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ABSTRACT

Synthesis of Bisphenol A Bis-2-Hydroxypropylmethacrylate (BISGMA) and Diethylchlorophosphate and 2-Hydroxyethylmethacrylate (DECP-HEMA) and Preparation of Dental Adhesives

by

Da Xie

BisGMA and DECP-HEMA were separately synthesized from Bisphenol A and glycidyl methacrylate and from diethylchlorophosphate and 2-hydroxyethyl-methacrylate. The structure of the monomer, BisGMA, was further analyzed by means of chromatography, VPO, IR, FTIR and GC-MASS.

Based on the main monomers, BisGMA, DECP-HEMA and an organosilane compound, a dental adhesive has been formulated. Although the tensile strength of the adhesive has been found to be not as good as the adhesive formulated by a previous worker (student), its applicability to teeth is more suitable for clinic practice.

SYNTHESIS OF BISPHENOL A BIS - 2-HYDROXYPROPYLMETHACRYLATE (BISGMA) AND DIETHYLCHLOROPHOSPHATE AND 2-HYDROXYETHYLMETHACRYLATE (DECP-HEMA) AND PREPARATION OF DENTAL ADHESIVES

by
Da Xie

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New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
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Department of Chemical Engineering, Chemistry,
and Environmental Science
October 1992

APPROVAL PAGE
Synthesis of Bisphenol A
Bis - 2-Hydroxypropylmethacrylate (BisGMA),
Diethylchlorophosphate and 2-Hydroxyethylmethacrylate
(DECP-HEMA) and Preparation of Dental Adhesives

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This thesis is dedicated to
my parents

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CHAPTER 1
INTRODUCTION

1.1 The History and Development of Polymer Adhesive Materials for Human Teeth

Usually, structural adhesives are composed of either inorganic or organic compounds. Inorganic adhesives which have been developed to date have low adhesive strength and their solubility in the oral fluids largely limit their service life.

Polymer materials appear to offer the best developmental approach for structural adhesives in dentistry and have been the principal type of structural adhesives introduced to dentistry in recent years.

During the early 1980s dentin - bonding systems utilizing phosphate esters of BisGMA ((isopropylidene bis [p-phenoxy (2-hydroxytrimethylene)]) dimethacrylat) were introduced in hopes of improving bonding strength by creating ionic bonds to the calcium component of dentin. These second - generation dentin bonding agents exhibit increased bonding strength to enamel and good adhesion to dentin [1].

But over a period of time, the dentin bonds have been shown to decrease in strength, probably due to the hydrolysis of the phosphate/calcium bond.

In order to further refine the dentine bonding system based on phosphorylated esters, research turned to several entirely new, but interrelated chemical approaches in the late of 1980s [2, 3, 4].

Multicomponent, multistage systems the third generation of dental-bonding agents, have been adopted by almost seven of ten dentists in the late 1980s, even though they are more difficult and time consuming to apply than the earlier phosphate ester formulations. Now researchers focus on the smear layer and modify this layer as well as a portion of the peritubular material, so that the tubules are exposed for

micro-mechanical bonding (see section 1.2 for a more detailed explanation of the structure of teeth).

Although the third generation dentin - bonding system is compatible with all composite resins, the composition of the pre-treatment primers that etch and or modify the dentin surface are specific to each system and cannot be interchanged with other bonding agents.

Leading researchers in the area of adhesive bonding indicate that further innovations and advancements in dentin - bonding systems are likely to focus on improving the longevity and reliability of the system rather than on enhancing bond strength [5].

1.2 Composition and Structure of Teeth

The tooth consists of the crown and the root. The crown is covered by a relatively thin (1-2 mm) coating of enamel. The enamel is a composite material consisting of about 95% hydroxide apatite, a composite phosphate mineral having the basic repeating unit $Ca_{10}(PO_4)_6(OH)_2$, with the remaining portion consisting mostly of keratin - like protein and water. Tooth enamel is characterized by hard, prism-like rods of hydroxide apatite which extend from the surface of the crown to the dentine.

Under the enamel surface and extending to the pulp is another composite called dentin which is about 60% hydroxide apatite and 20% organic material with the latter largely collagen, a fibrous protein.

The structure of dentin is highly tubular and these tubular walls contain a calcified matrix. The hydroxide apatite dentin crystals are only about one tenth the size of those in the enamel and are apparently embedded in or intimately mixed with the collagen fibrils [6] (see Figure 1).

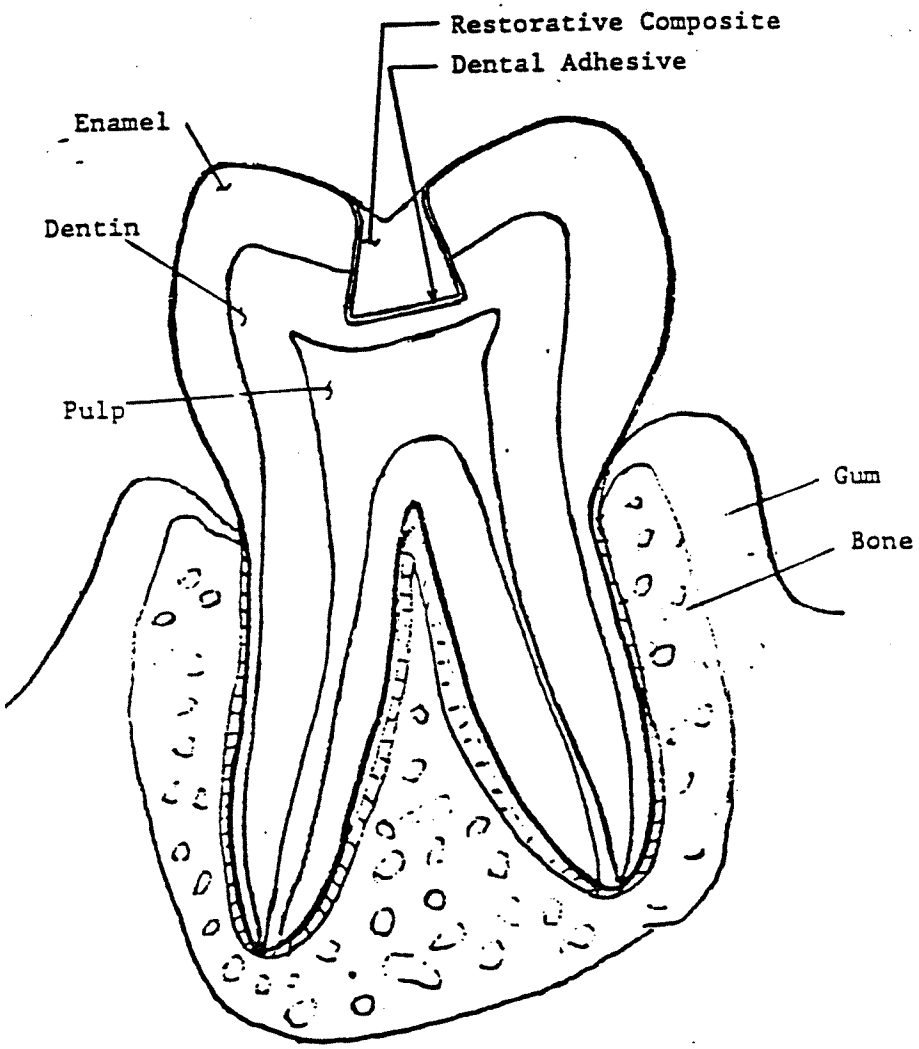


Fig.1 Tooth Structure

1.3 Mechanisms of Adhesion

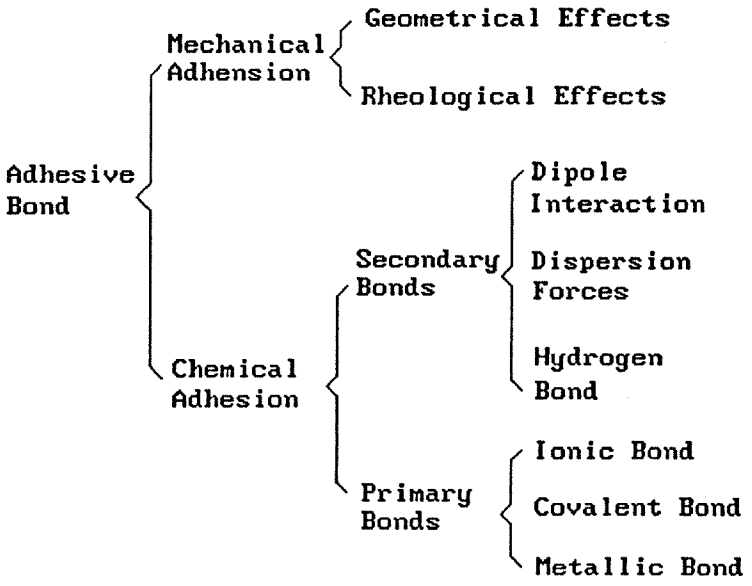
1.3.1 Types of Adhesion

An adhesive bond is a surface attachment due to mechanical and chemical adhesion.

Mechanical adhesion is attributed to two factors: geometrical effects and rheological effects. A geometrical effect is a mechanical retention caused by microscopic porosity or roughness of the surface which produces "mechanical hook" as the phenomenon is sometimes called. A rheological effect is a mechanical adhesion factor caused by the flow of the material in both the liquid and the solid phase that causes "shrink fit". Most shrinkage arises from polymerizatio or cooling .[7]

Chemical adhesion arises from two types of effects: secondary chemical bonds and primary chemical bonds. Secondary chemical bonds are intermolecular in nature. These secondary chemical bonds are the principal ones we look to when designing the adhesive. Primary chemical bonds are those types of bonds which hold atoms together to create molecules. They are designated as ionic, covalent, or metallic.[8]

The relations are shown as follows:



1.3.2 Criteria for Achieving High Adhesion

The following conditions must be present in order to achive good adhesion:

The surface of the substrate must be rough to increase the area of contact between the adhesive and the substrate, to provide perpendicular projections in order to resist shear force, and to introduce opportunities for geometrical and rheological mechanical ahesion.

The surface of the substrate must be free from grease, dust and any non-substrate material that would come between the adhesive and the substrate. This is usually accomplished using a suitable solvent.

The viscosity of the adhesive must be low enough to flow into all pores and crevices for maximum surface contact.

The adhesive must be chemically compatable with the substrate, meaning the polarity of the two should be similar. Usually this is a challenge in designing a good adhesive.

