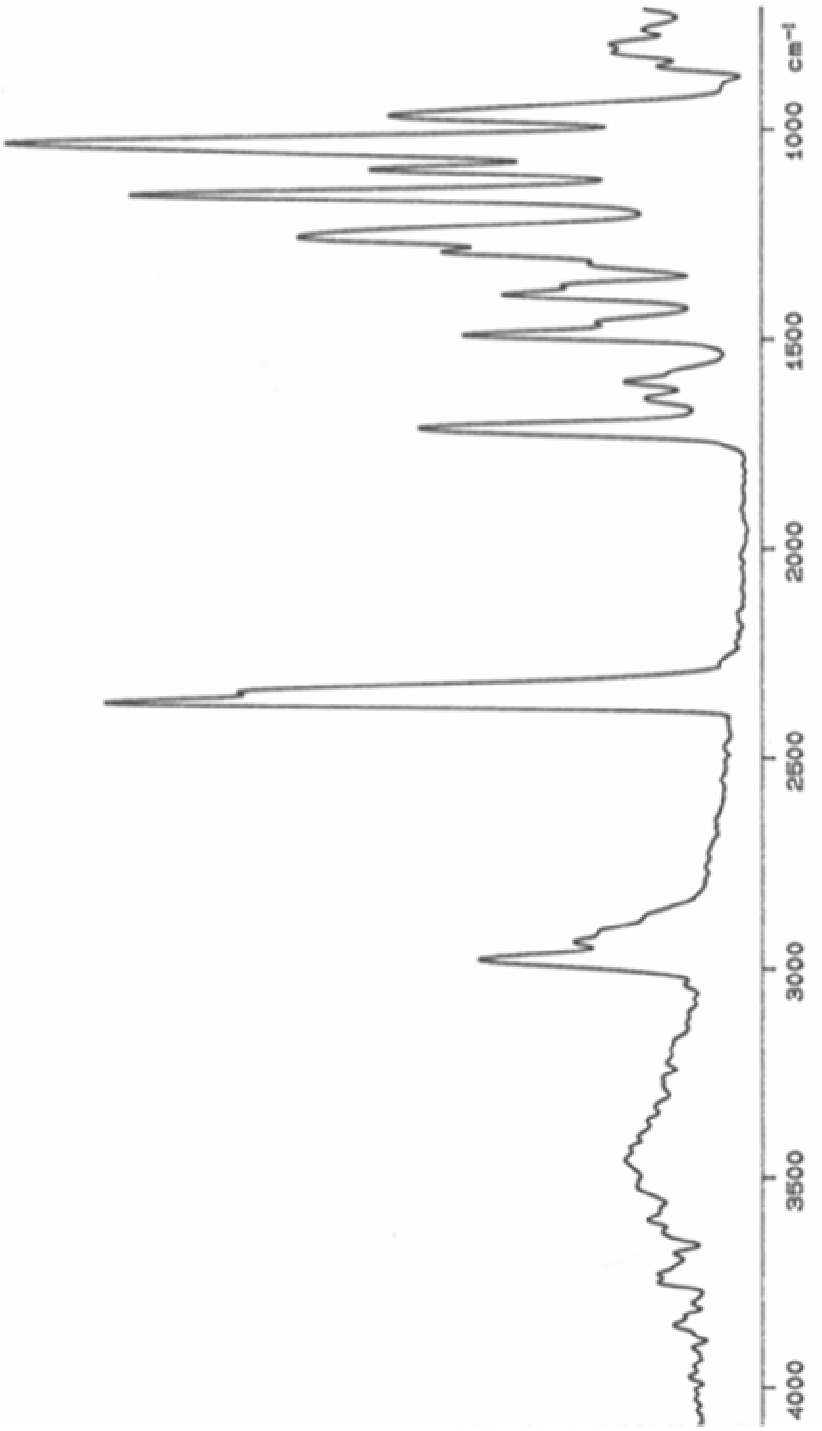
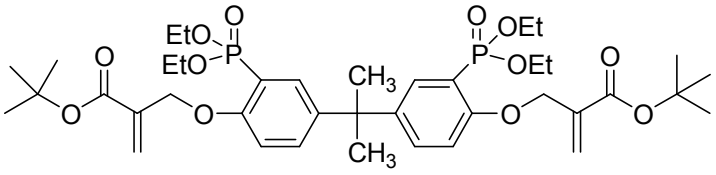
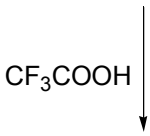


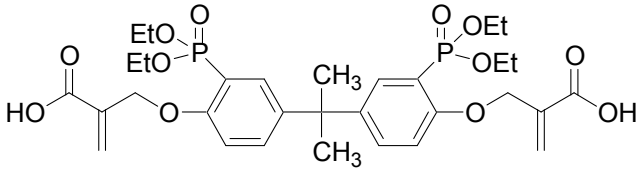
Figure 4.20. IR Spectrum of monomer **3**

T-butyl ester groups of monomer **3** was hydrolyzed with CF_3COOH (Figure 4.21). After recrystallization from acetone, the dicarboxylic acid monomer **4** was obtained in 32 per cent yield as a white solid.



Monomer **3**





Monomer **4**

Figure 4.21. Synthesis of monomer **4**

Monomer **4** was soluble in polar solvents like methanol, water, acetone, THF and methylene chloride but insoluble in ether, hexane, and petroleum ether. Solubility in water is very important for dental applications. This monomer is able to react with other monomers in dental formulations by radical polymerization. Also, it may react with the ions leached from the glass (Ca^{+2}, Al^{+3}) used in glass ionomer cements. This monomer is enable to make hydrogen bonding with the amino and hydroxyl groups of the organic component of tooth which is collagen. This binding process improves stability of dental materials.

The ^{13}C-NMR (Figure 4.22) and ^{1}H-NMR spectrum of this monomer (Figure 4.23) showed the disappearance of t-butyl peaks of monomer **3**.

The FT-IR spectrum of this monomer (Figure 4.24) showed a broad peak between 3500 and 2000 cm^{-1} due to carboxylic acid group.

