DEVELOPMENT OF REACTIVE PHOSPHONATE AND PHOSPHONIC ACID-CONTANING METHACRYLATES

by

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ABSTRACT

DEVELOPMENT OF REACTIVE PHOSPHONATE AND PHOSPHONIC ACID-CONTAINING METHACRYLATES

Four novel phosphonated methacrylate, two novel phosphonic acid-containing methacrylate and one phosphate-containing methacrylate monomers have been synthesized using three different routes and studied for their potential in dental materials.

First route for the synthesis of phosphonated monomers consists of a one step reaction of methacryloyl chloride with diethyl (2-hydroxyphenyl) phosphonate (monomer **1**) and tetraethyl (2,5-dihydroxy-1,4-phenylene) bisphosphonate (monomer **2**) in the presence of a base catalyst. Hydrolysis of the phosphonate groups of these monomers with trimethylsilyl bromide (TMSBr) gave phosphonic acid-containing monomers **1a** and **2a**.

Second route for the synthesis of phosphonated monomers involved two steps: (i) reaction of dimethyl (2-hydroxyphenyl) phosphonate and α-(chloromethyl)acryloyl chloride (CMAC) to give an intermediate (ii) reaction of this intermediate with benzoic (monomer **3**) and formic (monomer **4**) acids.

Third route involves reaction of glycidyl methacrylate (GMA) with diethyl hydrogen phosphate to give a phosphate-containing monomer (monomer **5**).

Thermal homopolymerization of monomers **1**, **3**, **4**, and **5** and copolymerization of monomer **1** with methyl methacrylate (MMA) were investigated using azobisisobutyronitrile (AIBN) at 60 ^{o}C. Glass transition temperatures were observed for poly-**1**, poly(MMA-co-**1**) (50:50), poly(MMA-co-**1**) (90:10), PMMA, poly-**3** and poly-**5** at 52, 90, 99, 129, 50 and 70 ºC, respectively. Thermogravimetric analysis (TGA) of these polymers indicated formation of char on combustion.

Homo- and/or copolymerization behavior of monomers **1-5** with 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propyloxy) phenyl] propane (Bis-GMA) were investigated with photo-differential scanning calorimetry at 40 ^{o}C using 2,2'-dimethoxy-2-phenyl acetophenone (DMPA) as photoinitiator. The maximum rate of polymerizations decreased in the following order: Bis-GMA~**3** > **1** > **4**. The conversions of monomers **1**, **3** and **4** (73.9, 85.9 and 98.2 %) were very high compared with Bis-GMA (40.5%).

The aqueous solution of the acid monomer (**2a)** was acidic enough (pH= 1.65) to etch enamel and dentin, but is prone to hydrolysis at long storage periods. The copolymerization behavior of this monomer with 2-hydroxyethyl methacrylate (HEMA) was investigated in water using photo-differential scanning calorimeter at 40 ^{o}C with bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO) as photoinitiator. The thermal solution copolymerization of this monomer with acrylamide (AAm) and HEMA gave crosslinked polymers, indicating its incorporation into the copolymers. The interaction of this monomer with hydroxyapatite was observed using FTIR spectroscopy. This monomer was found to be more suitable for dental composites than dental adhesives.

ÖZET

FOSFONAT VE FOSFONİK ASİT İÇEREN REAKTİF METAKRİLATLARIN GELİŞTİRİLMESİ

Fosfonat grubu içeren dört yeni metakrilat, fosfonik asit grubu içeren iki yeni metakrilat ve fosfat grubu içeren bir metakrilat monomeri üç farklı metod kullanılarak sentezlendi ve diş malzemelerinde kullanılma potansiyelleri incelendi.

Fosfonat grubu içeren monomerlerin sentezinde ilk metod, metakriloil klorürün dietil (2-hidroksifenil) fosfonatın (monomer **1**) tetraetil (2,5-dihidroksi-1,4-fenilen) bisfosfonat (monomer **2**) ile baz katalizörlüğünde tek basamaklı reaksiyonlarını içermektedir. Monomerlerin fosfonat gruplarının trimetilsilil bromür (TMSBr) ile hidrolizinden fosfonik asit grubu içeren iki yeni monomer (monomer **1a** ve **2a**) sentezlenmiştir.

Fosfonat grubu içeren monomerlerin sentezinde ikinci metod iki basamaktan oluşmaktadır: (i) dimetil (2-hidroksifenil) fosfonat ve α-(klorometil)akriloil klorür (CMAC)'ün reaksiyonu ile bir ara ürün oluşması, (ii) bu ara ürünün benzoik asit (monomer **3**) veya formik (monomer **4**) asitle reaksiyonları.

Üçüncü metot glisidil metakrilatın dietil hidrojen fosfat ile reaksiyonundan fosfat grubu içeren monomer **5**'in sentezini kapsamaktadır.

Monomerlerden **1, 3**, **4** ve **5**'in termal homopolimerizasyonları ve monomer **1**'in metil metakrilat (MMA) ile kopolimerizasyonu, 60 ^{o}C'de ve azobisisobütironitril varlığında incelendi. Poly-**1**, poly(MMA-co-**1**) (50:50), poly(MMA-co-**1**) (90:10), PMMA, poly-**3** ve poly-**5** için camsı geçiş sıcaklıkları 52, 90, 99, 129, 50 ve 70 ºC olarak bulundu. Bu polimerlerin termogravimetrik analizleri (TGA) yanma sırasında kül oluşumunu gösterdi.

Monomerlerin (**1**-**5**) homo- ve 2-bis[4-(2-hidroksi-3-metakriloiloksi propiloksi fenil] propan (Bis-GMA) ile kopolimerizasyonları 2,2'-dimetoksi-2-fenil asetofenon (DMPA) katalizörlüğünde 40 ºC'de foto diferansiyel taramalı kalorimetre ile incelendi. Maksimum polimerizasyon hızları şu sıra ile azalmaktadır: Bis-GMA~**3** > **1** > **4**. Monomer **1**, **3** ve **4**'ün polimere dönüşümleri (73.9, 85.9 and 98.2 %) Bis-GMA (40.5 %)'den yüksek bulundu.

Monomer **2a**'nın sulu çözeltisinin mine ve dentini aktive edebilecek kadar asidik (pH= 1.65) olduğu fakat monomerin uzun sure saklandığında hidroliz olabileceği bulundu. Bu monomerin 2-hidroksietil metakrilat (HEMA) ile kopolimerizasyonu suda 40 ^{o}C'de bis(2,4,6-trimetilbenzoil)fenilfosfin oksit (BAPO) fotobaşlatıcı kullanılarak çalışılmıştır. Monomerin akrilamid (AAm) ve HEMA ile termal polimerizasyonu çapraz bağlı polimerler vererek monomerin kopolimere katıldığını göstermiştir. Monomerin hidroksiapatit ile etkileşimi FTIR spektroskopi ile gözlenmiştir. Monomer **2a**'nın diş yapıştırıcıları için değil diş kompozitleri için daha uygun olduğu bulumuştur.

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LIST OF SYMBOLS/ABBREVIATIONS

Irgacure 651	2,2'-dimethoxy-2-phenylacetophenone
R_p	Rate of polymerization
T_g	Glass transition temperature
V-50	2,2'-azo-bis(2-amidinopropane)dihydrochloride
AIBN	2,2'-azobisisobutyronitrile
BAPO	Bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide
Bis-GMA	2,2-bis[4-(2-hydroxy-3-methacryloyloxy propyloxy) phenyl] propane
CMAC	α-(chloromethyl)acryloyl chloride
DABCO	1,4-diazobicyclo [2.2.2] octane
DSC	Differential Scanning Calorimetry
FT-IR	Fourier Transform Infrared Spectroscopy
GDMA	Glycerol dimethacrylate
HEMA	2-hydroxyethyl methacrylate
NMR	Nuclear Magnetic Resonance Spectroscopy
TBHMA	tert-butyl-α-hydroxymethyl acrylate
TEA	Triethylamine
TEGDMA	Triethyleneglycol dimethacrylate
TGA	Thermal Gravimetric Analysis
TMSBr	Trimethylsilyl bromide

1. INTRODUCTION

1.1. Synthetic Methods for Phosphorus-Containing Monomers

1.1.1. Arbuzov Reaction

The Michaelis-Arbuzov rearrangement, also known as the Arbuzov rearrangement, Arbuzov reaction, or Arbuzov transformation, is one of the most versatile pathways for the formation of carbon-phosphorus bonds and involves the reaction of an ester of trivalent phosphorus with alkyl halides. In its simplest form the Arbuzov arrangement is the reaction of an alkyl halide with a trialkyl phosphite yielding a dialkyl alkylphosphonate (Figure 1.1) [1].

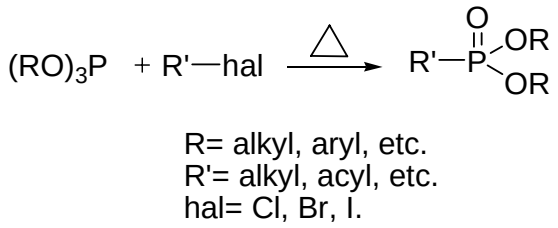


Figure 1.1. Arbuzov rearrangement

D'Alelio et al. carried out the Arbuzov reaction in order to synthesize phosphorus-containing monomers (Figure 1.2) [2].

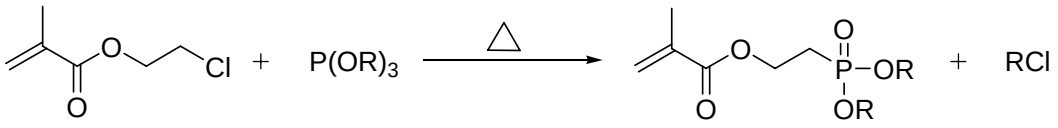


Figure 1.2. Synthesis of phosphorus-containing monomers from 2-methyl-acrylic acid 2-chloro-ethyl ester by Arbuzov reaction

New monomers were synthesized by the Arbuzov reaction of ethyl α-chloromethyl acrylate (ECMA) and t-butyl α-bromomethyl acrylate (TBBr) with triethyl phosphite (Figure 1.3) [3].

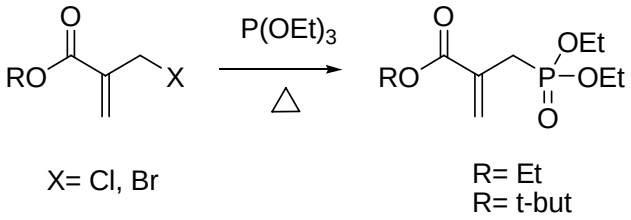


Figure 1.3. Synthesis of phosphorus-containing monomers from ECMA and TBBr by Arbuzov reaction

1.1.2. Michaelis-Becker Reaction

Michaelis Becker reaction involved the nucleophilic phosphorylation of a saturated carbon by the salts of dialkylphosphites (Figure 1.4). Michaelis-Becker reaction takes place as a biomolecular nuclephilic substitution. Numerous synthetic applications of this reaction have been already reviewed in the early literature [4].

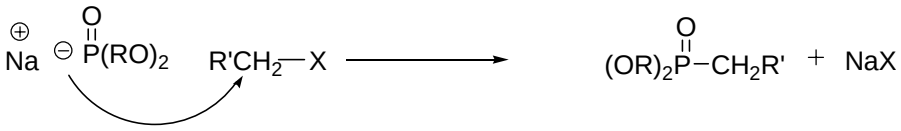
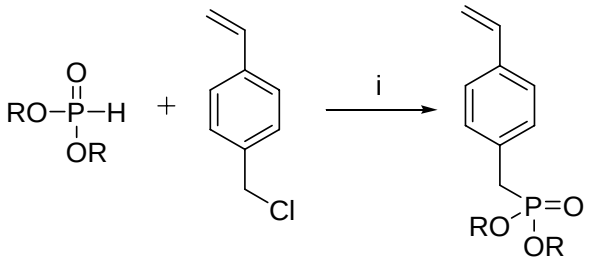


Figure 1.4. Michaelis-Becker reaction

The Michaelis–Becker procedure is shown to give ready access to higher dialkyl-p-vinylbenzyl phosphonates from Michaelis–Becker reactions of the appropriate dialkyl H-phosphonates with p-vinylbenzyl chloride (Figure 1.5) [5].



i: Potassium t-butoxide in THF, 20 ^{o}C
R= Me, Et, n-Bu, lauryl.

Figure 1.5. Synthesis of phosphorus-containing styrenic monomers

1.1.3. Michael Addition Reaction

Michael addition of either trialkylphosphites or dialkyl phosphonates to unsaturated C=C bonds gave phosphones (Figure 1.6).

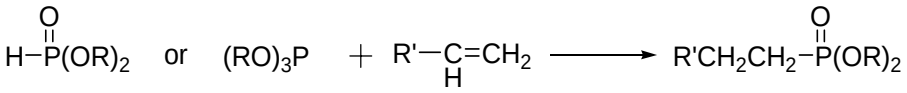


Figure 1.6. General synthesis of phosphones by the Michael addition reactions

Misato et al. described the radical addition of dialkyl hydrogenphosphonate (DAHP) on a vinyl methacrylate, shown in Figure 1.7 [6].

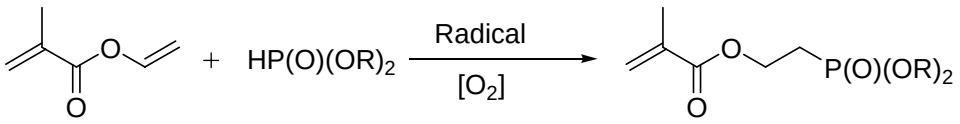


Figure 1.7. Synthesis of a phosphorus-containing methacrylate by radical addition

1.1.4. Ring Opening Reactions of Epoxides

Phosphorus-containing monomers can be obtained by ring opening polymerization of epoxy compounds by phosphorus-containing alcohols, acids and amines. Figure 1.8 shows

the general production of phosphoric esters. Van Den Bergen described the following synthesis where R=H or Me; R'=C_{1-24}alkyl, C_{6-20}(alk)aryl, C_{7-12}aralkyl; R''=H, C_{1-24}alkyl, C_{6-20}(alk)aryl, C_{7-12}aralkyl [7].

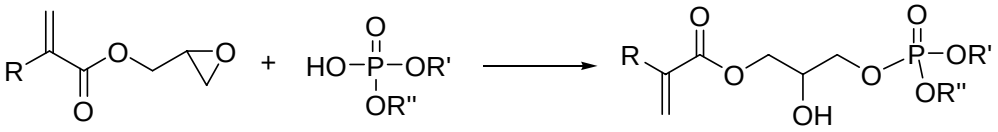


Figure 1.8. Synthesis of phosphorus-containing monomers by ring opening reactions

Figure 1.9 also shows the monomers synthesized by ring opening reaction of glycidyl methacrylate with (diethoxy-phosphoryl)-acetic acid and (2-hydroxy-ethyl)-phosphonic acid dimethyl ester [7].

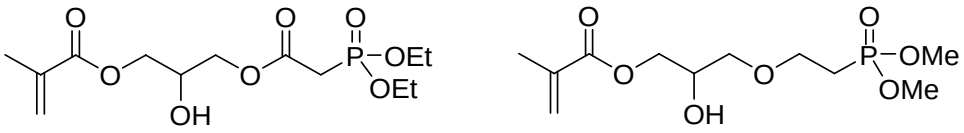


Figure 1.9. Structures of monomers synthesized from GMA

The ring opening reaction of Bisphenol A diglycidylether (DER) with (diethoxy-phosphoryl)-acetic acid was used to prepare a diol intermediate which was then converted to a dimethacrylate using methacryloyl chloride (Figure 1.10) [8].

N. Sibold et al. synthesized aromatic mono- and di(phosphonate) monomers bearing mono- and di(methacrylate) functions from readily available mono- and bis(sulfanyl phenyl phosphonate) and GMA (Figure 1.11) [9].

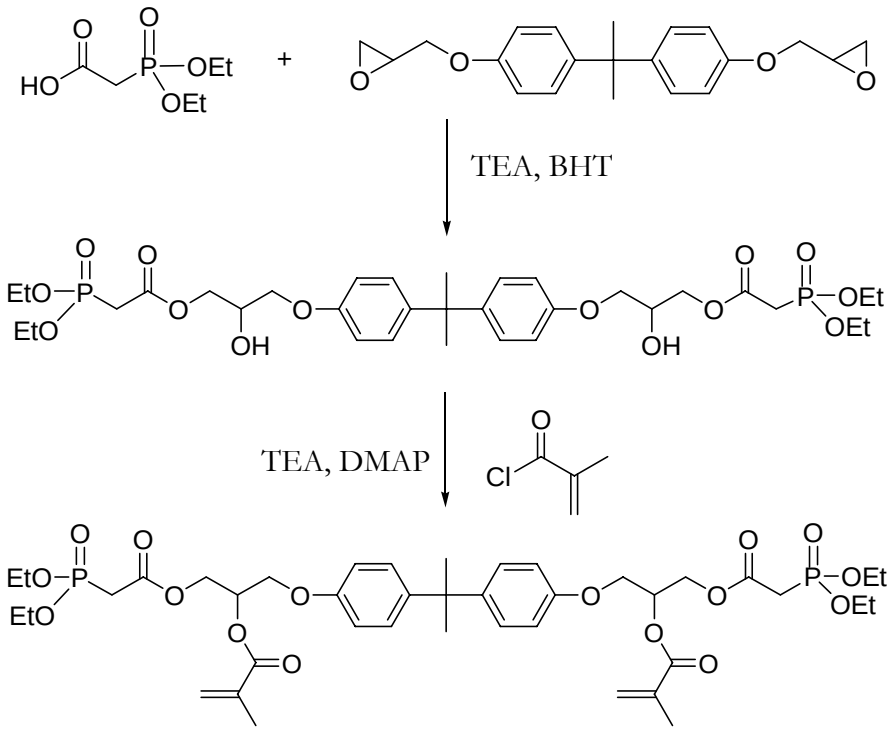


Figure 1.10. Synthesis of a phosphonated dimethacrylate from DER

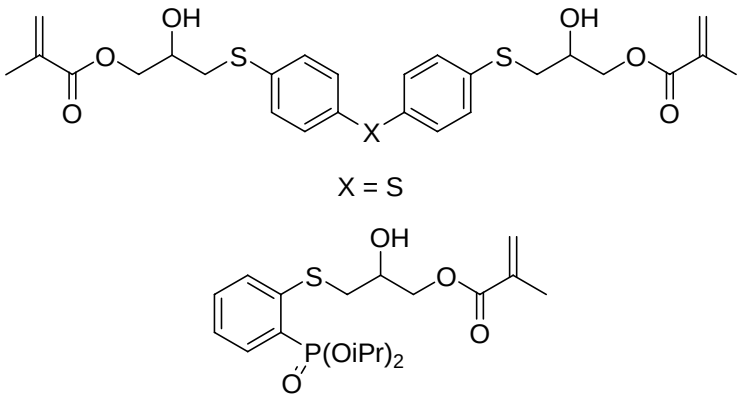


Figure 1.11. Aromatic methacrylate monomers synthesized from a bis(thiol) and thiol

1.1.5. Reactions of Alcohols with Phosphorus Oxychloride ($POCl_3$) and Its Derivatives

Phosphoric acid derivatives can be synthesized by reacting alcohols with $POCl_3$ (Figure 1.12).

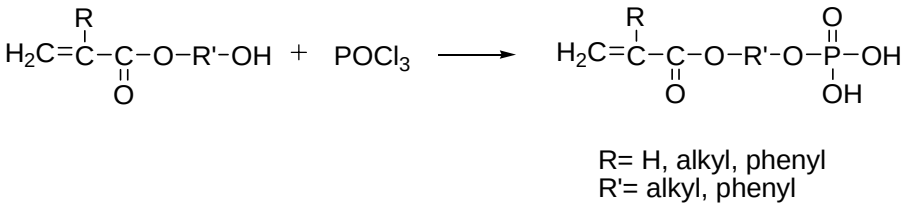


Figure 1.12. General synthesis of polymerizable phosphates using $POCl_3$

As an example, the reaction of $POCl_3$ with 10-hydroxydecyl methacrylate in the presence of triethyl amine (TEA) at -30 to -40 ^{o}C resulted in methacryloyloxydecyl dihydrogen phosphate (MDP) [10]. The reaction of a secondary alcohol, glycerol dimethacrylate (GDMA) with $POCl_3$ gives glycerol dimethacrylate ester of phosphoric acid (GDMP) (Figure 1.13) [11]. In the literature, there are a number of polymerizable phosphoric acids synthesized to be used as adhesives [12].

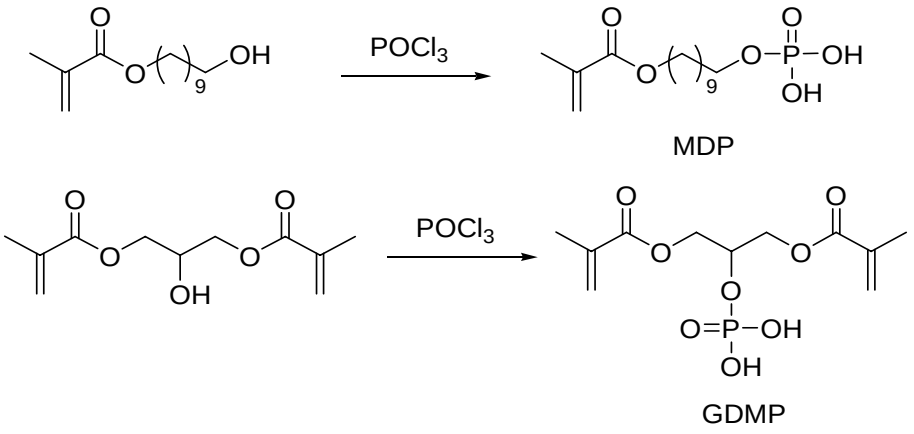


Figure 1.13. Synthesis of MDP and GDMP

Moszner et al. also investigated synthesis of a bis(methacrylamide) containing dihydrogen phosphate, shown in Figure 1.14 [13].

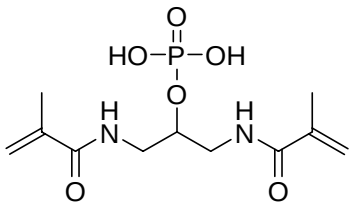


Figure 1.14. Structure of 1,3-bis(methacrylamido)propane-2-yl dihydrogen phosphate

Previously, phosphorus-containing acrylate/(di)methacrylate monomers based on 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM) were prepared by two different methods [14]. The first method involved reaction of AHM with diethylchlorophosphate to produce a phosphate-containing acrylate/methacrylate monomer followed by Michael addition of this monomer with dihexyl amine. In the second method, a hydroxyl containing dimethacrylate monomer was prepared via Michael addition of ethanol amine to AHM followed by its reaction with diethylchlorophosphate (Figure 1.15).

H. Wang et al. investigated the synthesis of phosphorus–nitrogen containing hyperbranched polyphosphonate acrylate (HBPPA) [15]. Figure 1.16 shows the reaction of phenylphosphonic dichloride (BPOD) with hydroxylethyl acrylate (HEA). The formed di(acryloyloxyethyl) benzenephosphonate (DABP) and N-(2-aminoethyl)-piperazine were reacted to give hyperbranched polyphosphonate acrylate.

1.1.6. Reactions of Phosphorus-Containing Alcohols and Amines with Acids and Acid Chlorides

Another way to synthesize phosphorus-containing monomers is the reaction of acid chlorides with phosphorus-containing alcohols or amines. Introducing polymerizable methacrylate groups to phosphorus-containing precursors is important to achieve free-radical polymerization.

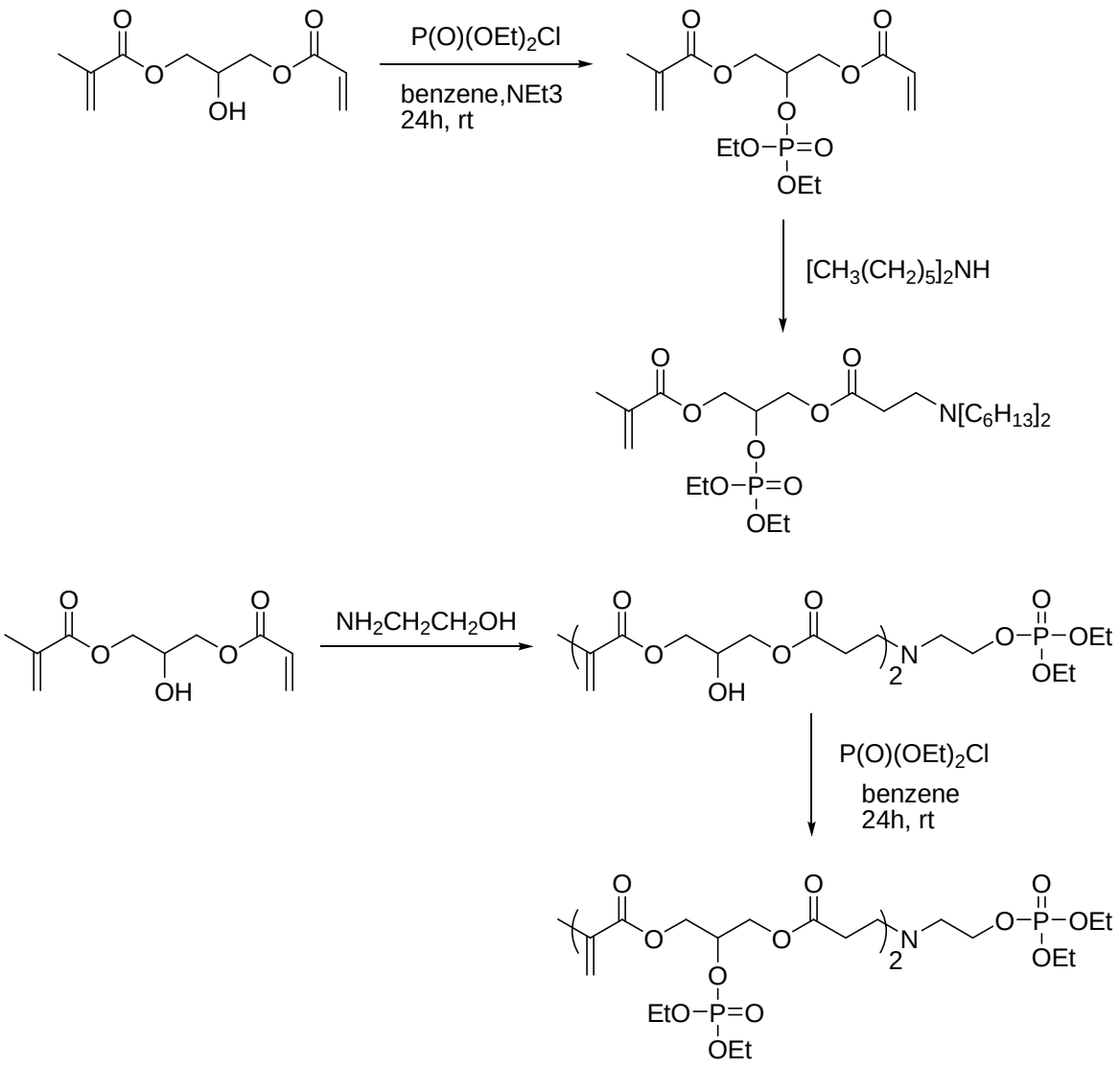


Figure 1.15. Synthesis of phosphate-containing methacrylates from AHM

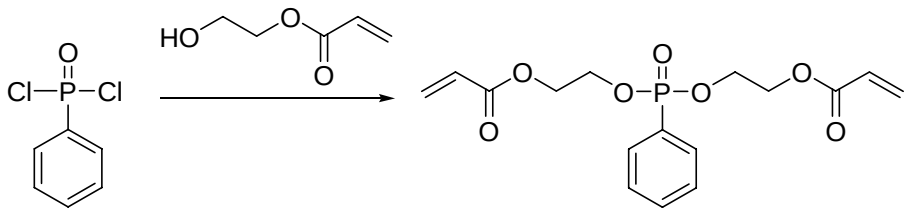


Figure 1.16. Synthesis of DABP

1.1.6.1. Reactions of Alcohols Synthesis of dialkyl(11-methacryloyloxyundecyl) phosphonate (DAHP) was described by the following method (Figure 1.17) [16].

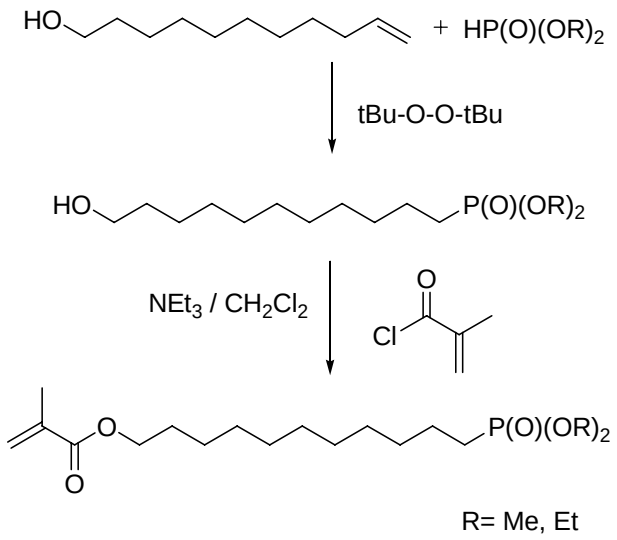


Figure 1.17. Synthesis of DAHP

Boutevin et al showed the synthesis of acrylic and methacrylic phosphonates presenting a sulfur bridge Figure 1.18 [17]. In the first step, thioethanol is added to the double bond of diethyl allylphosphonate. In the second step, the obtained alcohol reacts with methacryloyl chloride in the presence of TEA and hydroquinone.

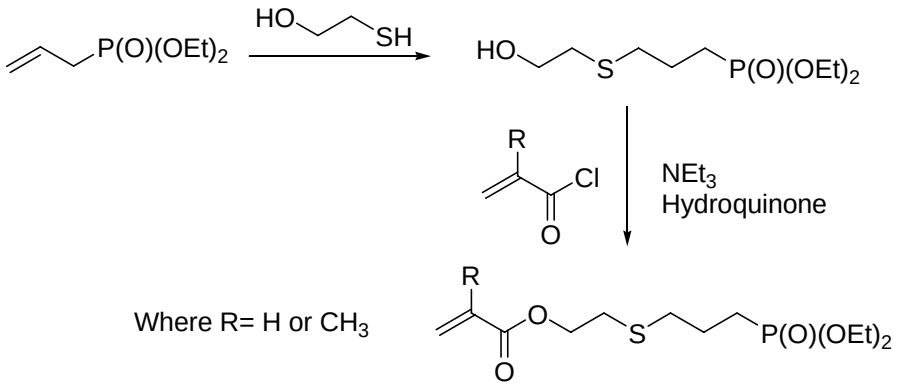


Figure 1.18. (Meth)acrylic phosphonates containing sulfur

The synthesis of a new phosphonated dimethacrylate was carried out by Quittmann et al. according to a classical esterification reaction (Figure 1.19) [18].

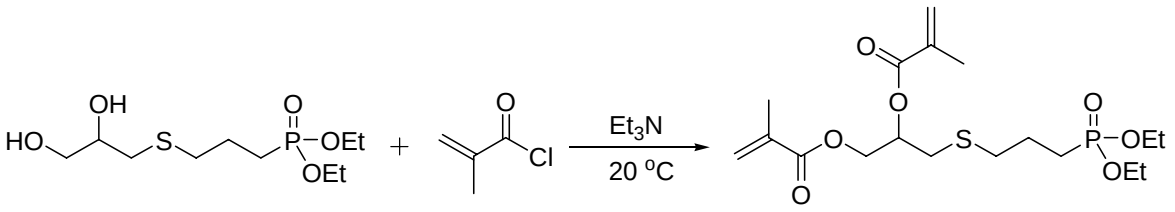
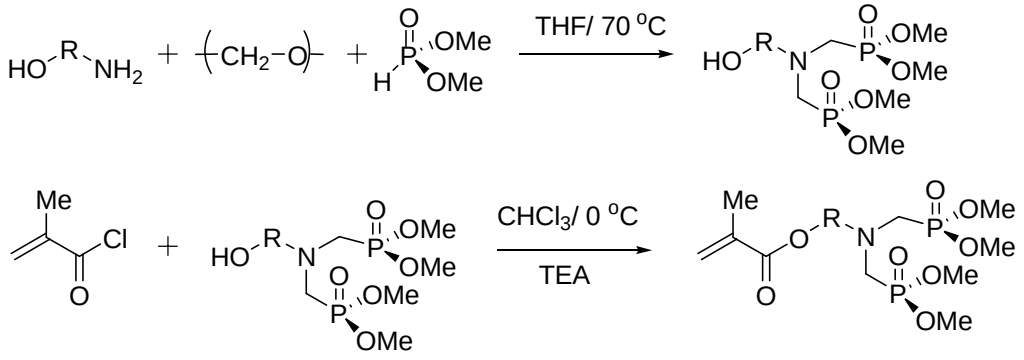


Figure 1.19. Synthesis of a phosphonated dimethacrylate containing sulfur

K. Chougrani et al. successfully synthesized hydroxy-amino-diphosphonates (HO–C_n–NH_2), with 2≤n≤11 via the Kabachnick-Field reaction with high yields. These hydroxy compounds were then reacted with methacryloyl chloride to lead to novel amino-diphosphonate methacrylates MAC_nNP_2 (with 2≤n≤11) (Figure 1.20) [19].



R= C_2H_4; C_3H_8; C_5H_{10}; C_6H_{12}

Figure 1.20. Synthetic pathway to nitrogen-containing bisphosphonated methacrylates via the Kabachnik-Fields reaction

A new phosphonated monomer for cyclopolymerization was synthesized by our group [20] from the reaction of ether dimer of RHMA with diethyl hydroxymethylphosphonate(Figure 1.21).

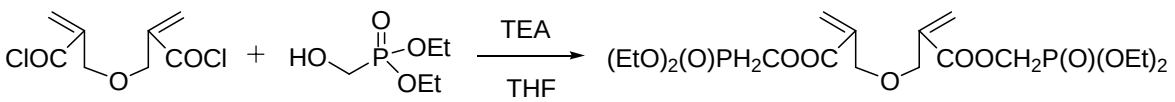


Figure 1.21. Synthesis of a phosphorus-containing monomer from the ether dimer of tert-butyl α-hydroxymethyl acrylate

Asri et al. investigated the synthesis of dimethyl(methacryloyloxy)-methyl phosphonate from the reaction of methacrylic acid and hydroxymethyl-phosphonic acid dimethyl ester (Figure 1.22) [31].