The adhesive must solidify with low shrinkage.[9]

1.4 Criteria for Choosing Suitable Monomers as an Adhesive

1.4.1 General Criteria

The most critical criterion that the monomer must meet is that it harden with minimal shrinkage. If the monomer hardens with high shrinkage it is probable that the shrinkage forces will be of the same order of magnitude as the adhesion forces because both arise from intermolecular forces. So the adhesive bond will be ruptured during hardening, or the adhesive will crack, or the adhesive bond will be so highly pre-stressed that it will exhibit poor bond strength in service.

Shrinkage occurs in the polymerization of monomers from:

1). Evaporation of reaction by - products.

2). Primary bond formation.

3). Cooling from the heat of polymerization and curing.

The evaporation of reaction by-products means by-products from condensation polymers. These are usually water or other low molecular weight compounds which evaporate from the glueline during polymerization and the curing period, which may last for several weeks. This creates shrinkage or shrinkage strains.

Primary bond formation occurs in both condensation and addition polymers, because small molecules are reacting to form macromolecules. Before reaction these small molecules are separated by a distance of about 4A, the Van der Waal's distance. After reaction, the ends of the molecules are no longer separated by Van der Waal's distances but by atomic bond distances, which for covalent bonds is an inter-atomic distance of less than 1.9A.

If a resin is cooled from an elevated curing temperature, thermal shrinkage will be superimposed on polymerization shrinkage. Thus to meet the criterion of low shrinkage the choice of monomer is critical.

One way of reducing shrinkage is to choose a low shrinkage monomer. In general, condensation polymerization produces the highest shrinkage. Addition polymerization also produces high shrinkage, but less than condensation polymerization. Addition polymerization of ring - opening species produces the lowest shrinkage. This is because when the ring is opened the reaction products occupy about a 4% larger molecular volume than the precursors.

Another way of reducing shrinkage is to use bigger monomers, such that the polymerization volume change is a lower percentage of the overall volume. This is why diacrylate is used as the monomer instead of methyl methacrylate.

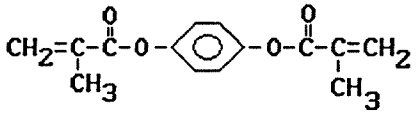
A third way of reducing shrinkage is to have the cure temperature at the service temperature (room temperature/ body temperature).

The fourth way to reduce shrinkage is to optimize the monomer blends such that gelation viscosity is not reached until a higher percentage of monomer has pre-reacted.[10]

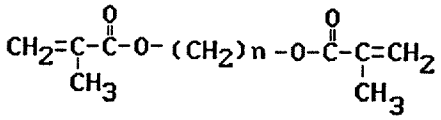
1.4.2 Specific Choices

a). The monomer, BisGMA

Despite the introduction of many new polymers, methacrylates have continued to be the most extensively used dental resins. Most successful have been studies with modified bifunctional acrylic monomers. A highly rigid material is obtained with an aromatic dimethacrylate (I) whereas aliphatic dimethacrylates incorporating a long chain of methylene groups (II) are considerably more flexible.



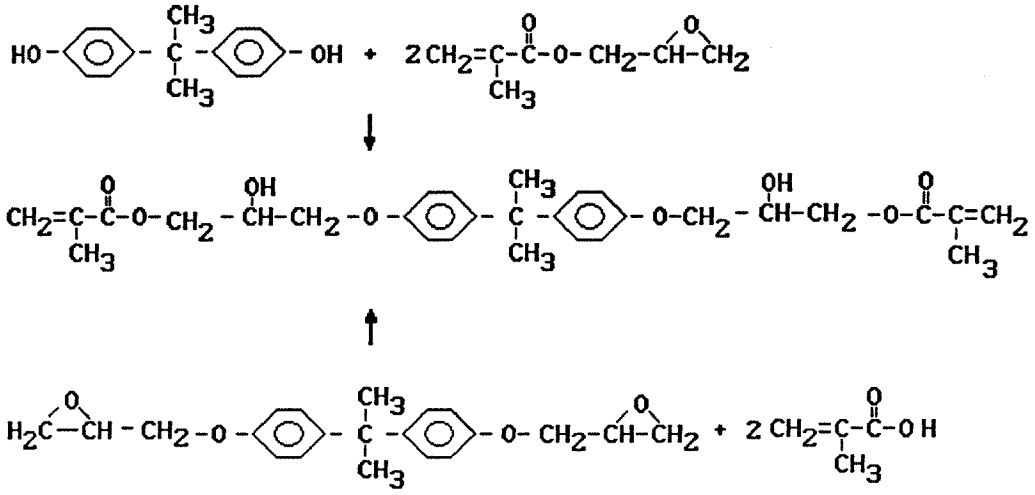
(I) Aromatic acrylic monomer



(II) Aliphatic dimethacrylates

Hydrophilic groups, such as hydroxyl groups, can be incorporated into the basic monomer unit to yield a polymer, which in the presence of water, forms a soft gel[11].

BisGMA (isopropylidene bis [p-phenoxy (2-hydroxytrimethylene)] dimethacrylate)



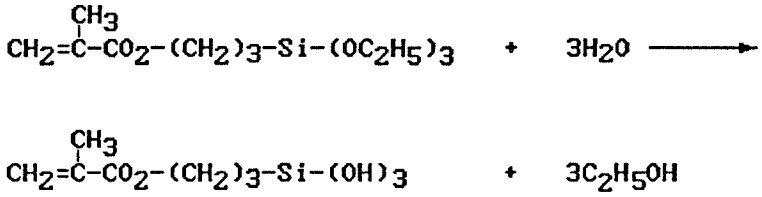
can be synthesized from Bisphenol A ([2,2 - bis(4 - hydroxyphenyl)propane]) and glycidyl methacrylate (top) or the glycidyl ether of Bisphenol A and methacrylic acid (bottom) [12,13]. BisGMA monomer diluted with copolymerizable solvents such as methyl methacrylate and dimethacrylate is the liquid component of most composite resins. Since the monomer is a complex mixture of high molecular weight optical isomers, purification on a large scale is difficult. The highly viscous nature of the monomer necessitates the use of volatile diluents, which increase curing shrinkage and toxicity.

Therefore, in this research, we attempted to make and purify the monomer and pre-polymer synthesized from bisphenol A and glycidyl methacrylate.

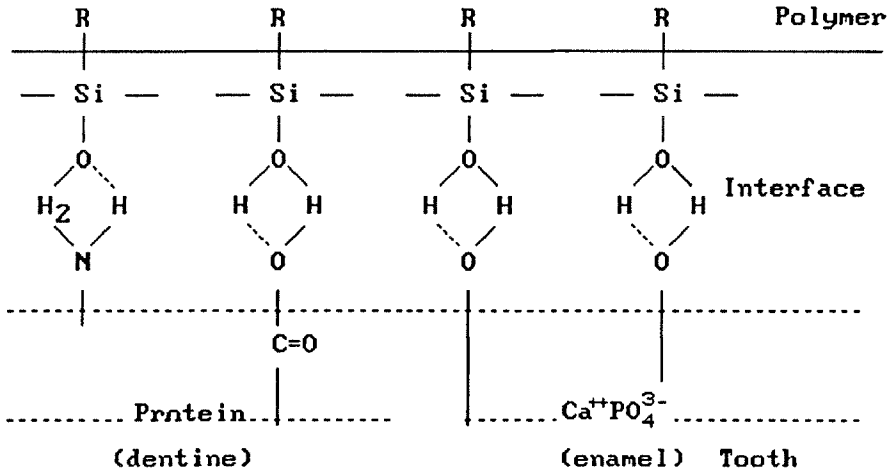
b). The monomer, G-methacryloxypropyltriethoxysilane.

The adhesion reaction existing between polymer - silane - mineral is based on the hydrolysis of the silane. The chemical reaction at the adhesion surface depends on the surface chemical structure and the silane functional groups.

The tooth structure consists of two main parts: dentin and enamel, each of which contains a large portion of water and protein. In dentin the protein has $-NH_2$, -OH, and -COOH groups. In the enamel the protein contains hydroxyapatite $(Ca_{10}(OH)_2PO_4)_6$. When the adhesive containing silane is applied to the surface of the tooth, the intermediate silanols will be generated because of the presence of the water in the tooth structure. The reaction is shown as follows:



It is proposed that in the chemical reaction between the silane and the tooth structure that the silane coupling agents provide H-bonding at the interface between the adhesive polymer and the surface of the tooth [14]. The adhesion between the polymer, the silane, the tooth surface can be shown as [15]:



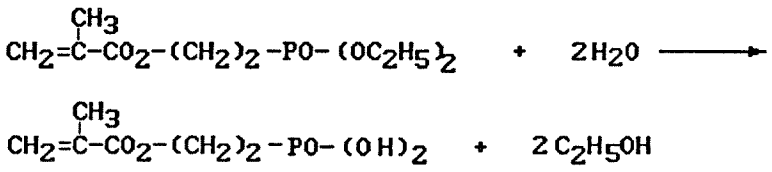
c). The monomer, organic phosphonate [15,16]

The enamel and dentine consist mainly of hydroxyapatite, which is a kind of calcium phosphate mineral. The polymer containing phosphonate adheres to the tooth by forming chemical (ionic) bonds between the calcium hydroxyapatite and the phosphonate groups of the polymer. This increases the adhesion of the restorative material to the tooth and prevents the seepage of fluids into the restoration-tissue interface.

The chemical reaction between the tooth and organic phosphonate occurs because hydroxyapatite crystals carry three PO_4^{3-} ions per unit cell which are readily exchangeable with the phosphonate ions. Phosphonate ions, RPO_3^{2-}, can exchange with the phosphate ions on hydroxyapatite crystals. A polymer carrying many phosphonate groups is expected to have an even higher affinity for the surface of hydroxyapatite crystals because the polymer can attach itself to many sites simultaneously.

The adhesion between the tooth and the polymeric phosphonate is based on the hydrolysis of the polymeric phosphonate, which happens as soon as the monomer is applied to the tooth surface, where water exists.