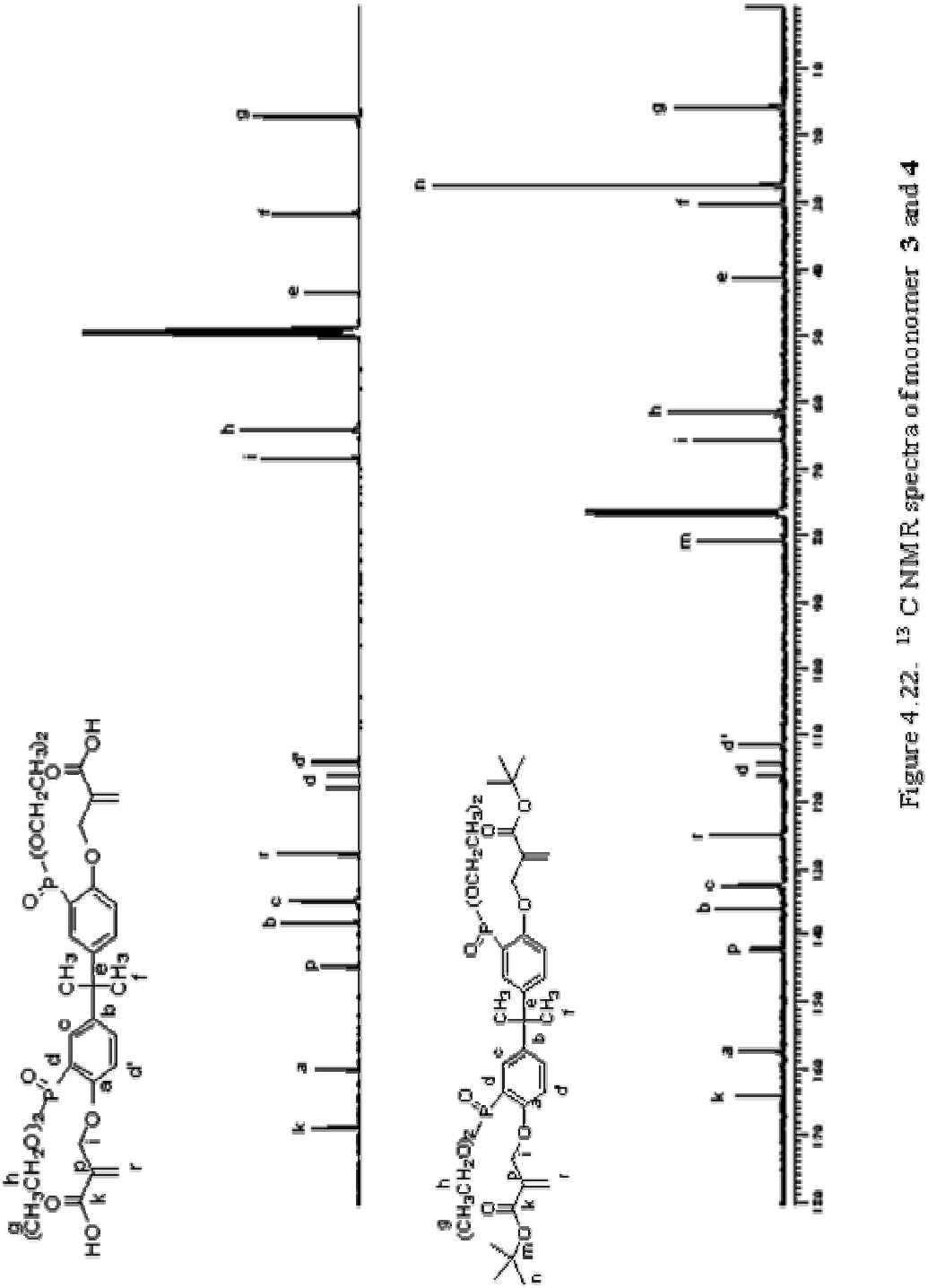


Figure 4.22. ^{13}C NMR spectra of monomer **3** and **4**

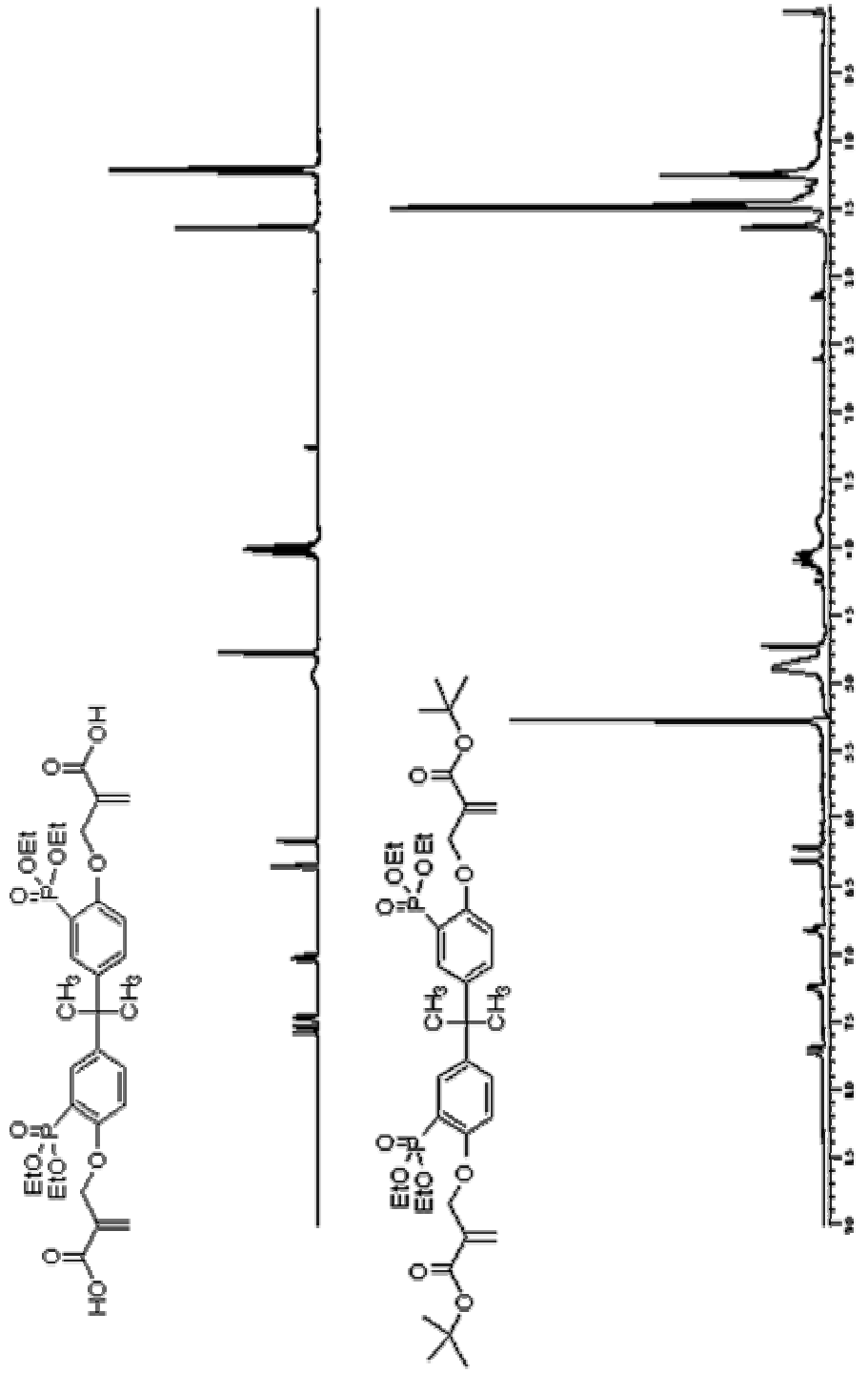


Figure 4.23. ^{1}H NMR spectra of monomer **3** and **4**

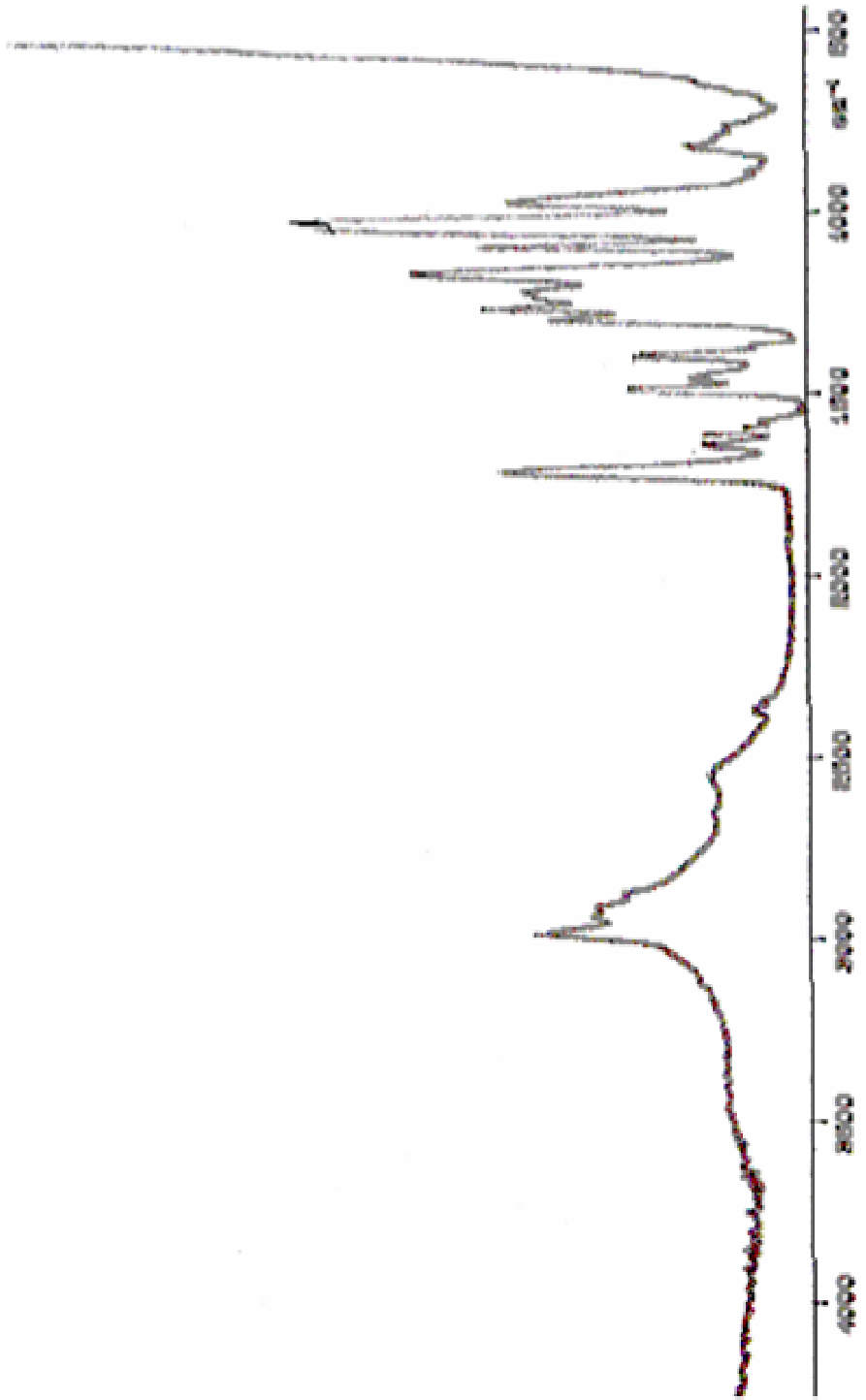


Figure 4.24. IR Spectrum of monomer 4

Phosphonate groups of monomer **3** were also hydrolyzed. The silylation of monomer **3** by TMSBr in dry CH_2Cl_2 followed by methanolysis of the silyl ester gave monomer **5** (Figure 4.25). During this process t-butyl groups are also hydrolyzed.

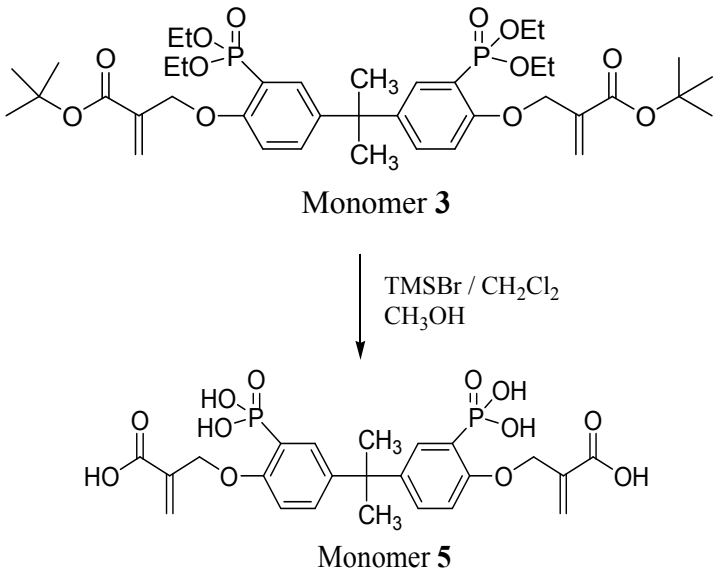


Figure 4.25. Synthesis of monomer **5**

This monomer was soluble in acetone, methylene chloride, water, THF and methanol, whereas it was insoluble in hexane, ether and petroleum ether.

The ^{13}C-NMR spectrum of monomer **5** showed the disappearance of t-butyl and ethyl peaks of monomer **3**.

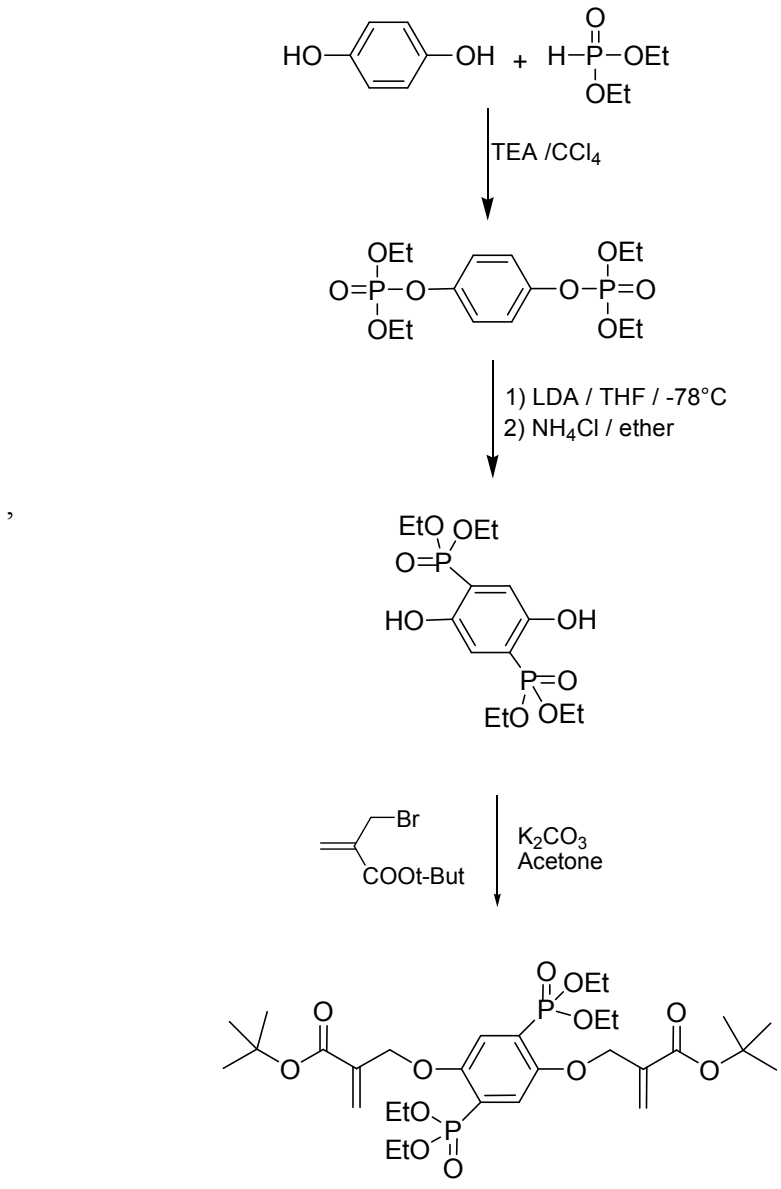
Purification of this monomer was not successful so it was not studied in photopolymerization.

This crosslinker contains dimethacrylic acid double bonds so it can polymerize radically. It will give a crosslinked polymer with good mechanical and thermal properties because of rigid Bisphenol A group. The phosphonic acids incorporated in the aromatic rings increase the hydrolytic stability; also they are attached to the double bond through an ether linkage which makes them more stable. Moreover, incorporation of phosphonic acid function into monomer structures would result in increased biocompatibility and adhesion

to tooth due to chelation with Ca^{+2} ions in the tooth surface, present carboxylic acids also support this chelation. Phosphonic acids are also able to etch the tooth surface.