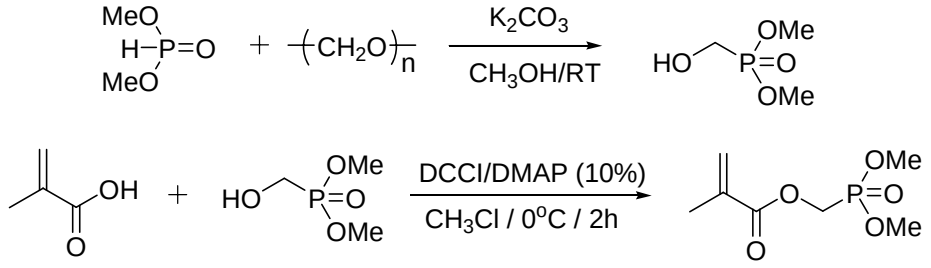


Figure 1.22. Synthesis of dimethyl(methacryloyloxy)-methyl phosphonate

1.1.6.2. Reactions of Amines Xu et al. introduced dental monomers with methacrylamidoethyl phosphonic acid groups by reacting amines containing phosphonic acids with methacryloyl chloride. One example to these monomers was shown in Figure 1.23 [21].

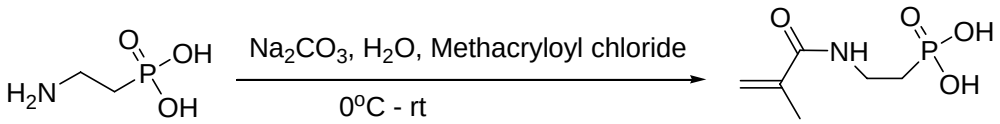


Figure 1.23. One-step reaction of 2-aminoethylphosphonic acid with methacryloyl chloride

Catel et al. also investigated acrylamide-containing phosphonic acids to be used as self-etching adhesives (Figure 1.24) [22].

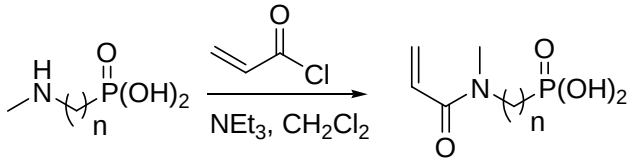


Figure 1.24. Synthesis of acrylamide-containing phosphonic acids

Catel et al. also showed the synthesis of new bisphosphonates from the reaction of acryloyl chloride and tetraethyl 3-(N-alkylamino)-propylidene bisphosphonates Figure 1.25 [23]. Finally, the bisphosphonates were deprotected by TMSBr to obtain new self etching adhesives.

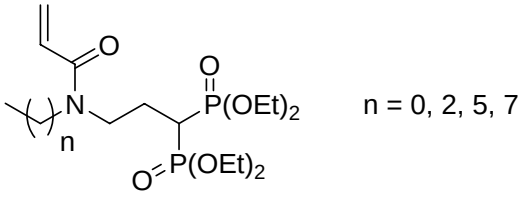


Figure 1.25. Structures of bisphosphonate-containing acrylamides

1.1.7. Reactions of Phosphorus-Containing Phenols and Alcohols with Alkyl Halides

1.1.7.1. Reactions of Phenols The phosphate-phosphonate rearrangement is an isomerization reaction which is characterised by base-induced migration of a dialkoxyphosphoryl group from oxygen to carbon (Figure 1.26). The driving force for the reaction is that the Li-O bond is stronger than the C-Li bond, which outweighs the loss in energy in going from a P-O to a P-C bond [24].

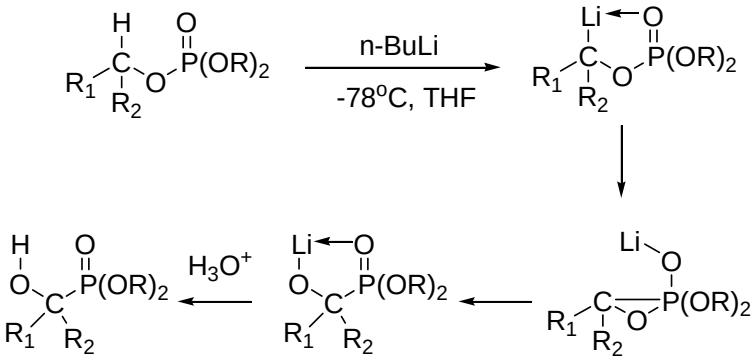


Figure 1.26. The mechanism of phosphate-phosphonate rearrangement

The rearrangement of dialkyl arylphosphates to dialkyl arylphosphonates was reported independently in two routes, one using proton-metal exchange with LDA and the other halogen metal exchange with n-BuLi. Phosphate esters of substituted phenols, readily

obtained from phenols and dialkylphosphites in CCl_4 in the presence of TEA (Atherton-Todd reaction), on treatment at low temperature with a strong base such as LDA, n-BuLi in THF or KNH_2 in liquid ammonia THF, produce excellent overall yields of 2-hydroxyphenylphosphonates (Figure 1.27).

This rearrangement was used for the synthesis of new phosphonated dental monomers. For example, two monomers were obtained by the reaction of diethyl (2-hydroxyphenyl) phosphonate and tetraethyl (2,5-dihydroxy-1,4-phenylene)bisphosphonate with TBBr using K_2CO_3 in refluxing acetone (Figure 1.28) [25]

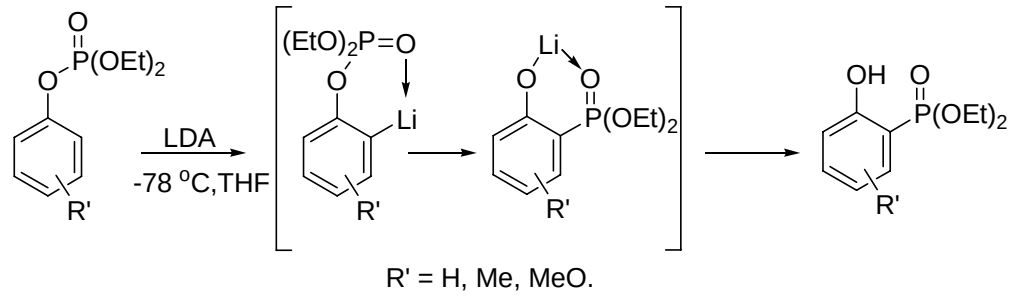


Figure 1.27. The rearrangement of dialkyl arylphosphates to dialkyl arylphosphonates

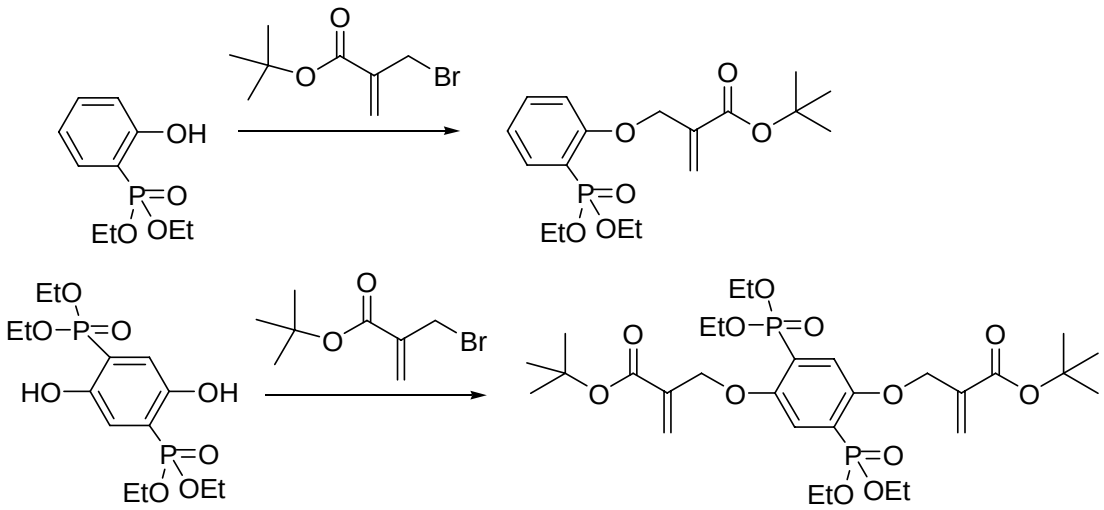


Figure 1.28. Synthesis of o-hydroxyaryl phosphonate-based monomers

1.1.7.2. Reactions of Alcohols A new route to highly reactive phosphorus-containing monomers was described by Avci et. al. (Figure 1.29) [2,26]. α-(Chloromethyl)acryloyl chloride (CMAC) was first reacted with a phosphorus-containing alcohol and then with salts of various carboxylic acids to give derivatives with mixed ester groups. Changing the structure of the acid allowed control of the polymerizability.

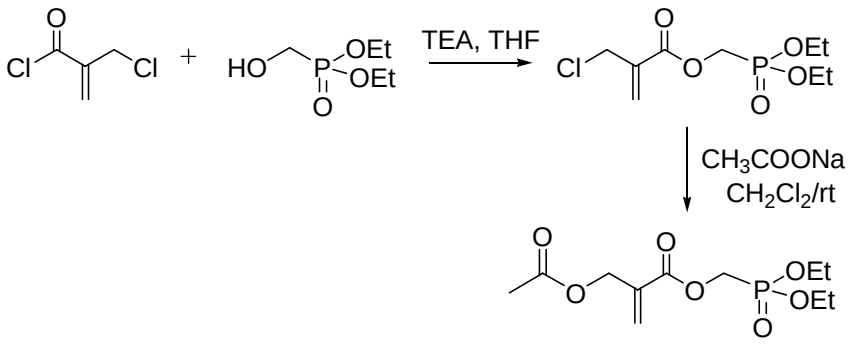


Figure 1.29. Synthesis of a phosphorus-containing monomer from CMAC

Moszner et al. synthesized new series of phosphonated monomers by the reaction of of alkyl α-bromomethacrylates and its derivatives (Figure 1.30) [27,28].

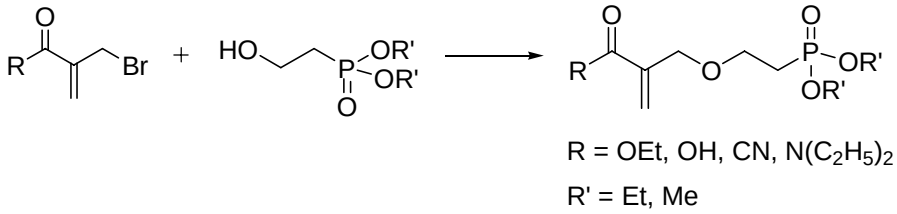


Figure 1.30. Synthesis of hydrolytically stable phosphorus-containing monomers

Moszner et al. prepared a hydrolytically stable acrylic ether phosphonic acid monomer (MAEPA) from the esterification of 2-[2-(dimethoxy-phosphoryl)-ethoxymethyl]acrylic acid with mesitol followed by hydrolysis of the phosphonate groups (Figure 1.31) [29].

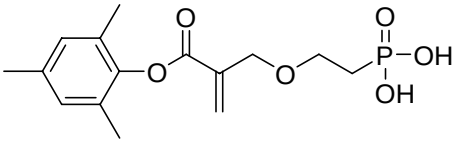


Figure 1.31. Structure of MAEPA

1.1.8. Deprotection of Phosphonates

The most conventional route toward hydrolysis of the phosphonate ester groups into phosphonic acid groups is based on silylation of the phosphonate groups with trimethyl silyl bromide (TMSBr) or tert-butyl-methoxy-phenylbromosilane (tBMPBrS) followed by methanolysis of the silyl ester groups (Figure 1.32).

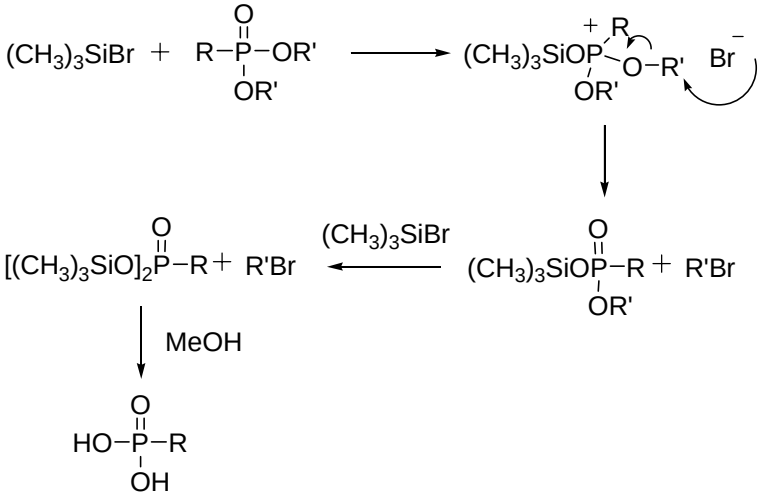


Figure 1.32. The mechanism of hydrolysis of the phosphonate groups into phosphonic acid groups

This route was used for the synthesis of many phosphonic acid-containing monomers [30]. One example is shown in Figure 1.33.

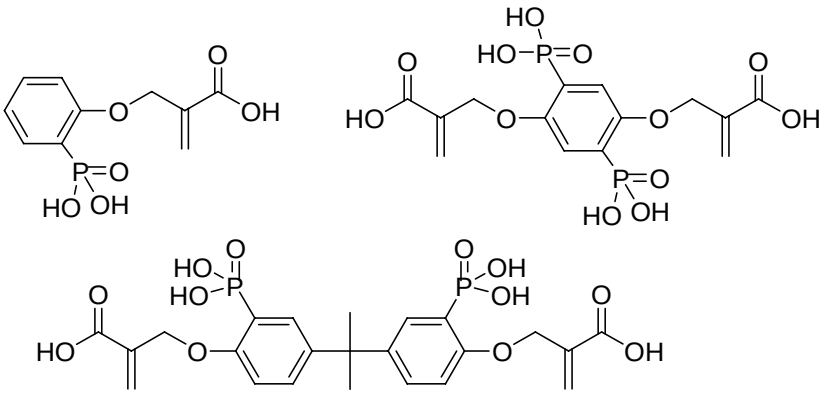
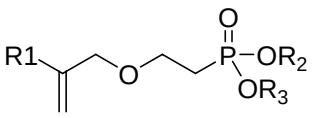


Figure 1.33. Structures of phosphonic acid-containing monomers from o-hydroxyaryl phosphonates

By using the same deprotection method, Moszner et al. demonstrated a new class of monomers in which the polymerizable group is connected to the phosphonic acid group via hydrolytically stable ether bond Figure 1.34. Therefore these monomers show an enhanced hydrolytic stability and can be used in dentine adhesives [28].



	R_1	R_2	R_3
1	$OC-OC_2H_5$	H	H
2	$OC-OC_2H_5$	H	CH_3
3	COOH	H	H
4	COOH	CH_3	$CH_3iC_2H_5$
5	COOH	H	CH_3
6	CN	CH_3	CH_3
7	CN	H	H
8	$OC-N(C_2H_5)_2$	CH_3	CH_3
9	$OC-N(C_2H_5)_2$	H	H

Figure 1.34. Examples of hydrolytically stable phosphonic acid monomers from alkyl α-hydroxymethacrylates

When they used tBMPBrS for silylation of ethyl ester monomer, they obtained phosphonic hemiacid (Figure 1.35).

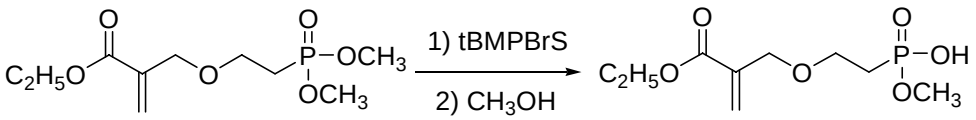


Figure 1.35. Synthesis of a phosphonic hemiacid

Asri et al. used NaBr for selective hydrolysis of the phosphonate group. Monodealkylation was performed in cyclohexanone in the presence of NaBr to give the corresponding monosalt and methyl(methacryloxy)-methyl phosphonic hemi-acid is subsequently obtained by acidification of the monosalt (Figure 1.36) [31].

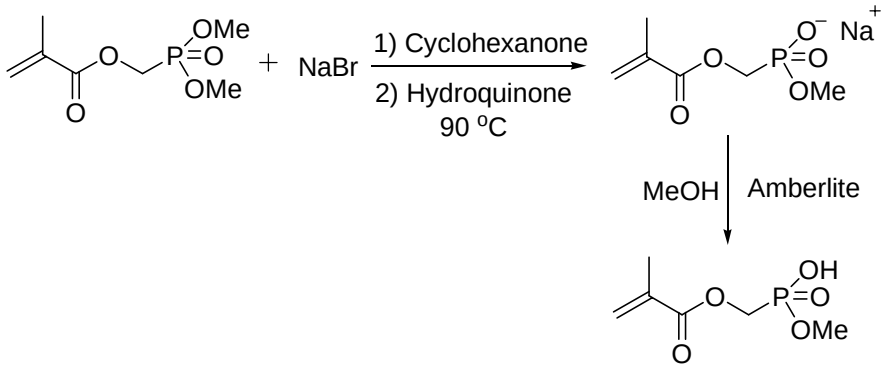


Figure 1.36. Selective hydrolysis to phosphonic hemi-acid using NaBr

The blends of organophosphorus copolymers with poly(vinylidene fluoride) (PVDF) powders were investigated to enhance adhesive and anticorrosive properties of fluoropolymer coatings. Figure 1.37 shows the synthesis of methacrylic monomers bearing phosphonic diacid and hemiacid groups from the corresponding dimethyl phosphonate monomer by two routes. The first one consists of using an excess of bromotrimethylsilane followed by a methyl alcohol hydrolysis, and the second one uses an equivalent amount of sodium iodide followed by an acidification step [32,33,34].

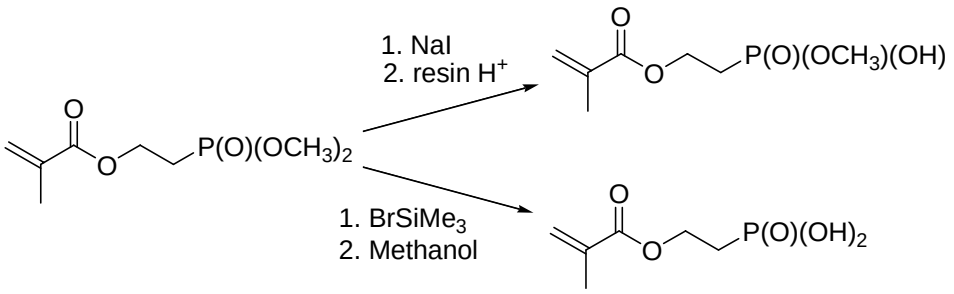


Figure 1.37. Synthesis of methacrylic monomers bearing phosphonic diacid and hemiacid groups

1.1.9. Other Reactions

Nazakin described the Michael addition of methacrylic acid on the dialkyl vinyl phosphonate, shown in Figure 1.38 [35].

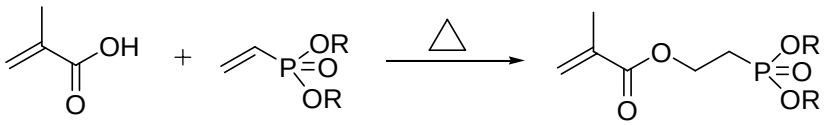


Figure 1.38. Synthesis of phosphorus-containing methacrylates by Michael addition

Carbamoyl phosphonate derivatives of methacrylic acid and α-methyl styrene were synthesized by reacting dimethyl and diethylphosphite with isocyanato ethylmethacrylate (IEM) or with meta-isopropenyl-α,α-dimethylbenzylisocyanate (m-TMI) [220]. Figure 1.39 shows the structures of dimethyl N-2-(rnethacryloyloxy)ethyl carbamoylphosphonate (IEM-DMP) and diethyl N-2 (methacryloy1oxy)ethyl carbarmoylphosphonate (IEM-DEP).

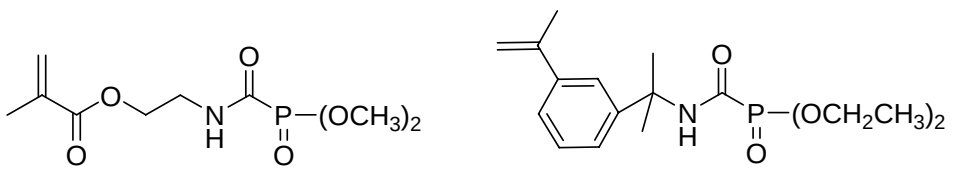


Figure 1.39. Structures of carbamoyl phosphonate monomers

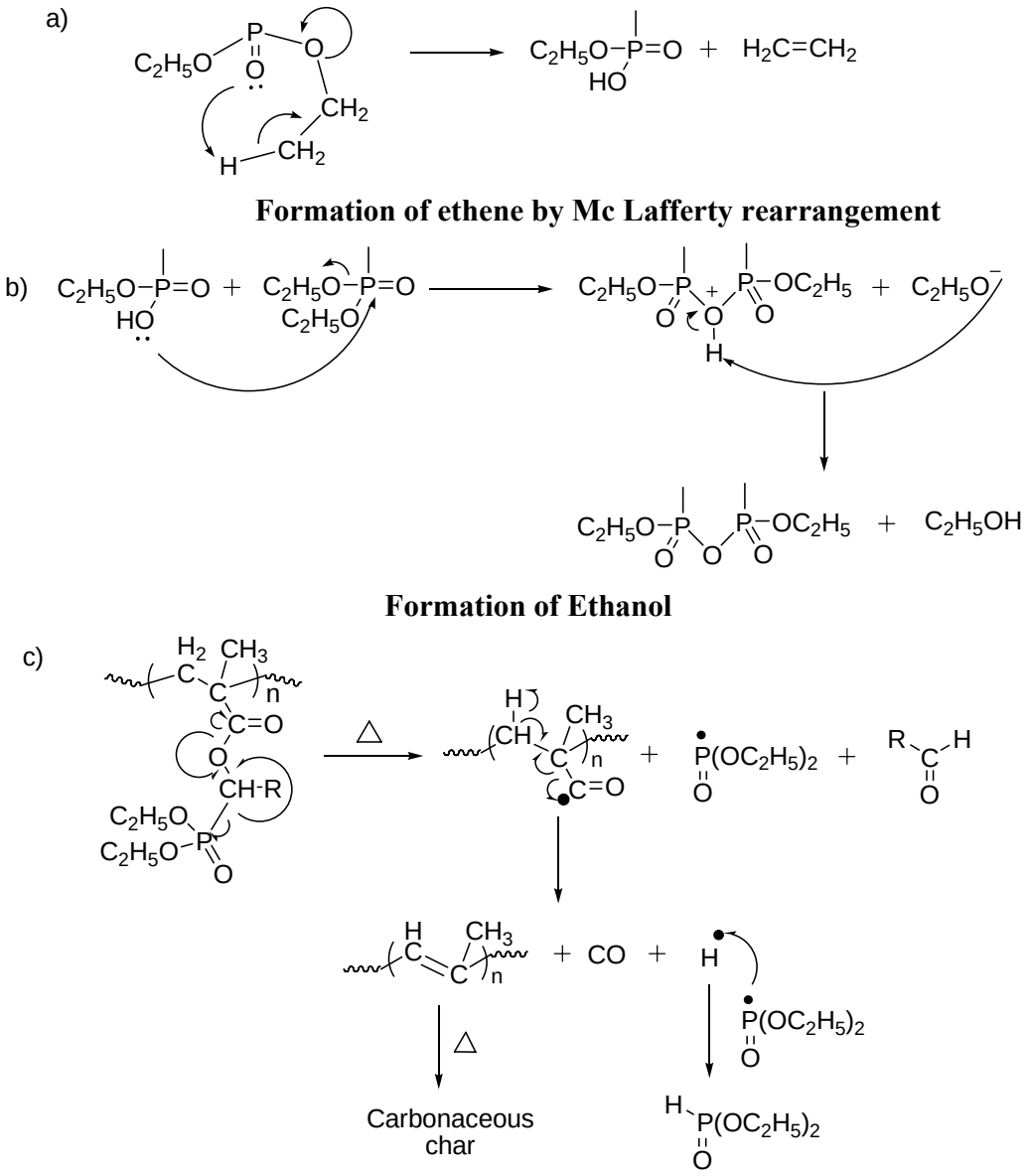
1.2. Advantages and Applications of Phosphorus-Containing Monomers and Polymers

1.2.1.Fire Retardant Materials

Flame retardants based on organic phosphorus compounds are known to be one of the most promising candidates that can replace the halogen-based flame retardants. The advantage of phosphorus-containing flame retardants is environmental friendliness. They generate less toxic gases and smoke than halogen-containing compounds.[36].

Organic phosphorus compounds act according to several mechanisms: in the condensed phase or in the gas phase. [37]. In the solid state, poly(phosphoric acid) forms on heating which catalyzes the formation of an intumescent char to protect the surface from further burning [38].

The thermal degradation mechanism of a phosphorus-containing polymer suggested by TGA-FT-IR and pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC–MS), is shown in Figure 1.40. During the first stage (Tmax~300 ^{o}C), ethene and semiacid were formed by a McLafferty rearrangement. Then –P-OH reacts with another phosphonated group to form P–O–P inter- or intramolecular links by giving off ethanol. The formation of other gases: diethylphosphite, aldehyde, triethyl phosphite and carbon monoxide, can be explained by a successive homolytic breaking of the side chain. At the end of the thermal degradation, polymeric chains with several double bonds, present in the residue, aromatize on heating, to give carbonaceous char [39].



Formation of ethene by Mc Lafferty rearrangement

Formation of Ethanol

Homolytic breaking of the side chain

Formation of triethylphosphite

Figure 1.40. Suggested mechanism for thermal degradation of phosphorous-containing polymers

1.2.2. Adhesives

One other interesting feature of phosphorus-containing polymers is adhesion to metals, bone and dental tissues [40,41].

1.2.2.1. Metals It is known that in coatings technology certain additives are used to improve adhesion on substrates. These compounds contain amine, silane, titanate, and phosphoric or carboxylic acid groups. Previously, Boutevin et al. were investigated the synthesis of (meth) acrylic monomer bearing phosphonic esters, phosphonic acids, and semisalts (Figure 1.41) [42].

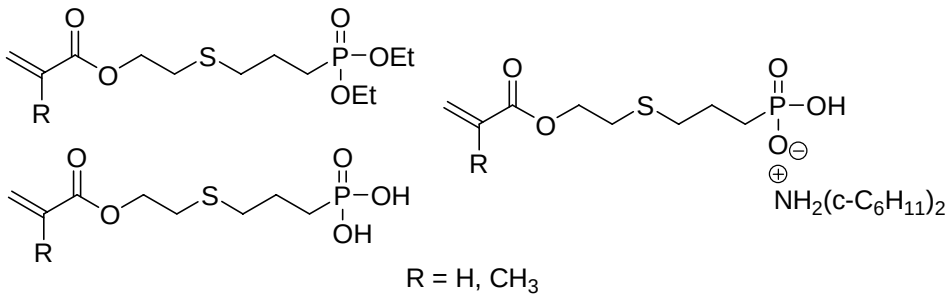


Figure 1.41. Structure of some phosphonated monomers used in coatings

Phosphonic acids and phosphonate esters are versatile complexing agents and are known to interact with a large number of transition and nontransition metal salts to form a variety of monomeric and polymeric complexes. In most of these complexes, a coordination bond is formed between the phosphoryl oxygen and the metal component of a metal salt [-C-P=O→M]. The relatively large fraction of the heavy metal salts that is miscible with the phosphonate esters reflects the strong interactions between the two species. Structures of some of the acrylated phosphonates derived from glycerol and mannitol were shown in Figure 1.42 [43].

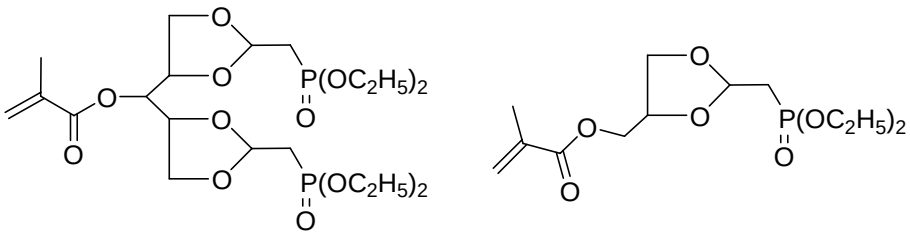


Figure 1.42. Structures of acrylated phosphonates derived from glycerol and D-mannitol

Ion exchange and adsorption are well-established techniques for the removal of trace concentrations of toxic metal pollutants from large volumes of potable water and waste-water aqueous solutions (e.g., amino methyl phosphonic acids) (Figure 1.43) [44,45]. The sorbents used for this purpose must possess good mechanical stability, resistance to aggressive media, high sorption capacity and selectivity, good kinetic properties and osmotic resistance during sequential sorption–regeneration cycles.

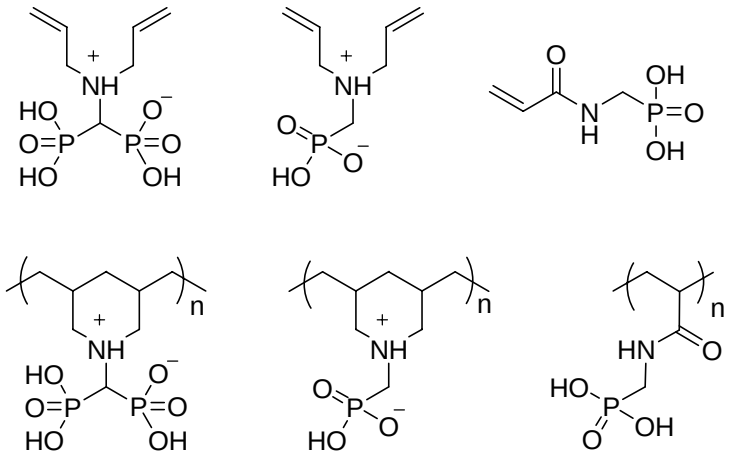


Figure 1.43. Monomeric and polymeric aminomethyl phosphonic acids

Various phosphorus-containing functional groups on the carbon surface are responsible for the improved selectivity towards lead(II) over copper(II), nickel(II) and cadmium(II). The phosphorus functionality imparts hydrophilicity and resistance towards oxidation as well as enhancing the ion-exchange properties of the carbon surface [46].

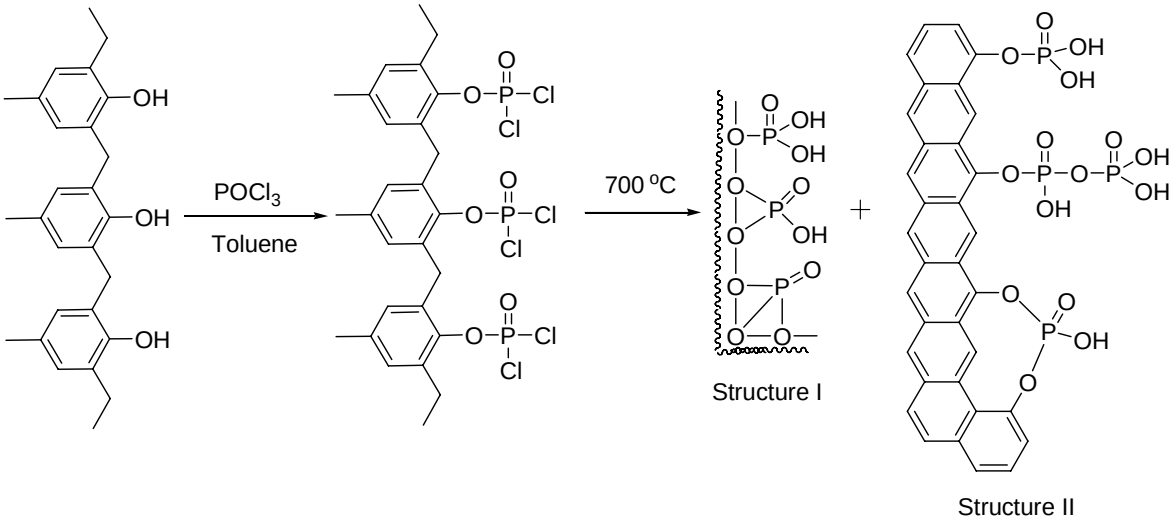


Figure 1.44. Reaction scheme of the phosphorus-containing active carbon (PGP-P)

1.2.2.2. Dental Materials Phosphorus-containing monomers with phosphoric acid, phosphonic acid and phosphinic acid esters have been synthesized and used in dental composites and dental adhesives [9,12,16,21,47].

- Dental Composites

Dental composites consist of an organic matrix and inorganic filler (Table 1.1).

Table 1.1. Typical composition of dental composites

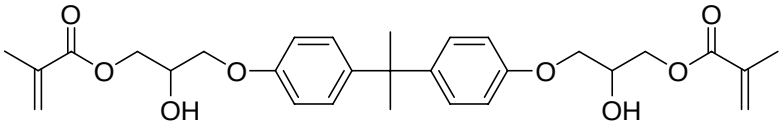
Dental composites		
Inorganic filler	75-85 wt %	Barium alumino silica glass Quartz etc..
Organic filler	15-25 wt %	Polymerizable monomers Initiator system Stabilizer, pigments

The organic matrix mainly contains methacrylic monomers, generally Bis-GMA patented by Bowen [48]. Structures of Bis-GMA and other commercial methacrylate based

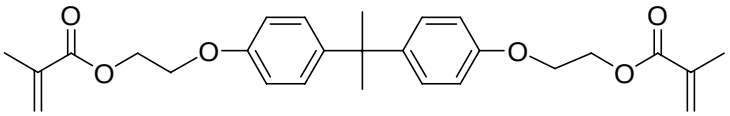
monomers used in dental composite materials are shown in Figure 1.45. Bis-GMA shows low polymerization shrinkage and good mechanical properties due to aromatic groups in its structure [49]. Reduced toxicity and diffusion to tissues are other advantages. Bis-GMA also contains hydroxyl groups which enhance the adhesion of the material to tooth. However, these groups are also responsible for high viscosity (1.0-1.2 kPa.s at 23 °C) and sorption of water. The high viscosity of Bis-GMA cause low conversion to polymer. Therefore, dilution of Bis-GMA with 30-50 wt per cent of low viscosity monomer, such as triethyleneglycol dimethacrylate (TEGDMA) and ethyleneglycol dimethacrylate (EGDMA) is required. Incorporation of diluent monomer leads to easier handling and greater extent of polymerization. The conversion of Bis-GMA/TEGDMA system has been increased to 60-75 per cent compared with 40-50 per cent conversion of Bis-GMA. However, this system has a disadvantage of increased volume shrinkage which damages the composite/tooth bonding, initiates bacterial leakage and limits the lifetime of dental composites [50,51].

Also, the residual monomer in Bis-GMA/TEGDMA system can leach into the body where various fates are possible. The unreacted monomer that remains in the restoration may act as a plasticizer and decrease the mechanical properties of the system when compared to a fully cured specimen [52].