The reaction can be shown as follows:



CHAPTER 2
EXPERIMENT

2.1 Synthesis of Diethylchlorophosphate and 2-Hydroxyethylmethacrylate

2.1.1 Purification of HEMA

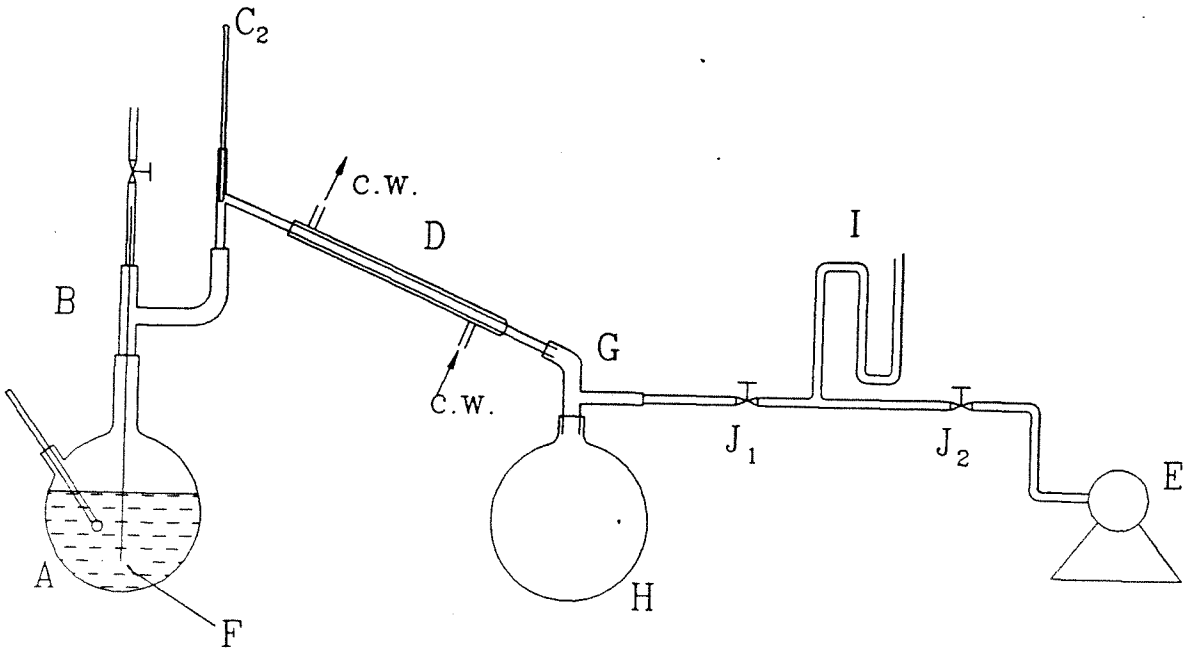
100 ml hydroxyethylmethacrylate (HEMA) was placed into a 250 ml flask equipped with two thermometers, a magnetic stirrer, a condensor, a receiver and a vacuum pump system. (See figure 2). 2 or 3 drops of chloranil were added to the flask as inhibitor. The flask was heated slowly to 85^{o}C in a silicon oil bath.

The distillation was maintained under a vacuum of 1 to 2 mm Hg and at a temperature of 85-90^{o}C. The initial portion of the distillate was discarded. Approximately 50 ml of distillate was collected. The distillate was stored in a refrigerator at about 5^{o}C to avoid self-polymerization.

2.1.2 Reaction Procedure

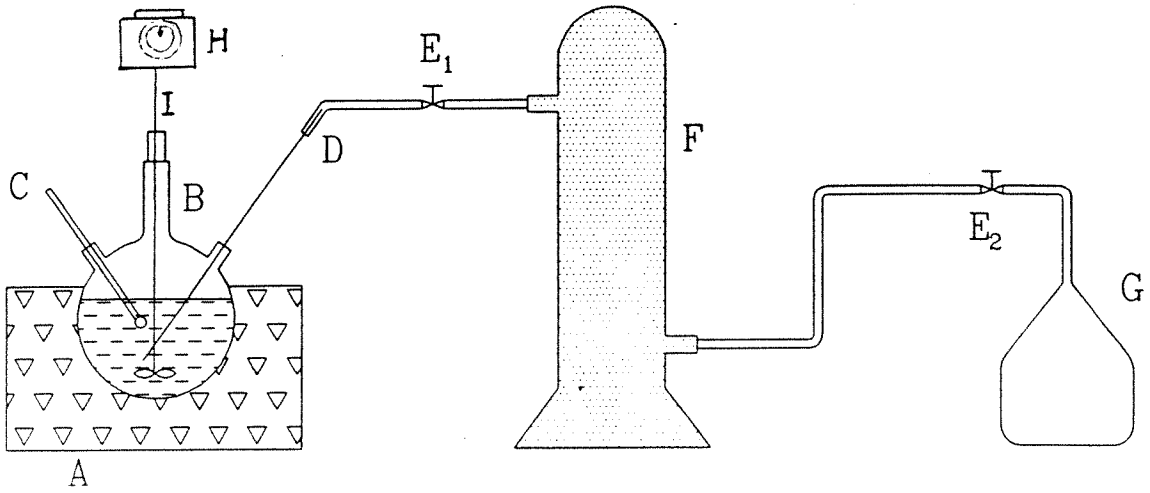
25.89 g diethylchlorophosphate (DECP) and 19.38 g freshly distilled HEMA were placed into a 500 ml three-necked flask equipped with a thermometer, a glass stirrer rod and a glass tube for introducing NH_3 gas. Five drops of pyridine were put into the flask as catalyst (see Fig.3).

After the flask was placed into an ice-bath, the reactants were stirred continuously throught the reaction. It took approximately 10 minutes for the temperature of the reactants to drop to 8--5^{o}C. Meanwhile, from a gas cylinder, NH_3 gas was introduced to the flask with a glass capillary. As the gas bubbled through the reactants it reacted with the by-product HCl to form a white precipitate, NH_4Cl. This began about 5 minutes after the introduction of the NH_3 gas. Since the formation of NH_4Cl is an exothermic reaction, the temperature of the flask tended to rise. However the temperature of the reactants was kept between 10--15^{o}C by periodically



A. flask
B. adapter
C1 & C2. thermometers
D. condenser
E. vacuum pump
F. capillary bubbler
G. adapter
H. collecting flask
I. manometer
J1 & J2. valves

Fig.2 HEMA Distillation Apparatus

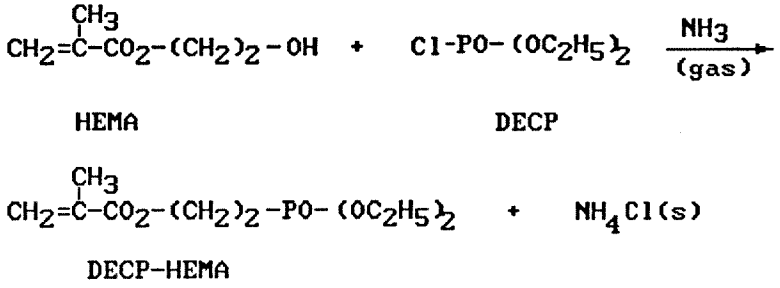


A. ice bath
B. flask
C. thermometer
D. NH_3 gas introducing capilary
E1. value
E2. value
F. gas dryer
G. NH_3 gas cylinder
H. stirring motor
I. glass stirring

Fig. 3 DECP-HEMA reaction apparatus

mixing ice and salt into the bath as needed. The reaction was completed in about 3 hours. By the end of the reaction, the reaction mixture had a PH of 4.5 to 5, as measured by litmus paper.

The reaction is shown as follows:



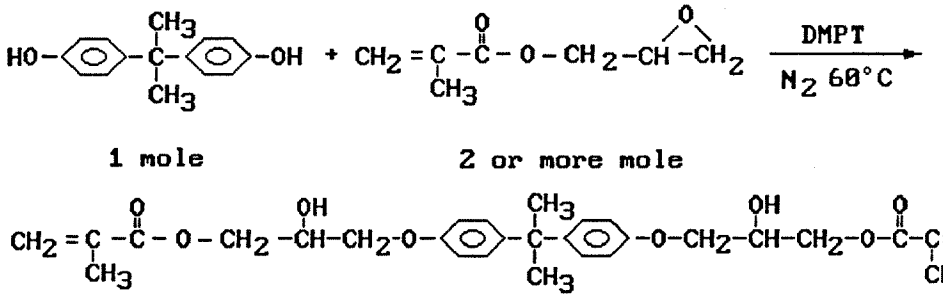
2.1.3 Collection of Product

The reaction mixture was left to settle at room temperature for about one hour. Removal of the precipitate, NH_4Cl, was carried out in a Buchner porous glass filter. The filtrate was further centrifuged at high speed for one hour to settle the fine NH_4Cl particles. Finally, the supernatant liquid was collected.

2.2 Synthesis of BisGMA

2.2.1 Method of Preparation

Two or more moles of glycidyl methacrylate were reacted with one mole of the bisphenol A (bis(4-hydroxyphenyl)dimethyl methane) or (4,4-Isopropylidene-diphenol). This polymerizable intermediate or monomer is shown below. The tertiary amine, dimethyl-para-toluidene (DMPT) catalyzes the addition of the phenolic hydroxyl groups to the epoxide groups.



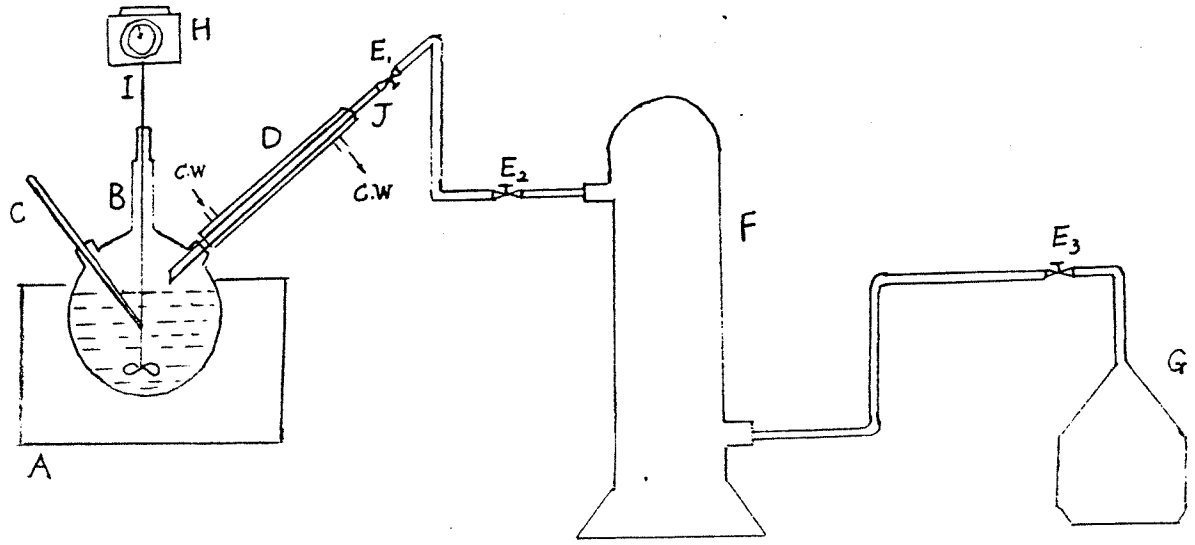
To arrive at a procedure that would yield this result, a series of experiments were conducted. In each case the Bisphenol A and GMA were placed in a 250ml, three-necked flask with continual stirring via a glass rod through one of the necks, with N_2 bubbled through another of the necks. The third neck was used for the thermometer and sampling. The flask was put in a temperature controlled water bath to control the reaction temperature (Fig. 4). Either the visual viscosity appearance was observed or the epoxy value was measured.