4.3.2 Syhthesis of Monomers 6, 7 and 8 from Hydroquinone

A novel phosphonic acid monomer was prepared by the base catalyzed rearrangement of diethyl phosphate derivative of hydroquinone. Synthesis of monomer involved four steps (Figure 4.26).



Monomer **6**

Figure 4.26. Synthesis of monomer **6**

In the first step, hydroquinone was readily converted into its phosphate ester upon treatment with diethyl phosphate in presence of triethyl amine (Figure 4.26).

The ^{13}C-NMR spectrum (Figure 4.27) of the phosphate compound is characterized by ethyl carbons at 14.8 and 63.4 ppm and aromatic carbons at 119.9 and 146.3 ppm.

Treatment of the phosphate compound with an excess lithium diisopropyl amide resulted in rearrangement that involves the fission of an oxygen-phosphorus bond and formation of a carbon-phosphorus bond, yielding the phosphonate compound (Figure 4.26).

The ^{13}C NMR spectrum (Figure 4.27) showed a doublet at 114.5 ppm due to aromatic carbon attached to phosphorus.

The reaction of TBBr with phosphonated hydroquinone in the presence of K_2CO_3 as catalyst gave monomer **6** as a red paste. The pure product was obtained by precipitation into ether (43 per cent yield) (Figure 4.26).

The monomer **6** was soluble in methanol, dichloromethane and THF, but it is insoluble in ether and hexane.

The ^{13}C-NMR spectrum (Figure 4.27) showed t-butyl carbons at 27.7 and 81.0 ppm, ethyl carbons at 16.0 and 62.0 ppm, methylene attached to oxygen at 67.0 ppm, double bond carbons at 125.2 and 136.4 ppm, aromatic ring carbons at 118.7, 121.4 123.2 and 153.3 ppm and a carbonyl carbon at 164.1 ppm.

The ^{1}H-NMR spectrum (Figure 4.28) showed methyl and t-butyl hydrogens at 1.2 and 1.5 ppm, ethyl methylenes at 4.1 ppm, methylene hydrogens attached to oxygen at 4.7 ppm, double bond hydrogens at 6.2 and 6.3 ppm and aromatic hydrogens at 7.4-7.5 ppm.

The IR spectrum of this monomer (Figure 4.29) showed the C-H, C=O, C=C, P=O and P-OEt peaks at 2973, 1700, 1636, 1231 and 1025 cm^{-1}.

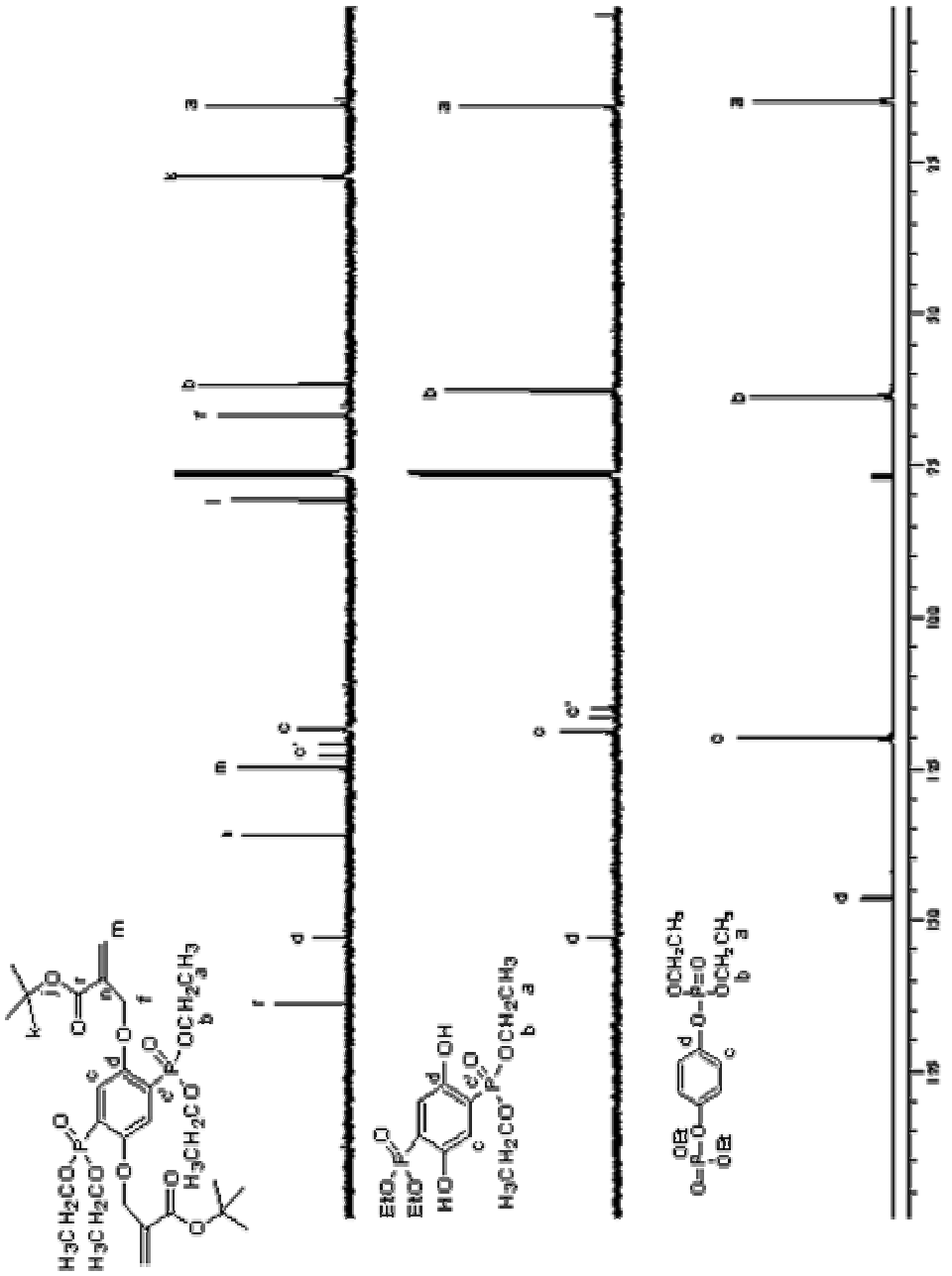


Figure 4.27. 13 C NMR spectra of phosphated hydroquinone, phosphonated hydroquinone and monomer 6