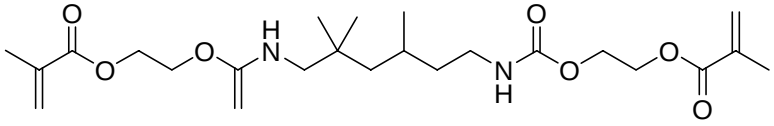
Many approaches have been developed to improve properties of dental composites. As viscosity modifiers, monomethacrylates such as tetrahydrofurfuryl methacrylate (THFMA), hydroxypropyl methacrylate (HPMA) and isobornyl methacrylate (IsoBMA) were copolymerized with Bis-GMA. Although copolymerization of Bis-GMA with these monomethacrylates exhibited lower shrinkage than Bis-GMA/TEGDMA, conversions to polymer were decreased [53].



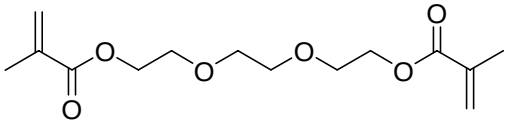
Bisphenol A glycolate dimethacrylate (Bis-GMA)



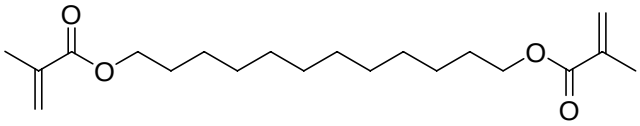
Bisphenol A ethoxylated dimethacrylate (EBPDMA)



Urethane dimethacrylate (UDMA)



Triethyleneglycol dimethacrylate (TEGDMA)



Dodecanediol dimethacrylate (D_3MA)

Figure 1.45. Structure of dimethacrylates frequently used in dental composites

New acrylic monomers with oxetane, dioxolane, oxazolidone, carbonate, carbamate, morpholine groups were found to be very promising to replace TEGDMA as reactive diluents (Figure 1.46) [54]. These monomers showed very high polymerization rates and gave crosslinked polymers due to chain transfer reactions.

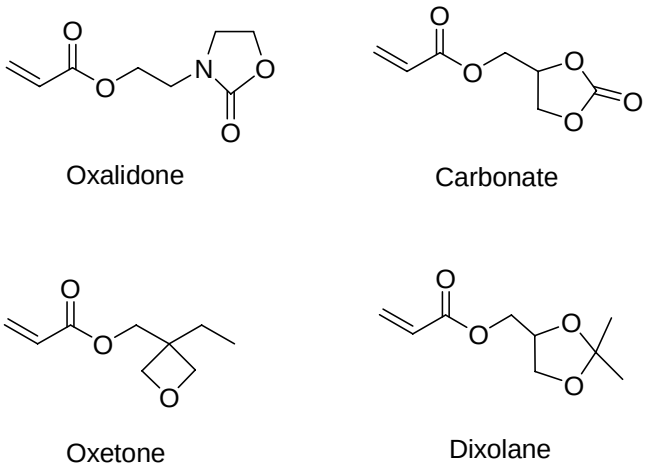


Figure 1.46. Acrylic monomers containing oxetane, dioxolane, oxalidone or carbonate groups

As an alternative way of eliminating TEGDMA from Bis-GMA/TEGDMA resin system, Moszner et al. introduced multifunctional urethane methacrylates with lower viscosity than Bis-GMA, comparable mechanical properties with Bis-GMA and improved hydrolytic stability. Some urethane dimethacrylates proposed are shown in Figure 1.47 [55].

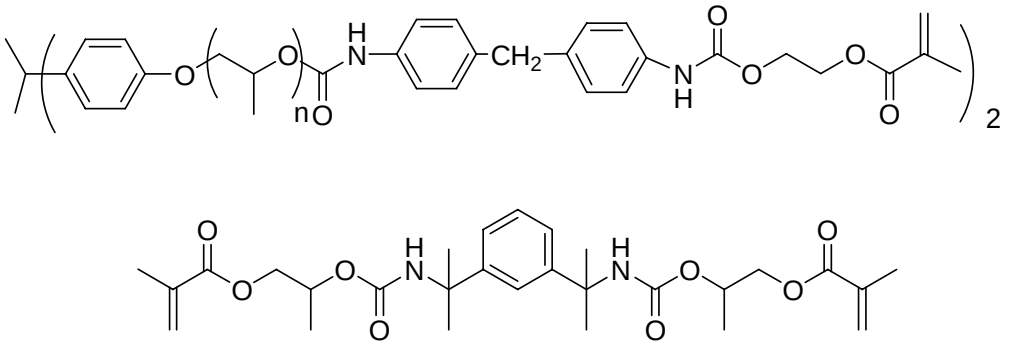


Figure 1.47. Examples of urethane dimethacrylates

Fluorinated resins can provide inert polymers that display excellent hydrophobicity and resistance to softening by a wide range of chemicals. Therefore several investigations have examined a variety of fluorinated monomers for use in dental resins as additive

comonomers that would favorably reduce water uptake and possible polymerization shrinkage [56].

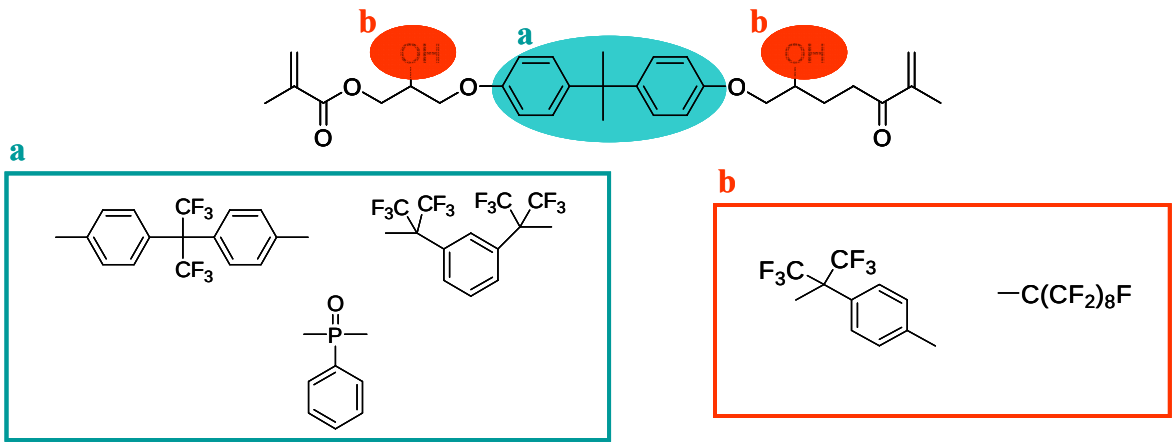


Figure 1.48. Fluorinated Bis-GMA analogs

One of the major problems encountered with the dental compositesis the lack of bonding to the tooth material. To address that problem, novel monomers with binding ability have been designed. In general this binding ability is provided by acid functionalized groups such as carboxylic, phosphonic and phosphoric acids, which form chelates with the calcium ions in the tooth surface.

Recently phosphonated mono and dimethacrylate monomers were synthesized for their potential use in dental composites. Sibold et al. studied on the reactivity of phosphonated aromatic methacrylate monomers synthesized from thiols or bis-thiols with GMA (Figure 1.11) [9]. Due to the presence of phosphonate functions, their adhesive bonding properties were better to that of the bisphenol A type epoxy resin.

Mou et al. synthesized a phosphonic acid monomer for use in dental composites by the base-catalyzed rearrangement of the corresponding diethyl aryl phosphonate [47]. They claimed that this aromatic monomer would yield materials with improved binding ability to tooth tissue and mechanical properties (Figure 1.49).

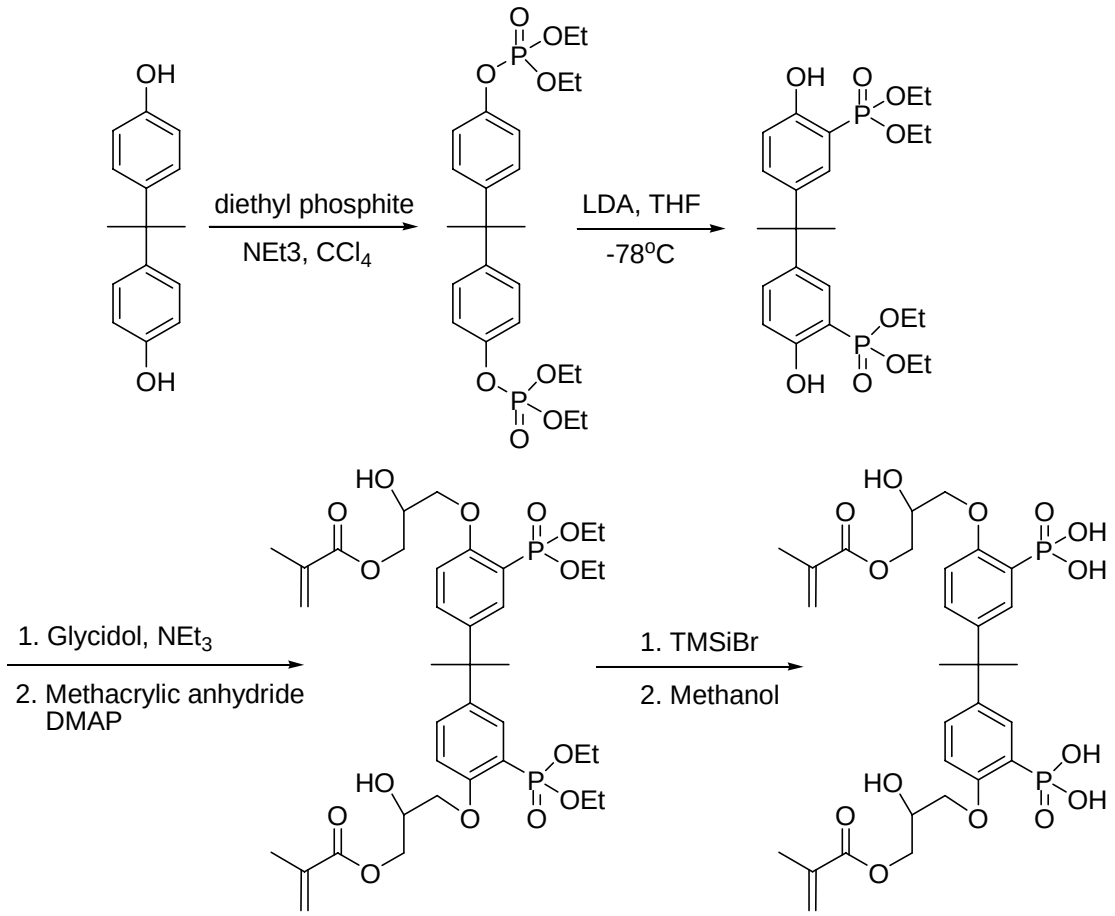


Figure 1.49. Synthesis of a phosphonic acid-containing dimethacrylate monomer

- Dental Adhesives

Formation of a strong and permanent bond between composite filling material and tooth tissue (dentin and enamel) increases life time of dental materials. Two different techniques can be used to achieve good bonding efficiency: acid etching and self-etching methods. In acid etching method, an acidic conditioner (generally 37 % solution of phosphoric acid) removes the smear layer by demineralizing the hydroxyapatite and generates a surface with cavities in which monomers can diffuse. After it is applied, washing with water and drying of tooth surface is necessary [57].

In the other technique, self-etchning adhesive systems are used. Major advantage of self-etching systems is that there is no need to be rinsed off. Commercial self-etching

adhesive systems consist of a mixture of self-etching adhesive monomers, cross-linking monomers and additives (Figure 1.50) [58].

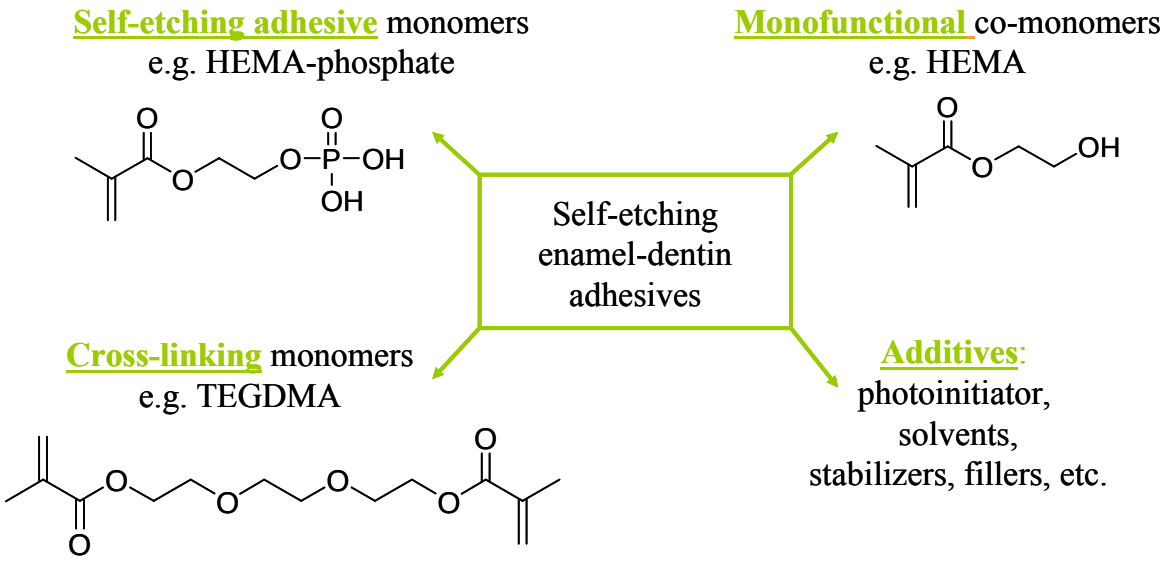


Figure 1.50. Components of currently available self-etching enamel-dentin primers/adhesives

All of the monomers used in self-etching systems should have the following properties;

- High rate of free-radical homopolymerization or copolymerization with the other monomers in the adhesive set.
- Optimal solubility in the aqueous solutions of acetone and ethanol, which are mainly used solvents in commercial self-etching adhesives.
- Sufficient stability of the monomer and the polymer against premature polymerization and also against degradation by oxygen, light, heat and water during storage.
- Minimal water uptake and low swelling degree of the formed polymer.
- Low shrinkage of the monomers during polymerization.
- Low oral toxicity and cytotoxicity of the monomers.

The general structure of a self-etching adhesive monomer is given in Figure 1.51.

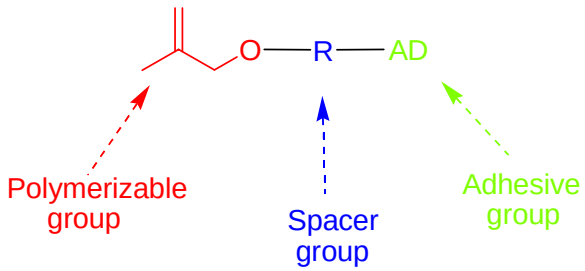


Figure 1.51. General structure of a self etching adhesive monomer

Polymerizable group reacts both with the other monomers of the adhesive and the restorative material by copolymerization. Generally free-radically polymerizable, methacrylate functionalized monomers are used. (Figure 1.52).

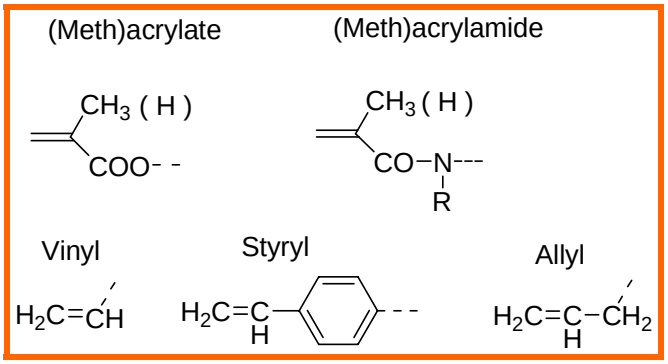


Figure 1.52. Example of polymerizable groups

Spacer groups have an effect on the adhesive monomer by changing solubility, flexibility, volatility and wetting properties. Figure 1.53 shows common examples of spacer groups.

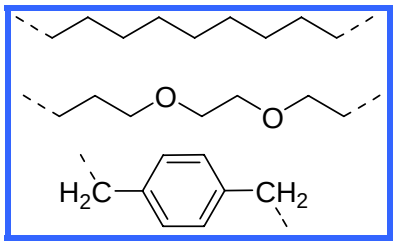


Figure 1.53 Examples of spacer groups R in adhesive monomers

The adhesive group (AD) has the capability of penetrating, for example, into the dentinal tubules and interacts with components of the dental hard tissue. As a result, ionic bonds are formed by the acidic groups reacting with the main inorganic component of the dental hard tissue, which is hydroxyapatite. A great number of acidic monomers with the potential for generating a self-etching enamel–dentin adhesive have been described in the literature (Figure 1.54).

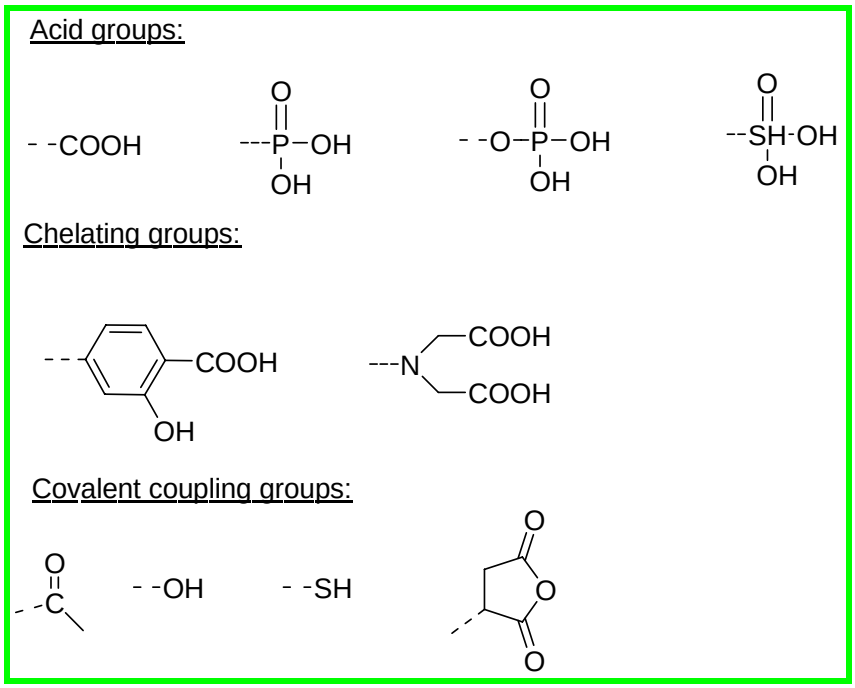


Figure 1.54. Adhesive groups AD enable chemical adhesion to enamel or dentin

Suitable adhesive groups are acidic groups such as phosphonic acid and mono-or dihydrogenphosphate groups, which form stronger acids than the corresponding carboxylic acids. The acidity of the monomers increases in the following order:

carboxylic acids < phosphonic acids < acid phosphates < sulfonic acids

Examples of commercial adhesive monomers are, 4-methacryloyloxyethyl trimellitic acid (4-MET), 10-methacryloyloxydecyl dihydrogen phosphate (MDP), methacryloyloxyethyl phenyl hydrogen phosphate (MEP-P) and methacryloyloxyethyl dihydrogen phosphate (MEP, HEMA-phosphate), [58].

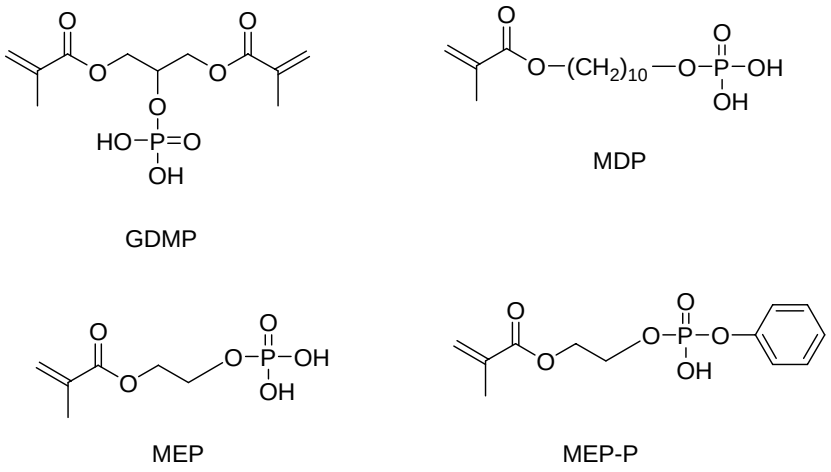


Figure 1.55. Examples of polymerizable acidic phosphates used in dentin adhesives

The adhesive monomers based on alkyl α-hydroxy methacrylates (RHMA) and containing both phosphorus and carboxylic acid groups were synthesized by our group previously (Figure 1.56) [25,30].

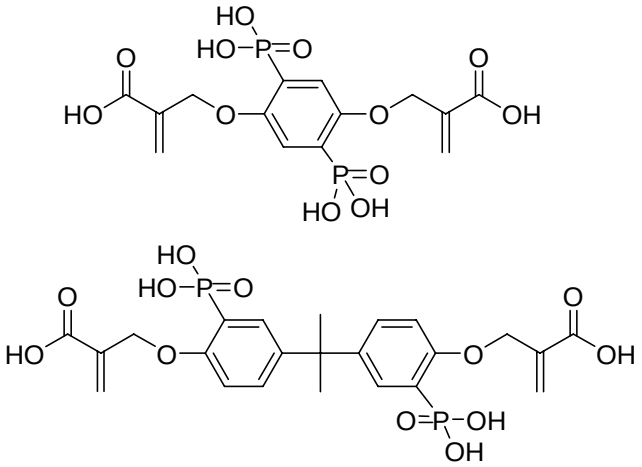


Figure 1.56. The structures of adhesive monomers based on RHMA

The invention of more hydrolytically stable acrylic phosponic acids have improved the self-etching adhesive systems remarkably [27]. Figure 1.57 shows the structures of some acrylic groups containing phosphonic acids, synthesized by Moszner et al.

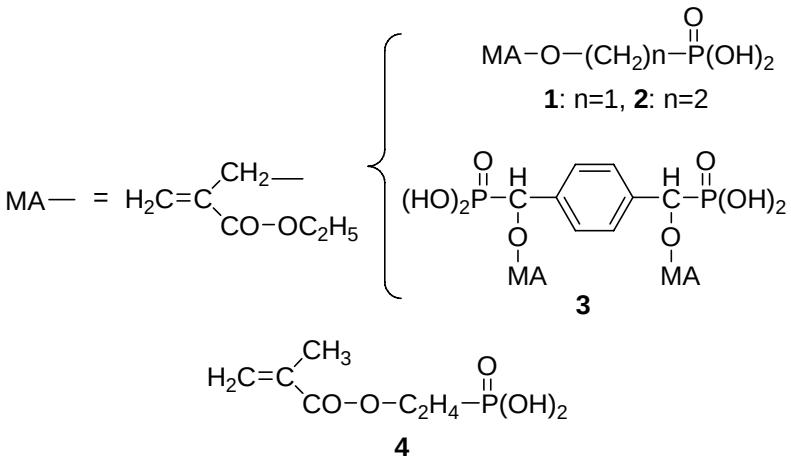


Figure 1.57. Structures of some acrylic groups containing phosphonic acids

Monofunctional co-monomers and cross-linking monomers are also have importance in influencing the properties of self-etching adhesives system. Mostly used comonomer is HEMA due to its low viscosity and high solubility in water and other components of adhesive system.

Cross-linking monomers in commercial adhesives also play an important role in polymerization rate of the system and mechanical properties of the cured dental material. They form polymer network and polymerization rate increases due to gel effect. Insoluble crosslinked layer formed leads to lower volume shrinkage. Mechanical properties are also increased with respect to linear polymers [12]. Most common cross-linking dimethacrylates used in dentin adhesives are TEGDMA, Bis-GMA, UDMA, and GDMA.

1.3. Photopolymerization

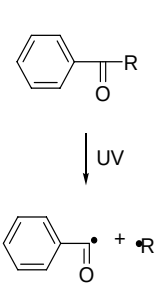
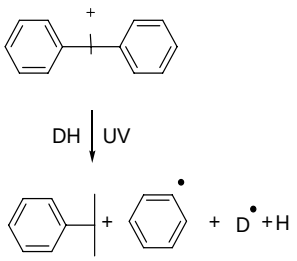
Light-induced polymerization of multifunctional monomers or oligomers, also called UV radiation curing, has become a well-accepted technology in dental applications. Photopolymerization provide a fast process at room temperature. In addition to this, the process is solvent-free, energy efficient and generally economical.

Polymerizable systems are usually made of three main components [51]:

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

There are two types of photopolymerization depending on the way chain reaction proceeds; cationic type or radical type mechanism. In radical type polymerization, aromatic ketones are used as initiators to generate free radical and initiate the polymerization of vinyl monomers by a step growth addition mechanism to get crosslinked polymer network. However, in cationic type polymerization, a protonic acid is produced by photolysis of triarylsulfonium (TAS) or diaryliodonium salts to initiate the polymerization of epoxides or vinyl ethers [59]. Radical type system is mostly prefered in photo-induced curing applications.

Table 1.2. Radical and cationic types of photopolymerization

Mechanism	RADICAL	CATIONIC
Photoinitiator	Aromatic ketone 	Aryliodonium salt 

1.3.1. Photoinitiators

Photoinitiators have an important role in dental polymerizable systems. Presence of suitable photoiniator is effective on both the rate of polymerization and penetration of incident light into the sample. 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 such as iodonium and sulphonium salts and arene complexes which are able to initiate polymerizations via both cationic and radical processes.

There are two types of mechanism that produces the free-radical intermediates upon irradiation of the initiators [60]. Type-I describes the photofragmentation that generates radical pairs through a highly efficient L- cleavage process. Type-I class includes aromatic carbonyl compounds that are known to undergo a homolytic C-C bond scission upon UV exposure. Figure 1.58 shows mechanism of initiation as an example to type-I initiator. The most efficient photointiators include benzoin ether derivatives, benzyl, ketals, hydroxyalkylpheneones, L-aminoketones and acylphosphine oxides.

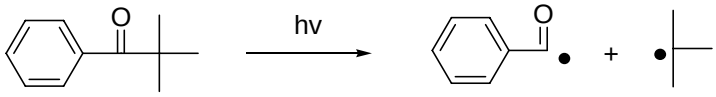


Figure 1.58. Example to type-I initiator

Type-II systems, in which photofragmentation that generates radical pairs through the H abstraction process from donor molecules, consist of two components which are aromatic ketone and a radical precursor. H-donor radical initiates polymerization by generating a ketyl radical and a donor radical from an aromatic ketone (Figure 1.59). Other examples are xanhones, thioxanthones, aromatic diketones, phenyl glyoxalates, 3-ketocoumarins, camporquinone, etc.

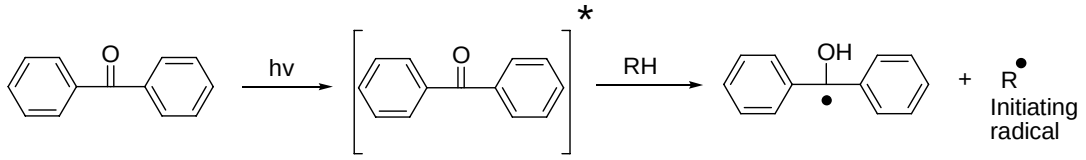


Figure 1.59. Example to type-II photoinitiator

The structures of some photoinitiators which are commonly used in both dentistry and other applications are shown in figure 1.60.

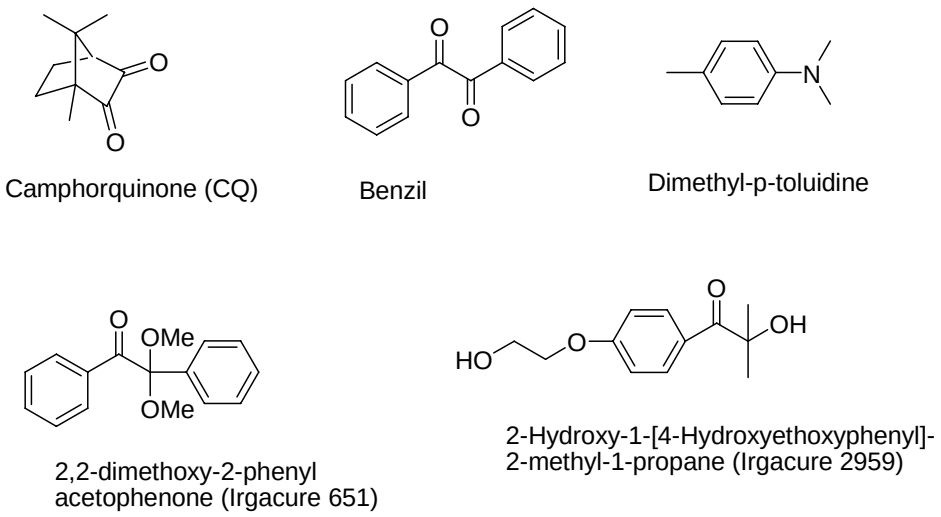


Figure 1.60. Commonly used initiators

Among these initiators, Camhorquinone (CQ) is widely used in visible light curing dental materials [61,62]. Camphorquinone (CQ) which has an absorption maximum at 468 nm is commonly used as the photoinitiator along with an amine accelarator such as ethyl p-dimethylaminobenzoate (DMAB) as a co-initiator (CI) in dental composites. In this case initiating radicals are formed via proton and electron transfer (Figure 1.61).

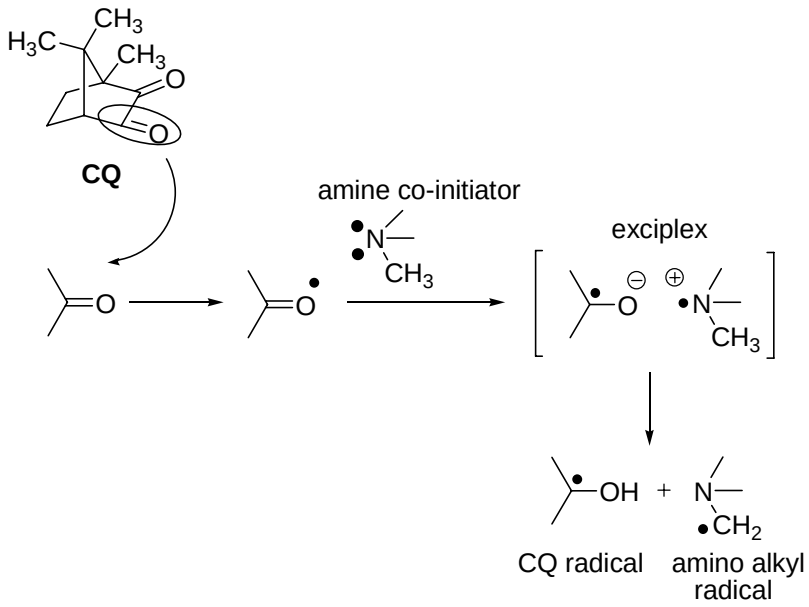
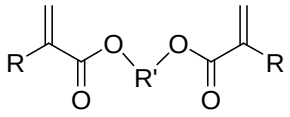


Figure 1.61. Initiator system for camphorquinone type initiators

1.3.2. Monomers

In photoinitiator systems, multifunctional acrylates and methacrylates are commonly used monomers due to their high reactivity. Figure 1.62 shows the general structure of the commonly used acrylate/methacrylate based resin systems [60].



R= H, CH_3
R' = polyether, polyester

Figure 1.62. 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 1.63).

The rate of mono or multi-functional (meth)acrylate polymerizations depends on many factors such as reactivity of the functional groups, its concentration, viscosity of the resin, distance and flexiblity between the functional groups, etc. These factors determine the final degree of polymerization, as well as the physical and chemical characteristics of the UV-cured polymer [60].

Three main mechanistic theories for the possible enhanced reactivity of these monoacrylates have been hypothesized, which include hydrogen abstraction and subsequent chain transfer, hydrogen bonding, and electronic and resonance effects.

Firstly, Decker et al. proposed a highly efficient hydrogen abstraction mechanism and subsequent chain transfer reaction to account for the increased reactivity and cross-linked polymer formation [54,59]

Importance of hydrogen bonding on the rate of acrylate photoinitiated polymerization was described by Jansen et al. [63]. It has been shown that hydrogen

bonding to the carbonyl group could alter the electron density of the acrylate double bond, thereby enhancing the rate constant for propagation. It was found that acrylates with urethane and amide side groups capable of hydrogen bonding exhibited very fast polymerization rates at room temperature: at high temperatures the rates decreased along with a reduction in the extent of hydrogen bonding measured by infrared analysis. He also determined that the rate of polymerization (R_p) of the hydrogen-bonding monomer, undecyl amide *N*-ethyl acrylate, was 9 mol/(L s) while the non-hydrogen-bonding analogue pentyl amide *N*-methyl *N*-ethyl acrylate gave a much lower R_p of 1.9 mol/(L s).

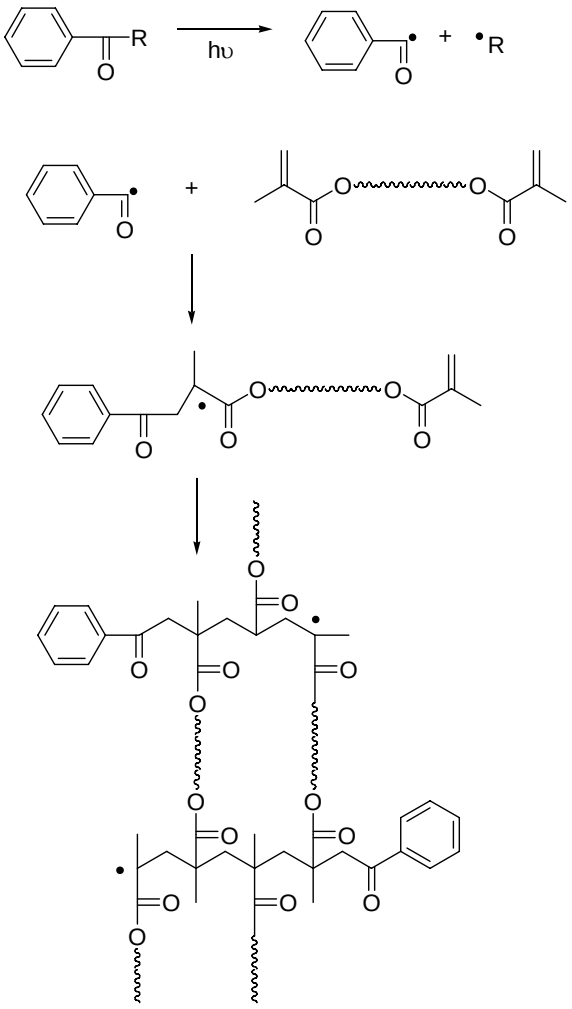


Figure 1.63. Mechanism of the photopolymerization of a dimethacrylate monomer

Jansen also reported that when the dipole moment (μ_{calc}) is above a threshold value (~ 3.5), the polymerization rate of some novel monoacrylates increases linearly with dipole moment (electronic effect) [63,64].