Table 1 summarizes the results of the first series of experiments where the Bisphenol A/GMA ratio was varied and presents the reaction times when gel products appeared.

Table 2 summarizes the results of the second series of experiments where the effect of DMPT was studied. After reacting for 60 minutes the product did not gel but maintained low viscosity in the third experiment of this series.

Table 3 presents the results of the effect of temperature on the reaction. The epoxy value was measured to determine the optimum temperature (for epoxy value, the lower the better).

The effect of time on the reaction was studied in the fourth series of experiments and is summarized in Table 4. For this set of experiments 1.071 grams of hydroquinone was added as inhibitor. Again the epoxy values were measured at the end of each reaction.



A. ice bath
B. flask
C. thermometer
D. condenser
E_1. value
E_2. value
E_3. value
F. gas dryer
G. N_2 gas cylinder
H. stirring motor
I. glass stirring
J N_2 gas introducing tube

Fig. 4 BisGMA reaction apparatus

The effects of two inhibitors on the reaction were also studied. The result are listed in Table 5.

After these five series of experiments, the final Bis-GMA synthesis experiment was carried out with 0.5 mole of GMA and 0.2 mole of Bisphenol A in a 250ml, three necked flask, with continual stirring, N_2 bubbling, and the temperature held constant at 60°C. Once the reactants were completely dissolved, 0.3577 grams of DMPT were added to the flask. After 1 hour, a small sample was taken out for the analysis of the epoxy value, after which 0.0589 grams of hydroquinone was added to the reaction mixture. At hour 3, 5, 7, and 9, samples were withdrawn to determine the epoxy value. After each sampling, 0.3577g of DMPT was added, except at hour 9. The epoxy value at hour nine indicated that the reaction was complete. These results are summarized in Table 6.

Table 1 The Effects of Bisphenol A and GMA Ratio

Bisphenol A (mole)	GMA (mole)	DMPT (gram)	Time (min)	Appearance
0.2	0.532	2.094	30	gel
0.2	0.516	2.094	45	gel
0.2	0.5	2.094	49	gel

Table 2 The Effect of Different Amounts of DMPT

Bis-A* (mole)	GMA (mole)	DMPT (gram)	Epoxy (mole)	Time (min)	Appearanc
0.2	0.5	1.75	-	10	gel
0.2	0.5	1.05	-	30	gel
0.2	0.5	0.3577	0.4428	60	Low Viscosity

* Bis-A = Bisphenol A

Table 3 The Effect of Temperature

Bis-A (mole)	GMA (mole)	Temp (^{o}C)	DMPT (gram)	Epoxy (mole)	Appearance
0.2	0.5	70	0.3577	-	gel
0.2	0.5	60	0.3577	0.4428	Low Viscosity
0.2	0.5	50	0.3577	0.4540	Low Viscosity

Table 4 The Effect of Time

Bis-A (mole)	GMA (mole)	DMPT (gram)	Time (hour)	Hydroquinone (gram)	Epoxy (mole)
0.2	0.5	0.3577	1	1.071	0.4428
0.2	0.5	0.3577	5	1.071	0.3771
0.2	0.5	0.3577	9	1.071	0.3557

Table 5 The Effect of Different Inhibitors

Bis-A (mole)	GMA (mole)	DMPT (gram)	Inhibitor (gram)	Time (hour)	Epoxy (mole)
0.2	0.57	1.057	Chloranil 0.016	9	0.4901
0.2	0.57	1.428	hydroquinone 1.071	-	-

Table 6 Reaction Procedure

Time (hour)	0	1	2	3	4	5	6	7	8	9
GMA (mole)	0.5	-	-	-	-	-	-	-	-	-
Bis* (mole)	0.2	-	-	-	-	-	-	-	-	-
DMPT (g)	0.3577	-	-	0.3577	-	0.3577	-	0.3577	-	-
HQ (g)	-	0.059	-	-	-	-	-	-	-	-
Epoxy (mole)	-	T*	-	T	-	T	-	T	-	0.1958

* Bis = Bisphenol A
*HQ = Hydroquinone
*T = Epoxy value has been tested

2.2.2 Epoxy Group Testing [17,18]

The chemical reactions involved in of the epoxy value determination are discussed in section 3.3.2. The following procedure was followed to determine the epoxy value:

1). Magnesium chloride was added to 0.1N standard hydrochloric acid solution until the solution was saturated. The saturated acid solution was titrated with 0.1N NaOH alkali to determine the exact equivalent concentration of the $MgCl_2$ saturated solution.

2). The sample was weighed out in a 1 ml glass ampoule (10.5mm dia. * 67mm length) which was sealed and placed in a 250 ml conical flask containing a measured excess of the acid solution. The flask was stoppered and shaken vigorously to break the ampoule. About 5 minutes later, the solution was titrated with 0.1 N NaOH alkali standard solution to the methyl orange end point. The moles of acid consumed is a measure of the epoxide content of the sample.

2.2.3 Thin Layer Chromatography of the Product [19]

1). Choice of the Eluent: The solubility of Bisphenol A, GMA, and BisGMA in methanol, THF,toluene, acetone, hexane and cyclohexane is summarized in Table 7. Toluene was chosen as the main TLC solvent for the BisGMA products. Since the migration of the spots with toluene solvent is too slow, methanol was added to increase the polarity of the solvent. THF was also added to increase the solubility of methnol in toluene. The toluene : methanol : THF ratio was 100 : 4 : 4.

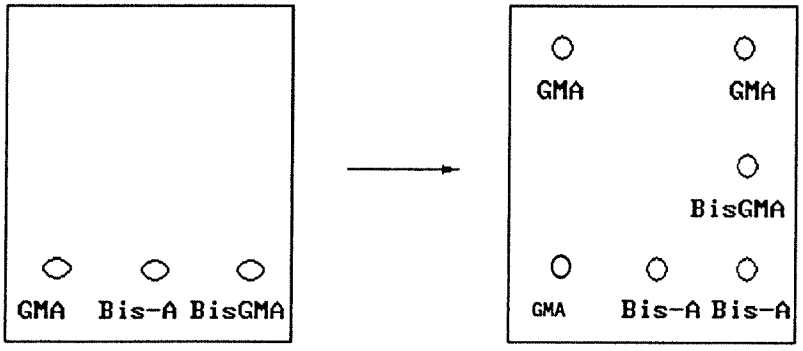
2). Application of Sample: In a 10 * 75mm test tube, the sample to be applied was dissolved in the solvent mixture, ie. toluene - methnol - THF, to obtain a roughly 5 to 10 percent solution of the sample. A capillary tube was dipped into the sample solution and then touched very lightly to the TLC slide (silica gel) so that the spot

would not spread to a diameter more than 1 mm. The spot was placed about 1 cm from the end of the TLC slide.

3). Application of the Bisphenol A and GMA: Standard solutions of Bisphenol A and GMA were prepared similarly and applied next to the product sample on the TLC slide.

4). Development: The developing chamber is a wide mouthed bottle with a snap - on plastic lid. The bottle was filled with solvent to a depth of about 0.5cm, so that the level was below the sample spots. A piece of filter paper was fitted around the inside wall to serve as a wick for maintaining an atmosphere of solvent vapor. The slide was put into the chamber and the lid was secured. When the solvent had risen to about 1 cm from the top of the slide, the plate was removed and stood vertically for 10 minutes to dry completely.

5). Visualization: Since BisGMA and the other two compounds are colorless, UV light was used to visualize them. From the product sample spot, three different Rf circles were seen. The first was Bisphenol A, moving the same distance as the Bisphenol A standard. The second spot, which moved further, was the BisGMA product. The third spot, which moved the furthest, was GMA. It moved the same distance as the GMA standard. This is shown below:



Before Developing

After Developing

Table 7 The Solubility of GMA, Bisphenol A and BisGMA in Various Solvents

	GMA	Bisphenol A	BisGMA
CH_3OH	S	S	S
THF	S	S	S
Toluene	S	INS	S
Acetone	S	S	S
Hexane	S	INS	INS
Cyclohexane	S	INS	INS

S: soluble
INS: insuble

2.2.4 Column Chromatography of BisGMA Products[20]

1). Glass wool was stuffed into the bottom of a glass tube of 5.5 cm I.D. and 70 cm length. The tube was clamped in a vertical position and rinsed with about 20 ml of toluene.

2). In a 1000 ml beaker, a slurry of 300 g silica gel (70-230 mesh) and about 500 ml toluene was prepared. The slurry was carefully poured into the dry tube to avoid bubbles. The tube was gently tapped to remove bubbles which did get trapped, as well as to level the silica gel.

3). The toluene that was filtered through the glass wool was collected and used to rinse the slurry that remained in the beaker.

4). After the silica gel packing had settled, a small filter paper circle was dropped onto the top of the packing to keep the packing from being disturbed by the addition of eluent and/or sample.

5). A solution of 15 g of the sample and 50g of toluene was prepared.

6). When the last drop of toluene from the toluene - silica gel mixture exited the column, the sample solution was added to the top of the column.

7). The eluent ratio was toluene : methnol : THF=100 : 4 : 4.

8). Once the sample solution penetrated the gel, eluent was added to wash down any sample adhering to the wall.

9). After the eluent penetrated the gel, the tube was filled with the eluent and the chromatography was allowed to develop. During development, three layers appeared.

10). From the previous TLC experiment the three compounds were identified. The first layer through the column was glycidyl methacrylate, the second was BisGMA, and the third layer was Bisphenol A.

11). After the BisGMA layer was collected, it was filtered to remove the silicon gel.