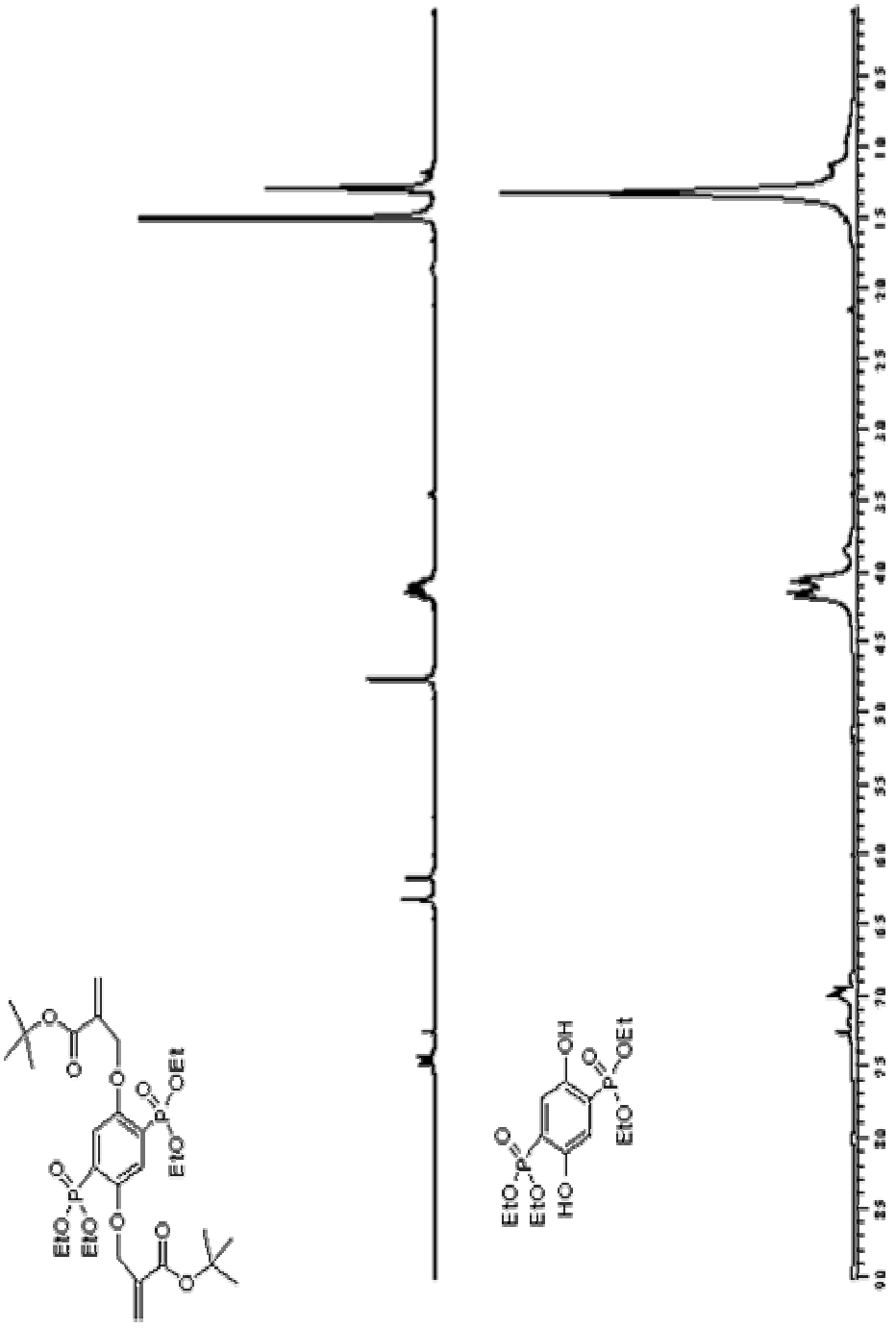


Figure 4.28. ^{1}H NMR spectra phosphonated hydroquinone and monomer **6**

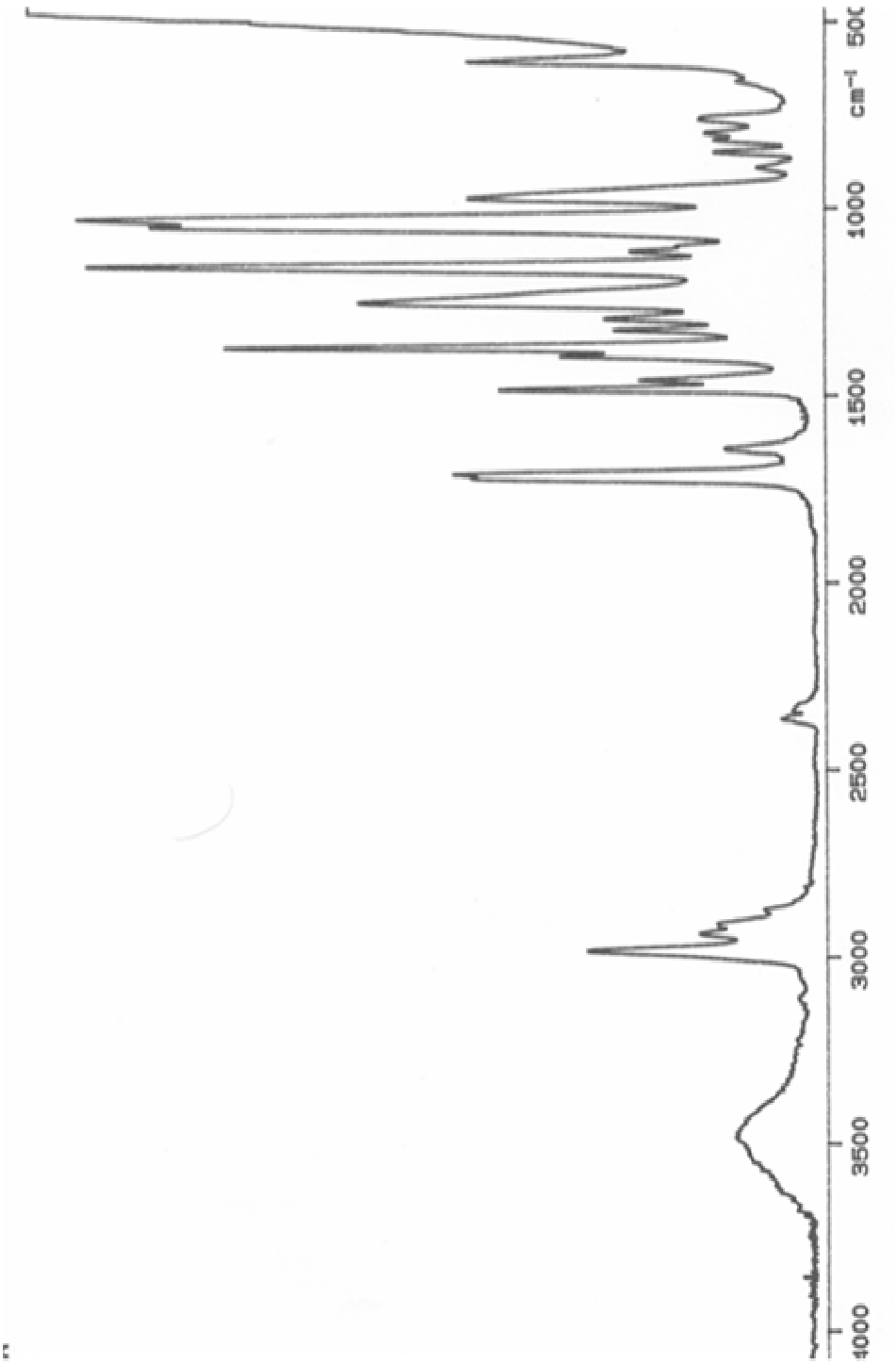
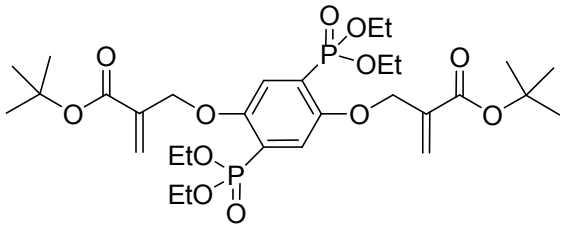
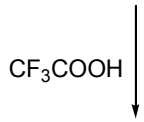


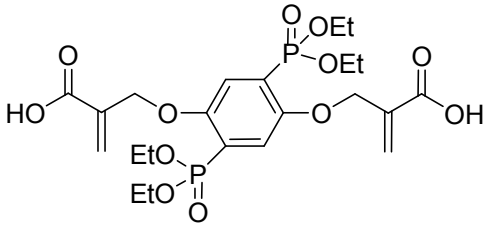
Figure 4.29. IR Spectrum of monomer **6**

This monomer (monomer **6**) has two sides to be hydrolysed namely carboxylate and phosphonate groups. Treatment of monomer **6** with CF_3COOH for 24 hour at room temperature gave monomer **7**. It was precipitated into methanol as a white solid (Figure 4.30).



Monomer **6**





Monomer **7**

Figure 4.30. Synthesis of monomer **7**

The ^{13}C-NMR spectrum (Figure 4.31) proved the hydrolysis by the absence of the t-butyl peaks at 27.7 and 81.0 ppm.

The ^{1}H-NMR spectrum (Figure 4.32) showed ethyl hydrogens at 1.2 and 4.1 ppm, methylene hydrogens attached to the oxygen at 4.8 ppm, double bond hydrogens at 6.1 and 6.3 ppm and aromatic hydrogens at 7.3 ppm.

The FT-IR spectrum of the product (Figure 4.33) showed a broad O-H peak at 3500-2500 cm^{-1} due to carboxylic acid groups.

The product has two dimethacrylic double bonds so it can act as a radically polymerizable crosslinker. The phosphonate ester increases the dental interact ion and the carboxylic acid group may form chelates with Ca^{+2} ions of tooth surface.