Andrzejewska et al. reported the effect of heteroatoms including oxygen and sulfur in enhancing the rate of dimethacrylate polymerization in the presence and absence of oxygen as a function of temperature [60].

1.3.3. Light sources

Another important factor in the photo-curing process is the light source because the initiation rate strongly depends on the light intensity. There are two types of light sources mainly used:

i. Arc light
ii. Laser light

An arc lamp produces light by an electric arc (or voltaic arc). The lamp consists of two electrodes typically made of tungsten which are seperated by a gas. When a direct current is applied through electrodes, the gas is discharged and light is emitted. The most commonly used gases contained in the bulb are mercury, xenon, sodium, metal halide, and mercury [65].

The word 'LASER' is an acronym which stands for 'Light Amplification by Stimulated Emission of Radiation'. Lasers offer the prospect of an excitation source of exceedingly high intensity compared to classical light sources. The outputs of a laser are available in both UV and visible wavelengths. Some lasers offer fixed wavelength, whereas some others offer tunable wavelengths [65]. In dentistry, 420-500 nm light in visible region is used.

1.3.4. Photopolymerization kinetics

Photopolymerization can be studied with various methods such as differential scanning calorimetry, dilatometry, fluorescence spectroscopy and RT-FT-IR spectroscopy.

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 equations in Figure 1.64.

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 (0.3 s), 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 (Figure 1.65) [65].

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

(Q/s) : heat flow per second during reaction
M : molar mass of the monomer
n : number of double bonds per monomer molecule
ΔHp : 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
e : extinction coefficient of the initiator
[A] : initiator concentration

Figure 1.64. Equations of the rate of polymerization

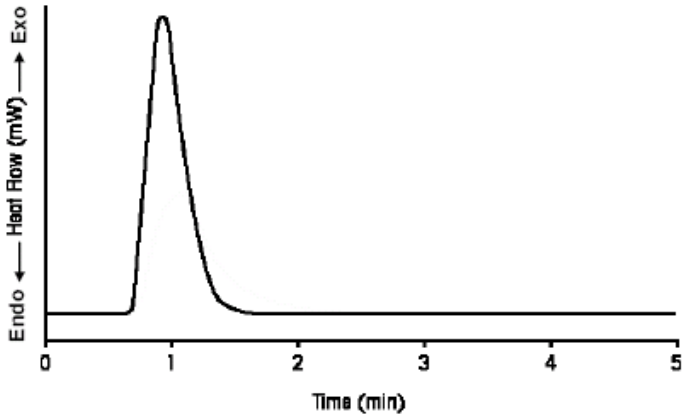


Figure 1.65. Representative heat flow versus time plot obtained from differential scanning calorimetry technique

1.3.5. 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 information storage systems, aspherical lenses for CD applications, microcircuits, and contact lenses are some of the other areas which photocuring technology is used [59,63,66].

2. OBJECTIVES

Our goal is to synthesize new reactive phophonates, phosphonic acids and phosphate-containing monomers and investigate their polymerization behavior.

Phosphonic acid-containing monomers are expected to have properties such as solubility in water and ethanol, homo- and copolymerization reactivity and binding ability in the ranges desired for dental materials. The phosphonate- and phosphate-containing monomers have potential in dental materials (reactive diluents) and flame retardants.

The monomers to be synthesized are based on methacrylate esters of o-hydroxyaryl phosphonates, phosphonate esters of RHMA and phosphate esters of GMA.

The properties to be investigated are photopolymerization behavior, binding ability (to HAP for potential dental materials) and various properties of their polymers.

3. EXPERIMENTAL

3.1. Materials and Apparatus

3.1.1. Materials

Diethyl (2-hydroxyphenyl) phosphonate, tetraethyl (2,5-dihydroxy-1,4-phenylene)bisphosphonate and 2-(chloromethyl)acryloyl chloride (CMAC) were synthesized using literature procedures [67,68,69,70]. Glycidyl methacrylate (GMA), glycerol dimethacrylate (GDMA), diethyl chlorophosphate (DECP), triethyl amine (TEA), 2-hydroxyethyl methacrylate (HEMA), 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propyloxy) phenyl] propane (Bis-GMA), Hydroxyapatite (HAP), methyl methacrylate (MMA), t-butyl acrylate, thionyl chloride ($SOCl_2$), lithium diisopropylamide (LDA), phenol, hydroquinone, 1,4-diazabicyclo[2.2.2]octane (DABCO) and Na_2SO_4 were purchased from Aldrich and used as received. Trimethylsilyl bromide (TMSBr) (Aldrich, Taufkirchen, Germany) was distilled before use. Methacryloyl chloride was obtained from Fluka and distilled before use. (2-hydroxy-ethyl)-phosphonic acid dimethyl ester was a gift from Ivoclar Vivadent.

The photoinitiators 2,2-dimethoxy-2-phenylacetophenone (DMPA from Aldrich) and bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide (BAPO from Aldrich) and thermal initiators azobisisobutyronitrile (AIBN from Fluka) and 2,2'-azo-bis(2-amidinopropane)dihydrochloride (V-50 from Aldrich) were used as recieved.

3.1.2.Apparatus

^{1}H, ^{13}C and ^{31}P-NMR spectroscopies were taken with Varian Gemini 200 MHz instrument. Fourier transform infrared (FT-IR) spectroscopy was performed on a Thermo Scientific Nicolet 380 FT-IR spectrophotometer. Photopolymerizations were carried out on a TA Instruments Q100 differential photocalorimeter (DPC). Thermogravimetric analysis

(TGA) was carried out with a TA Instruments (Q50). Gel permeation chromatography (Viscotek) was carried out with THF solvent using polystyrene standarts.

3.2. Synthesis of Novel Phosphonated Monomers

3.2.1. Synthesis of Monomers from o-Hydroxyaryl Phosphonates

3.2.1.1. Synthesis of Diethyl (2-hydroxyphenyl) Phosphonate To a mixture of phenol (8.80 g, 93.5 mmol) and diethylphosphite (18 ml, 143.5 mmol) in 40 ml CCl_4, TEA (20 ml, 143.5 mmol) was added dropwise in an ice bath. The reaction mixture was stirred overnight at room temperature. Then, it was extracted with water and the organic layer was dried with Na_2SO_4. After removal of solvent, diethyl phenyl phosphate was obtained as yellow liquid in a 86 per cent yield.

To a mixture of 25 ml THF and 25 ml LDA (2M, 0.050 mol) at -78 ^oC diethyl phenyl phosphate (5.23 g, 0.023 mol) in 25 ml THF was added. The mixture was stirred for 1 h at -78 ^oC and stirring was continued at 0 ^oC for an additional 30 min. The mixture was poured to a mixture of 75 ml of saturated aqueous NH_4Cl and 75 ml ether. The organic layer was separated and dried with anhydrous Na_2SO_4. After removal of solvents a red liquid was obtained. The pure product, diethyl (2-hydroxyphenyl) phosphonate was obtained as a yellow viscous liquid after column chromatography, using hexane:CH_2Cl_2 (50:50) initially and gradually changing to CH_2Cl_2:MeOH (100:1) as eluent. (85 per cent yield).

^{1}H-NMR ($CDCl_3$): δ= 1.26 (t, 6H, CH_2-C*H*$_3$), 4.04 (m, 4H, C*H*$_2$-CH_3), 6.84, 7.29 (dd, 2H, CH-Ar), 6.89, 7.38 (t, 1H, CH-Ar), 10.19 (s, 1H, -OH) ppm.

^{13}C-NMR ($CDCl_3$): δ= 16.6 (*C*H_3-CH_2), 63.1 (CH_3-*C*H_2), 107.9, 109.8 (d, C-P), 118.0, 119.8, 131.9, 135.4 (Ar-CH), 162.4 (C(Ar)-O) ppm.

FT-IR (NaCl): 3075 (b, -OH), 2984 (m, C-H), 1598, 1446 (m, C=C), 1391, 1197 (m, C-O), 1250 (m, P=O), 1163/cm (P-OEt).

3.2.1.2. Synthesis of Tetraethyl (2,5-dihydroxy-1,4-phenylene)bisphosphonate To a mixture of hydroquinone (3.96 g, 36.0 mmol) and diethylphosphite (10.38 g, 75.3 mmol) in 24 ml CCl_4, TEA (7.56 g, 75.0 mmol) was added dropwise at 0 ^oC. The reaction mixture was stirred overnight at room temperature. Then, it was extracted with water and the organic layer was dried with Na_2SO_4. After removal of solvent, 1,4-phenylene tetraethyl diphosphate was obtained as light brown liquid in a 72 per cent yield.

To a mixture of 25 ml THF and 25 ml LDA (2M, 0.050 mol) at -78 ^oC 1,4-phenylene tetraethyl diphosphate (4.29 g, 0.011 mol) in 25 ml THF was added. The mixture was stirred for 1 h and stirring was continued at 0^oC for an additional 30 min. The mixture was poured to a mixture of 50 ml of saturated aqueous NH_4Cl and 50 ml ether. The organic layer was separated and dried with anhydrous Na_2SO_4. After removal of solvents a red liquid was obtained. The pure product was obtained as a light yellow liquid after recrystalization in ethyl acetate in 86 per cent yield.

^{1}H-NMR ($CDCl_3$): δ= 1.34 (t, 12H, CH_2-C*H*$_3$), 4.19 (q, 8H, C*H*$_2$-CH_3), 7.10 (s, 2H, CH-Ar), 9.62 (s, 2H, -OH) ppm.

^{13}C-NMR ($CDCl_3$): δ= 15.2 (*C*H_3-CH_2), 62.2 (CH_3-*C*H_2), 114.1, 116.2 (d, C-P), 118.0 (Ar-CH), 152.5 (C(Ar)-O) ppm.

FT-IR (NaCl): 3076 (b, -OH), 2985 (m, C-H), 1523 (m, C=C), 1406, 1198 (m, C-O), 1284 (m, P=O), 1162,974/cm (P-OEt).

3.2.1.3. Monomer **1.** To a mixture of diethyl (2-hydroxyphenyl) phosphonate (1.92 g, 8.34 mmol) and TEA (1.6 g, 15.84 mmol) in an ice bath methacryloyl chloride (1.08 g, 10.43 mmol) in THF (12 ml) was added dropwise under N_2. After 12 h of stirring at room temperature, the solution was filtered and the solvent was evaporated. The residue was dissolved in petroleum ether and stored in the refrigirator for a day. The crude product precipitated as a brown oil, was purified by column chromatography using hexane initially and gradually changing to CH_2Cl_2 as eluent. The pure product was obtained as a viscous yellow oil in a 74.8 per cent yield.

^{1}H-NMR ($CDCl_3$): δ= 1.3 (t, 6H, C*H*$_3$-CH_2), 2.1 (s, 3H, CH_3-C), 4.0-4.1 (m, 4H, CH_2-O), 5.8, 6.4 (s, 2H, CH_2=C), 7.1, 7.3 (t, 2H, CH-Ar), 7.6, 8.0 (m, 2H, CH-Ar) ppm.

^{13}C-NMR ($CDCl_3$): δ= 16.2 (*C*H_3-CH_2), 18.3 (*C*H_3-C), 62.3 (CH_2-O), 120.3, 122.1 (C-P), 123.7, 125.8, 133.8, 135.0 (Ar-CH), 127.8 (*C*H_2-C), 135.6 (*C*-CH_2), 152.4 (C(Ar)-O), 165.4 (C=O) ppm.

FT-IR: 2984 (C-H), 1739 (C=O), 1633 (C=C), 1243 (P=O), 1014/cm (P-OEt).

^{31}P-NMR ($CDCl_3$): 16.3 ppm.

3.2.1.4. Monomer **1a.** TMSBr (0.51 g, 3.35 mmol) was added dropwise to a solution of monomer **1** (0.2 g, 0.67 mmol) in 2 ml of dried dichloromethane in ice bath under nitrogen and then the solution was refluxed at 40 ^{o}C for 2 h. After evaporation of the solvent, 2 ml of methanol was added and the mixture was stirred at room temperature for 18 h. After evaporation of methanol two different products were obtained. These are monomer **1a** and diethyl 2-hydroxyphenyl phosphonic acid.

^{1}H-NMR ($CDCl_3$): δ= 1.9 (s, 3H, CH_3-C), 5.6, 6.2 (s, 2H, CH_2=C), 6.6-6.7 (m, 2H, CH-Ar), 7.0, 7.3, 7.4, 7.7 (m, 4H, CH-Ar) ppm.

3.2.1.5. Monomer **2.** To a mixture of tetraethyl (2,5-dihydroxy-1,4-phenylene) bisphosphonate (0.38 g, 1.0 mmol) and TEA (0.24 g, 2.4 mmol) in an ice bath methacryloyl chloride (0.25 g, 2.4 mmol) in THF (8 ml) was added dropwise under N_2. After 12 h of stirring at room temperature, the solution was filtered and the solvent was evaporated. The residue was diluted with 5 mL of CH_2Cl_2 and extracted with water (3 mL). After the drying of the organic phase with anhydrous Na_2SO_4 and the evaporation of the solvent, the residue was recrystallized from acetone. The white, solid product with a melting point of 132 ^{o}C was obtained in 31 per cent yield.

^{1}H-NMR ($CDCl_3$): δ= 1.3 (t, 12H, C*H*$_3$-CH_2), 2.1 (s, 6H, (CH_3)-C), 4.0-4.1 (m, 8H, CH_2-O), 5.8, 6.4 (s, 4H, CH_2=C), 7.8 (m, 2H, CH-Ar) ppm.

^{13}C-NMR ($CDCl_3$): δ= 16.1 (CH_3-CH_2), 18.2 (CH_3-C), 62.7 (CH_2-O), 126.4 (d,C(Ar)-P), 128.2 (CH_2-C), 130.1 (C-CH_2), 135.2 (Ar-CH), 149.3 (C(Ar)-O), 165.1 (C=O) ppm.

FT-IR: 2987 (C-H), 1745 (C=O), 1632 (C=C), 1244 (P=O), 1018/cm (P-OEt).

^{31}P-NMR ($CDCl_3$): 13.1 ppm.

3.2.1.6. Monomer **2a.** TMSBr (0.36 g, 2.35 mmol) was added dropwise to a solution of monomer **2** (0.28 g, 0.53 mmol) in 2 ml of dried dichloromethane in ice bath under nitrogen and then the solution was refluxed at 40 ^{o}C for 2 h. After evaporation of the solvent, 7 ml of methanol was added and the mixture was stirred at room temperature for 18 h. After evaporation of methanol the residue was washed with ether and acetonitrile twice and pure product was obtained as a white solid in 92 per cent yield.

^{1}H-NMR ($CDCl_3$): δ= 2.1 (s, 6H, (CH_3)-C), 5.8, 6.4 (s, 4H, CH_2=C), 7.7 (m, 2H, CH Ar) ppm.

^{13}C-NMR ($CDCl_3$): δ= 18.5 (CH_3-C), 128.7 (CH_2=C), 129.5, 129.6 (d,C-P), 130.2 (C=CH_2), 136.9 (Ar-CH), 150.6 [C(Ar)-O], 166.9 (C=O) ppm.

FT-IR: 2677 (O-H), 1740 (C=O), 1633 (C=C), 1470, 1376 (C=C, arom.), 1309 (P=O), 1177, 1092, 1061 (C-O), 1017, 925, 592 (P-O) cm^{-1}.

^{31}P NMR ($CDCl_3$): 8.31 ppm.

3.2.2. Synthesis of Monomers from Dimethyl (2-hydroxyethyl) Phosphonate

3.2.2.1. Synthesis of 2-Chloromethyl-Acryloyl Chloride (CMAC) Thionyl chloride was added dropwise to tert-butyl-α-hydroxymethyl acrylate (TBHMA) in an ice bath under nitrogen. The reaction mixture was stirred overnight. After removal of excess thionyl

chloride, product was obtained as light yellow liquid was get in a 35 per cent yield.

^{1}H-NMR ($CDCl_3$): δ= 4.26 (s, 2H, CH_2-Cl), 6.41, 6.74 (2H, CH_2=C) ppm.

^{13}C-NMR ($CDCl_3$): δ= 41.99 (CH_2-Cl), 136.21 (C=*C*H_2), 141.44 (*C*=CH_2), 166.90 (C=O) ppm.

FT-IR (neat): 2966 (C-H), 1747 (m, C=O), 1640 (C=C), 896 (C-Cl)/cm.

3.2.2.2. Monomer **3.** 2-(chloromethyl)acryloyl chloride (2.00 g, 14.38 mmol) was added dropwise to the mixture of dimethyl (2-hydroxyethyl) phosphonate (2.21 g, 14.38 mmol) and triethylamine (1.45 g, 14.38 mmol) in 10 ml of dry THF at -10 ^{o}C. After 12 h of stirring at room temperature, the solvent was evaporated. The residue was diluted with CH_2Cl_2 and extracted twice with water. The organic layer was separated and dried with sodium sulfate. The evaporation of the solvent gave a viscous yellow oil in a 49.4 per cent yield, forming our intermediate for monomers **3** and **4**.

To this intermediate, benzoic acid (0.86 g, 7.09 mmol) and K_2CO_3 (0.98 g, 7.09 mmol) in 20 ml MEK were added. The mixture was stirred for overnight at 55 ^{o}C. The solution was filtered and MEK was evaporated. The crude product was purified by column chromatography using CH_2Cl_2 initially and gradually changing to 2 per cent methanol in CH_2Cl_2 as eluent. The pure product was obtained as a viscous yellow oil in a 33.5 per cent yield.

^{1}H-NMR ($CDCl_3$): δ= 2.2 (m, 2H, CH_2-P), 3.7 (d, 6H, CH_3-O), 4.4 (m, 2H, CH_2-O), 5.1 (s, 2H, CH_2-O), 6.0, 6.4 (s, 2H, *C*H_2=C), 7.5 (t, 2H, CH-Ar) ,7.6 (t, 1H, CH-Ar), 8.0 (d, 2H, CH-Ar) ppm.

^{13}C-NMR ($CDCl_3$): δ= 23.9, 25.3 (d, C-P), 58.7 (CH_3-O), 52.4, 62.4 (CH_2-O), 128.2, 129.3, 132.9 (Ar-CH), 127.6 (*C*H_2=C), 129.5 (*C*(Ar)-C=O), 134.8 (*C*=CH_2), 164.4, 165.6 (C=O) ppm.

FT-IR: 2956 (C-H), 1718 (C=O), 1632 (C=C), 1265 (P=O), 1021/cm (P-O-Me).

^{31}P NMR ($CDCl_3$): 29.4 ppm.

3.2.2.3. Monomer **4.** To our intermediate, formic acid (0.33 g, 7.09 mmol) and K_2CO_3 (0.98 g, 7.09 mmol) in 20 ml MEK were added. The mixture was stirred overnight at 55^{o}C. After filtration, MEK was evaporated. The crude product was purified by column chromatography using CH_2Cl_2 initially and gradually changing to 2 per cent methanol in CH_2Cl_2 as eluent. The pure product was obtained as a viscous yellow oil.

^{1}H-NMR ($CDCl_3$): δ= 2.2 (m, 2H, CH_2-P), 3.7 (d, 6H, CH_3-O), 4.4 (m, 2H, CH_2-O), 4.9 (s, 2H, CH_2-O), 5.9, 6.4 (s, 2H, C*H*$_2$=C), 8.0 (s, 1H, CH=O) ppm.

^{13}C-NMR ($CDCl_3$): δ= 24.1, 25.5 (d, C-P), 59.0 (CH_3-O), 52.5, 61.6 (CH_2-O), 128.7 (*C*H_2=C), 134.3 (*C*=CH_2), 160.2, 164.5 (C=O) ppm.

FT-IR: 2957 (C-H), 1718 (C=O), 1640 (C=C), 1250 (P=O), 1020/cm (P-O-Me).

^{31}P NMR ($CDCl_3$): 29.3 ppm.

3.2.3. Synthesis of Monomers from Diethyl Hydrogen Phosphate

3.2.3.1. Monomer **5.** Diethyl chlorophosphate (5.0 g, 28.9 mmol) and H_2O (3.1 g, 173.9 mmol) were added to a round bottom flask and the mixture was stirred at room temperature for 1 hour. The aqueous phase was extracted with dichloromethane, then the organic phase was dried with Na_2SO_4, filtered and concentrated.

The formed product, diethyl hydrogen phosphate (1.75 g, 11.36 mmol) and GMA (1.34 g, 9.47 mmol) were added to a round bottom flask with a nitrogen inlet. The mixture was stirred at 50 ^{o}C for 5 h. The crude product was washed with water three times, then with cyclohexane and petroleum ether. Then the crude product was purified by column chromatography using CH_2Cl_2 initially and gradually changing to 1 % methanol in CH_2Cl_2 as eluent. The pure product was obtained as a viscous yellow oil in a 31.5 % yield.

^{1}H-NMR ($CDCl_3$) : 1.3 (s, 3H, CH_3-CH_2), 1.9 (t, 3H, CH_3-C), 2.6 (b, 1H, C-OH), 4.1-4.2 (m, 7H, CH_2-O, *C*H_2-CH_3), 5.6, 6.1 (s, 2H, *C*H_2=C) ppm.

^{13}C-NMR ($CDCl_3$) : 16.4 (*C*H_3-CH_2), 18.6 (*C*H_3-C), 64.6, 68.9 (CH_2-O), 65.0 (*C*H_2-CH_3), 69.1 (CH-OH), 126.6 (*C*H_2=C), 136.1 (*C*=CH_2), 167.5 (C=O) ppm.

FT-IR: 3379 (O-H), 2983 (C-H), 1717 (C=O), 1637 (C=C), 1249 (P=O), 1017/cm^{-1} (P-O-Me).

3.3. Free Radical Polymerizations in Bulk and Solution

3.3.1. Polymerization Procedure

Bulk polymerizations of monomers **1**, **3**, **4** and **5** were carried out in an oil bath at 60 ºC with AIBN (0.5 wt%) in septum-sealed glass tubes using standard freeze-evacuate-thaw procedures. For the polymerizations in solution, the tube was charged with the monomer, solvent and the initiator. The viscous polymer solutions were dissolved first in a suitable solvent and precipitated into a nonsolvent, filtered and dried.

Solution copolymerization of monomer **2a** with acrylamide was carried out in water at 50 ^{o}C using V-50 as an initiator. For example, acrylamide (94.5 mg, 1.32 mmol), **2a** (10.75 mg, 0.026 mmol) and V-50 (2.8 mg, 0.010 mmol) in 0.4 ml H_2O were added to a septum–sealed tube. The tube was subjected to freeze-evacuate-thaw procedure and placed in a 50 ^{o}C oil bath. After 10 minutes, the gel formed was placed into large quantity of water to remove unreacted monomers.

Solution copolymerization of monomer **2a** with HEMA was carried out in ethanol at 50 ^{o}C using AIBN. For example, HEMA (26.0 mg, 0.2 mmol), **2a** (16.2 mg, 0.04 mmol) and AIBN (3.3 mg, 0.02 mmol) in ethanol were added to a septum-sealed tube. The tube was subjected to freeze-evacuate-thaw procedure and placed in 50 ^{o}C oil bath. After 2 hours, the gel formed was placed into large quantity of water to remove unreacted monomers.

3.4. Photopolymerizations

3.4.1. Polymerization Procedure

The photopolymerization behaviors of the synthesized monomers were investigated using photo-differential scanning calorimeter (Photo-DSC). All the polymerizations were performed under identical conditions of UV light intensity (20 mW/cm^2) and temperature (40 ^oC).

Approximately 3.0 mg of sample was placed in an aluminium DSC pan. A CH_2Cl_2 solution of the photoinitiator was added with a microsyringe to give a final concentration in the monomer after evaporation of the solvent. Heats of photoreactions were measured using a DPC equipped with a mercury arc lamp. The DSC chamber was purged with nitrogen to remove air and CH_2Cl_2 for 10 min before polymerization and purging was continued during polymerization. The samples were irradiated with UV-light (intensity =20 mW/cm^2) for 10 min at 40 $^{\circ}C$. The heat flux as a function of reaction time was monitored using DSC under isothermal conditions, and both the rate of polymerization and conversion were calculated as a function of time. The theoretical values used for the heats of reaction (ΔH_p) were 13.1 kcal/mol for methacrylate double bonds [71,72]. Rates of polymerization were calculated according to the formula given in figure 1.64

3.5. Hydrolytic Stability of Monomers 1, 2 and 2a

The hydrolytic stabilities of the synthesized monomers **1** and **2** were investigated by means of ^1H NMR measurements of 20 wt.-% solutions of the monomers in methanol-d_6/D2O (1/1) after storage at 37 ^oC for 55 days.

The hydrolytic stability of the monomer **2a** was investigated by means of ^1H-NMR measurements of 2 wt % solutions of the monomers in methanol-d_6/D_2O (3/2) after storage at 37 ^oC for 40 days.

3.6. Interactions of Monomer 2a with Hydroxyapatite

3.6.1. FT-IR Spectroscopy Technique

FT-IR spectrum of the monomer **2a** with and without HAP were obtained. 40 mg of monomer was dissolved in 1.63 gr of 20 wt % D_2O/H_2O. To 0.6 gr of this solution, 20 mg of HAP was added. After the suspension was stirred at 37 ^oC for 1 h, the pH value was measured and FT-IR spectrum analysis was performed.

4. RESULTS AND DISCUSSION

4.1.Synthesis of Novel Phosphorus-Containing Monomers

Novel mono- and/or di-phosphonate, phosphonic acid and phosphate-containing monomers were synthesized using three different routes.

4.1.1. Synthesis of Monomers from o-Hydroxyaryl Phosphonates (First Route)

First route for the synthesis of phosphonated monomers consists of a one step reaction of diethyl (2-hydroxyphenyl) phosphonate and tetraethyl (2,5-dihydroxy-1,4-phenylene) bisphosphonate with methacryloyl chloride in the presence of a base catalyst.

Synthesis of the first pair of monomers (**1** and **1a**) is shown in Figure 4.1. Diethyl (2-hydroxyphenyl) phosphonate was used as a starting phosphonate compound for the synthesis of these monomers. It was synthesized in two steps. In the first step, phenol and diethyl phosphite were reacted in the presence of TEA as a catalyst in CCl_4 to give diethyl phenyl phosphate. In the second step, diethyl phenyl phosphate was treated with lithium diisopropylamide (LDA) in dry THF at -78 ^{o}C to give diethyl (2-hydroxyphenyl) phosphonate.

Reaction of methacryloyl chloride with diethyl (2-hydroxyphenyl) phosphonate in the presence of TEA at 0 ^{o}C gave monomer **1** which was obtained as a viscous yellow oil after purification with column chromatography. This monomer was soluble in ether, acetone, dichloromethane, THF and water but insoluble in petroleum ether and hexane.

The ^{13}C-NMR spectrum of monomer **1** showed characteristic peaks for methyl carbons at 16.2 and 18.3 ppm, methylene carbon at 62.3 ppm, carbon attached to phosphorus at 120.3, 122.1 ppm, aromatic carbons at 123.7, 125.8, 133.8, 135.0, 152.4 ppm, double bond carbons at 127.8 and 135.6 ppm and a carbonyl carbon at 165.4 ppm (Figure 4.2).

The ^{1}H-NMR spectrum of monomer **1** showed characteristic peaks for methyl protons at 1.3 ppm (triplet) and 2.1 ppm (singlet), methylene protons next to oxygen atoms at 4.0-4.1 ppm (multiplet), double bond protons at 5.8 and 6.4 ppm (singlet) and aromatic protons at 7.1, 7.3, 7.6, 8.0 ppm (Figure 4.3).

The FT-IR spectrum showed absorptions of CH, C=O, C=C, P=O and P-O-Et groups at 2984, 1739, 1633, 1243 and 1014 cm^{-1} (Figure 4.4).

The ^{31}P-NMR spectrum of this monomer, with one peak at 16.3 ppm, confirms the purity of the monomer (Figure 4.5).

The silylation of monomer **1** with TMSBr, followed by methanolysis of the silyl derivative was expected to give a new phosphonic acid monomer, monomer **1a**. However, the ^{1}H-NMR spectrum of the product indicated the presence of monomer **1a** as well as 2-hydroxyphenyl phosphonic acid which was not possible to remove. If this byproduct comes from hydrolysis of monomer **1** we would also see methacrylic acid peaks. But the ^{1}H-NMR spectrum did not show any indication of methacrylic acid protons (Figure 4.3).