2.2.5 Rotation Distillation

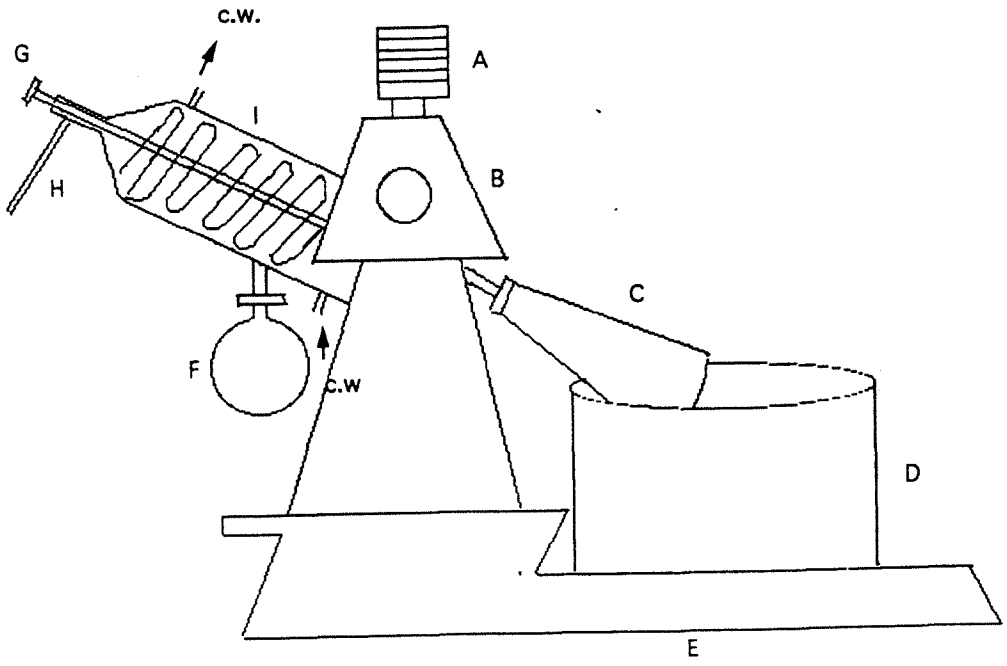
The BisGMA sample containing the eluent solvent was distilled in a rotary evaporator to remove the solvent. The temperature was maintained at 30°C by a water bath and keptunder a vacuum of 50 mm Hg. The apparatus setup is shown in Fig 5.

2.3 Characterization

2.3.1 VPO of DECP-HEMA and BisGMA[21]:

The temperature of the vapor pressure osmometer, (VPO) (Model 233, Wescan Instruments Inc.), was maintained at 50°C. Two syringes were filled with toluene and injected in turn until the respose was stable, and the voltage was recorded. The data was used as the solvent calibration.

Five concentrations of the standard, benzil, in toluene, were prepared. The voltage data of the above five standard solutions were taken.



A. motor
B. digital display of rotation speed
C. sample flask
D. heating bath
E. rack
F. receiving flask
G. tap
H. inlet feed tube
I. tap-water-cooled condenser

Fig. 5 Rotation distillation apparatus

The voltage was calculated by the equation V=Vsample-Vsolvent. The instrument constant, K, was determined from the intercept obtained by plotting V/C vs C.

Similarly, five concentrations of the sample DECP-HEMA, in toluene, were prepared. The voltage data of these solutions were taken. After plotting the V/C vs C, the molecular weight of DECP-HEMA was calculated from the intercept.

In the same manner, the molecular weight of BisGMA was determined. The data is list in Table 9 and 10.

2.3.2 IR Spectra of DECP, HEMA, DECP-HEMA and BisGMA

The IR spectra of DECP, HEMA, DECP-HEMA, BisGMA and the commercial produce BisGMA were obtained by using an infrared spectrophotometer, Perkin Elmer, model 1310. The salt plate smear method was used with THF as the solvent. The spectra were scanned over the wave numbers between 650 - 4000cm.$^{-1}$ The spectra are shown in Figures 6 through 10.

2.3.3 FTIR Spectra of BisGMA

The IR spectra of experimentally made BisGMA monomer and commercial BisGMA were obtained by using a Nicolet 5ZDX FTIR spectrometer. The experimentally made BisGMA monomer was measured by using the salt plate method with THF solvent. The commercial monomer was measured with the salt plate smear with air as the background, because the solvent, THF, absorbed too much such that the absorption of BisGMA could not be seen. The scanned ranges were between 500-4000 cm^{-1}, 500-2000cm^{-1} and 2000-4000cm^{-1}. The spectra are shown in Figures 11 through 16.