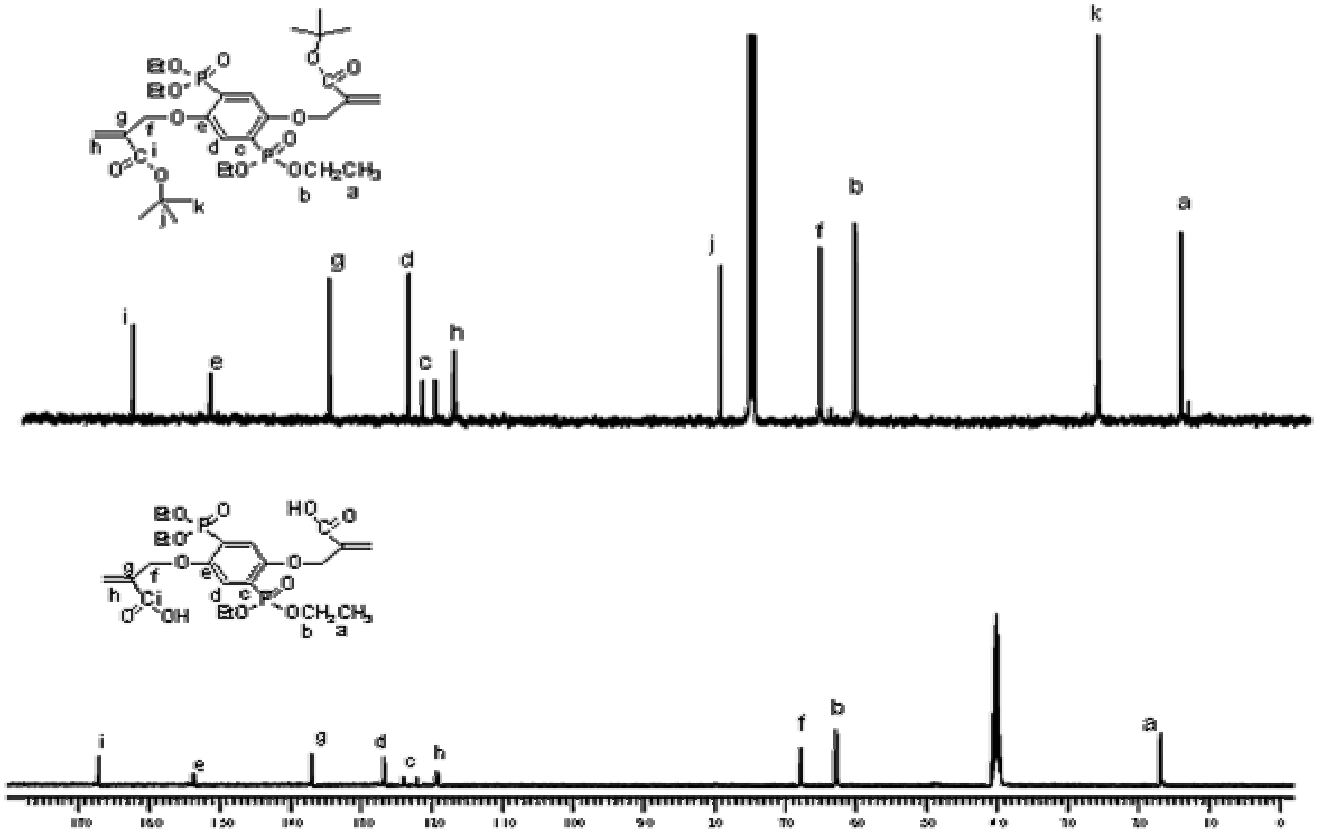


Figure 4.31. ^{13}C NMR spectra of monomer **6** and **7**

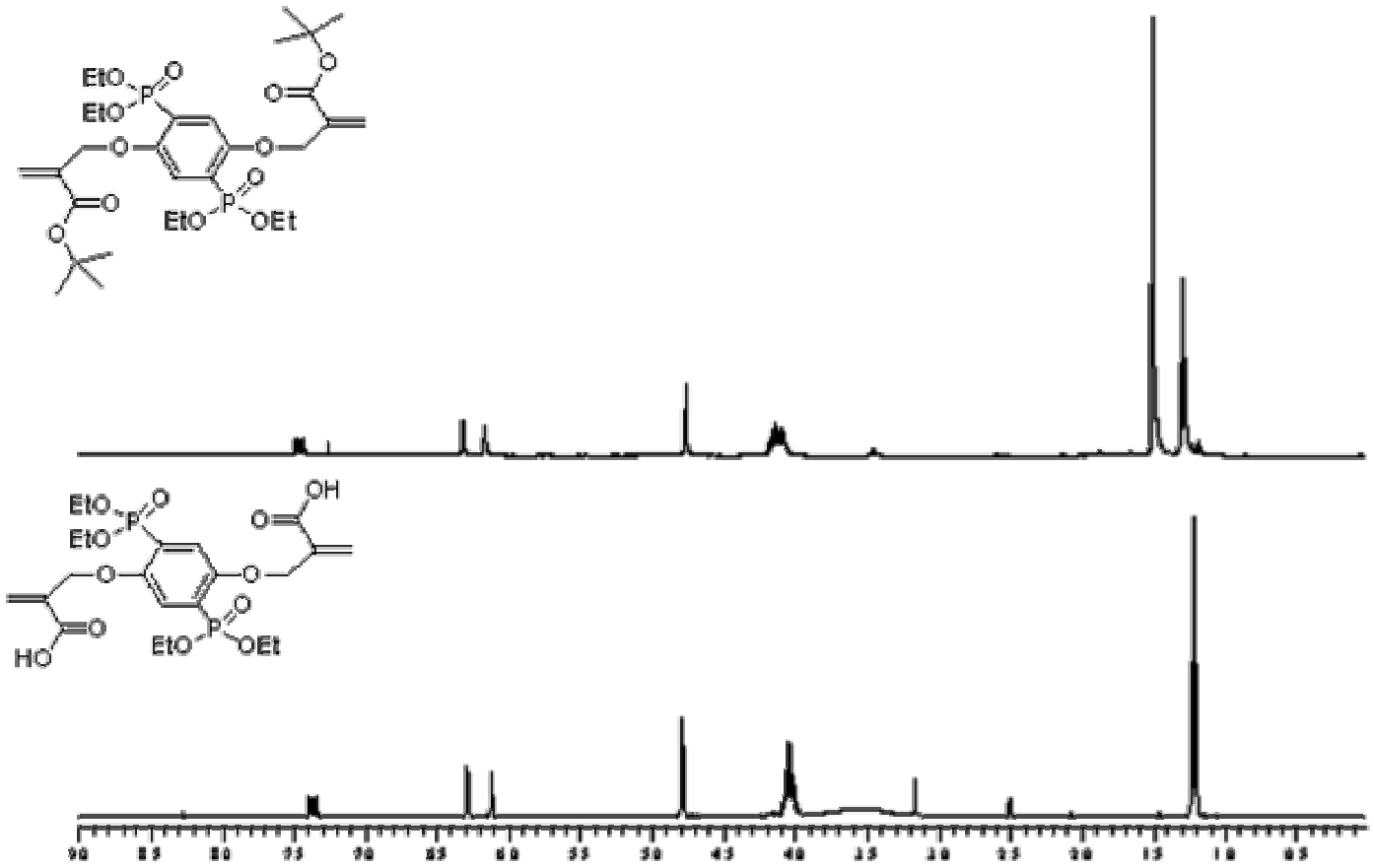


Figure 4.32. ^{1}H NMR spectra of monomer **6** and **7**

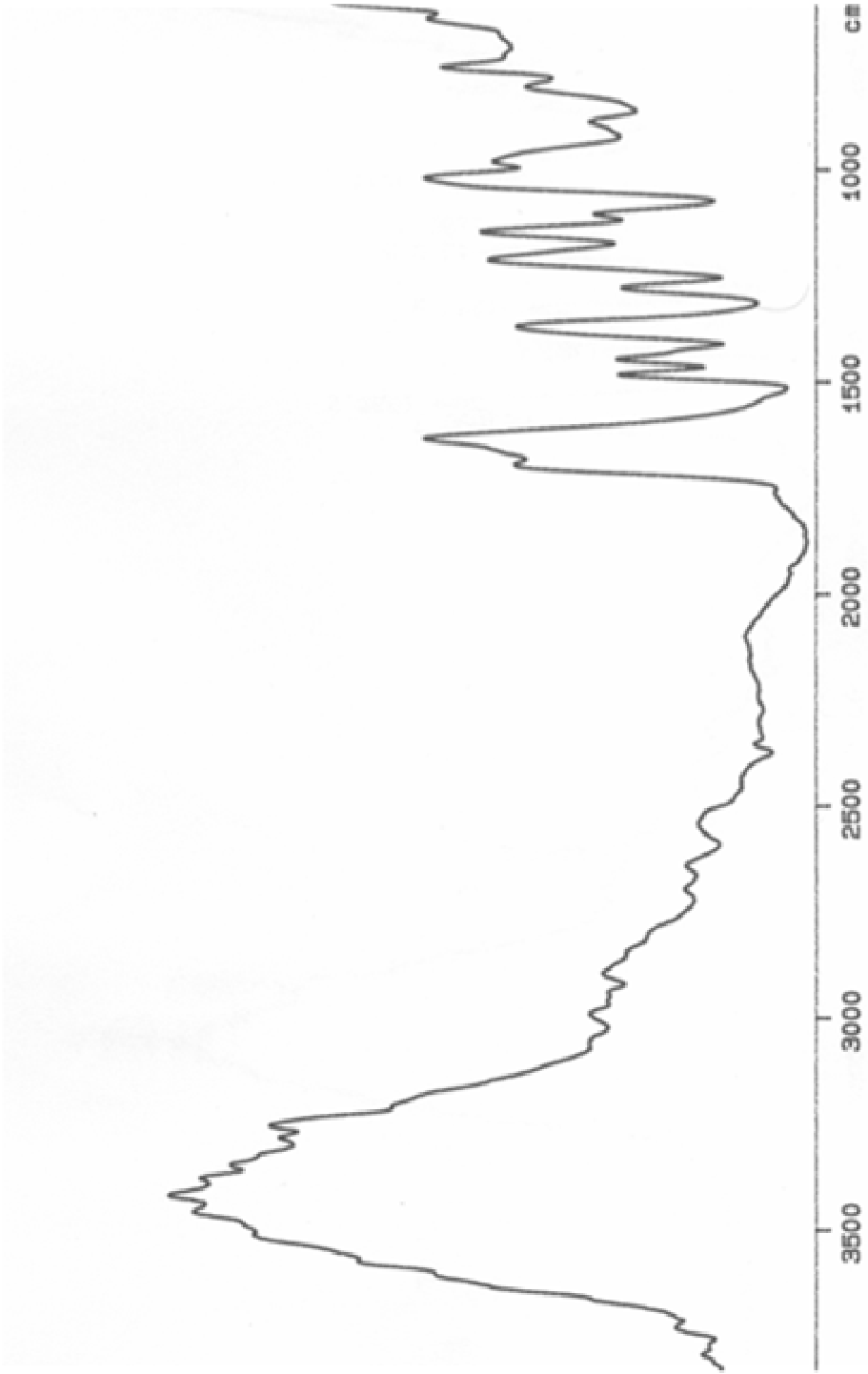
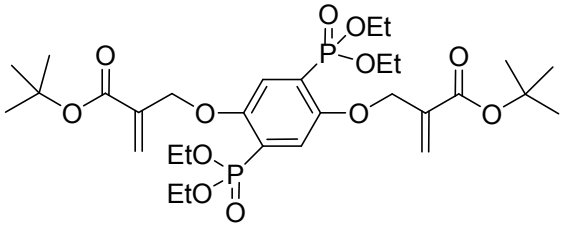
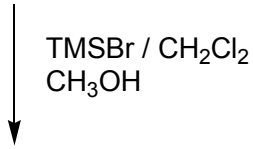


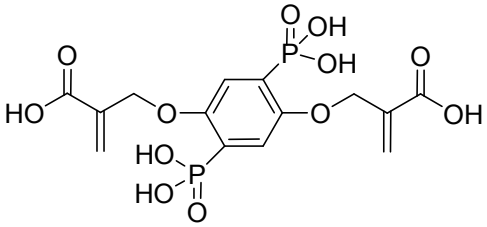
Figure 4.33. IR Spectrum of monomer 7

Monomer **6** was hydrolyzed with first silylation by TMSBr in dry CH_2Cl_2 and methanolysis of the silyl ester to the phosphonic acid (Figure 4.34). The product obtained as a white precipitate in acetone. Unexpectedly, the t-butyl groups of monomer **6** were also hydrolyzed.



Monomer **6**





Monomer **8**

Figure 4.34. Synthesis of monomer **8**

The product monomer **8** is soluble in methanol, but insoluble in dichloromethane, acetone, ether, and chloroform.

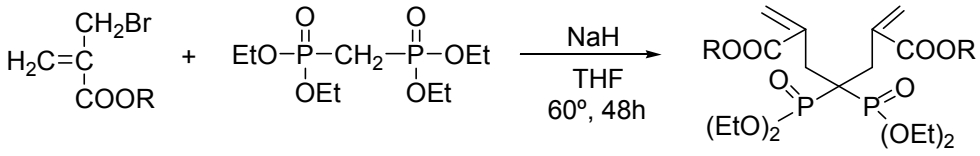
Although the disappearance of both phosphonate and carboxylate ester groups were shown, the purification of this monomer was not successful so it was not studied in photopolymerization.

The crosslinker contains dimethacrylic double bonds so it can be polymerize radically. The phosphonic acids are on the ring increases the hydrolytic stability; also they are attached to the double bond through an ether linkage which makes them more stable. Moreover, incorporation of phosphonic function into monomer structures would result in

increased biocompatibility and adhesion to tooth due to chelation with Ca^{+2} ions in the tooth surface. They are also able to etch the tooth surface.

4.4. Synthesis of A Cyclopolymerizable 4,4-Disubstituted Dimer

In this part, a cyclopolymerizable 1,6 heptadiene monomer (monomer **9**) with two phosphonate groups at 4,4′-position was synthesized. This monomer was prepared from the reaction of TBBr and tetraethyl methylenediphosphonate in presence of sodium hydride in THF (Figure 4.35). The pure product was obtained as colorless liquid after the column chromatography in 60 per cent yield [73].



R: T-Butyl

Figure 4.35. Synthesis of monomer **9**

The ^{13}C-NMR spectrum of the monomer (Figure 4.36) showed t-butyl carbons at 27.0 and 79.2 ppm, methylene carbon at 31.0 ppm, ethyl carbons of phosphonate group at 15.3 and 61.6 ppm, double bond carbons at 127.4 and 136.8 ppm, and carbonyl carbon peak at 165.8 ppm. The carbon attached to phosphorus gives a triplet at 45.6, 46.9, 48.2 ppm.

The ^{1}H-NMR spectrum of the monomer (Figure 4.37) showed tert-butyl hydrogens at 1.4 ppm, phosphonate hydrogens at 1.2 and 4.1 ppm, methylene protons at 2.9 ppm, and double bond protons at 5.8 and 6.1 ppm.

The FTIR of this monomer (Figure 4.38) showed C-H, C=O, C=C, P-O-Et vibrations at 2978, 1715, 1627, 1246 and1028 cm^{-1}.

Since this monomer **9** has a 1,6-heptadiene structure it will form five and six membered rings as repeat unit during polymerization

The initiator attacks to the double bond, to give a radical which undergoes intramolecular reaction resulting a polymer with a 6-membered ring at the backbone (Figure 4.39).

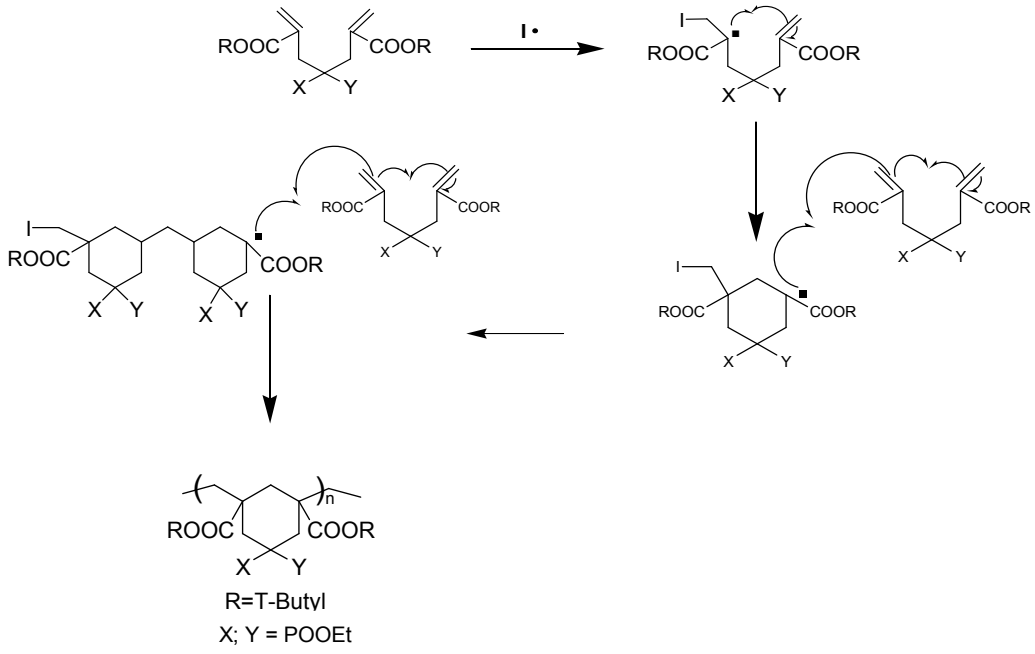


Figure 4.39. The mechanism of cyclopolymerization

The advantageous property of this monomer is capability of improving thermal and mechanical properties of the ultimate material; due to the rigidity of the 6 membered rings at the polymer back bone.