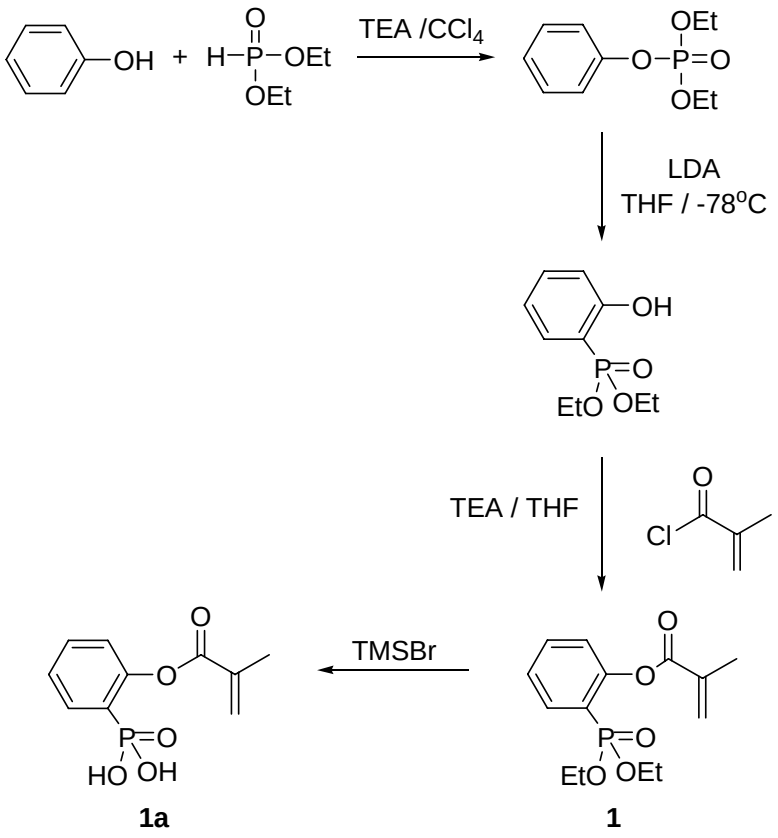


Figure 4.1. Synthesis of monomers **1** and **1a**

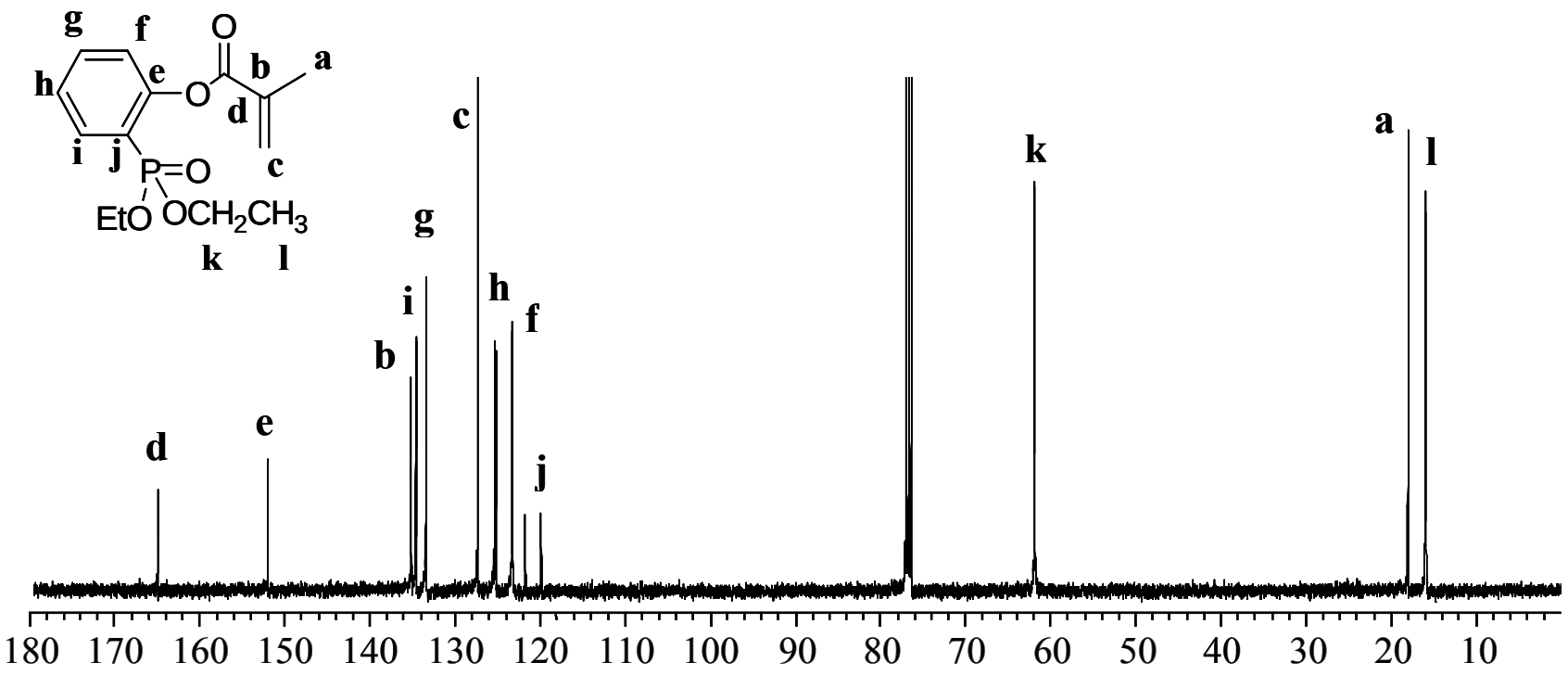


Figure 4.2. ^{13}C-NMR spectrum of monomer **1**

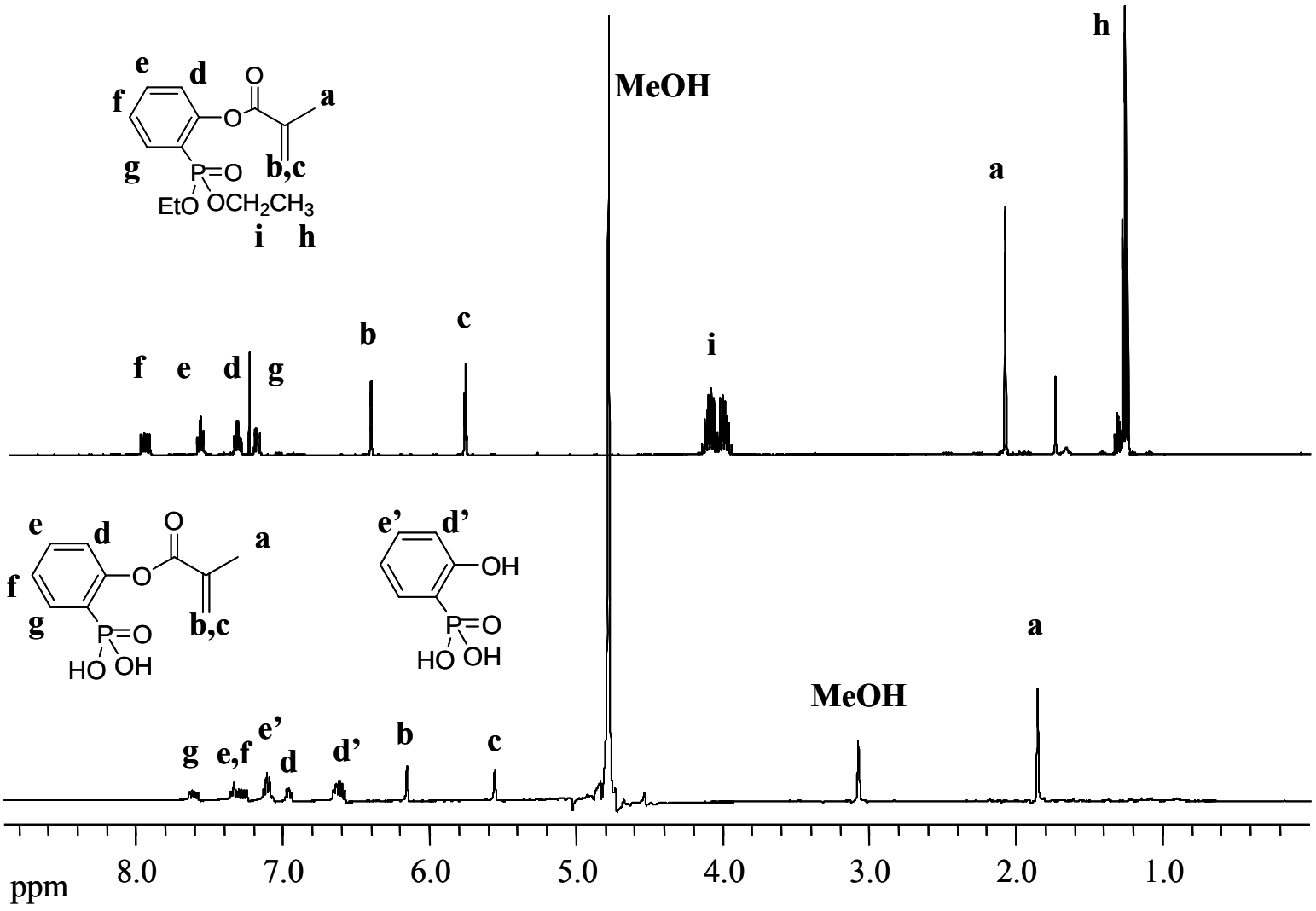


Figure 4.3. ^{1}H-NMR spectra of monomers **1** and **1a**

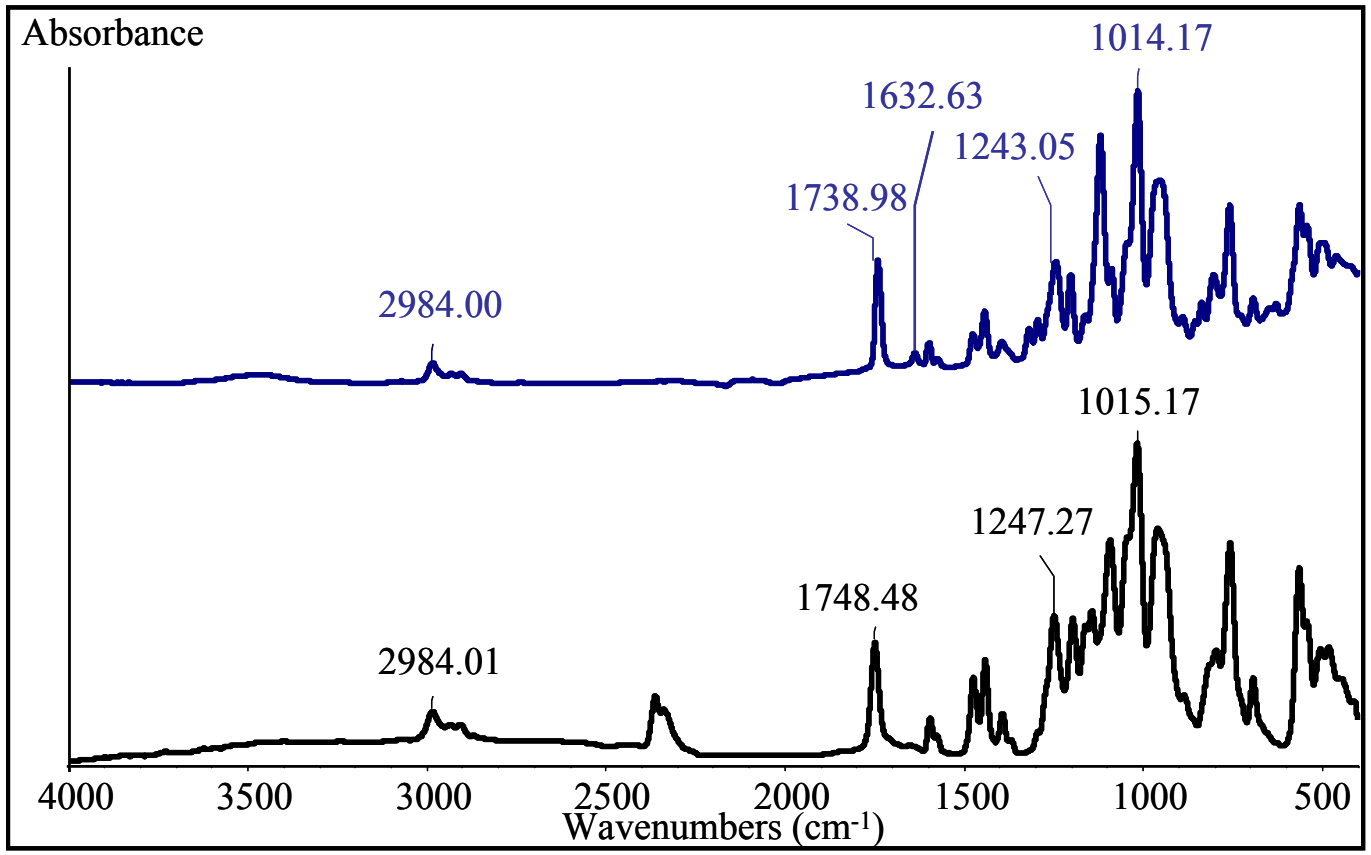


Figure 4.4. FT-IR spectrum of monomer **1** (blue) and it's polymer **1** (black)

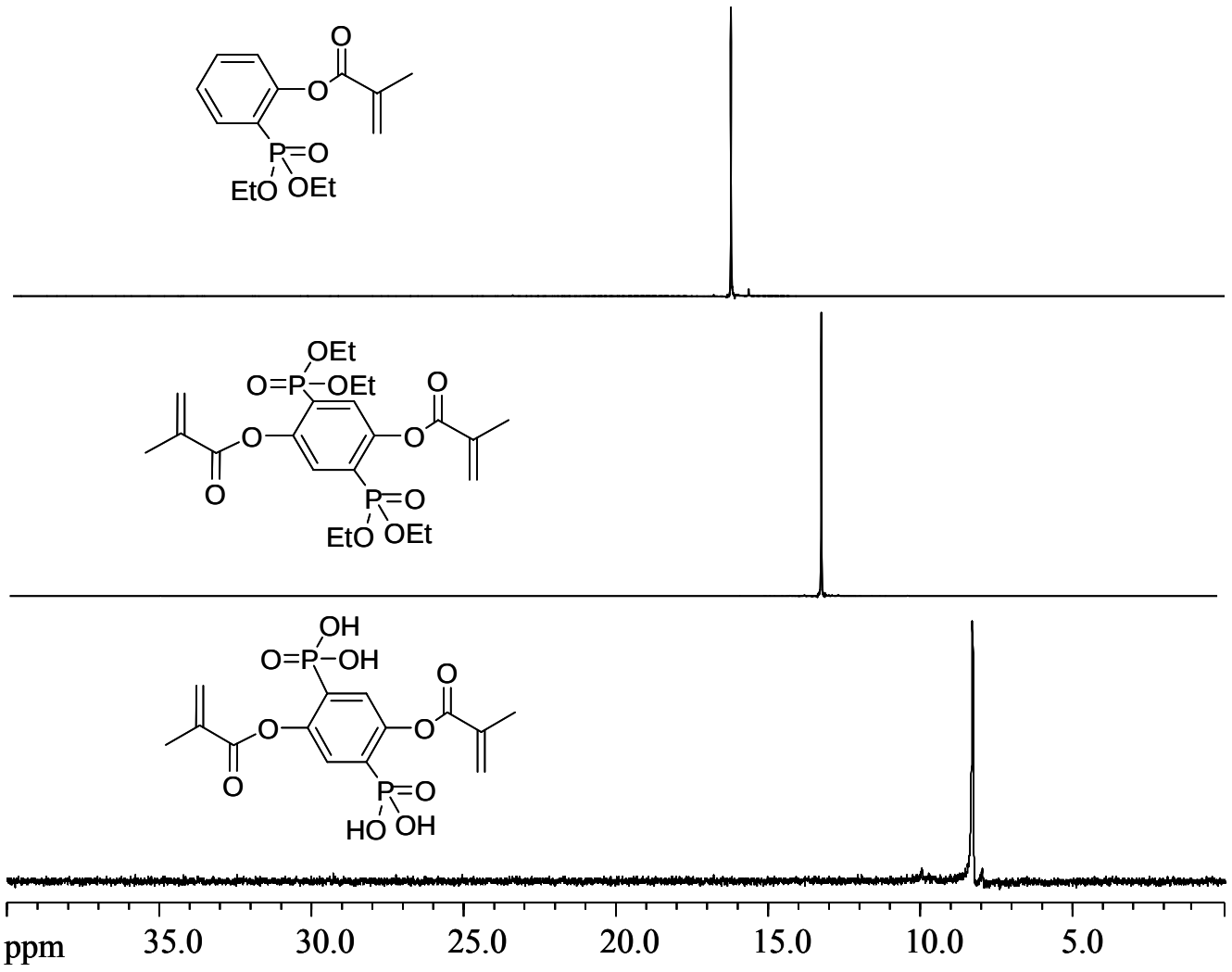


Figure 4.5. ^{31}P-NMR spectra of monomers **1**, **2**, **2a**

Synthesis of the second pair of monomers (monomer **2** and **2a**) is shown in Figure 4.6. Tetraethyl (2,5-dihydroxy-1,4-phenylene) bisphosphonate was used as a starting phosphonate compound for the synthesis of monomer **2** and **2a**. It was synthesized in two steps. In the first step, hydroquinone and diethyl phosphite were reacted in CCl_4 using TEA as a catalyst to give tetraethyl phenyl bisphosphate. In the second step, tetraethyl phenyl bisphosphate was treated with lithium diisopropylamide (LDA) in dry THF at -78 ^oC to give tetraethyl (2,5-dihydroxy-1,4-phenylene) bisphosphonate.

Reaction of methacryloyl chloride with tetraethyl (2,5-dihydroxy-1,4-phenylene) bisphosphonate in the presence of TEA at 0 ^oC gave monomer **2** as a white solid with a melting point of 132 ºC after recrystallization from acetone. This monomer was soluble in ether, acetone, dichloromethane and THF but insoluble in water and hexane.

The ^{13}C-NMR spectrum of monomer **2** showed characteristic peaks for methyl carbons at 16.1 and 18.2 ppm, methylene carbon attached to oxygen at 62.7 ppm, carbon attached to phosphorus at 126.4 ppm as doublet, double bond carbons at 128.1 and 130.1 ppm, aromatic carbons at 135.2, 149.3 ppm, and a carbonyl carbon at 165.1 ppm (Figure 4.7).

The ^{1}H-NMR spectrum of monomer **2** showed methyl protons at 1.3 and 2.1 ppm, methylene protons at 4.0-4.1 ppm, double bond carbons at 5.8 and 6.4 ppm and aromatic protons at 7.8 ppm (Figure 4.8).

The FT-IR spectrum showed peaks at 1745, 1632, 1244 and 1018 cm^{-1}, which can be assigned to C=O, C=C, P=O and P-O-Et (Figure 4.9).

The ^{31}P-NMR spectrum showed a peak at 13.1 ppm (Figure 4.5).

The synthesis of monomer **2a** involved the silylation reaction of monomer **2** with TMSBr, followed by methanolysis of the silyl derivative. After washing with acetonitrile to remove unreacted monomer, monomer **2a** was obtained as a white solid in 92 percent yield. Because of its crystalline structure this monomer is not highly soluble in polar solvents such as ethanol and water. For example, it has the solubility of 1.2 wt % in water

and 2.5 wt % in ethanol. An aqueous solution of this monomer (1 wt %) had a pH value of 1.65. Although this value was higher than pH of 1 wt % aqueous phosphoric acid solution (pH = 1.54), monomer **2a** is in the range of mild self-etching dental adhesive monomer.

The ^{1}H-NMR spectrum of monomer **2a** showed disappearance of the ethyl protons which confirmed the hydrolysis of phosphonate esters (Figure 4.8).

The FT-IR spectrum showed a broad peak at around 2677 cm^{-1} due to OH stretching vibrations of phosphonic acid groups (Figure 4.9).

The ^{31}P-NMR spectrum showed one peak at 8.31 ppm which corresponds to phosphonic acid group. (Figure 4.5).

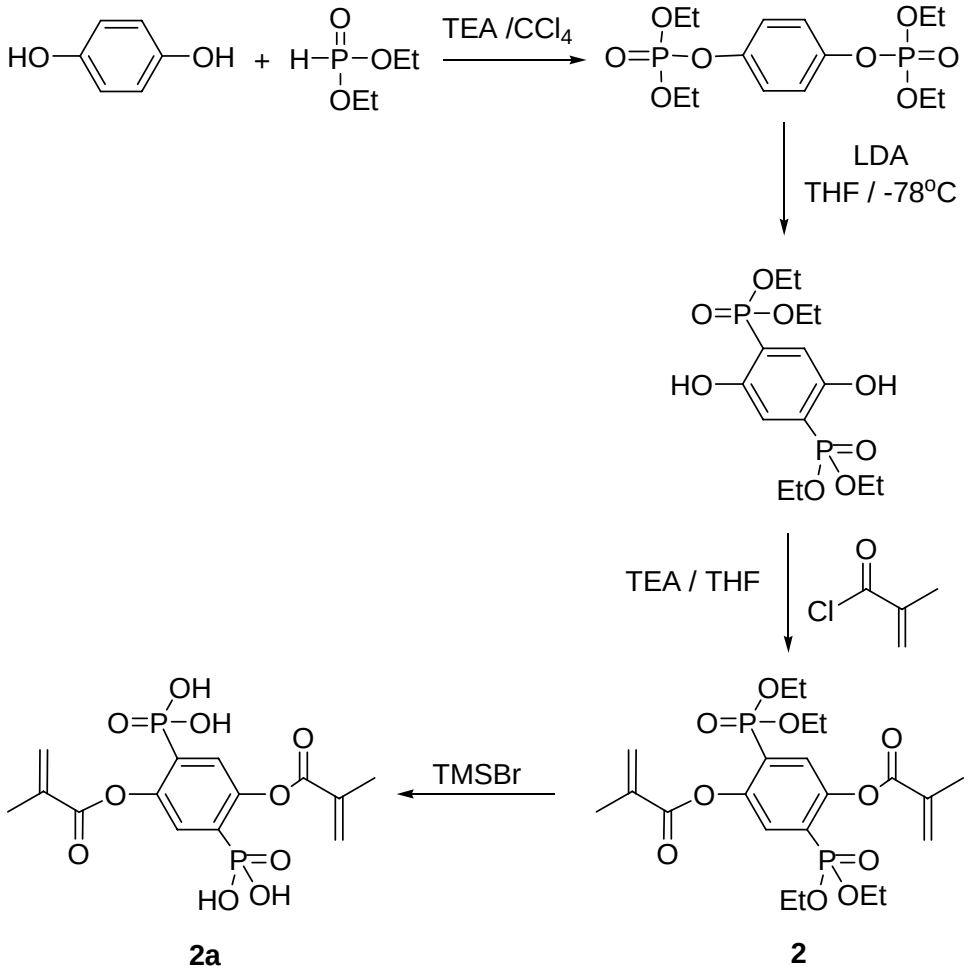


Figure 4.6. Synthesis of monomers **2** and **2a**

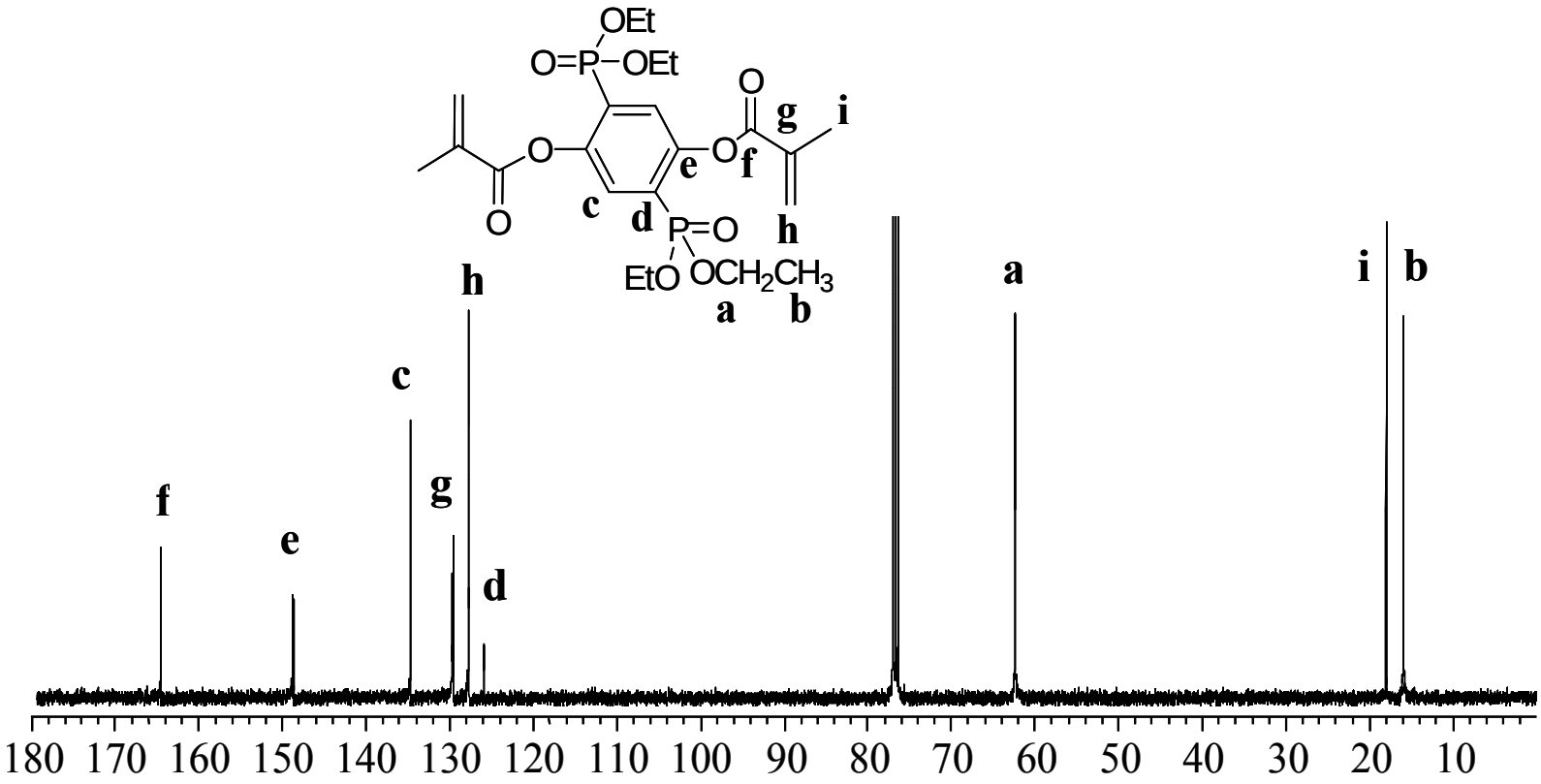


Figure 4.7. ^{13}C-NMR spectrum of monomer **2**

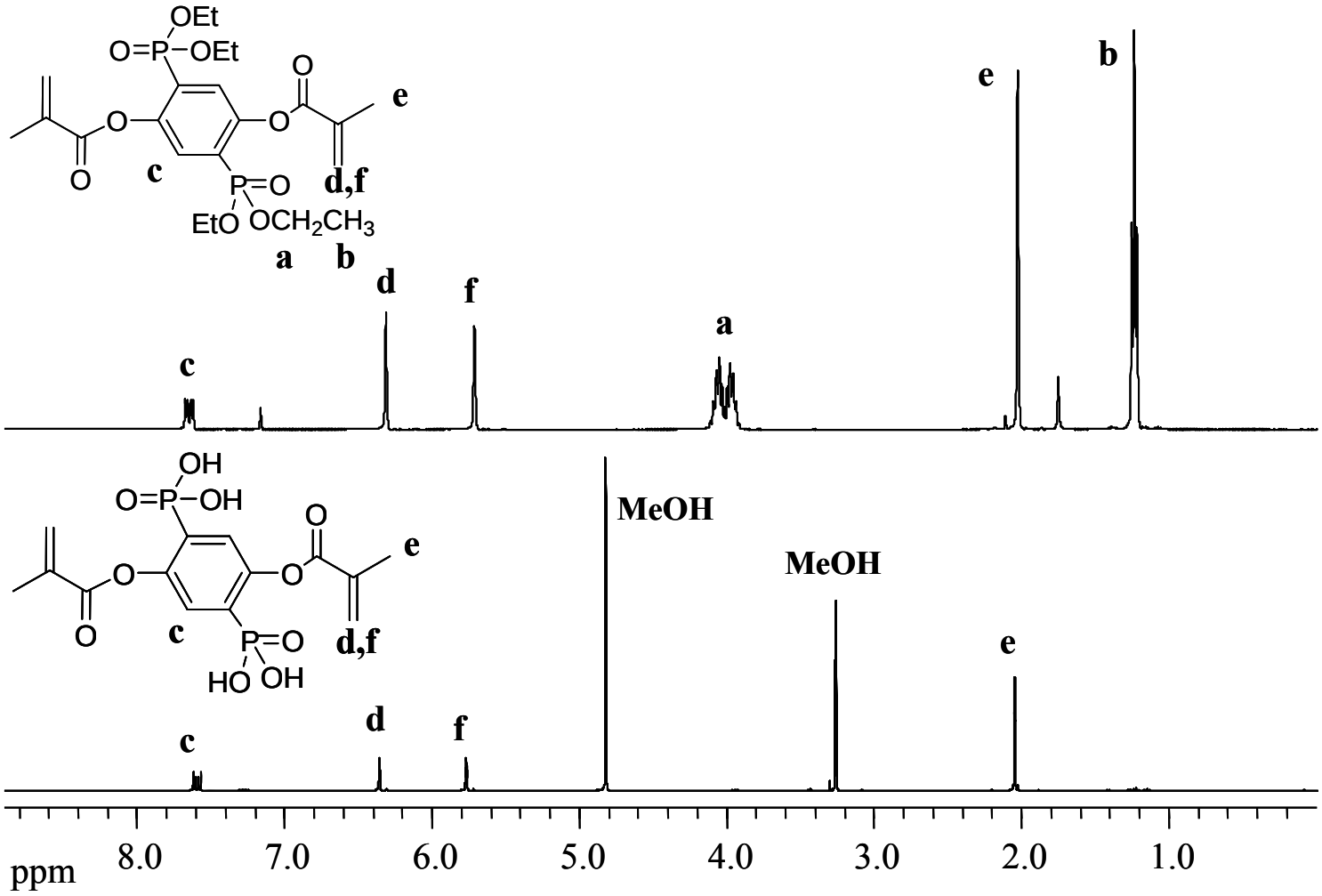


Figure 4.8. ^{1}H-NMR spectra of monomers **2** and **2a**

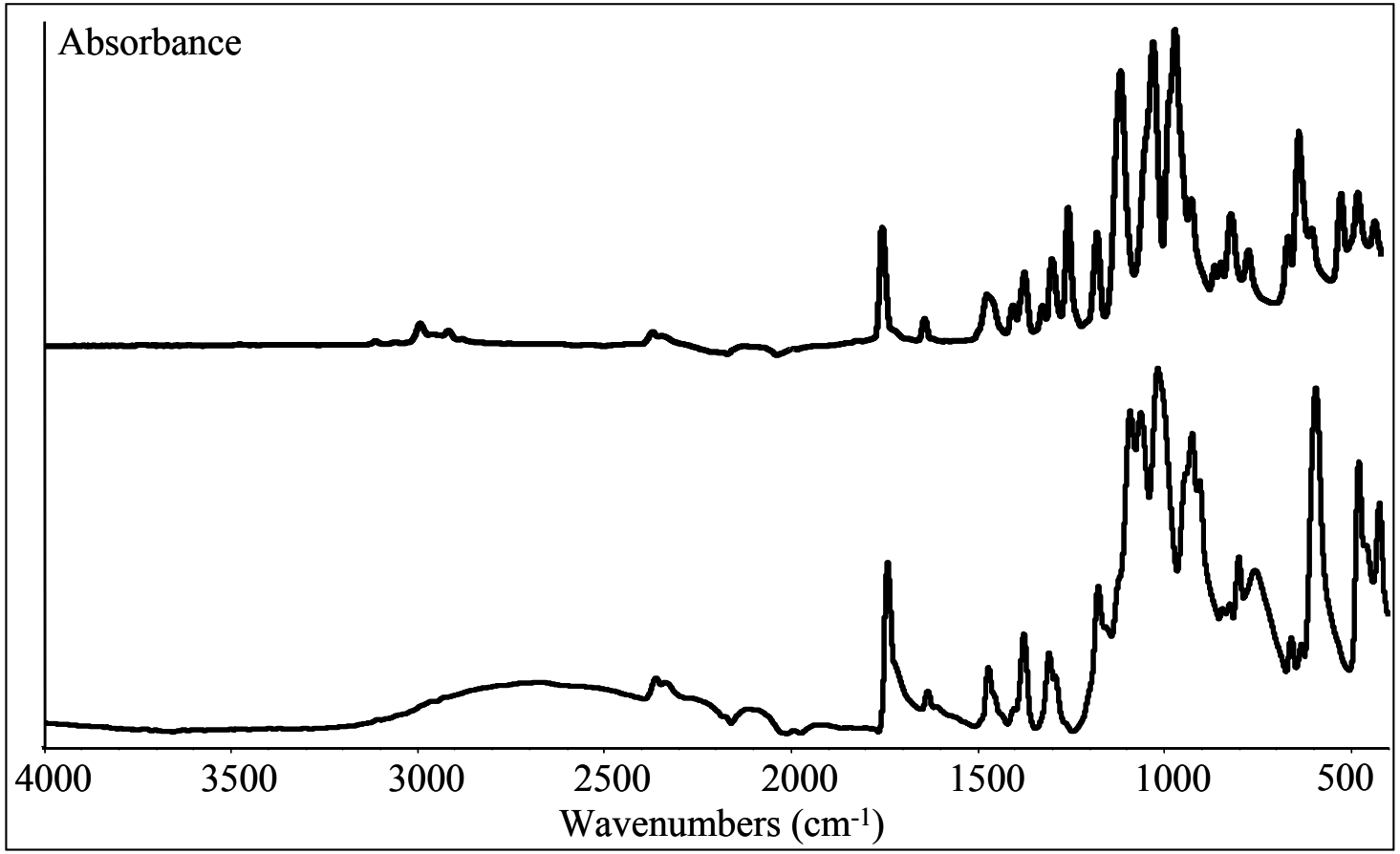


Figure 4.9. FT-IR spectra of monomers **2** and **2a**

4.1.2. Synthesis of Monomers from Dimethyl 2-Hydroxyethyl Phosphonate (Second Route)

Second route for the synthesis of phosphonated monomers involved two steps: (i) reaction of dimethyl (2-hydroxyphenyl) phosphonate and CMAC to give an intermediate (ii) reaction of this intermediate with carboxylic acids (Figure 4.10)

This route is a modification of a route to highly reactive methacrylate monomers using CMAC which developed in our group previously [3]. There, CMAC was reacted first with diethyl (hydroxymethyl) phosphonate to give an intermediate which was than reacted with sodium acetate in the presence of a phase-transfer catalyst. We would like to find alternative substituents to achieve higher polymerization reactivity.

Studies on the reactivities of several ester derivatives of ethyl α-hydroxymethyl acrylate indicated that aromatic esters are more reactive than nonaromatic ones. For example, photopolymerization rates of formate, acetate and benzoate derivatives were found to be 14, 15 and 71 kJ/mol min^{-1} [26]. The benzoate ester based on its k_p and k_t values obtained from solution polymerization (k_p= 990, k_t= $2.9x10^{-6}$ L/mol s^{-1}) is more reactive than ether derivatives of ethyl α-hydroxymethyl acrylate and methyl α-acetoxymethyl acrylate (k_p= 350, k_t= $2.1x10^{-6}$ L/mol s-1) and methyl methacrylate (k_p= 510, k_t= $42x10^{-6}$ L/mol s^{-1}). Based on the reactivities of the ester substituents, here, we report synthesis of two new phosphonated monomers with mixed ester groups to investigate the effect of the substituents on reactivity.

Synthesis of the monomers (monomer **3** and **4**) is shown in (Figure 4.10). CMAC was reacted with equal moles of dimethyl (2-hydroxyphenyl) phosphonate in the presence of TEA as catalyst. The monosubstituted product was than reacted with benzoic and formic acids in the presence of potassium carbonate to obtain benzoate (monomer **3**) and formate esters (monomer **4**).

The pure product of monomer **3** was obtained as a viscous yellow oil after column chromatography in 49.4 per cent yield. This monomer was soluble in ether, dichloromethane, THF and acetone, but insoluble in petroleum ether, water and hexane.

The ^{13}C-NMR spectrum of monomer **3** was characterized by carbon attached to phosphorus at 23.9 and 25.3 ppm, methyl carbon at 58.7 ppm, methylene carbons at 52.4 and 62.4 ppm, aromatic carbons at 128.2, 129.3 and 132.9 ppm, double bond carbons at 127.6 and 134.8 ppm and two carbonyl carbons at 164.4, 165.6 ppm (Figure 4.11).

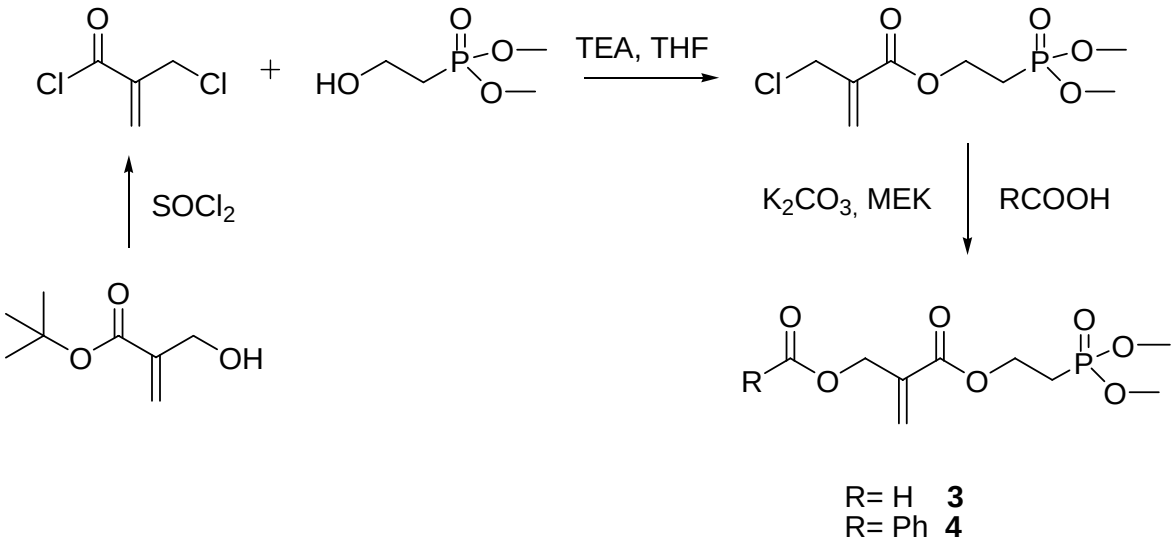


Figure 4.10. Synthesis of monomers **3** and **4**

The ^{1}H-NMR spectrum of monomer **3** showed characteristic peaks for methylene protons attached to phosphorus at 2.2 ppm (multiplet), methyl protons at 3.7 ppm (doublet), methylene protons next to oxygen atoms at 4.4 ppm (multiplet) and 5.1 ppm (singlet), double bond protons at 6.0 and 6.4 ppm and aromatic protons at 7.5-8.0 ppm (Figure 4.12).

The FT-IR spectrum showed peaks at 2956, 1718, 1632, 1265 and 1021 cm^{-1}, which can be assigned to C-H C=O, C=C, P=O and P-O-Me (Figure 4.13).

The ^{31}P-NMR spectrum showed one peak at 29.4 ppm (Figure 4.14).

The pure product of monomer **4** was obtained as a viscous yellow oil after column chromatography in 12.7 per cent yield. This monomer was soluble in dichloromethane, THF and acetone, but insoluble in ether, petroleum ether, water and hexane.

The ^{13}C-NMR spectrum proved the structure of the monomer **4** (Figure 4.11).

The ^{1}H-NMR spectrum of monomer **4** showed methyl protons at 3.7 ppm as doublet, methylene protons next to oxygen atoms at 4.4 and 4.9 ppm, double bond protons at 5.9 and 6.4 ppm and a formate proton at 8.0 ppm (Figure 4.12).

The FT-IR spectrum of this monomer showed the presence of the characteristic peaks due to C=O, C=C, P=O, P-O-Et at 1718, 1640, 1250 and 1020 cm^{-1} (Figure 4.13).

The ^{31}P-NMR spectrum showed one peak at 29.3 ppm (Figure 4.14).