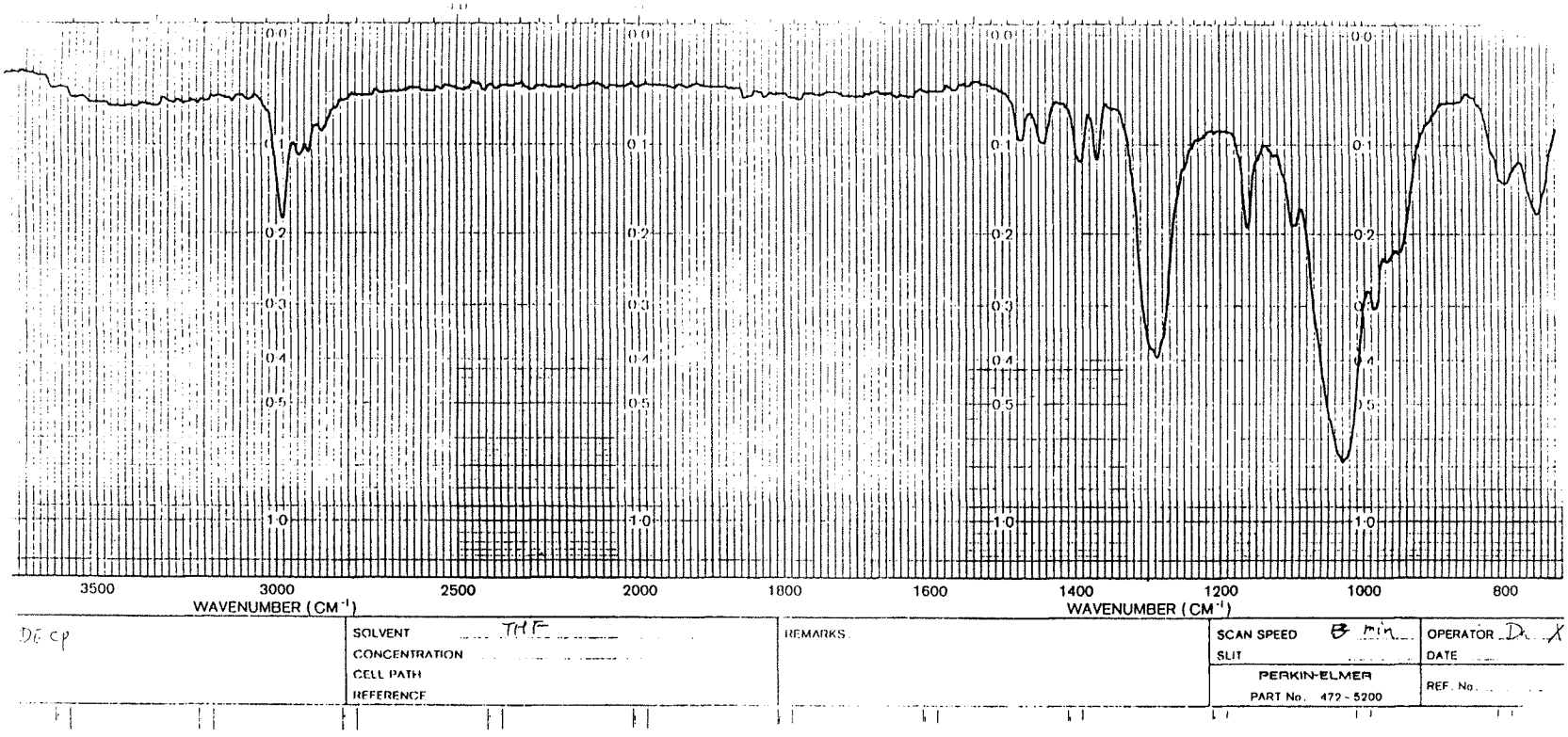


Fig. 6 IR spectra of DECP

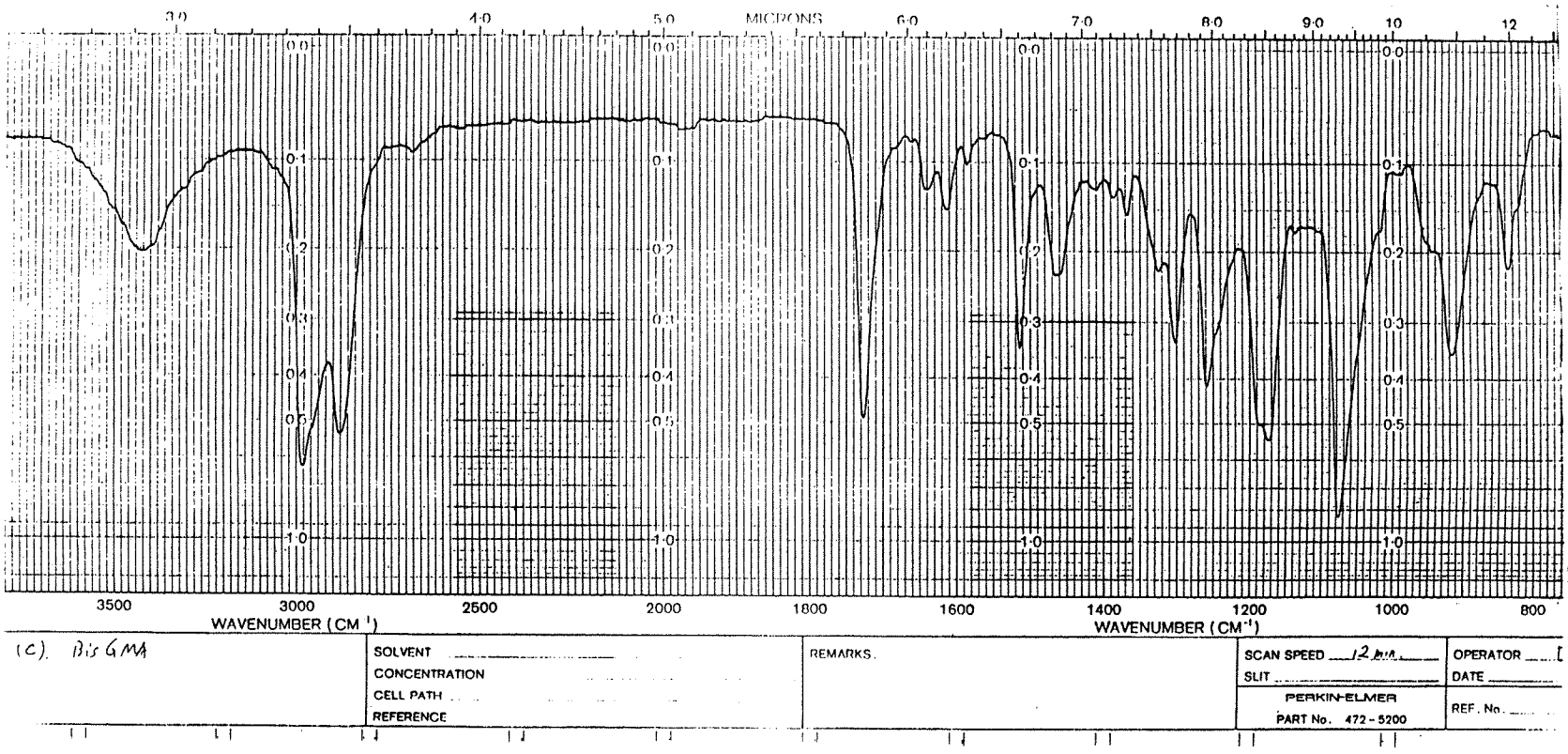


Fig.7 IR spectra of HEMA

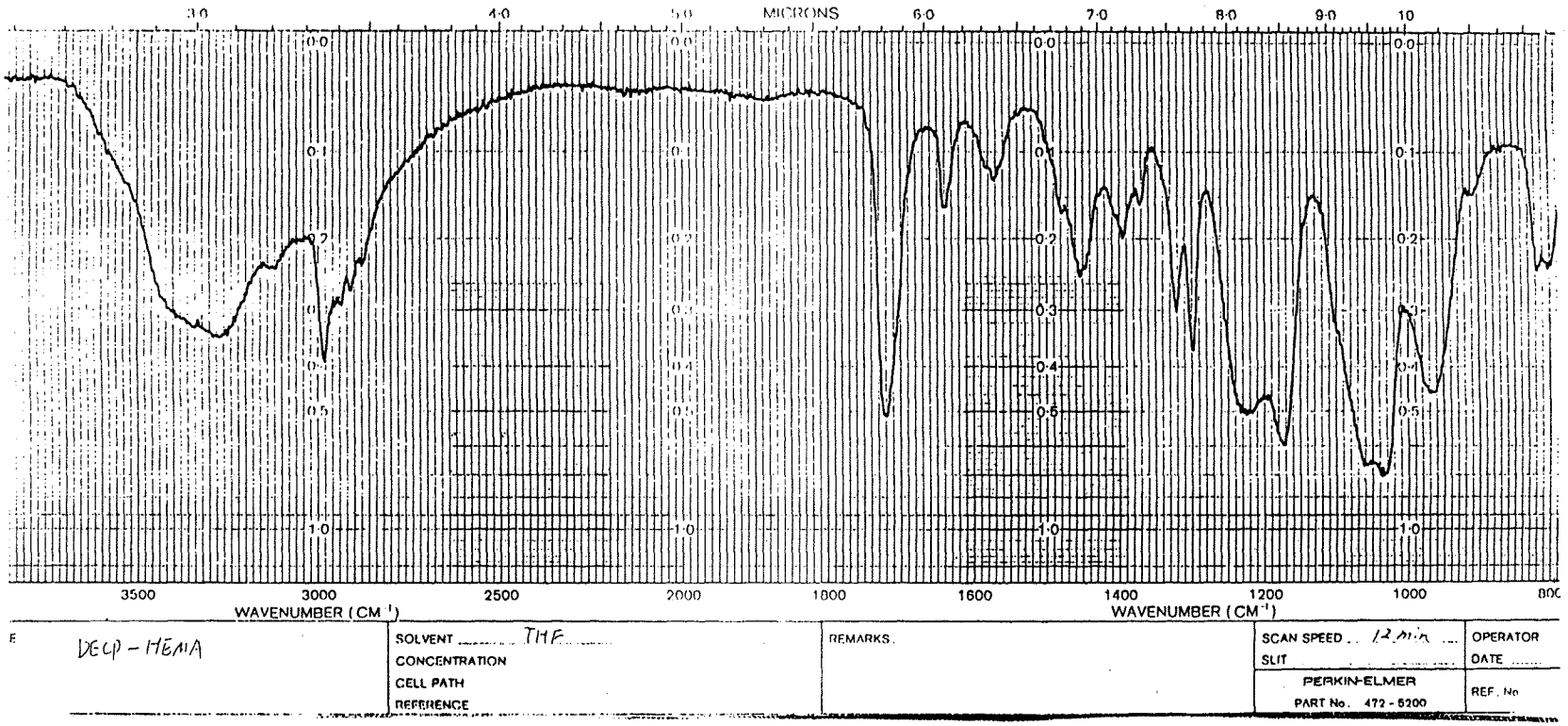


Fig.8 IR spectra of DECP-HEMA

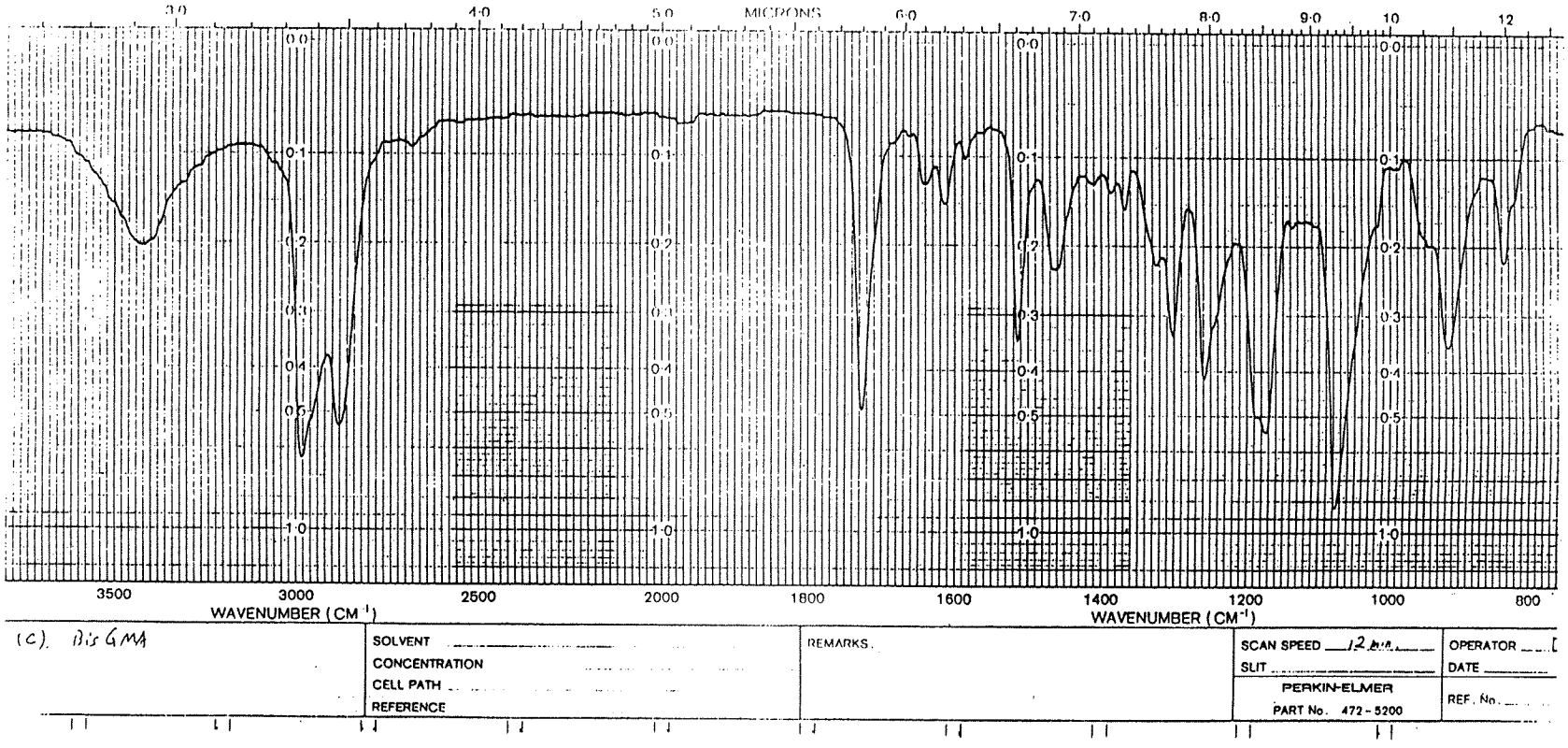


Fig.9 IR spectra of BisGMA (commercial)