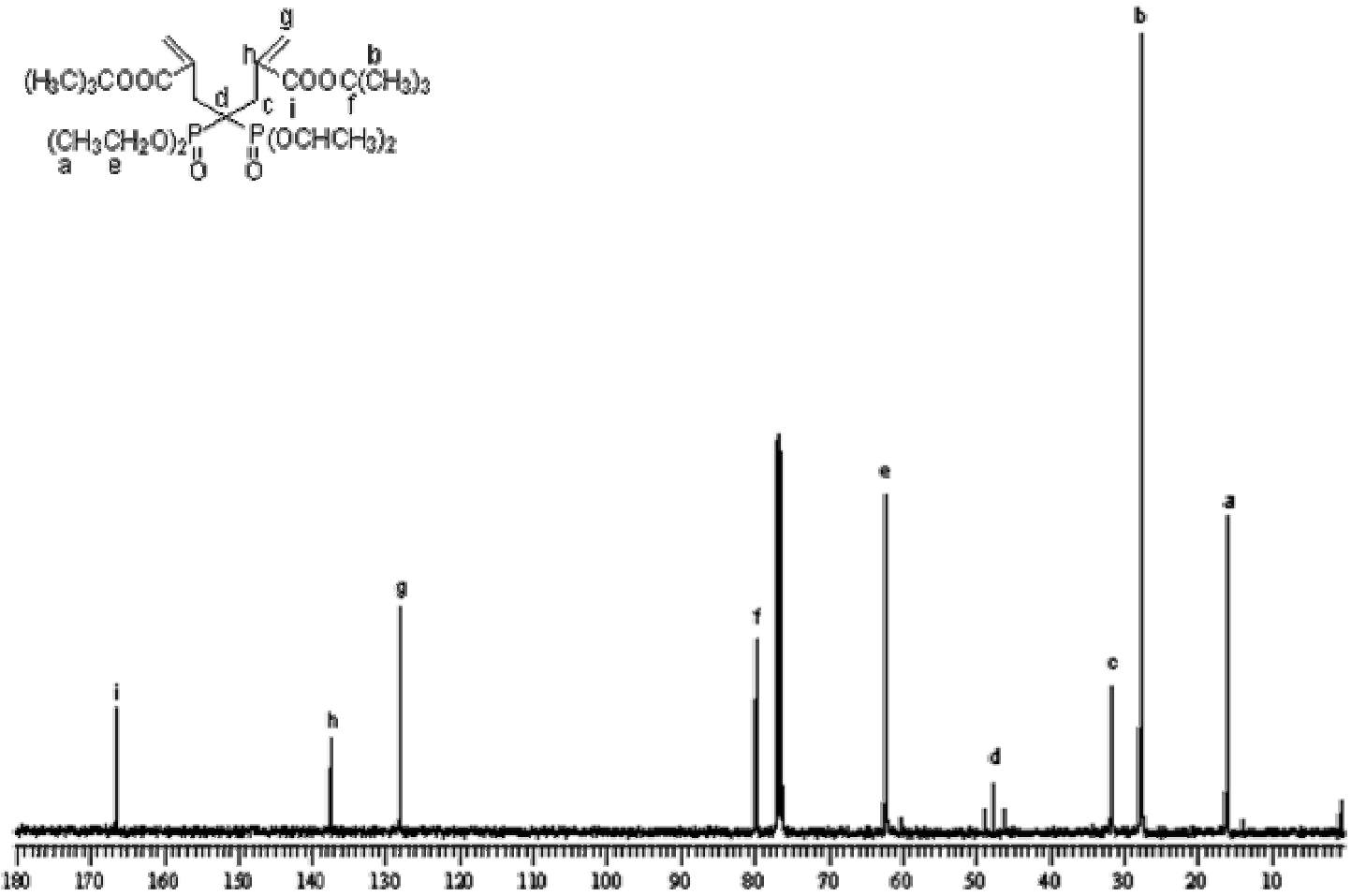


Figure 4.36. ^{13}C NMR spectrum of monomer 9

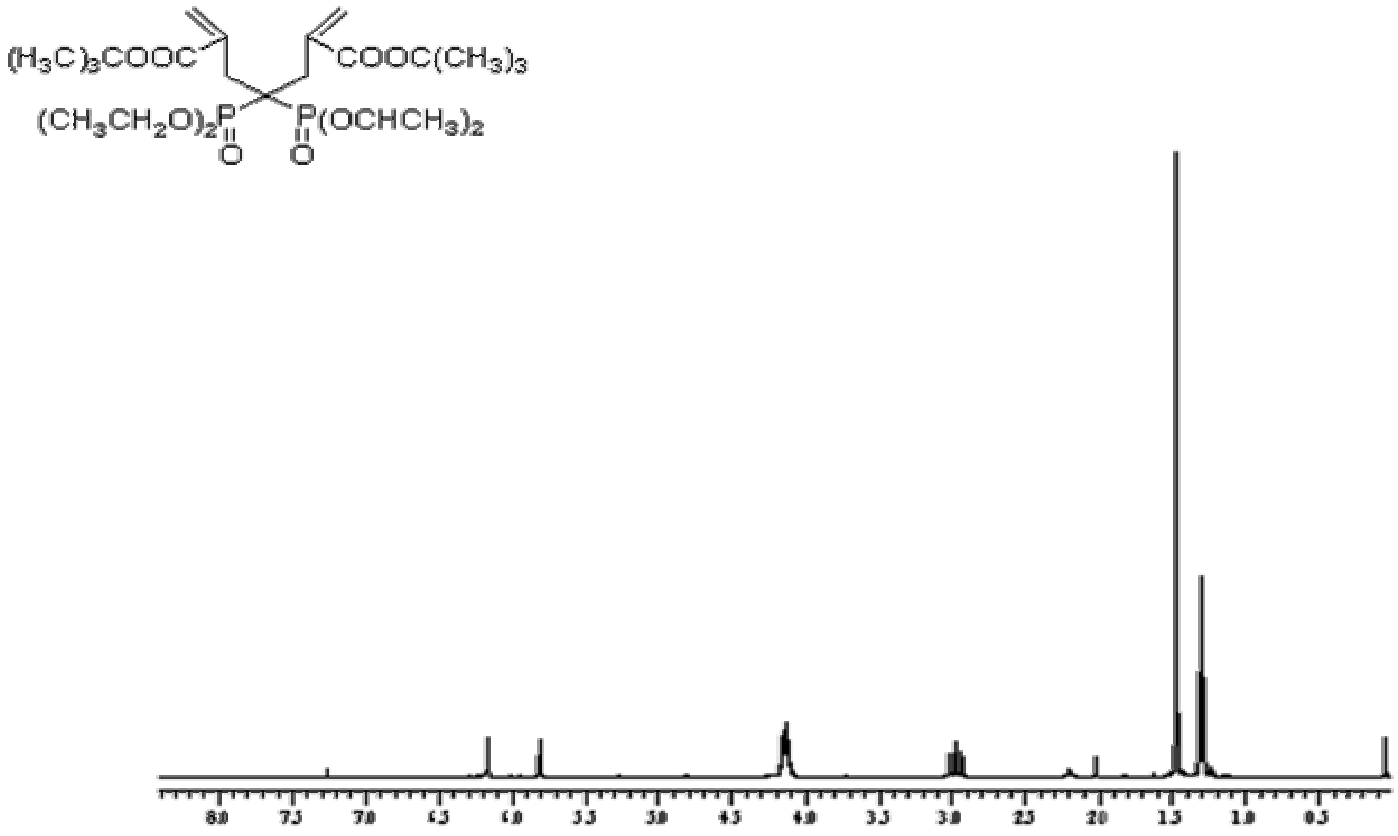


Figure 4.37. ^{1}H-NMR spectrum of monomer **9**

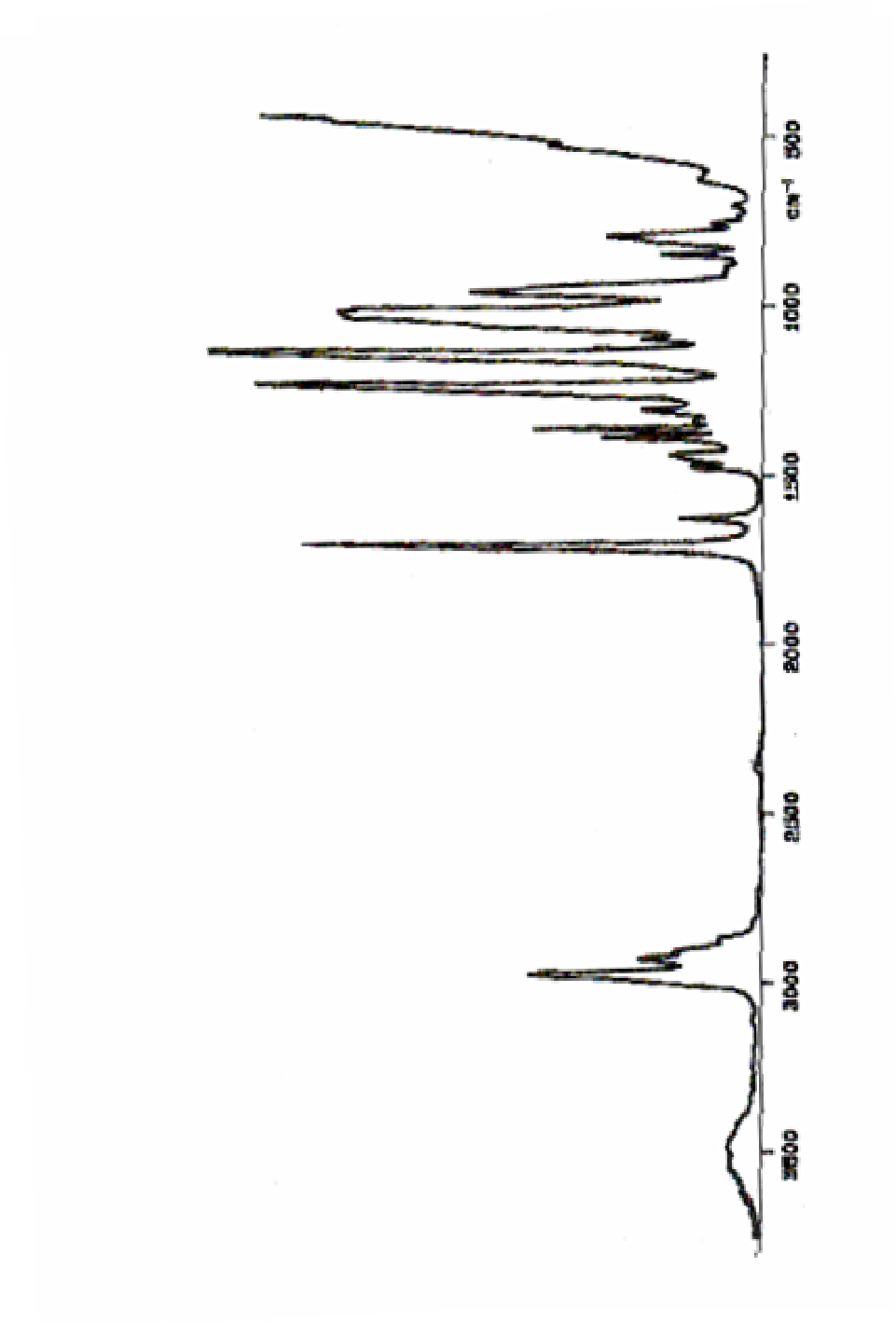


Figure 4.38. IR spectrum of monomer 9

4.5. Photopolymerizations

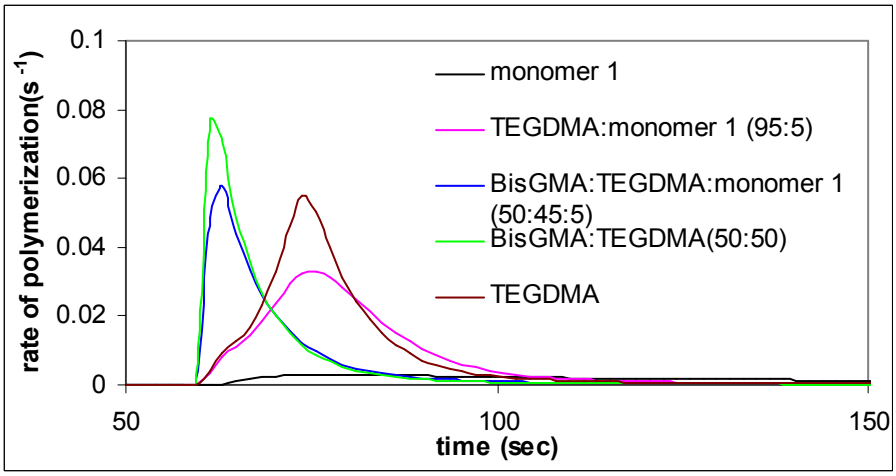
The photopolymerization behavior of the synthesized monomers was investigated using photodifferential scanning calorimeter (Photo-DSC). All the polymerizations were performed under identical conditions of initiator concentration (2.0 mol peer cent) and UV light intensity (15 mW/cm^2) and temperature (40 ^oC).