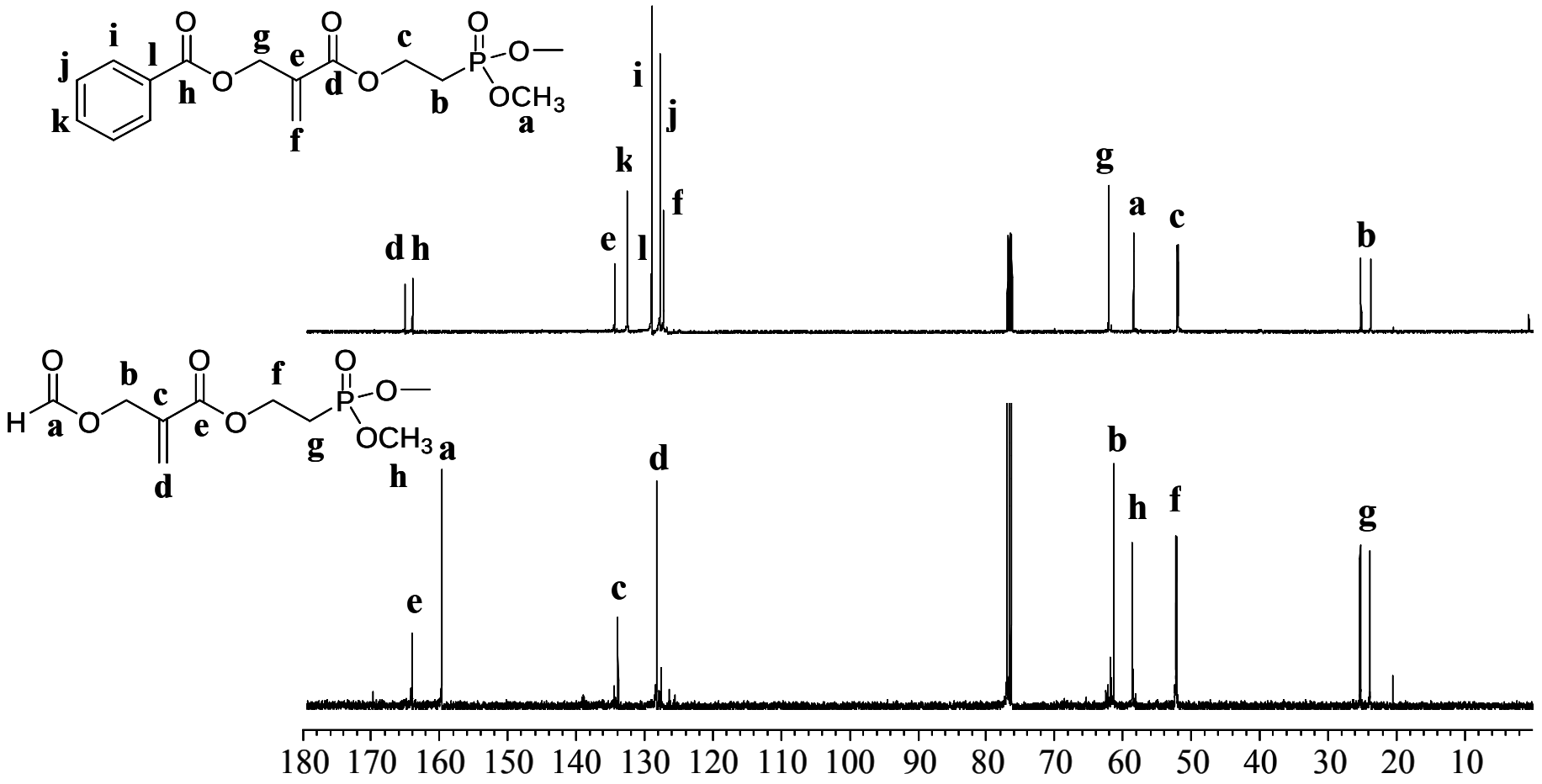


Figure 4.11. ^{13}C-NMR spectra of monomers **3** and **4**

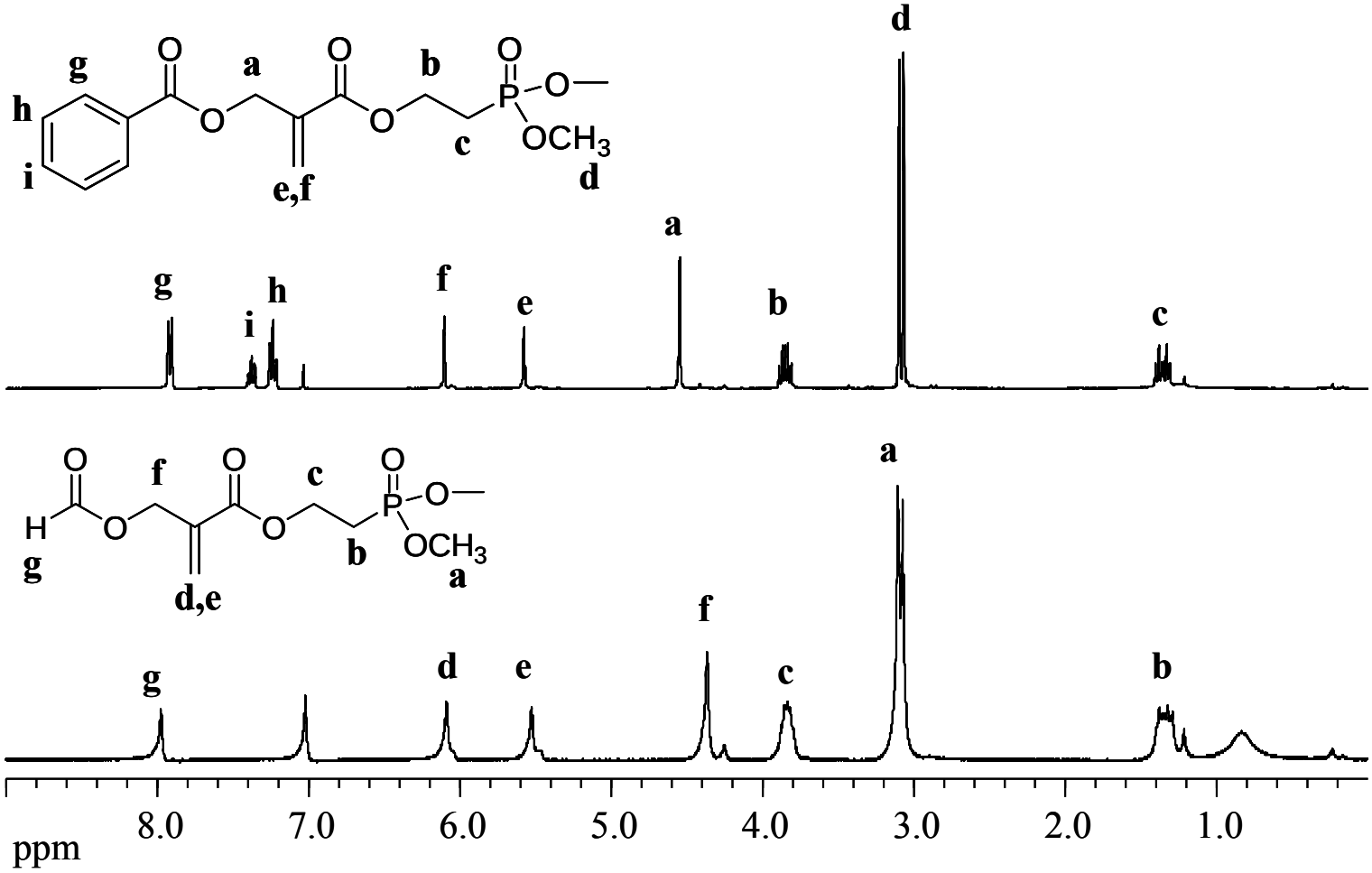


Figure 4.12. ^{1}H-NMR spectra of monomers **3** and **4**

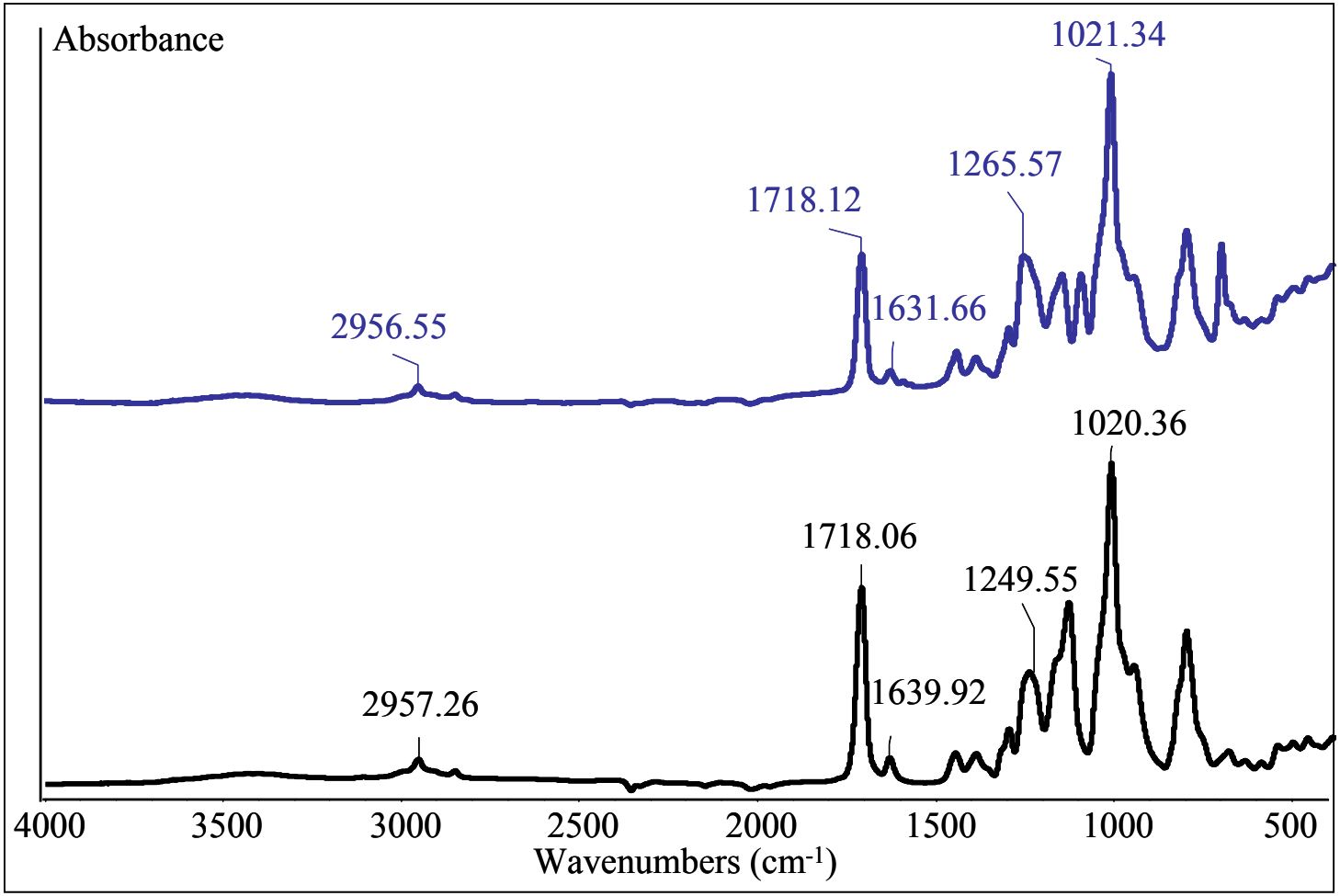


Figure 4.13. FT-IR spectra of monomers **3** (blue) and **4** (black)

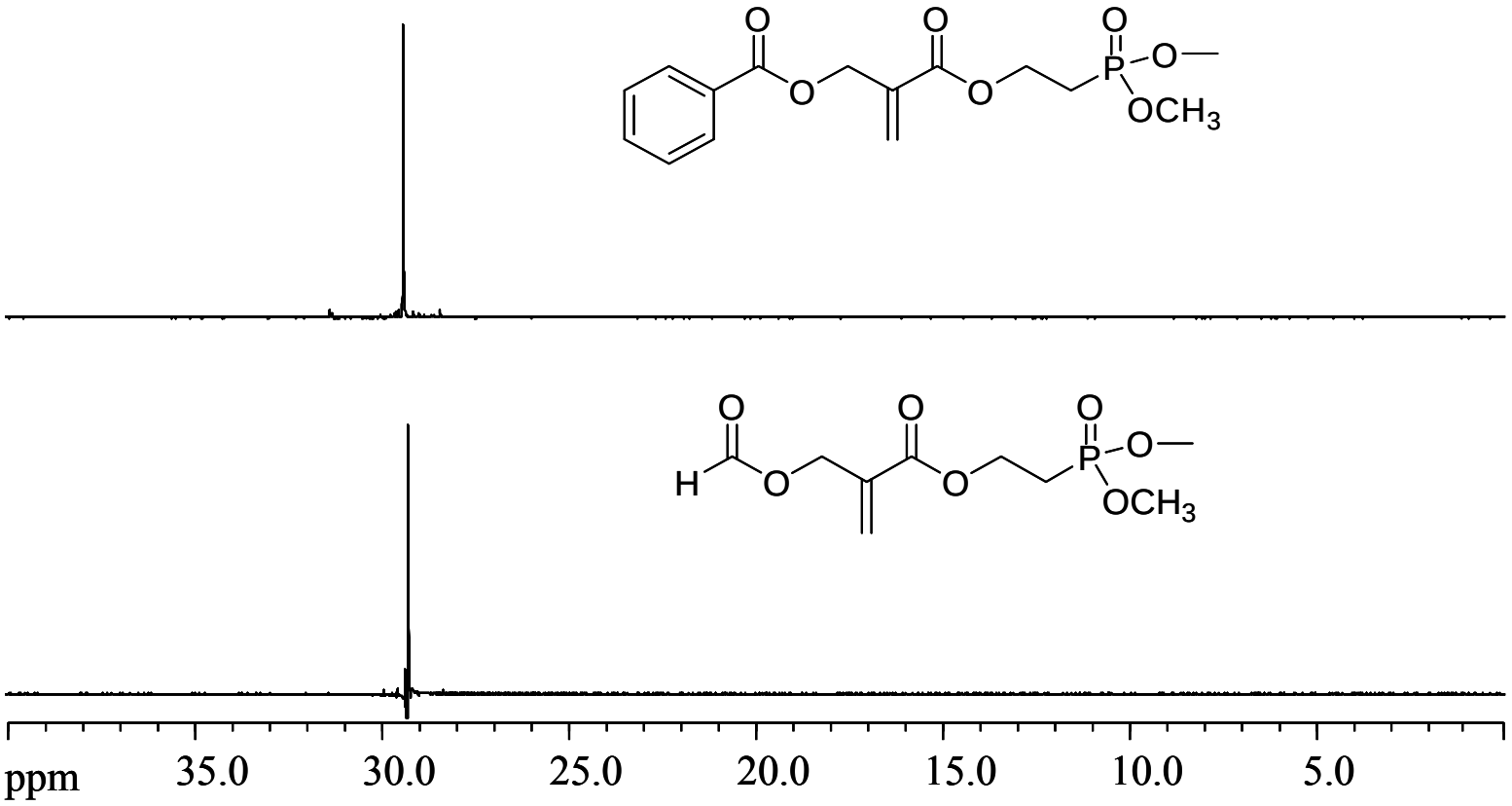


Figure 4.14. ^{31}P-NMR spectra of monomers **3** and **4**

4.1.3. Synthesis of Monomers from Diethyl Hydrogen Phosphate (Third Route)

This route for the synthesis of phosphonated monomers involves reaction of GMA and diethyl hydrogen phosphate.

First diethylchlorophosphate was converted to diethyl hydrogen phosphate by using H_2O. The acid was then reacted with GMA to give monomer **5** through ring opening reaction (Figure 4.15).

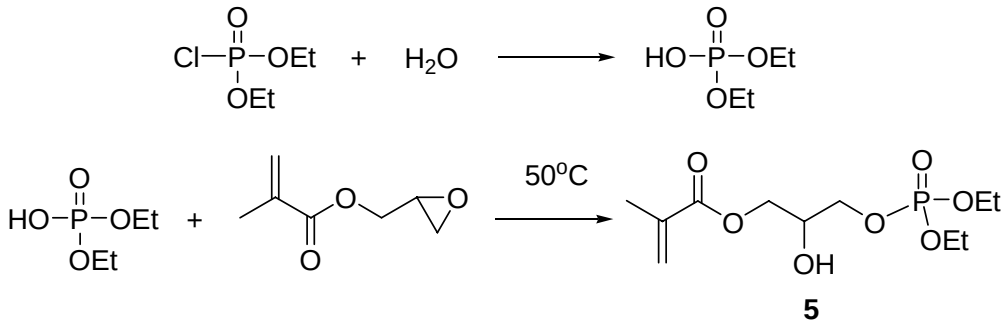


Figure 4.15. General mechanism for the synthesis of monomer **5**

The disappearance of the characteristic epoxy peaks at 64.6 and 68.9 ppm in the ^{13}C-NMR spectra were used to follow product formation.The yield of monomer **5** was 47.8 per cent. Monomer **5** was soluble in almost all organic solvents such as ether, acetone, dichloromethane, THF and methanol except hexane and it was also soluble in water.

The ^{13}C-NMR spectrum of monomer **5** also confirmed product formation (Figure 4.14) with the characterictic peaks for ethyl group at 16.4 and 65.0 ppm, methyl carbon at 18.6 ppm, methylene carbons attached to oxygen at 64.6 and 68.9 ppm, carbon attached to hydroxyl group at 69.1 ppm, double bond carbons at 126.6 and 136.1 ppm and a carbonyl carbon at 167.5 ppm (Figure 4.16).

The ^{1}H NMR spectrum of this monomer was characterized by methyl protons at 1.3 and 1.9 ppm, hydroxyl proton at 2.6 ppm, methylene protons attached to oxygen and between 4.1 and 4.2 ppm and double bond protons at 5.6 and 6.1 (Figure 4.17).

The FT-IR spectrum showed the presence of alcoholic OH peak at 3379 cm^{-1}, the characteristic ester C=O peak at 1717 cm^{-1}, the double bond peak at 1637 cm^{-1} and the peaks due to phosphonate group at 1249 and 1017 cm^{-1} (Figure 4.18).

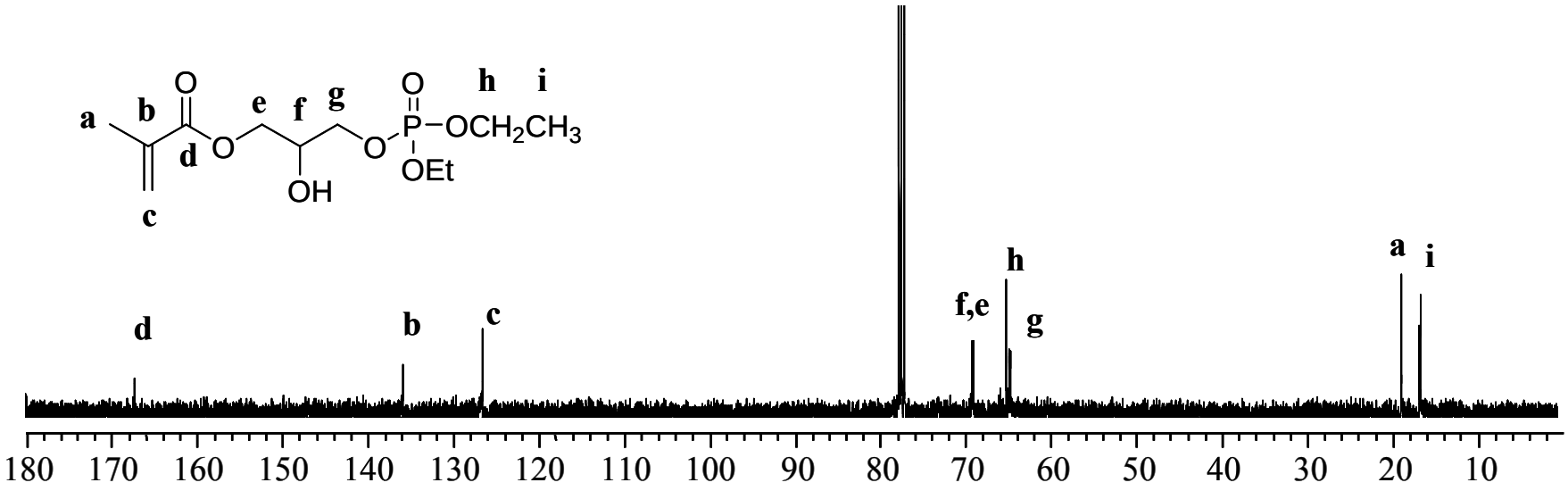


Figure 4.16. ^{13}C-NMR spectra of monomer **5**

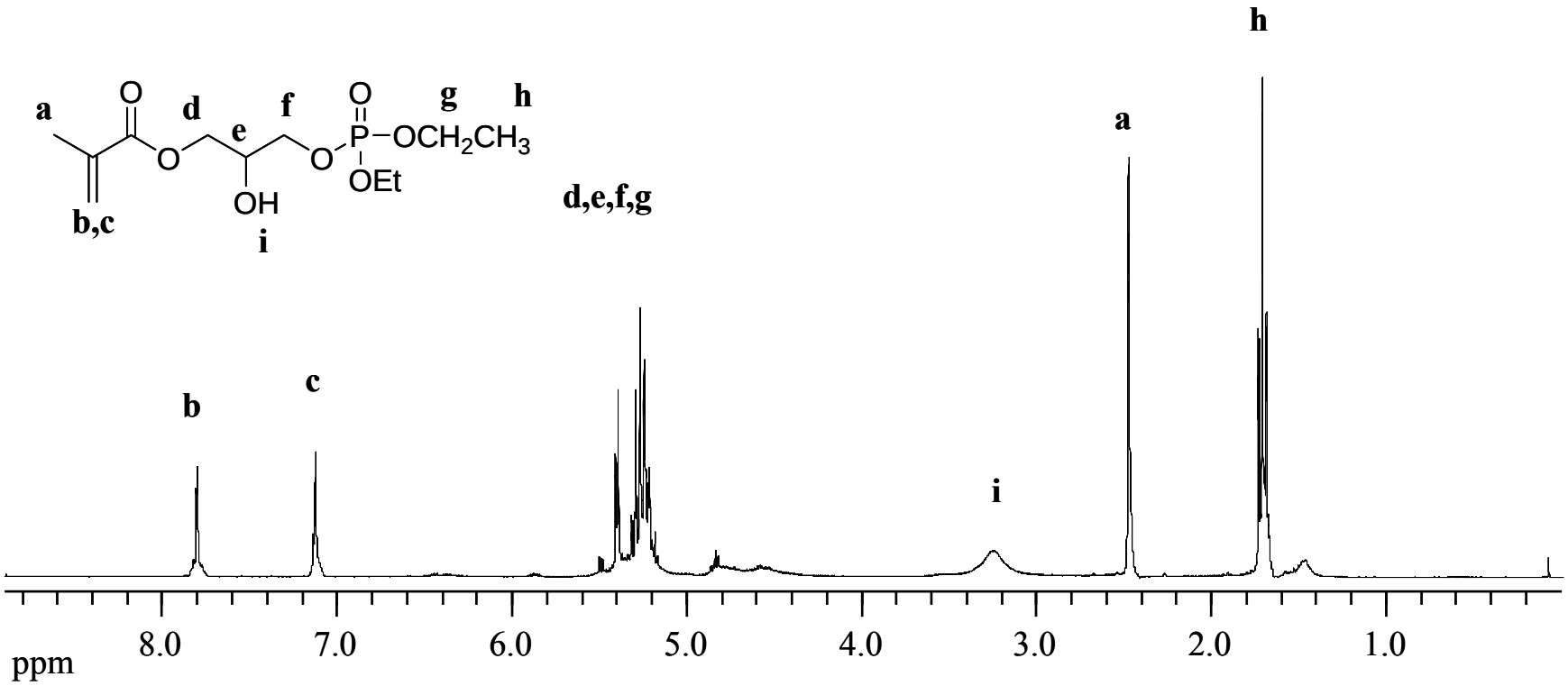


Figure 4.17. ^{1}H-NMR spectra of monomer **5**

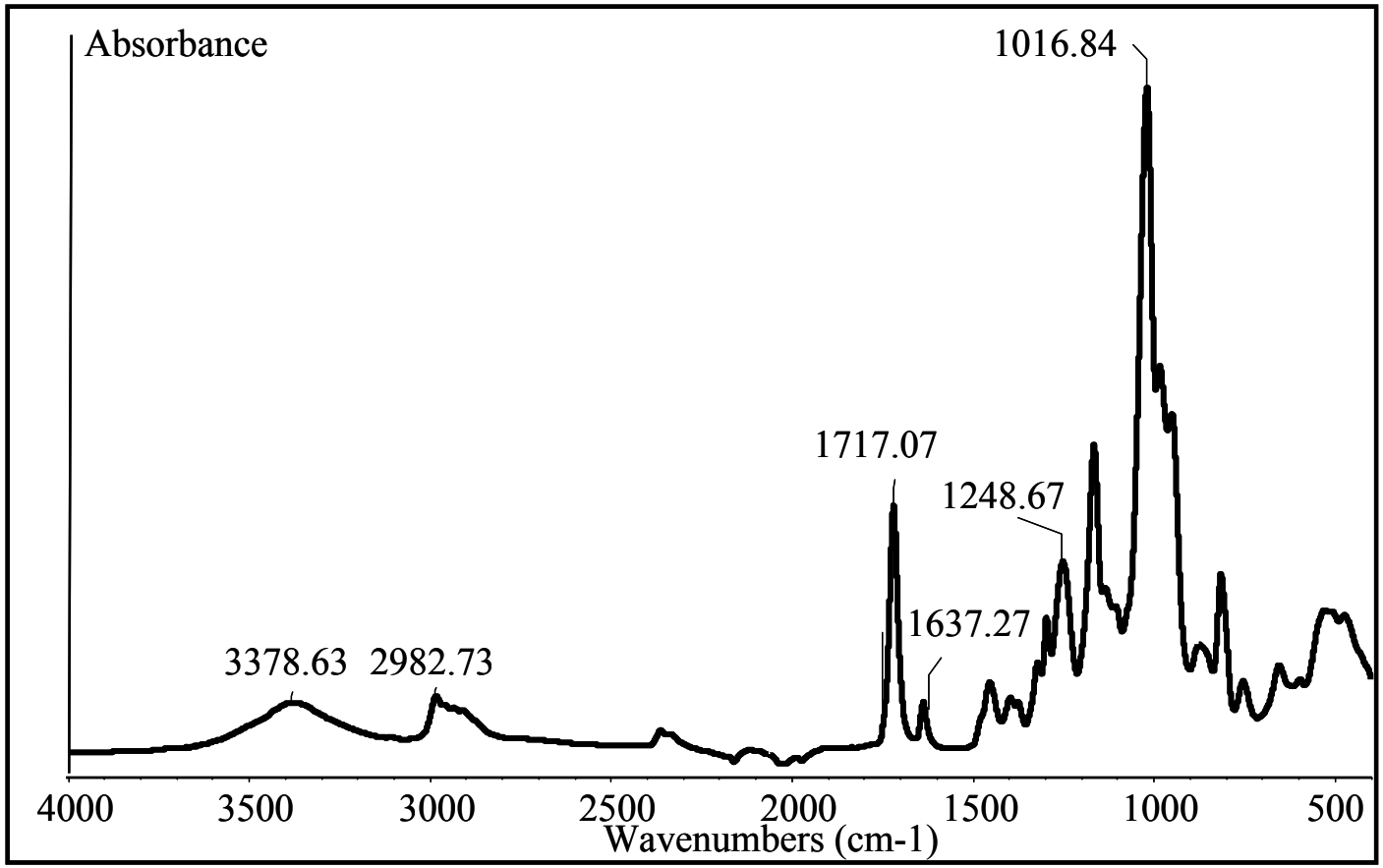


Figure 4.18. FT-IR spectrum of monomer **5**

4.2. Evaluation of Synthesized Monomers

4.2.1. Thermal Polymerizations of Monomers

4.2.1.1. Homo and Copolymerizations of Monomer **1** Monomer **1** was a very reactive monomer which polymerized in a vacuum oven without an initiator in 24 h. Bulk polymerization of this monomer was carried out with AIBN at 60 ºC using standard freeze-evacuate-thaw procedures.(Figure 4.19). The polymer was obtained as a white solid after precipitation into water. The polymer was soluble in THF, acetone and methylene chloride but insoluble in water and ether.

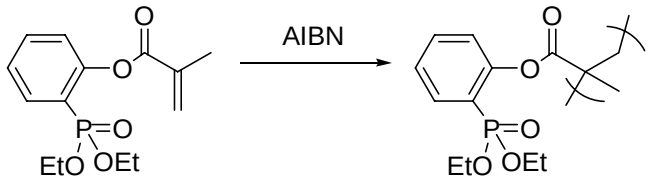


Figure 4.19. Polymerization scheme of monomer **1**

^{1}H-NMR spectrum of the poly-**1** with its monomer are shown in Figure 4.21. The double bond peaks at 5.8 and 6.4 ppm completely disappeared from the monomer after polymerization. The FT-IR spectrum of poly-**1** showed disappearance of double bond peak in Figure 4.4. The number average molecular weight (M_n) for this polymer was around 23560 as estimated by size exclusion chromatography (Table 4.1).

Thermal copolymerization of monomer **1** with methyl methacrylate (MMA) in bulk were run at 60 ^{0}C using 0.5 wt per cent AIBN (Figure 4.20). Table 4.1 shows the copolymerization conditions and characteristics of the resulting polymers. The homopolymerization reactivity of the monomer **1** was higher than those of its copolymerization with MMA. For example, the conversion reached for monomer **1** was 26 per cent in 4 h whereas conversions of 10.2 and 6.8 per cent were reached for the copolymers. The higher homopolymerization reactivity of this monomer may be due to the higher viscosity of this monomer compared to MMA mixtures and electronic effect of the substituent.

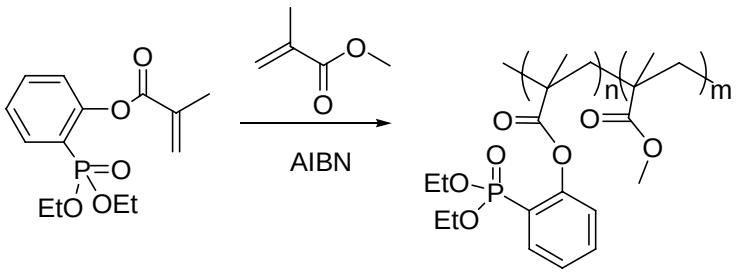


Figure 4.20. Copolymerization of monomer **1** with MMA

The copolymers were purified by precipitation first into ether in which MMA is soluble and then into water to remove residual monomer **1**. The solubility of the copolymers was same with poly-**1**. The copolymer compositions were determined from integrated ^{1}H-NMR spectra using the ratio of peak areas of CH_2-O groups of monomer **1** (4.0-4.2 ppm) to CH_3-O groups of MMA (3.6 ppm) (Figure 4.21). The results shown in Table 4.1 confirm incorporation of monomer **1** into the copolymers.

The molecular weights for the copolymers were higher than that of poly-**1** and decreased with increasing monomer **1** in the copolymer. For example, M_n values of the copolymers MMA/**1** (90:10) and MMA/**1** (50:50) were 54920 and 31530 (Table 4.1). The reason for this decrease may be because of residual diethyl (2-hydroxyphenyl) phosphonate.

The T_g values of the polymers were determined by using DSC, at a scanning rate of 10 ºC/min (Figure 4.22 and Table 4.1). In general, the incorporation of phosphorus into a polymer often results in a decrease of the glass transition temperature. As expected, it was observed that the poly-**1** gives the lowest T_g (52 ºC). The addition of monomer **1** to MMA significantly plasticized PMMA. T_g of MMA/**1** copolymers (90 and 99 ºC) are lower than that of PMMA (129 ºC). However, the decrease in T_g of MMA/**1** copolymers is not proportional to the monomer **1** amount added. Price et al. reported that the T_g of PMMA containing 3.5 wt per cent diethyl ethyl phosphonate as additive is ca. 70 ºC [73]. However, they found that the chemical incorporation of the flame retardant as comonomer (3.5 wt % diethyl (methacryloyloxymethyl) phosphonate) to PMMA only slightly reduces T_g, from 124 to 117 ºC. Thus, they suggested that chemical modification of PMMA by

copolymerization should not effect mechanical properties as much as physical modification using additives, which is an important issue for the use of PMMA. In our work, the incorporation of polymerizable monomer 1 (13 and 59 mol per cent) also slightly reduced the T_g of PMMA.

Table 4.1. Homo- and copolymerization results of monomer **1** with MMA

Monomer	1 in feed	1 in copolymer	Yield (%) 4 h, 60 ºC	M_n	M_w	T_g
1	100	-	26.6	23560	40420	52
MMA/ 1	50	59	10.2	31530	85430	90
MMA/ 1	10	13	6.8	54920	112390	99

The thermal stabilities of the synthesized polymers together with poly-MMA were investigated by TGA under nitrogen (Figure 4.23). The PMMA showed a major weight loss starting at about 250 ºC due to random scissions within PMMA chain and gave no residue. The poly-**1** showed two step degradation at 226 and 352 ºC indicating (i) a different thermal degradation mechanism than that of PMMA, (ii) lower thermal stability than PMMA. The char yield of this polymer was unexpectedly low (3.41 %) compared to our previously synthesized phosphorous-containing monomers from alkyl α-hydroxymethacrylates with 20-30 % residue [3,74]. The copolymers gave char yields of 2.58 and 2.61 %. The formation of char indicates a condensed phase mechanism for flame retardance. The char yields were comparable with copolymers of MMA with 2-methacryloxyethyl phenyl phosphate [75].