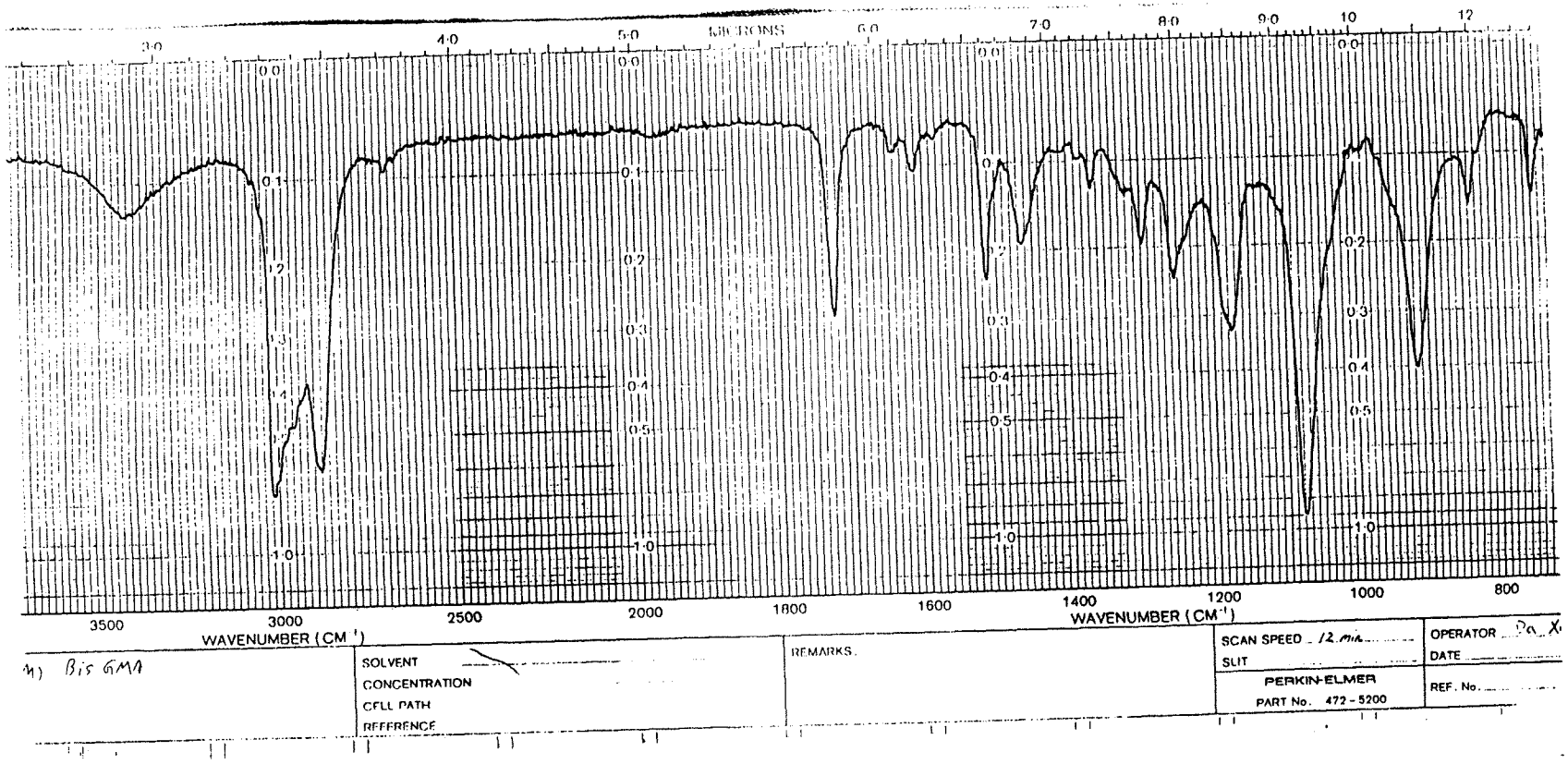


Fig.10 IR spectra of BisGMA (made)

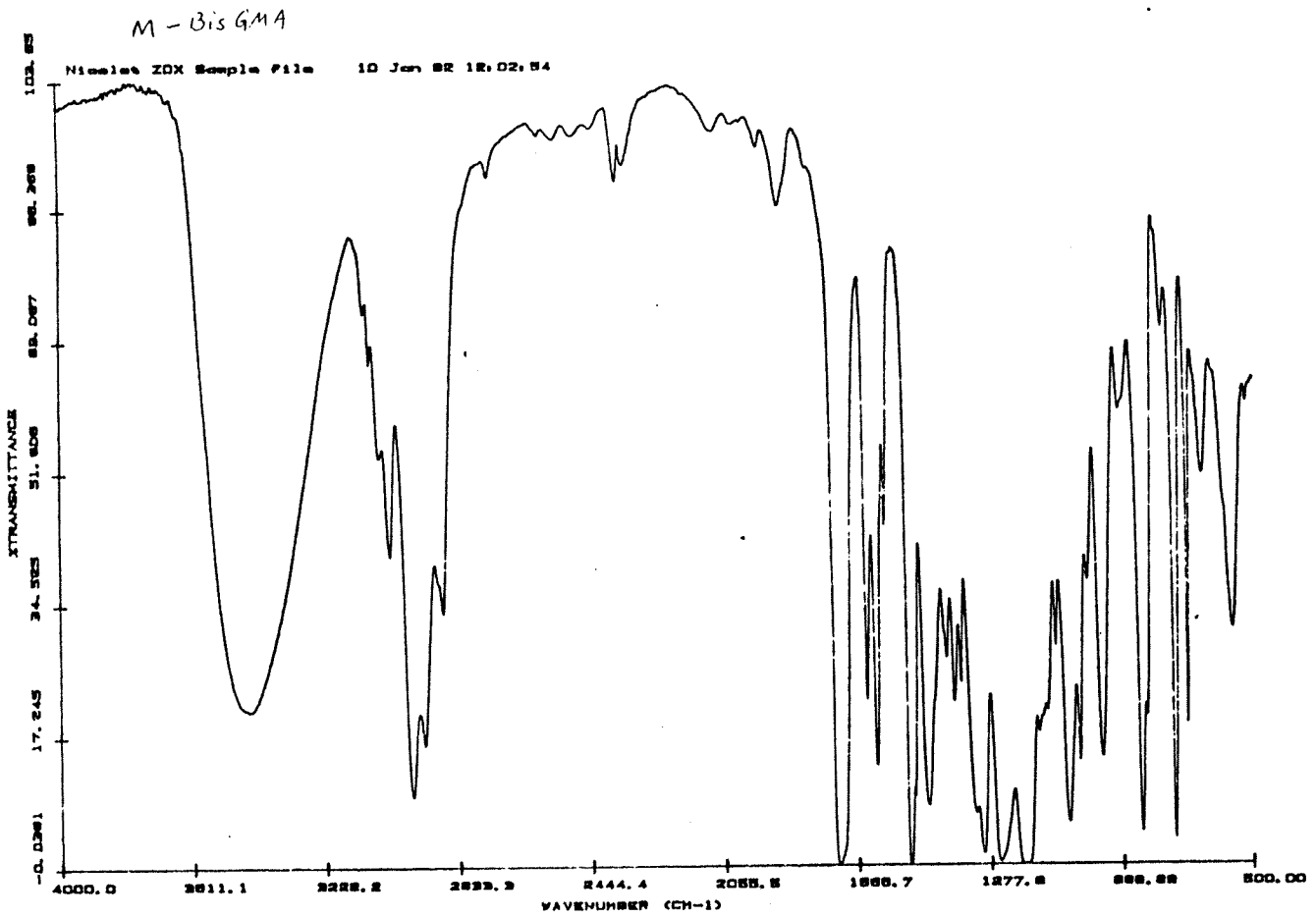


Fig.11 FTIR of BisGMA (monomer)

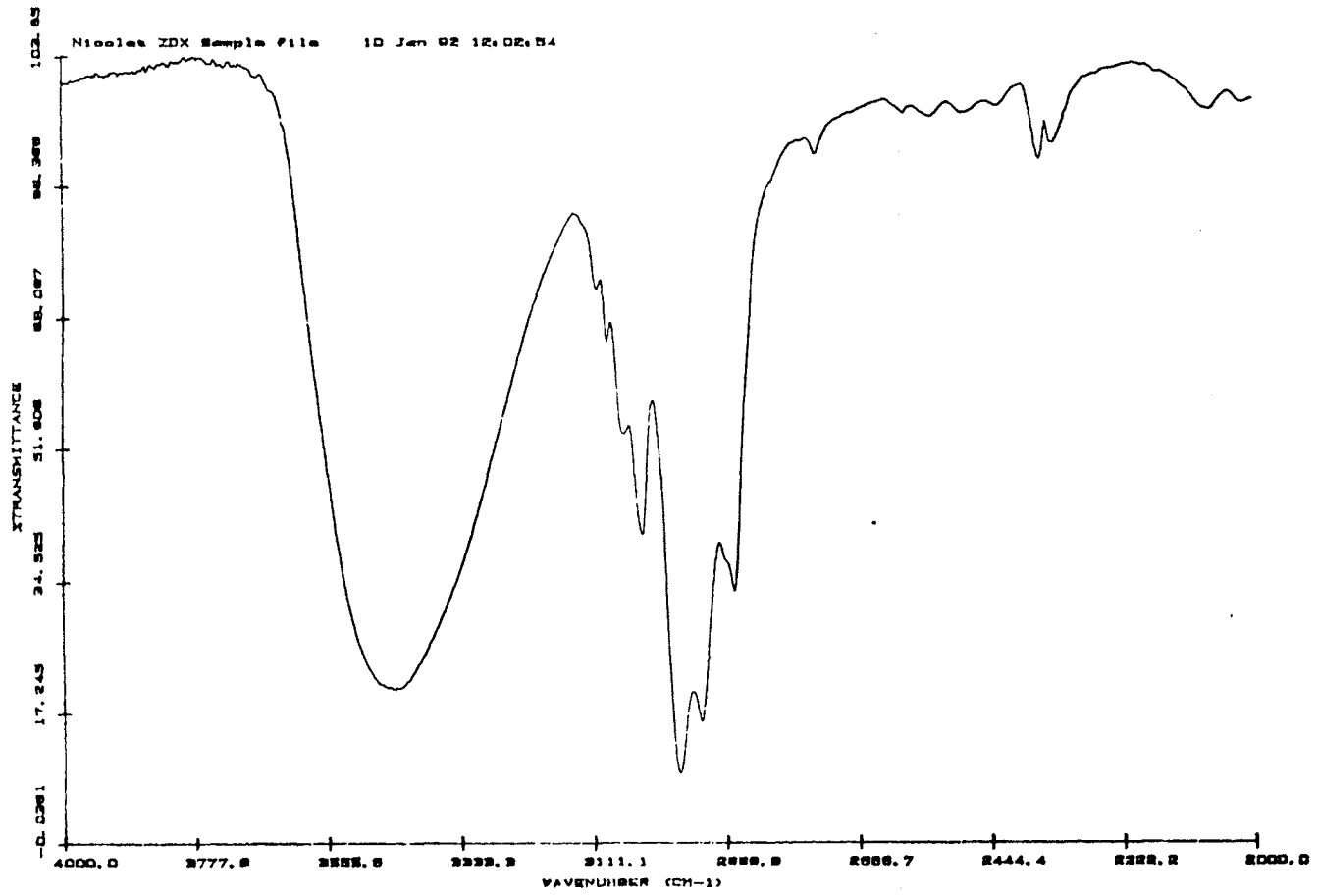


Fig.12 FTIR of BisGMA (monomer)