Mixtures of the synthesized monomers with the common monomers used in dentistry, TEGDMA (triethyleneglycol dimethacrylate) and BisGMA (2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane) or GDMA (glycerol dimethacrylate) were prepared. BisGMA is very rigid and H-bonding monomer while TEGDMA is flexible and non H-bonding.

4.5.1. Photopolymerizations of monomer 1

Monomer **1** showed very low reactivity in homopolymerization. The maximum rate of polymerization and conversion were 0.00299 s^{-1} (Figure 4.40) and 30.8 percent (Figure 4.41). The low reactivity of this monomer can be explained by steric effect of the phosphonate ester groups close to the double bond.

When monomer **1** was copolymerized with TEGDMA and BisGMA, it was observed that the rate of polymerizations of TEGDMA and BisGMA decreased. For example, the maximum rate of polymerization of BisGMA: TEGDMA (50:50 mol per cent) and BisGMA: TEGDMA: monomer **1** (50:45:5 mol per cent) were 0.7689 s^{-1} and 0.5781 s^{-1}. Similarly, the conversion values of these mixtures decreased by incorporation of monomer **1**.



4.40. Rate versus time plot of monomer **1** and its mixtures with TEGDMA and Bis-GMA

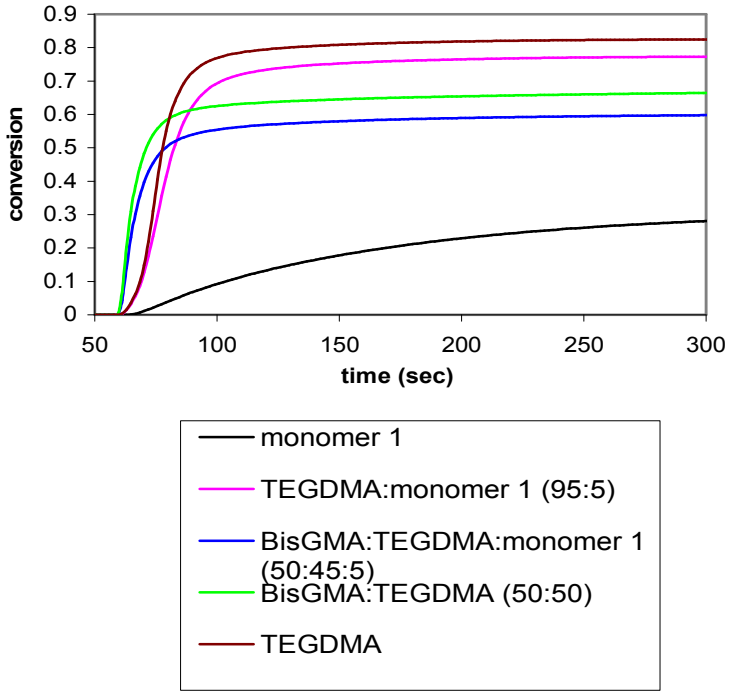


Figure 4.41. Conversion versus time plot of monomer **1** and its mixtures with TEGDMA and Bis-GMA

4.5.2. Photopolymerizations of monomer 3

Figure 4.42 shows the photopolymerization rates of monomer **3**, TEGDMA: monomer **3** (95:5 mol per cent), BisGMA:TEGDMA:monomer **3** (50:45:5 mol per cent), TEGDMA and TEGDMA: BisGMA (50:50 mol per cent). No exotherm was obtained with monomer **3**. The failure of this monomer to homopolymerize is probably due to steric effects in the propagation reaction. Bulky end groups close to the double bond prevented polymerization of this monomer. The presence of monomer **3** in TEGDMA: monomer **3** (95:5 mol per cent) and BisGMA: TEGDMA: monomer 3 (50:45:5 mol per cent) mixtures decreased the rate.

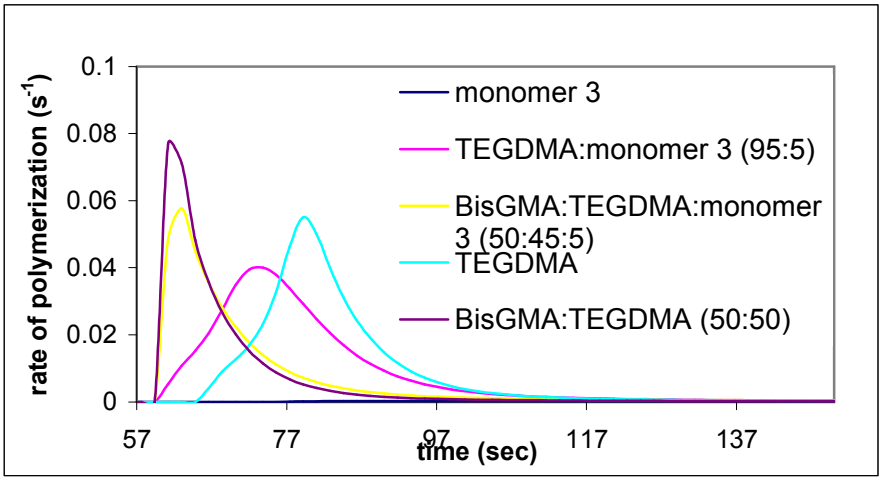


Figure 4.42. Rate versus time plot of monomer **3** and its mixtures with TEGDMA and Bis-GMA

The overall conversions were shown in Figure 4.43. It was observed that addition of 5 per cent of monomer **3** did not change the conversions of TEGDMA and BisGMA: TEGDMA (50:50 mol per cent).

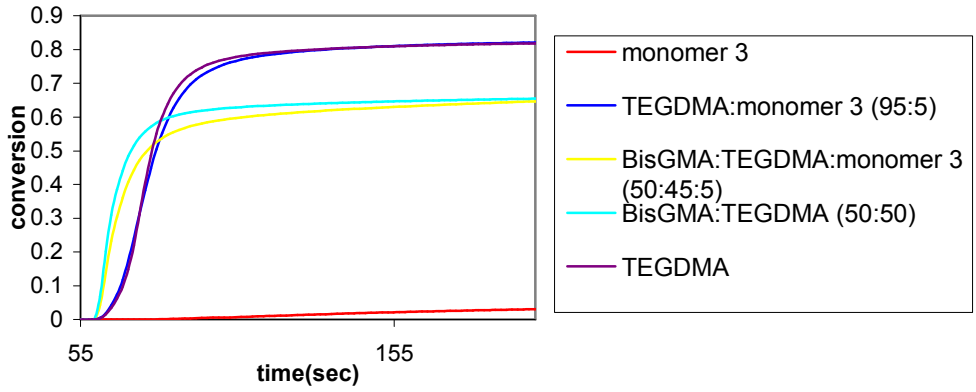


Figure 4.43. Conversion versus time plot of monomer **3** and its mixtures with TEGDMA and Bis-GMA

4.5.3. Photopolymerizations of monomer 4

Since monomer **4** was a solid with high melting point (above 300 °C), so it was not homopolymerized. The mixtures of this monomer with TEGDMA and GDMA were prepared. TEGDMA: monomer **4** (95:5 mol per cent) mixture was not homogeneous. The maximum rates of polymerizations were found as 0.4635 s^{-1}, 0.3620 s^{-1} for GDMA and GDMA: Monomer **4** (95:5 mole per cent). For TEGDMA and TEGDMA: monomer 4 (95:5 mole per cent), the maximum rates of polymerization were found to be 0.05621 s^{-1} and 0.02766 s^{-1} (Figure 4.44).

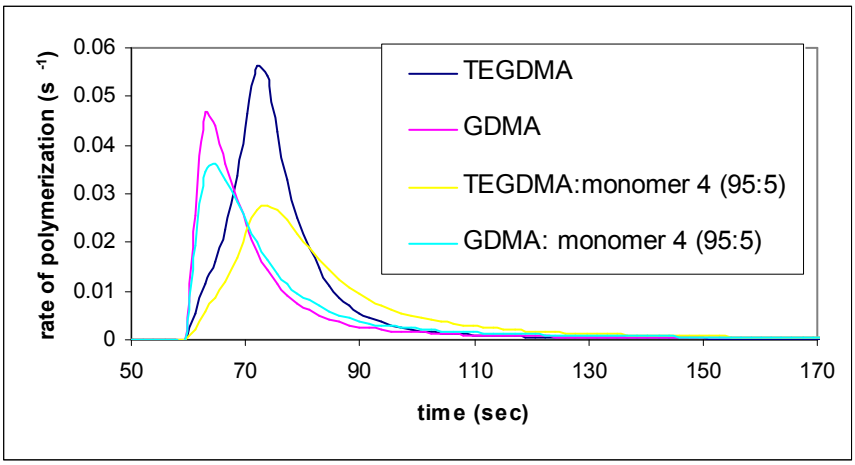


Figure 4.44. Rate versus time plot of monomer **4** and its mixtures with TEGDMA and GDMA

The overall conversions were shown in Figure 4.45; it was observed that addition of 5 per cent of monomer **4** decreased the conversions of TEGDMA. However, conversions of GDMA and GDMA: monomer **4** mixtures were similar.