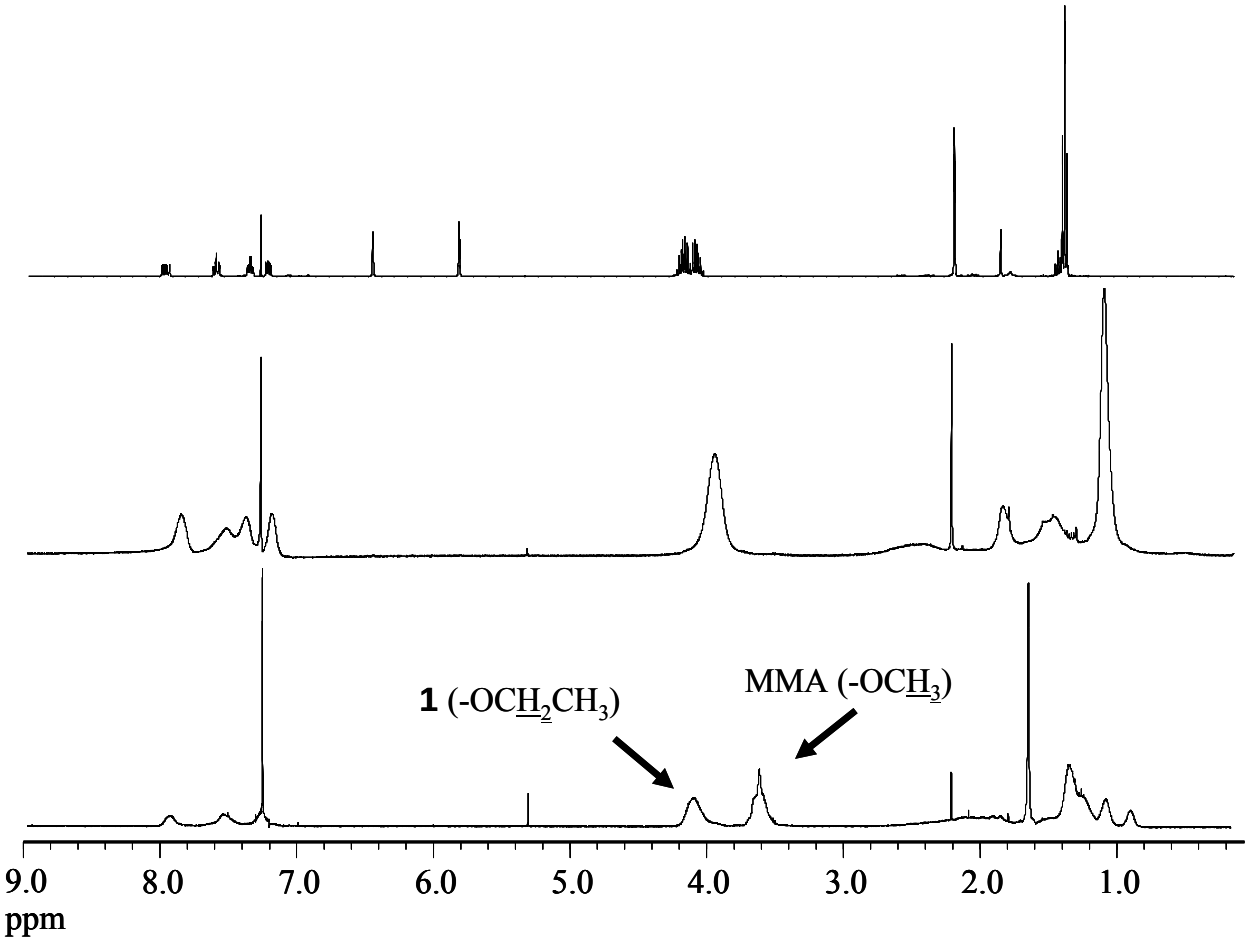


Figure 4.21.[1]H NMR spectra of **1**, poly-**1** and MMA-**1** (90:10) copolymer

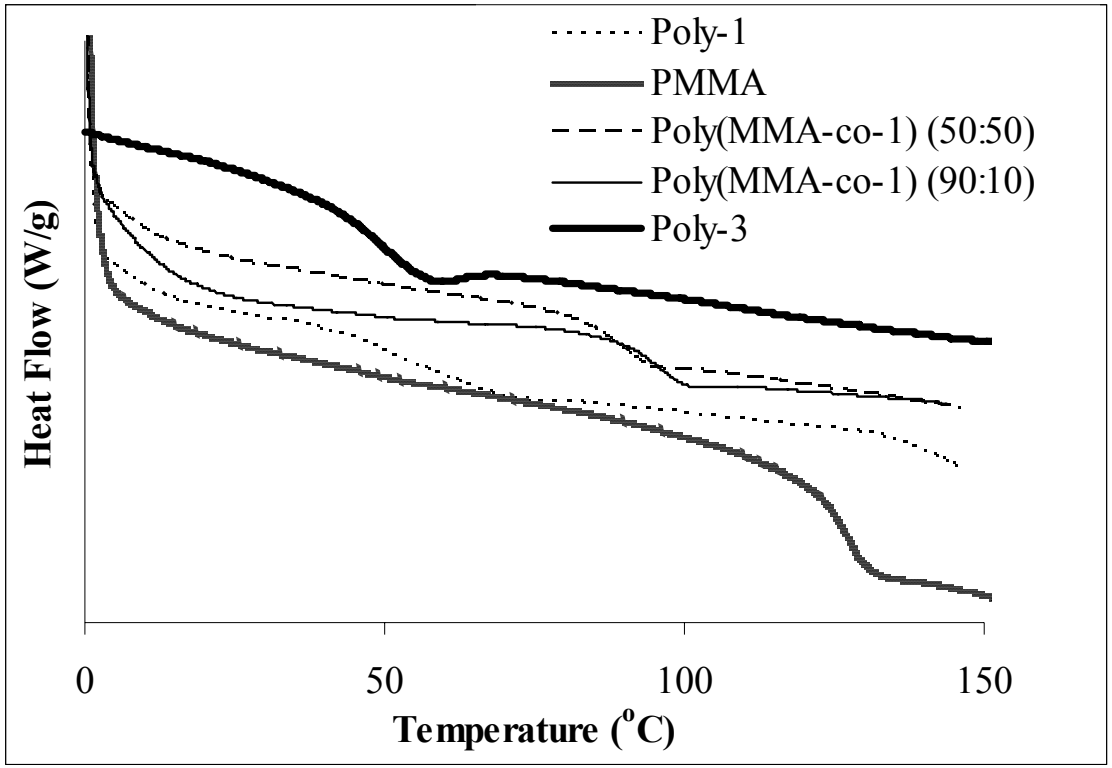


Figure 4.22. DSC curves of PMMA, poly-**1**, copolymers MMA:**1** (90:10 and 50:50 mol%) and poly-**3**

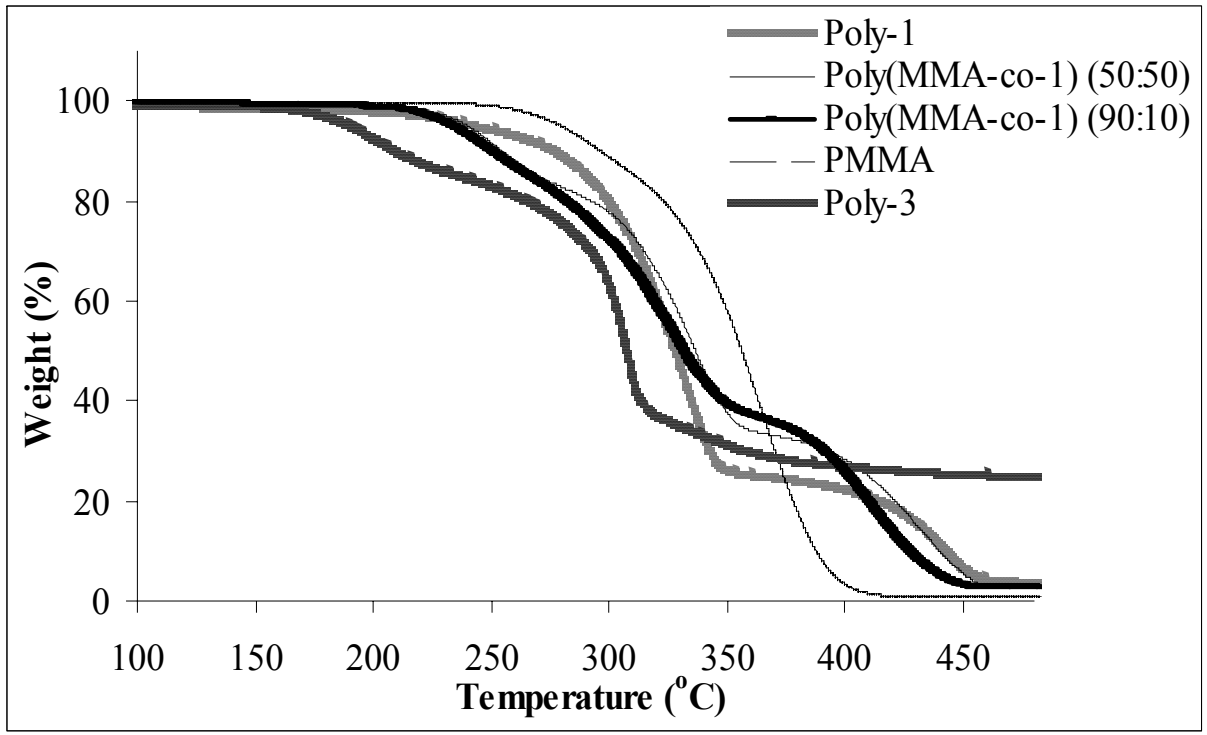


Figure 4.23. TGA curves of PMMA, poly-**1**, copolymers MMA:**1** (90:10 and 50:50 mol%) and poly-**3**

4.2.1.2. Homo and Copolymerizations of Monomer **2** and **2a** The thermal bulk homopolymerization of monomer **2** was not possible because of its high melting point (132 ºC). We did not investigate solution polymerization of this monomer.

Solution copolymerization of monomer **2a** with HEMA was carried out in ethanol at 50 ^{o}C with AIBN. For example, HEMA (26.0 mg, 0.2 mmol), monomer **2a** (16.2 mg, 0.04 mmol) and AIBN (3.3 mg, 0.02 mmol) in ethanol were added to a septum–sealed tube. The tube was subjected to freeze-evacuate-thaw procedure and placed in a 50 ^{o}C oil bath. After 2 h, the gel formed was placed into a large quantity of water to remove unreacted monomers and a crosslinked polymer was obtained in 27.7 % yield.

In order to check polymerizability of monomer **2a**, we conducted its solution free radical copolymerization with acrylamide in water at 50 ^{o}C using V-50 as an initiator.Because of its low solubility only 2 mol % of monomer **2a** was used for 98 mol % of acrylamide. After 10 minutes of polymerization with acrylamide a crosslinked polymer was obtained in a 7.22 per cent yield, indicating incorporation of monomer **2a** in copolymers.

The thermal stabilities of monomer **2a**, poly-HEMA and copolymer of **2a** with HEMA were investigated by TGA under nitrogen at a heating rate of 10 ºC/min (Figure 4.24). The monomer **2a** showed two-stage decomposition starting at 200 ºC and 450 ºC and giving a char yield of 51% at 575 ºC. Poly-HEMA had a char yield of 2% at 575 ºC. The incorporation of monomer **2a** to HEMA increased char yield to 32%.

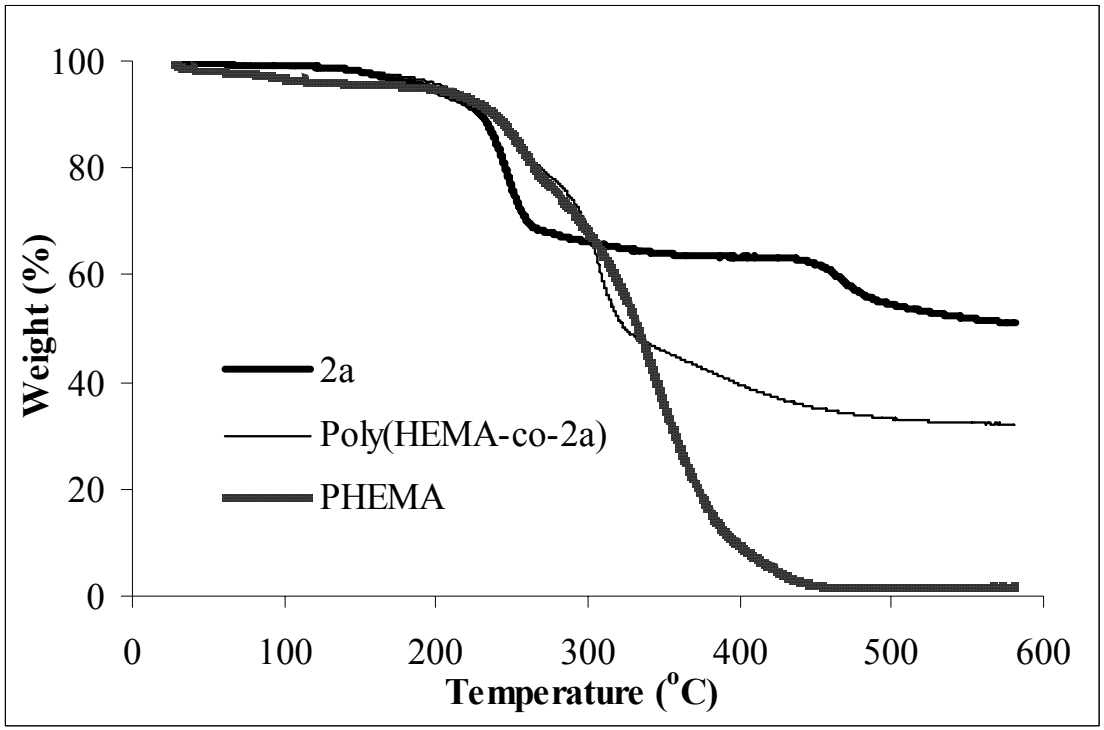


Figure 4.24. TGA curves of PHEMA, poly(HEMA-co-**2a**) and **2a**

4.2.1.3. Homopolymerizations of Monomers **3** and **4** The thermal bulk polymerization of monomers **3** and **4** was carried out with 0.5 wt % AIBN at 60 ºC using standard freeze-evacuate-thaw procedures (Table 4.2). Monomer **3** gave soluble or crosslinked polymers depending on the purity of the sample. The polymerization of the monomer after column chromatography gave only crosslinked polymers. The soluble polymers were purified by precipitation into ether. This polymer was soluble in THF and acetone but insoluble in water, ether and hexane.

^{1}H NMR spectrum of the polymer shows no double bond peaks (Figure 4.25). The number average molecular weight (M_n) for this polymer was 172240 as estimated by size exclusion chromatography (Table 4.2). The high molecular weight of this polymer is probably the result of autoacceleration due to diffusion controlled termination which was observed for the other ester derivatives of alkyl α-hydroxymethyl acrylates.

The DSC analysis of poly-**3** showed a T_g at 50 ^{o}C (Figure 4.22, Table 4.2). This value was much lower than benzoate ester derivative of ethyl α-hydroxymethacrylate (130 ^{0}C) confirming the plasticizing effect of phosphonate group. Thermogravimetric analysis of this polymer gave a char yield of 24 per cent which is much higher than that of poly-**1** and comparable to other phosphonated monomers obtained from alkyl α-hydroxymethacrylates (Figure 4.23).

Table 4.2. Homopolymerization conditions and polymer characterization results[a,b]

Monomer	Time (h)	Yield (%)	M_n	M_w	T_g
3	4	crosslinked	-	-	-
3	4[b]	10.6	172240	204850	50
4	4	crosslinked	-	-	-
4	18	crosslinked	-	-	-

[a][AIBN]= 0.5 wt%, temp= 60 ºC, [b]before column chromatography

The bulk polymerization of monomer **4** gave crosslinked polymers (Table 4.2). Therefore we could not characterize this polymer. The high crosslinking tendencies of monomers **3** and **4**, similar to CMAC-acetate derivative, can be explained by high reactivity of the monomers due to incorporation of ester group.

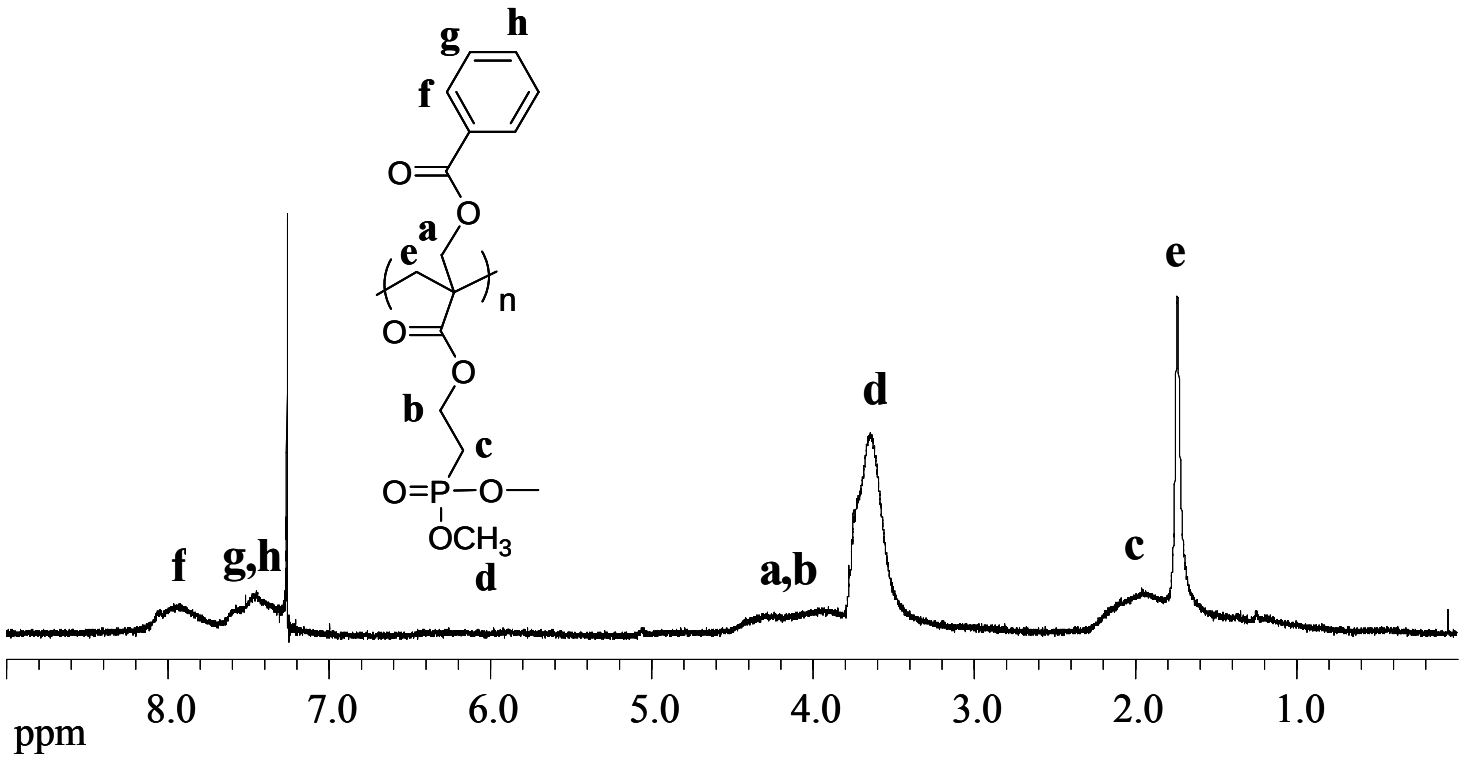


Figure 4.25. The ^{1}H-NMR spectrum of poly-**3**

4.2.1.4. Homopolymerization of Monomer **5** The thermal bulk and solution polymerization (1 M and 3 M in THF) of monomer **5** were carried out with 0.5 wt % AIBN at 60 ºC using standard freeze-evacuate-thaw procedures (Table 4.3). Monomer **5** gave crosslinked polymer at each trial.

Table 4.3. Bulk and solution polymerization results of monomer **5**

Trial (at 60 ºC)	[M]	Solvent	t(min)	Yield (%)
1	3.00	THF	60	Crosslinked
2	1.00	THF	15	Crosslinked
3	-	-	30	Crosslinked

Bahar and Gorkem et al. also synthesized phosphonated methacrylates based on a GMA for dental applications (Figure 4.26). These monomers polymerized rapidly despite having one double bond and showed tendencies to give crosslinked polymers due to a hydrogen abstraction mechanism. The high crosslinking tendency of this monomer can also be explained by a hydrogen abstraction/chain transfer reaction.

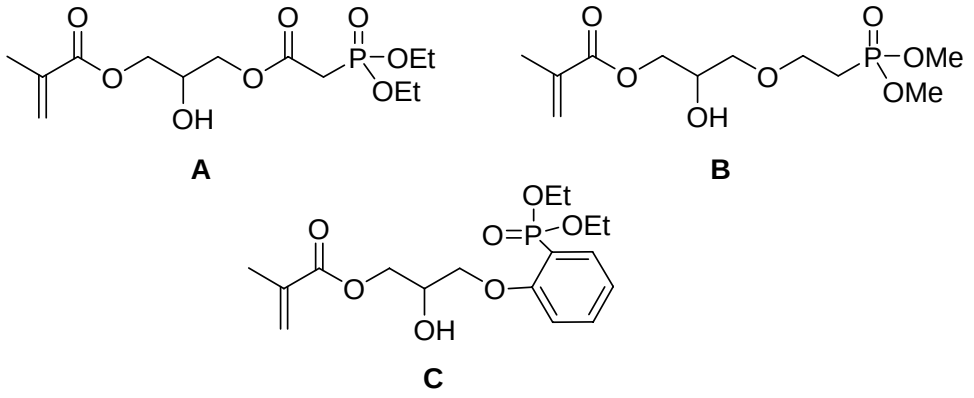


Figure 4.26. Structures of monomers A, B and C

The thermal stability of the polymer was investigated by thermogravimetric analysis (TGA) (Figure 4.27). It showed a weight loss around 270 ^{o}C a char yield of 33 %. This char yield was comparable to those of previously synthesized polymers from monomers A, B and C.

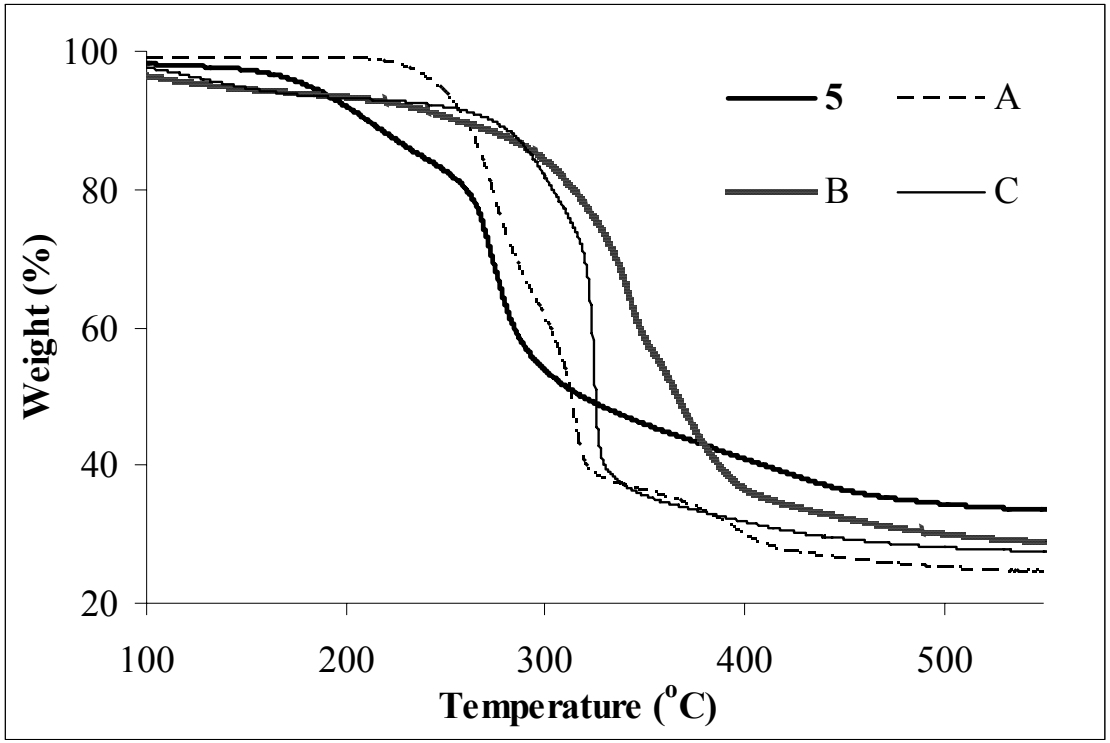


Figure 4.27. TGA curves of monomers **5**, A, B, C

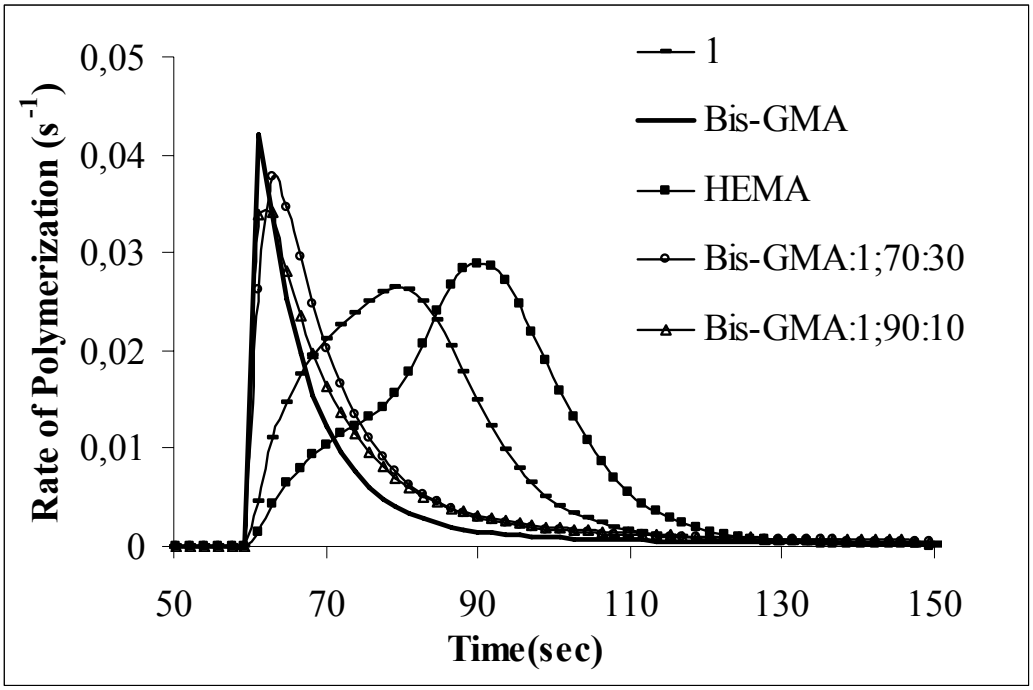
4.2.2. Photopolymerizations of Monomers

4.2.2.1. Photopolymerization of Monomer **1** First, the homopolymerization behavior of monomer **1** was investigated using DMPA as initiator and compared with those of the commercial monomers such as (2-hydroxyethyl methacrylate) HEMA and (2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane) Bis-GMA.

The rate vs. time and conversion vs. time curves are shown in Figure 4.28. The reactivity of monomer **1** (0.026 s^{-1}) was found to be lower than a dimethacrylate monomer, Bis-GMA (0.042 s^{-1}) and similar to a hydrogen bonding methacrylate monomer, HEMA (0.029 s^{-1}). However, conversions of monomer **1** (73.9 %) and HEMA (83.2 %) were higher than that of Bis-GMA (40.5 %). We also investigated copolymerization behavior of monomer **1** with Bis-GMA. Addition of 10 and 30 mol% of monomer **1** to Bis-GMA did not significantly effect the rate of Bis-GMA. But conversions were slightly improved by the addition of monomer **1**. The T_g value of a monomer is a measure of the flexibility of the monomer and mobility of the polymerizing system; a correlation between the conversion data and the monomeric T_g values was reported [76]. The monomeric T_g values of Bis-GMA, Bis-GMA:**1** (90:10), Bis-GMA:**1** (70:30) and monomer **1** were found to be -10, -13, -18 and -22 ^{0}C. Conversion values were in good correlation with the T_g values of the monomers, the most flexible monomer (monomer **1**) is giving the highest conversion (73.9 %) whereas Bis-GMA with the highest T_g showed the lowest conversion (40.5 %). The mixtures were found to be in between (54.3-57.0 %).

4.2.2.2.Photopolymerization of Monomer **2** To study the copolymerization with Bis-GMA, 10 and 30 mol % of monomer **2** was added to Bis-GMA Figure 4.29 shows the rates and conversions of the mixtures. Compared to Bis-GMA, the mixtures did not show noticeably different rates of polymerization, but they did show higher conversions (48.9, 55.8 %) and lower T_g (-12 and -13 ^{0}C). The increase in conversion was not monotonic with the monomer **2** mole fractions, an observation we interpret as competition between two effects changing the rigidity of the resulting copolymer: The addition of monomer **2** probably dilutes the hydrogen bonds which make Bis-GMA viscous. This initially increases the flexibility of the system, decreasing monomeric T_g and increasing polymer conversion. On the other hand, monomer **2** is itself very rigid, therefore increasing its mole fraction works

in the opposite direction. Both mixtures showed higher rates but lower conversions than HEMA.



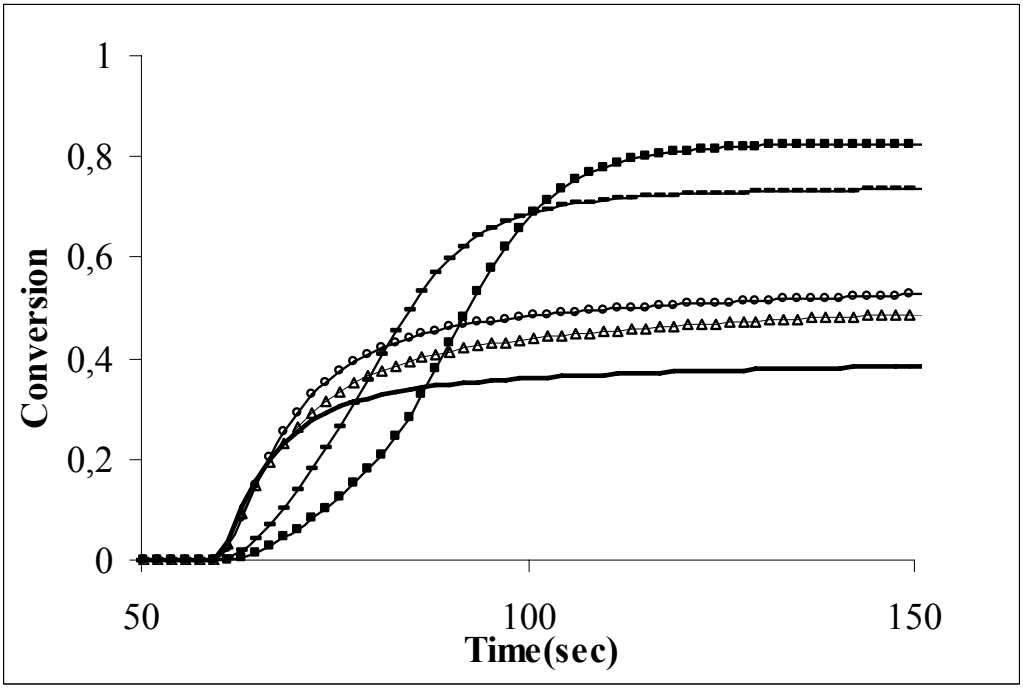
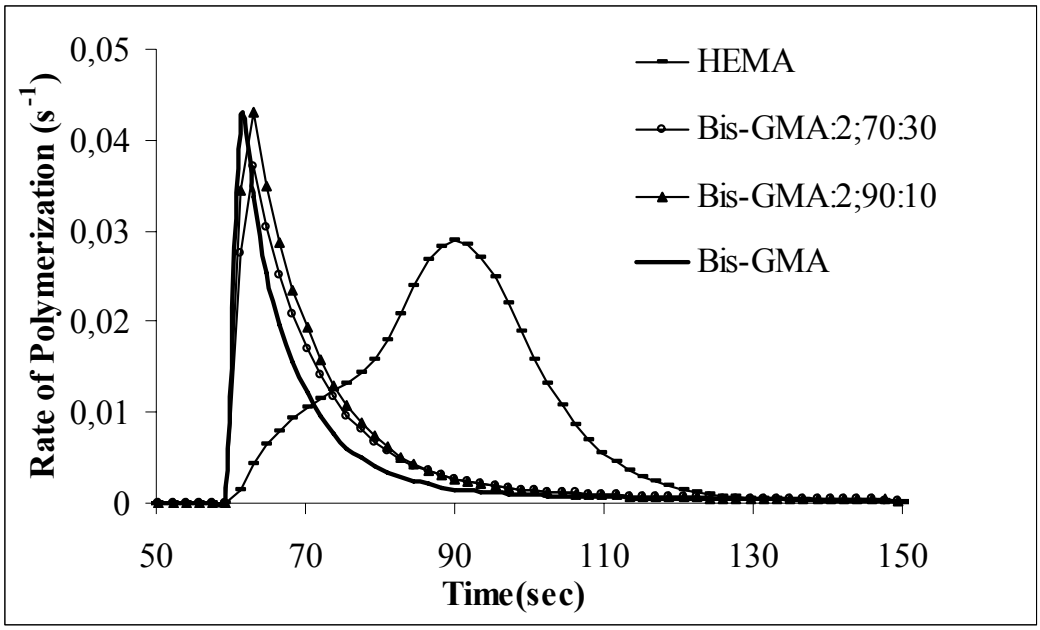


Figure 4.28. Rate of polymerization and conversions of HEMA, Bis-GMA, **1** and Bis-GMA:**1** (90:10 and 50:50 mol%)



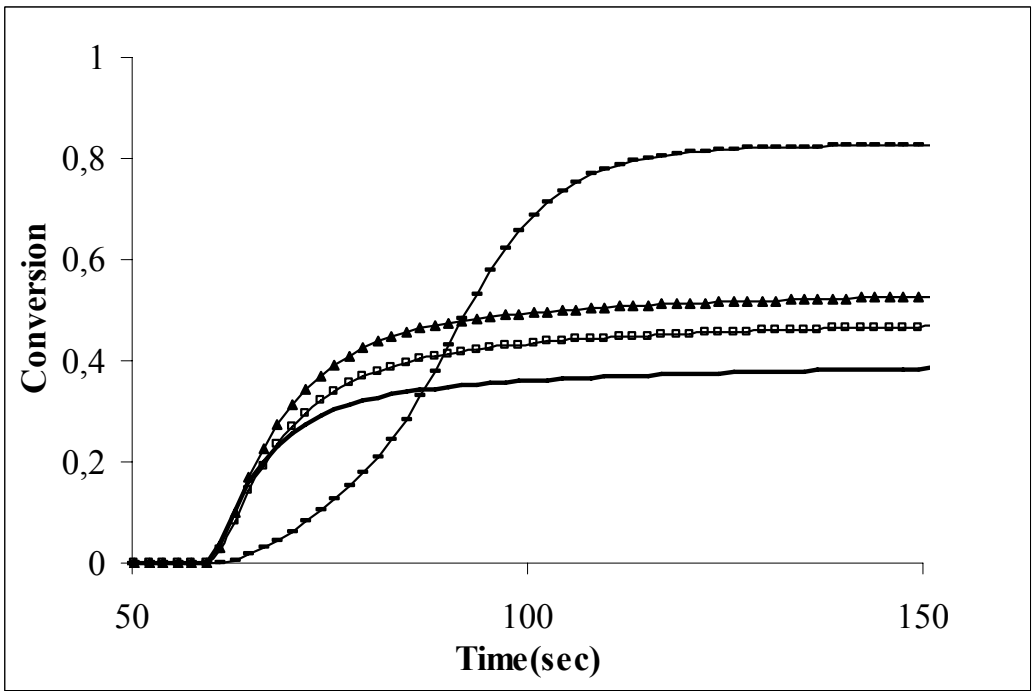


Figure 4.29. Rate of polymerization and conversions of HEMA, Bis-GMA and Bis-GMA:**2** (90:10 and 50:50 mol%)

4.2.2.3. Photopolymerization of Monomer **2a** Copolymerization behaviour of monomer **2a** with HEMA was investigated using photo-DSC. In general, camphorquinone-amine initiator systems are used in dental materials. However these initiating systems have disadvantages due to the possible reaction of the amine group with the acidic dental monomer which decreases the photoreactivity. Therefore we used an initiator without a base groups, BAPO, in our polymerization studies. Moszner et al. also showed that BAPO and its water soluble derivatives have high photoreactivity as well as storage stability [77].

Formulations consisting of mixtures of HEMA: water (40:60 wt.-%), HEMA: **2a**: water (40:20:40, 35:5:60 and 55:5:40 wt.-%) and GDMA: water (28:72 wt.-%) were prepared. They were milky solutions due to low water solubility of monomer **2a**. Homopolymerization of monomer **2a** was not possible due to its low solubility in water in these concentrations. Table 4.4 and Figure 4.31 show photopolymerization results. The maximum rate and conversion values for HEMA: water (40:60 wt.-%) were 0.028 and 83.5%. First, it was observed that for the monomer **2a**-containing mixtures autoacceleration begins earlier and maximum rate of polymerization was observed at lower conversions as expected for dimethacrylates. Second, addition of monomer **2a** to HEMA decreased both the rate and conversion of this monomer depending on the amount in feed. For example, HEMA: **2a**: water (55:5:40 wt.-%) mixture had a maximum polymerization rate and conversion of $0.026 s^{-1}$- 69.3 %, while HEMA: **2a**: water (40:20:40 wt.-%) gave polymerization rate and conversion of 0.02 s^{-1}- 54.3%. The reason for the decrease in the rate of polymerizations are probably due to the rigid structure of monomer **2a**. The lower conversions were typical for multifunctional methacrylates which was also observed during polymerization of GDMA under the same conditions.

Table 4.4. Photo-DSC results of acidic aqueous formulations of **2a** using BAPO

Monomer **2a** (wt. %)	HEMA (wt. %)	GDMA (wt. %)	Rp (s^{-1})	Conversion(%)
-	40.0	-	0.028	83.5
-	40.0	-	0.026	90.9
-	-	28	0.049	59.3
20.0	40.0	-	0.017	49.1
20.0	40.0	-	0.020	54.3
5.0	55.0	-	0,022	76.2
5.0	35.0	-	0,026	69.3
5.0	35.0	-	0,026	72.4

4.2.2.4.Photopolymerization of Monomer **3** and **4** Photopolymerization behavior of the monomers **3** and **4** were investigated using DMPA as initiator and compared with those of the commercial monomers such as HEMA and Bis-GMA and with the previously synthesized monomer, GMonomer. (Figure 4.32). GMonomer as a derivative of CMAC (monomer **5**) with identical ester and ether groups was synthesized by our group previously (Figure 4.30).

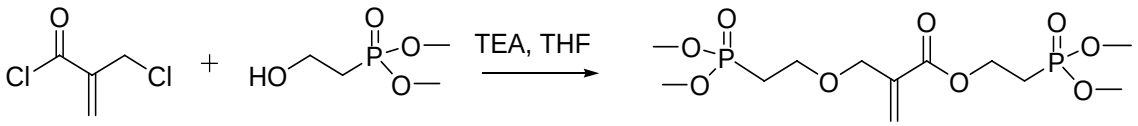


Figure 4.30. Synthesis of GMonomer

Maximum rate of polymerizations were found to be 0.043, 0.018, 0.0090, 0.029 and 0.042 s^{-1} for monomers **3**, **4**, GMonomer, HEMA and Bis-GMA. Rate of polymerization of monomer **3** was about 2.4 times higher than aliphatic ester derivative, monomer **4**. Also rate of polymerization of the ether derivative (GMonomer) was lower than those of the ester derivatives. This results were similar to those found for ester and ether derivatives of alkyl α-hydroxymethacrylates. The conversions reached (85.9, 98.2% for monomers **3** and **4**) were very high compared to Bis-GMA (40.5%) and comparable with HEMA (83.2%).

These values were also comparable to the CMAC-acetate derivative synthesized in our previous work (90%). The slowest monomer (Gmonomer) gave the lowest conversion (62.2%).

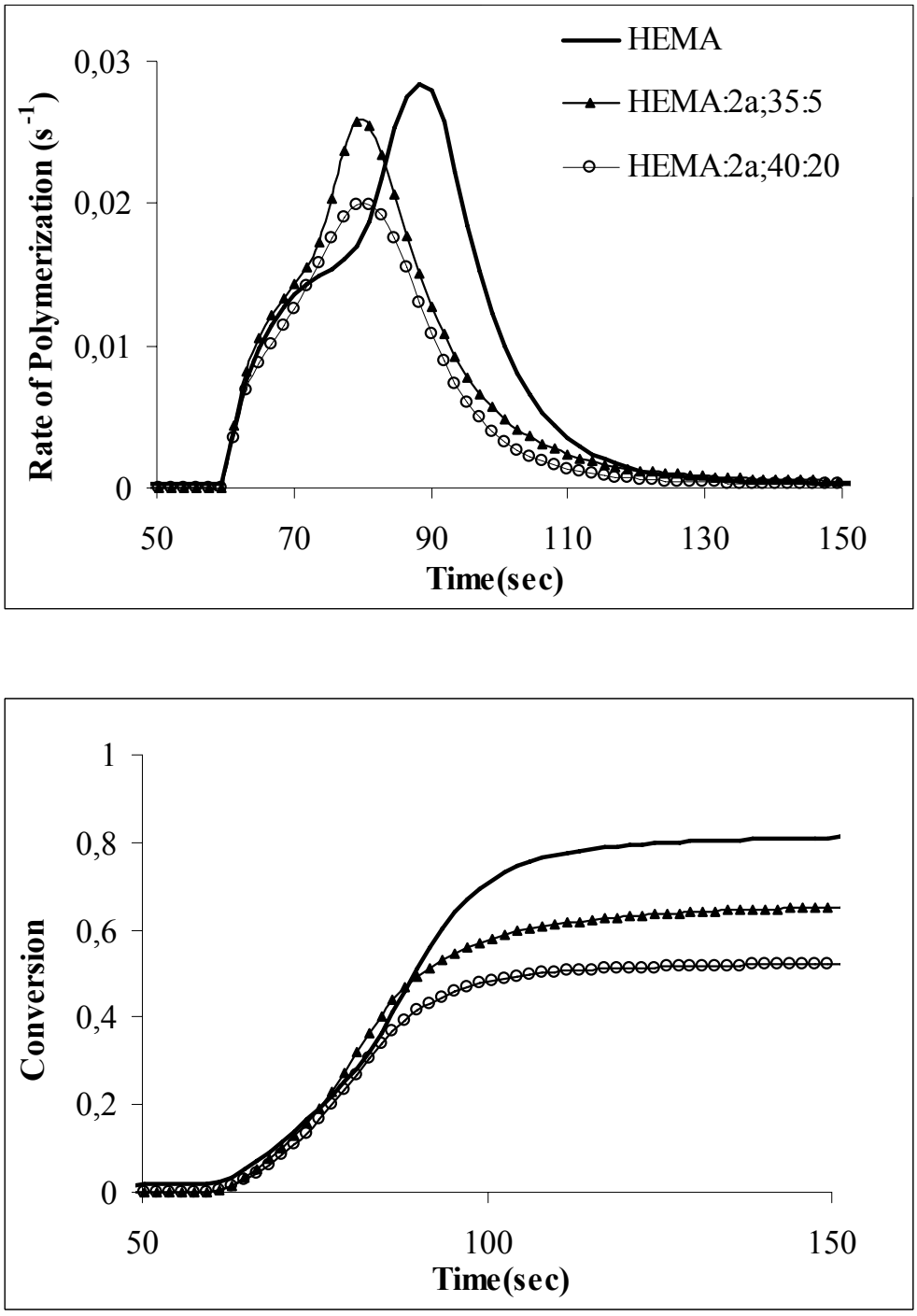


Figure 4.31. Rate of polymerization and conversions of HEMA, HEMA:**2a** (35:5) and HEMA:**2a** (40:20)

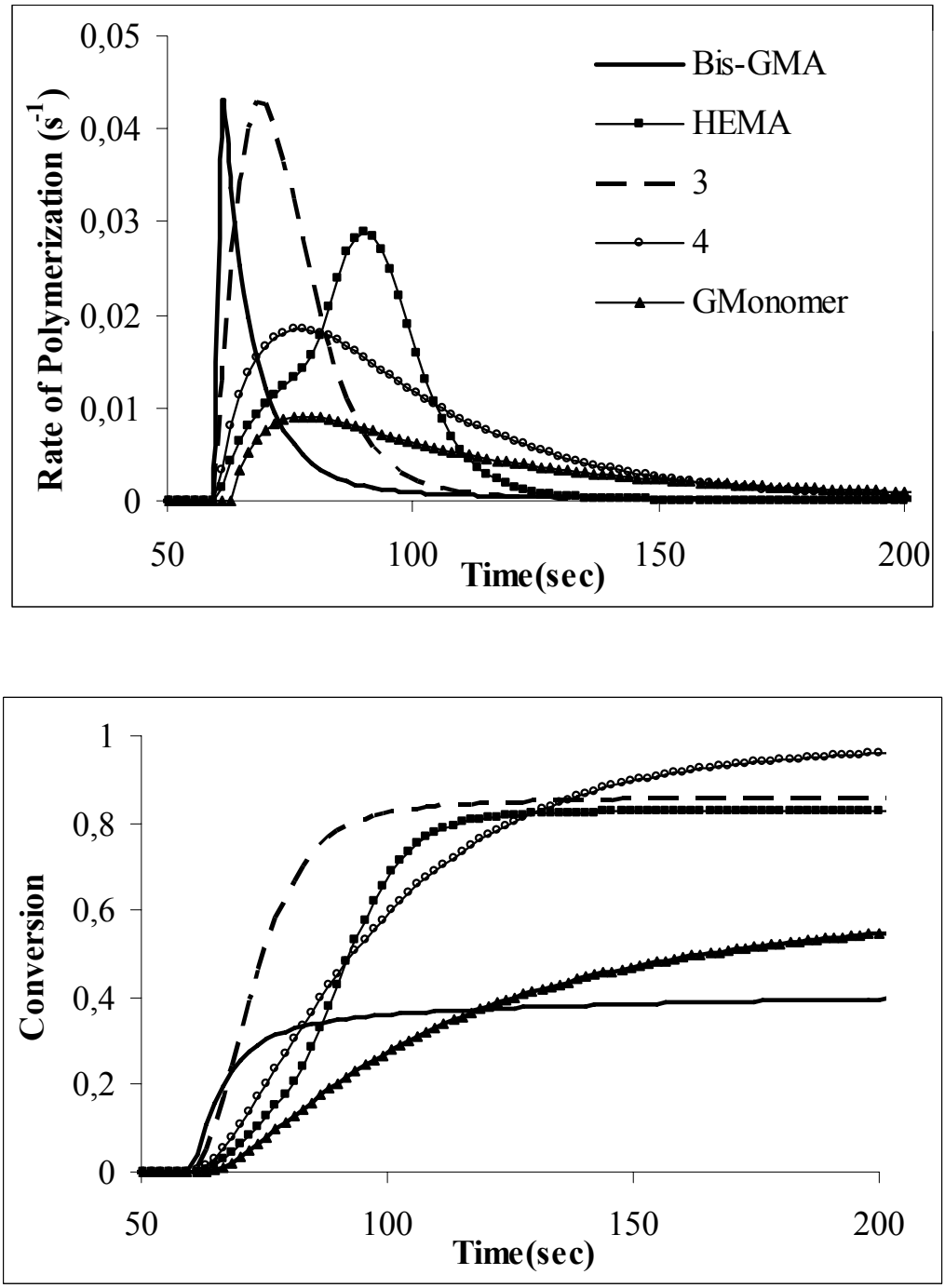


Figure 4.32. Rate of polymerization and conversions of HEMA, Bis-GMA, monomers **3**, **4** and GMonomer

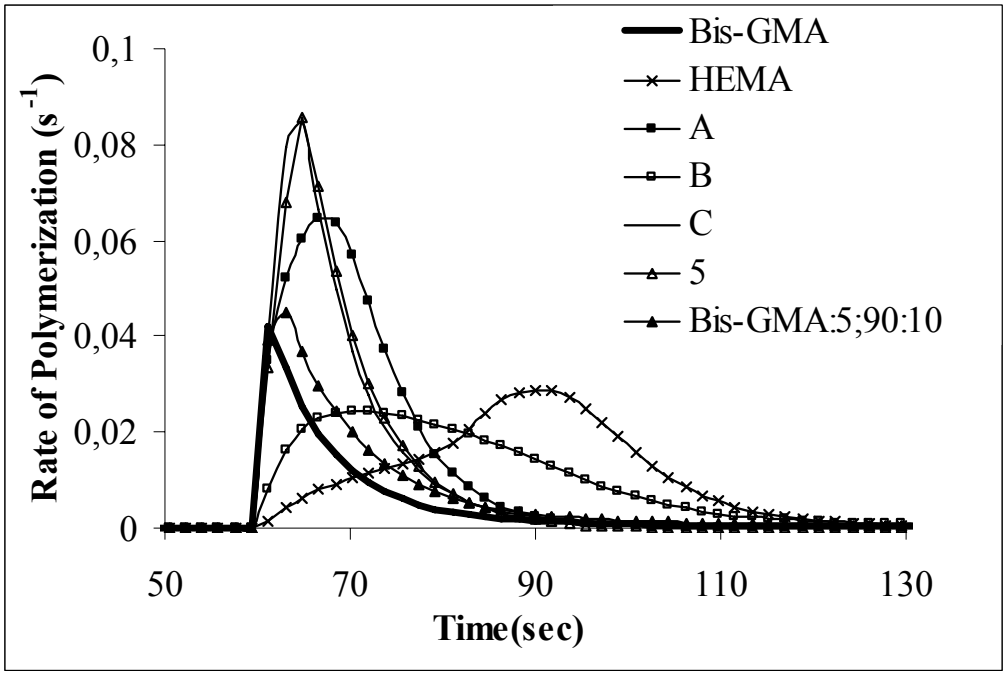
4.2.2.5. Photopolymerization of Monomer **5** Photopolymerization behavior of monomer **5** was investigated and compared with those of the commercial monomers such as HEMA and Bis-GMA and with the previously synthesized monomers, A, B and C (Figure 4.33).

Monomer **5** showed the higher maximum rate of polymerization (0.071 $\mathbf{s^{-1}}$) and conversion (85.2 %) than Bis-GMA and HEMA. This monomer with one vinyl group reacts very rapidly and forms a crosslinked network with low residual monomer. The crosslinking will cause high modulus and hardness of polymer.

Rate of polymerization of monomer was found to be comparable to monomer A and C but higher than monomer B. The reactivity difference between monomers was due to the electronic effect of substituents.

Table 4.5. Photopolymerization results of monomers (**5**, A, B, C, HEMA, Bis-GMA and copolymer of **1** with Bis-GMA (90:10 mol %))

Monomer	**R_p (s^{-1})**	**Conversion (%)**
A	0.064	94.2
B	0.025	83.9
C	0.084	87.2
5	0.071	85.2
BisGMA-**5** (90:10)	0.045	59.6
HEMA	0.029	83.2
Bis-GMA	0.042	40.5



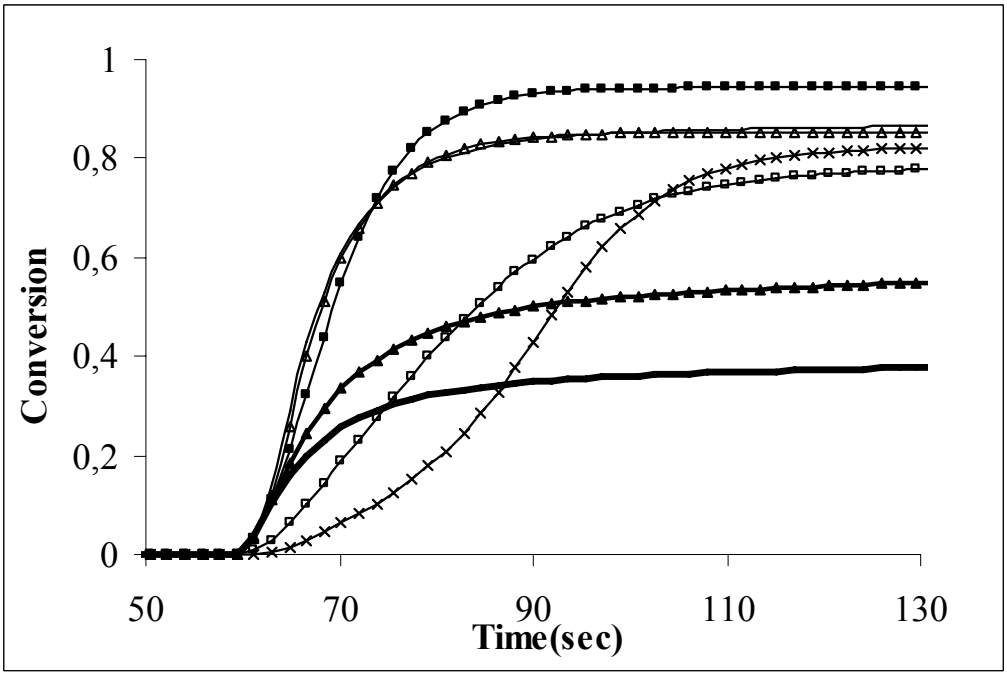


Figure 4.33. Rate of polymerization and conversions of HEMA, Bis-GMA, A, B, C, **5** and Bis-GMA:**5** (90:10 mol%)

4.3. Hydrolytic Stability of Monomers 1, 2 and 2a

The hydrolytic stabilities of the synthesized monomers **1** and **2** were investigated by means of ^{1}H-NMR measurements after storage at 37 ^{o}C for 55 days. ^{1}H-NMR spectrum of Monomer **1** after storage at 37 ^{o}C proved that Monomer **1** was hydrolyzed to diethyl (2-hydroxyphenyl) phosphonate and small amount of polymer was formed (Figure 4.34). On the other hand, monomer **2** was hydrolytically stable.

The major problem in self-etching adhesive systems is the hydrolysis of the ester groups in methacrylates under acidic conditions in the presence of water The hydrolytic stability of the monomer **2a** (2 wt %) in aqueous methanol (3/2) at 37 ^{o}C was investigated by ^{1}H-NMR spectroscopy measurements (Figure 4.35). After 40 days of storage ^{1}H-NMR spectrum a significant decrease of the peaks assigned to monomer **2a** and new peaks appeared in the methyl (a), double bond (b) and aromatic (c) region. These peaks are attributed to methacrylic acid and tetraethyl (2,5-dihydroxy-1,4-phenylene) bisphosphonic acid. The integration of two types of double bond peaks indicated that 87.5 % of monomer **2a** was hydrolyzed. This is to be compared with HEMA, the conventional methacrylate in self-etching adhesive systems, for which Nishiyama et al. [78] found hydrolysis fraction greater than 80 % when stored as 20 wt.-% solution in water (with a pH of 0.94) for 14 days. On the other hand, in our previous work, we reported monomers that are hydrolytically stable due to ether linkages [30]. The above properties of monomer **2a** indicate that it is more suitable for dental composites than dental adhesives. Because formulations of dental composites do not contain water, hydrolysis during storage will not be a problem, unlike dental adhesives. Phosphonic acid groups of this monomer will provide binding ability to tooth, while its rigid structure and crosslinking ability will improve mechanical properties of dental composites.

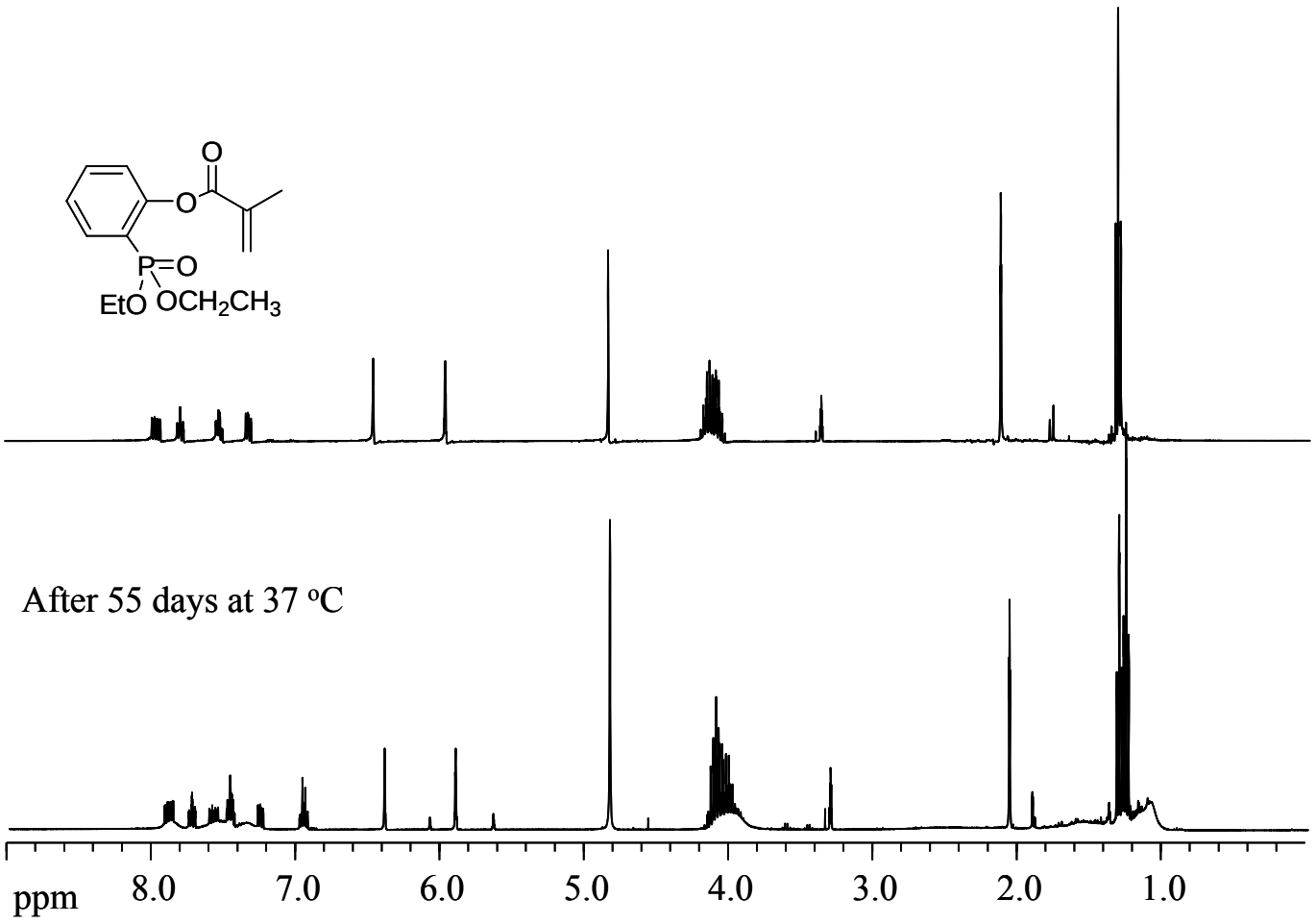


Figure 4.34. The ^{1}H-NMR spectra of Monomer **1** before and after storage at 37 ^{o}C for 55 days

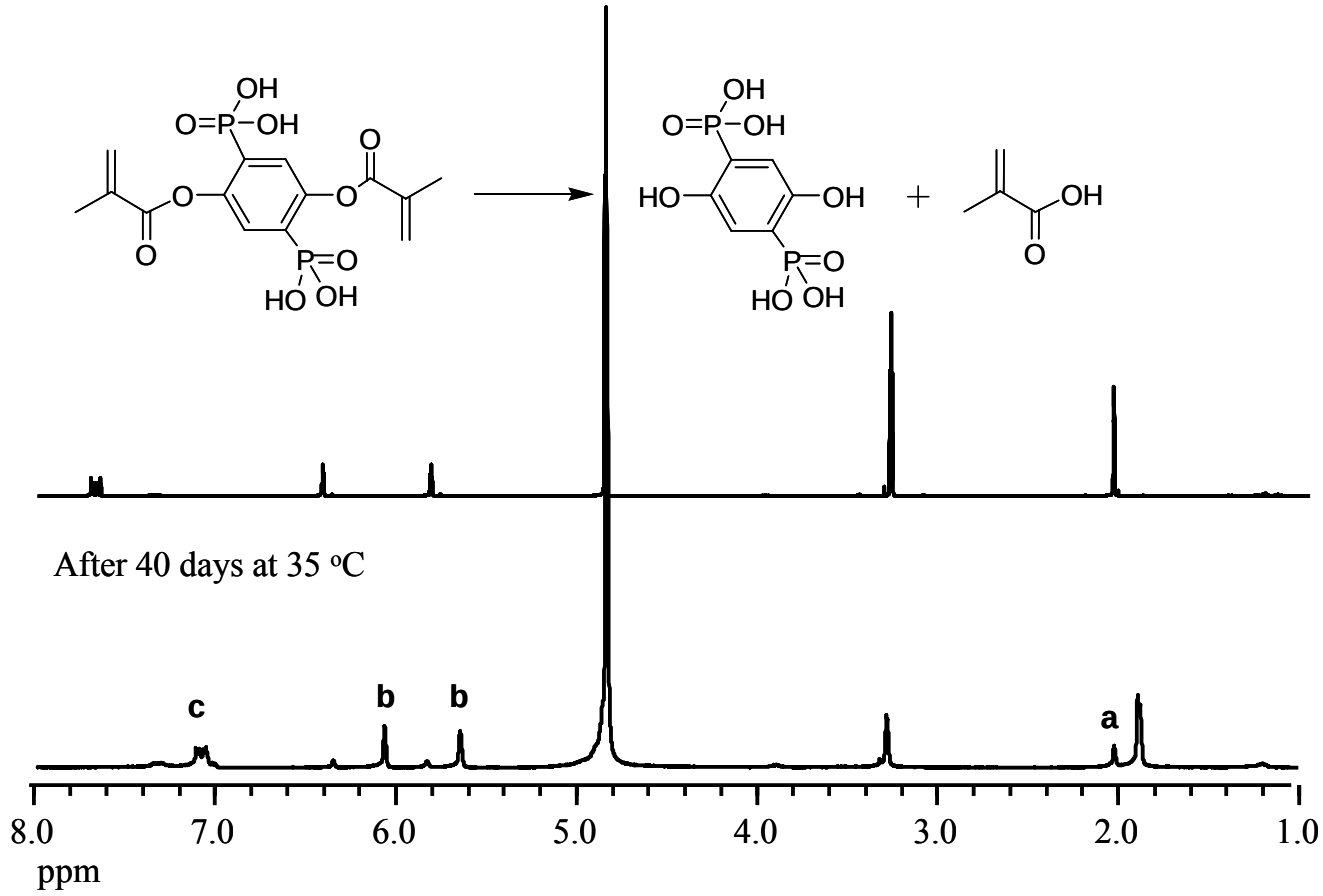


Figure 4.35. The ^{1}H-NMR spectra of Monomer **2a** before and after storage at 37 °C for 40 days

4.4. Interaction of Monomer 2a with Hydroxyapatite

The interaction of monomer **2a** with HAP was investigated using FT-IR spectroscopy (Figure 4.36). For the aqueous solution of monomer **2a**, 40 mg was dissolved in 1.63 g of 20 wt % D_2O/H_2O. First, HAP was added to the 0.6 gr of this aqueous solution of monomer 2a. The addition of 20 mg of HAP resulted in an increase in pH value from 1.71 to 4.22, indicating neutralization of the POOH groups with HAP. After removal of water, FT-IR spectrum was recorded.

Monomer **2a** showed the very broad OH peak of POOH at around 3000-2000 cm^{-1}, the C=O and P=O stretching vibrations are at ~1740 and ~1309 cm^{-1}. The P-O stretching and bending bands are at 1017, 925 and ~592 cm^{-1} respectively. HAP spectrum showed OH peak from lattice of HAP at 3564 cm^{-1}, symmetric and antisymmetric P-O stretching modes around 1000 and 1100 cm^{-1} and antisymmetric P-O bending modes in the 700-500 cm^{-1} region [78]. The mixture of monomer **2a** and HAP showed peaks due to both components, indicating adsorption of monomer **2a** on the HAP surface probably due to hydrogen bonding or complex formation. Also, C=O peak of monomer **2a** at 1740 cm^{-1} shifted to 1712 cm^{-1} after mixing with HAP. The interaction between phosphonic acid groups and HAP, changes the inductive contribution of the ester group to the C=O group, causing it to vibrate at lower frequency.

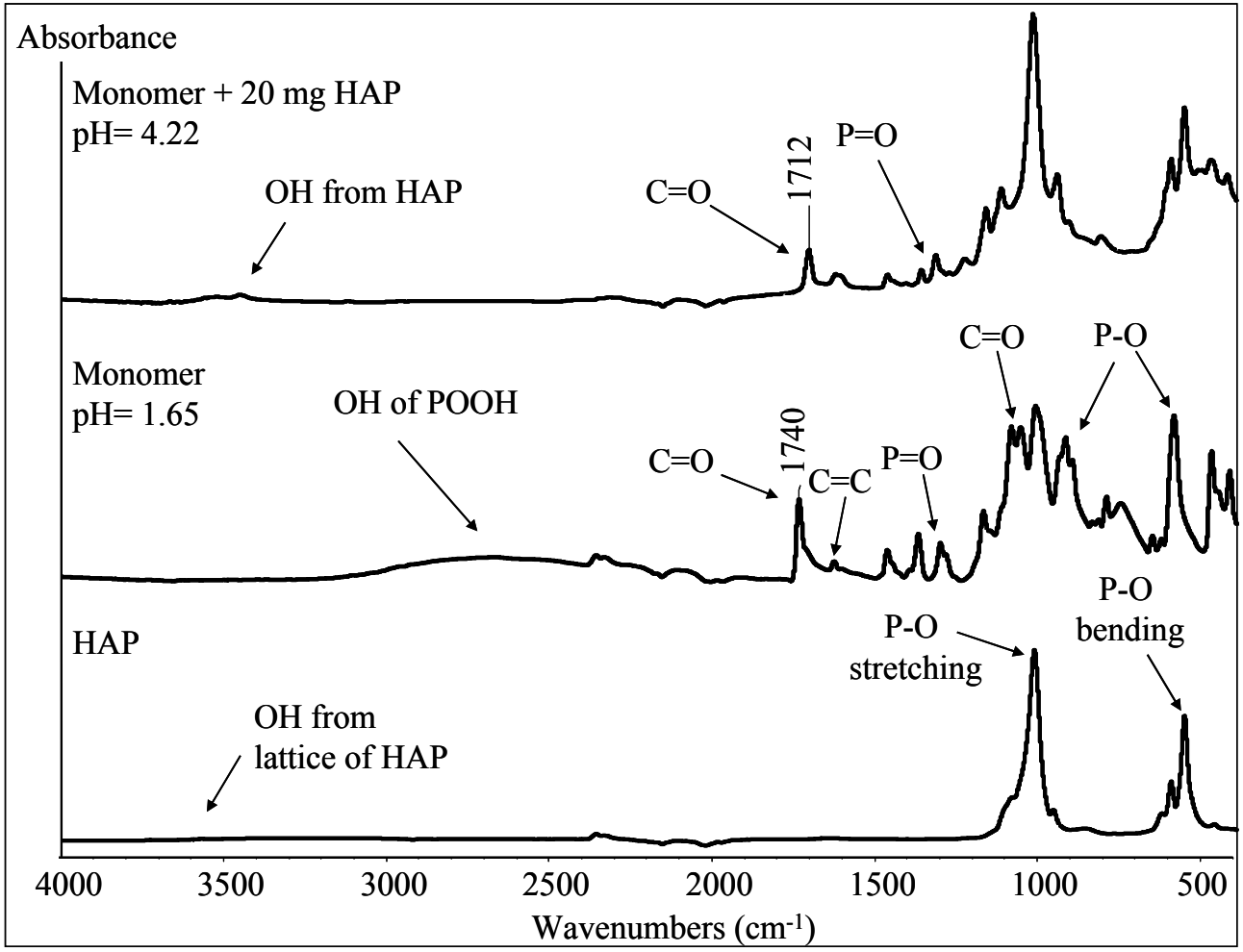


Figure 4.36. FT-IR spectra of HAP, Monomer **2a** and Monomer **2a** with 20 mg HAP

5. CONCLUSIONS

Novel four phosphonate-containing monomers (monomers **1**-**4**), two phosphonic acid-containing monomers (monomers **1a** and **2a**) and one phosphate-containing monomer (monomer **5**) were synthesized by three routes in order to be used in dental materials.

Four phosphonated-methacrylate monomers were successfully synthesized using two different routes. Reactions of two o-hydroxyaryl phosphonates with methacryloyl chloride gave the mono and difunctional monomers **1** and **2**; two stepwise reactions of CMAC with a phosphonated alcohol followed by an acid each gave ester-linked monomers **3** and **4**.

The synthesized monomers showed high reactivity during homo- and copolymerizations to give polymers with pendant phosphonate groups. During photopolymerizations, addition of monomers **1** and **2** to Bis-GMA increased conversion of this monomer without a significant change in the rate of polymerization of this monomer. Therefore these monomers can be used as reactive diluents to Bis-GMA.

It is possible to increase reactivity of CMAC-based monomers by changing the substituents, aromatic substituents being more reactive than aliphatic ones. Although it is a monomethacrylate, monomer **3** showed higher rate of polymerization and conversion than Bis-GMA. Monomers **3** and **4** showed high crosslinking tendencies during thermal bulk polymerizations.

The homopolymers and copolymers obtained produced char on burning indicating their potential as flame-retardant materials. The char yield of the polymer obtained from RHMA derivative (monomer **3**) was much higher than that obtained from methacryloyl chloride (monomer **1**).

Two new dimethacrylate monomers with phenyl phosphonic acid groups (monomer **1a** and **2a**) were synthesized by silylation of monomer **1** and **2** with trimethylsilyl bromide (TMSBr) followed by the hydrolysis of the silyl ester. Monomer **2a** was soluble in water

and pH of the aqueous solution (1.2 wt %) was found to be 1.65. Therefore this monomer was expected to etch enamel and dentin of tooth. The copolymerization behavior of monomer **2a** with 2-hydroxyethyl methacrylate (HEMA) was investigated in water using photo-differantial scanning calorimeter at 40 ^{o}C with bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO) as photoinitiator. It was observed that the addition of monomer **2a** to HEMA slightly decreased both the maximum rate of polymerization and conversion. FT-IR measurements indicated that this monomer can adhere to HAP. It can be copolymerized with other dental monomers to give crosslinked polymers. Hydrolytic stability measurements indicated that this monomer can hydrolyze in water if the storage duration is prolonged. These findings indicated that this monomer is more suitable to use for dental composites where the formulations do not contain water.

Monomer **5** was synthesized by the reaction of GMA and diethyl hydrogen phosphate. Thermal and photopolymerization behavior of this monomer were compared with the phosphonate-containing monomers previously synthesized from GMA. Although it is a monomethacrylate it gave crosslinked polymers probably due to a hydrogen abstraction mechanism. Monomer **5** showed higher rate of polymerization and conversion compared to Bis-GMA. Addition of this monomer (10 mol%) improved both the rate and conversion of Bis-GMA.

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