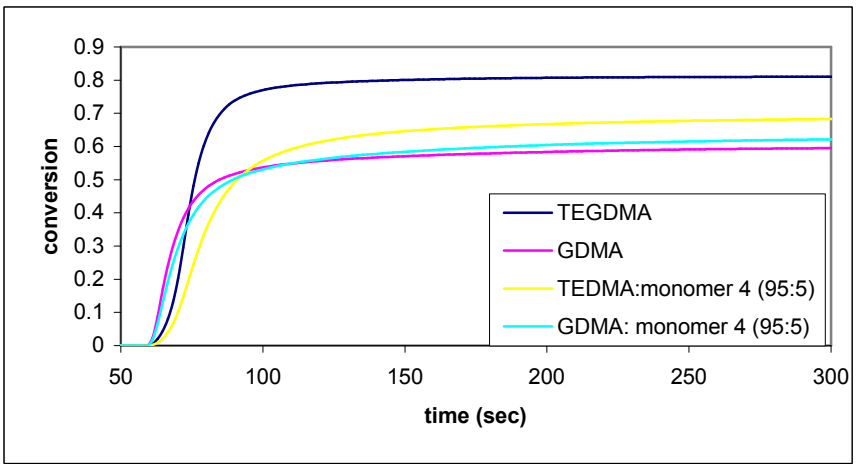
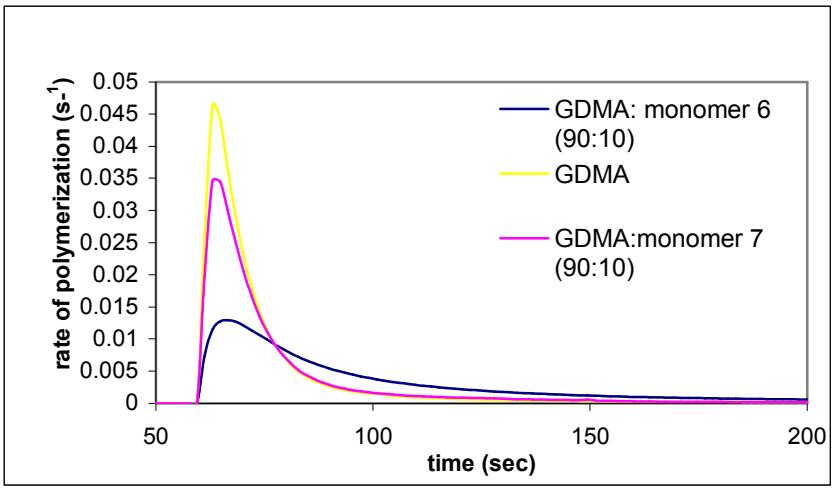


Figure 4.45. Conversion versus time plot of mixtures of monomer **4** with TEGDMA and GDMA

4.5.4. Photopolymerizations of monomer 6 and monomer 7

Since monomers **6** and **7** were solid, their mixtures with GDMA were studied. The rates of polymerizations were shown in Figure 4.46. The maximum rates of polymerizations were found to be 0.4635 s^{-1}, 0.1138 s^{-1}, 0.3463 s^{-1} for GDMA, GDMA: Monomer **6** (90:10 mol per cent), GDMA: Monomer **7** (90:10 mol per cent). Addition of either monomer **6** or monomer **7** decreased the rate of polymerization of GDMA. Polymerization reactivity of monomer **7** was found to be higher than monomer **6**. This may be due to a decrease in steric hindrance by hydrolysis of t-butyl groups or H-bonding effect of –COOH groups. It is known that H-bonding brings the double bonds close to each other and enhance polymerization.



4.46. Rate versus time plot of monomer **6** and monomer **7** with GDMA

The conversion values were 60.0, 53.1 and 51.7 per cent for GDMA, GDMA: monomer **6** (90:10 mole per cent), GDMA: monomer **7** (90:10 mol per cent) (Figure 4.47).

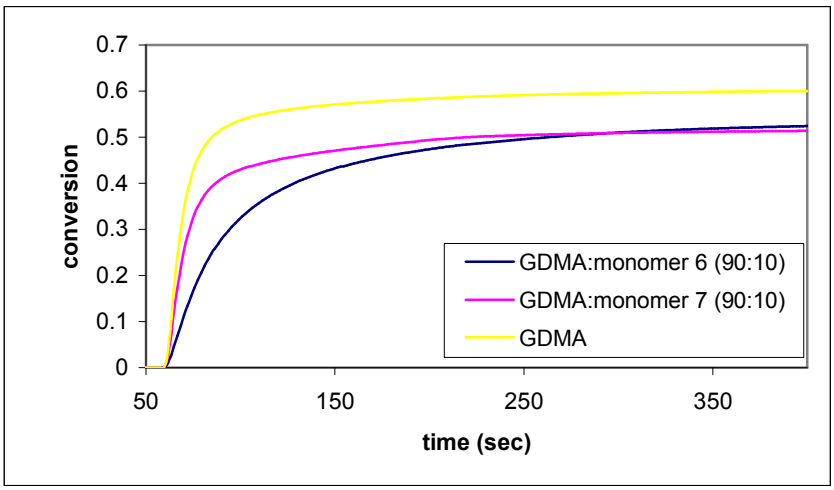


Figure 4.47. Conversion versus time plot of monomer **6** and monomer **7** with GDMA

When mixtures of monomer **6** and monomer **7** with TEGDMA were studied similar behavior to GDMA was observed (Figure 4.48).

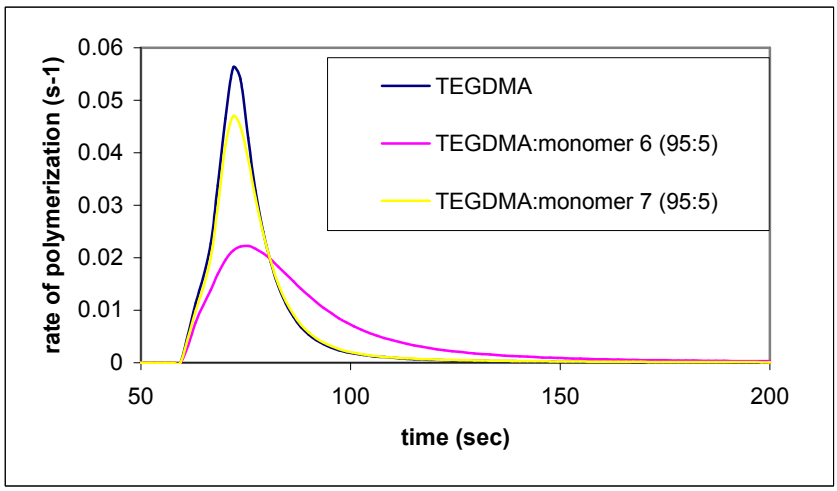


Figure 4.48. Rate versus time plot of monomer **6** and monomer **7** with TEGDMA

The conversion values were for TEGDMA, TEGDMA: Monomer **6** (95:5 mol per cent) and TEGDMA: monomer **7** (95:5 mol per cent) were 81.0 per cent, 76.4 per cent and 74.8 per cent (Figure 4.49). Rigid monomers (monomer **6** and monomer **7**) decreased the conversion by decreasing the flexibility of TEGDMA.

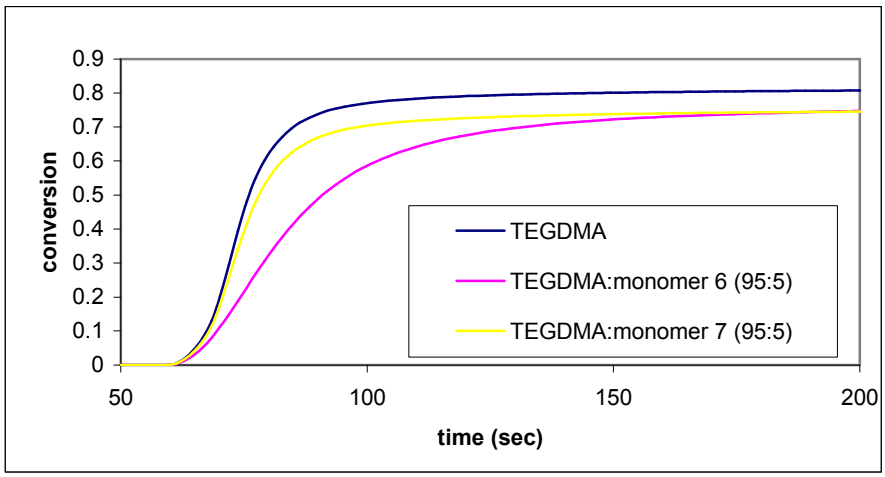


Figure 4.49. Conversion versus time plot of monomer **6** and monomer **7** with TEGDMA

4.5.5. Photopolymerization of monomer 9

The rate of polymerization versus time and conversion versus time plots of Monomer **9** were shown in Figure 4.50 and Figure 4.51. The polymerization rate of this monomer was found to be low. The maximum rate of polymerization and conversion were found to be 0.0069 s^{-1} and 62.8 per cent. The low reactivity of this monomer is probably due to bulky phosphonate and carboxylic ester groups close to the double bonds. Hydrolysis of carboxylic ester and phosphonate ester groups is expected to increase rate of polymerization of this monomer by decreasing steric hindrance.

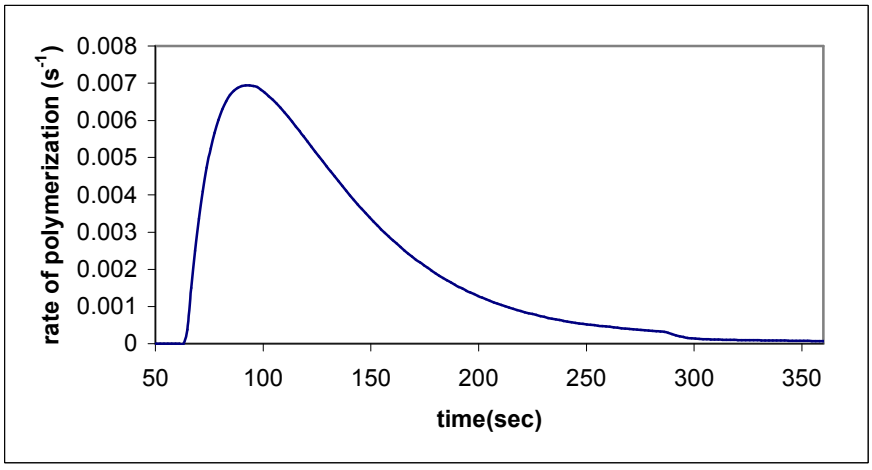


Figure 4.50. Rate versus time plot of monomer **9**

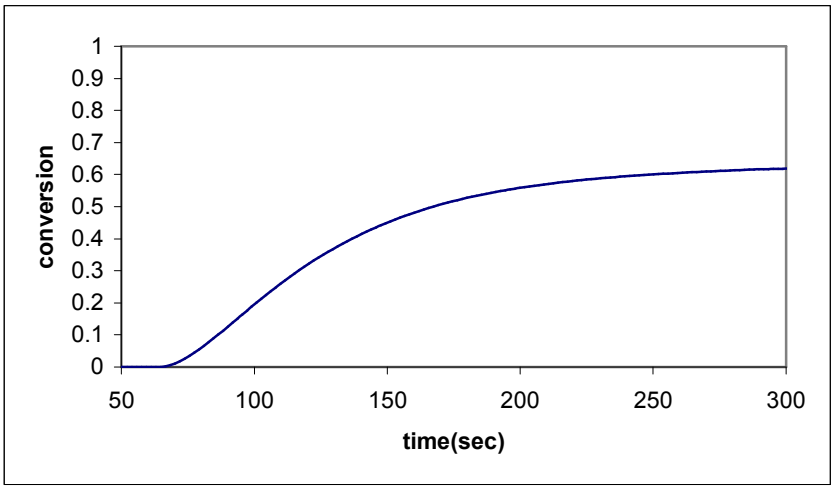


Figure 4.51. Conversion versus time plot of monomer **9**

Rate of polymerizations of the monomers increased by decreasing steric hindrance due to hydrolysis of butyl ester groups.

Monomers containing bulky t-butyl groups and phosphonate groups showed no polymerizability or very low polymerizability due to steric effect.

5. CONCLUSIONS

Novel eight crosslinking monomers and one cyclic monomer with adhesive groups to tooth tissue were synthesized from t-butyl α-hydroxymethyl acrylate using two different routes. The synthesized monomers will have good mechanical properties due to their rigid aromatic structures.

The phosphonic acid containing monomers were soluble in water which is important for dental applications. They are also expected to have good enamel and dentin etching properties. Monomers synthesized from o- hydroxyl aryl phosphonates have good stability and improved hydrolytic stability.

The photopolymerization behavior of the mixtures of the monomers with the commercial dental monomers were investigated with 2,2'-dimethoxy-2-phenyl acetophenone (DMPA) as photoinitiator using photo DSC.

Monomers containing bulky t butyl groups and phosphonate groups showed no polymerizability or very low polymerizability due to steric effect. Rate of polymerization of the monomers increased by decreasing steric hindrance due to hydrolysis of t butyl ester groups. The photopolymerization reactivity of phosphonate containing 1,6-heptadiene monomer was found to be low.

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