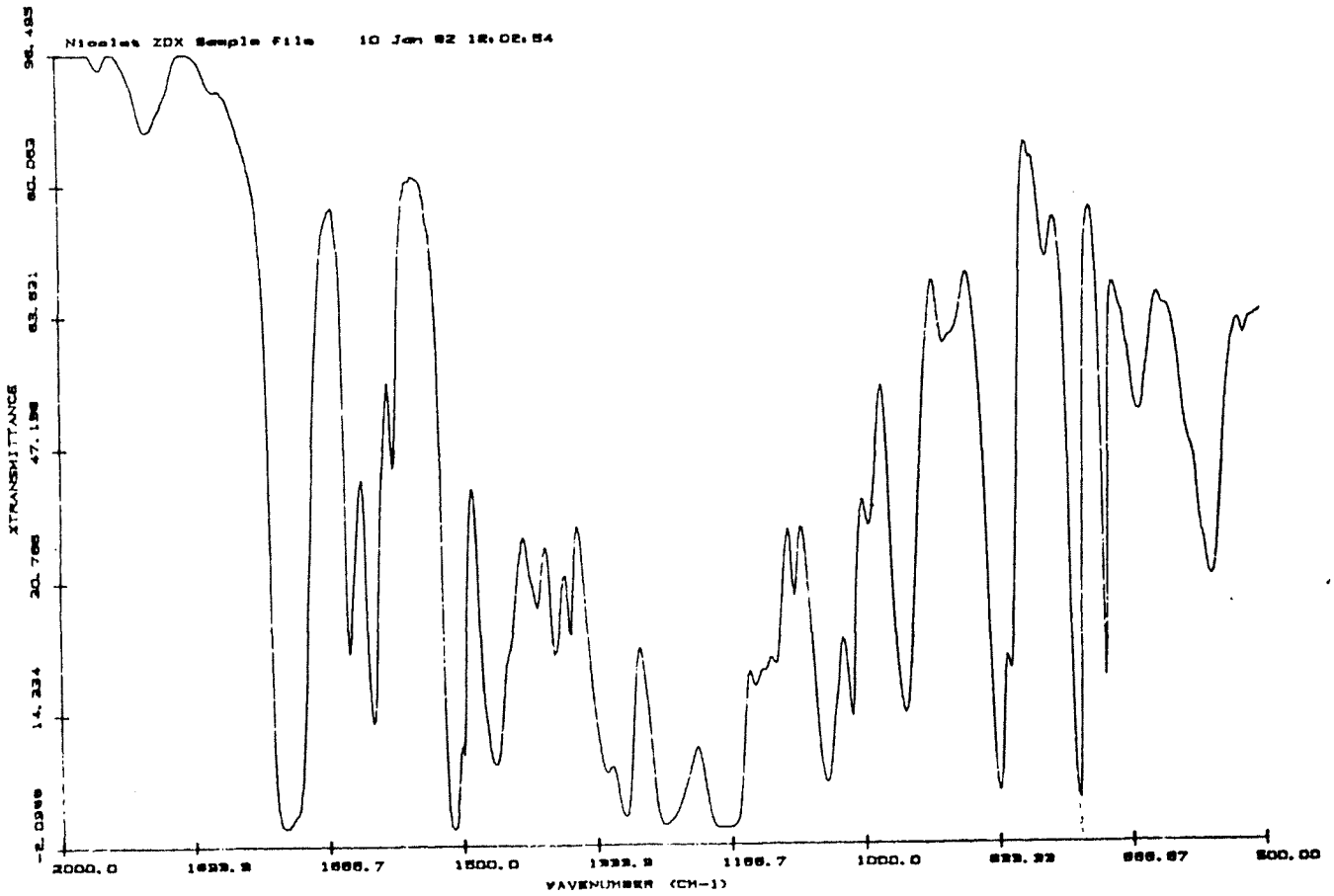


Fig.13 FTIR of BisGMA (monomer)

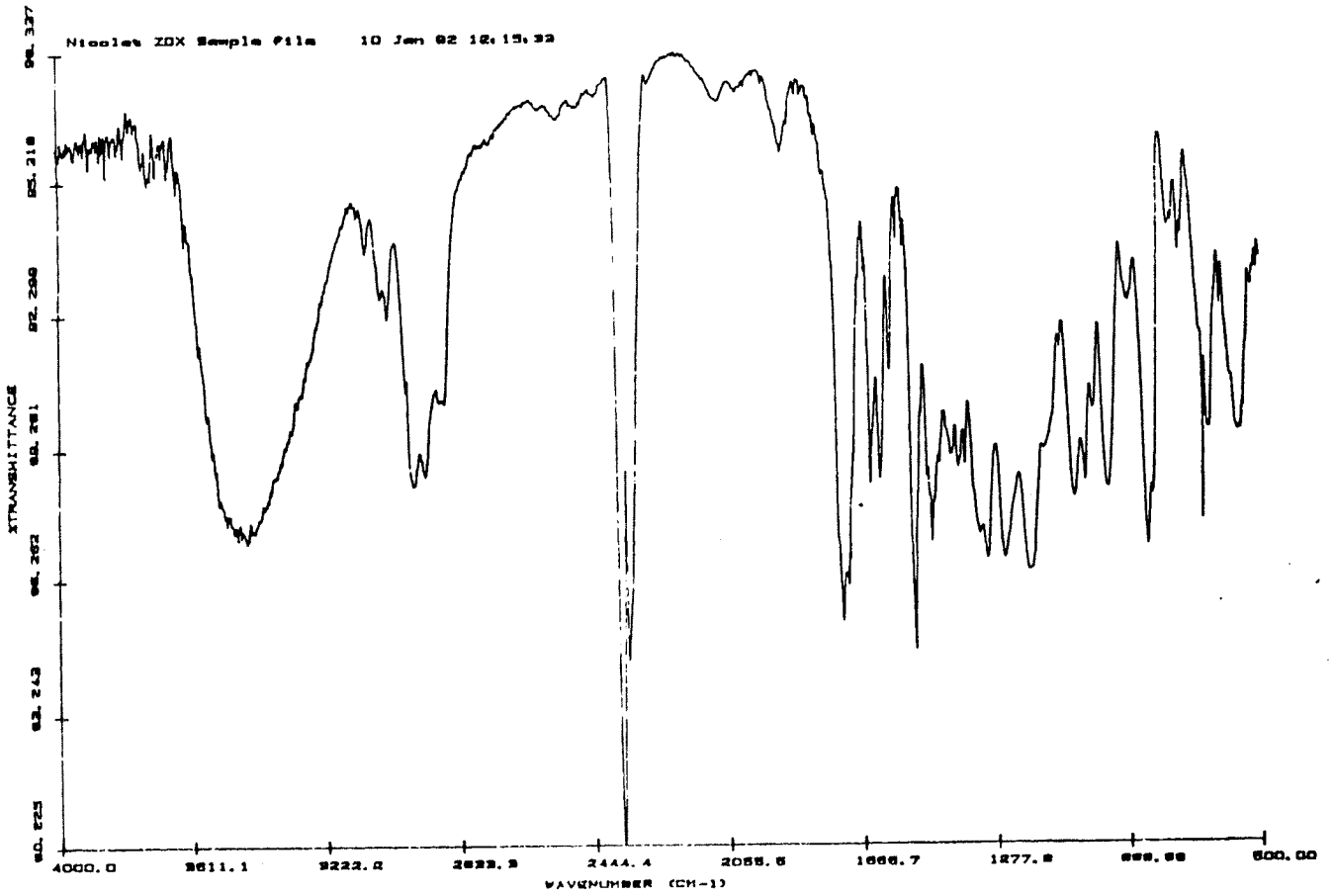


Fig.14 FTIR of BisGMA (commercial)

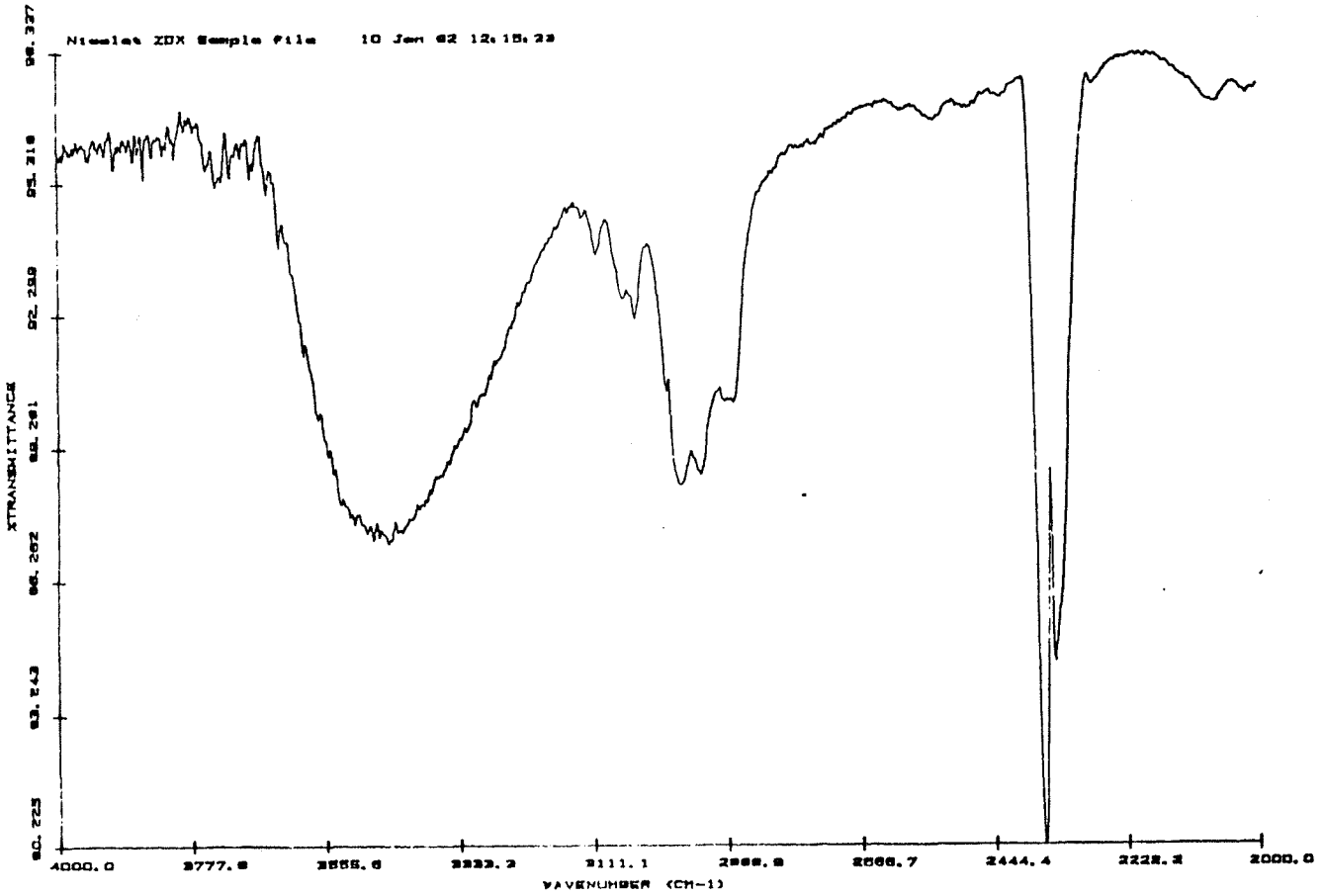


Fig.15 FTIR of BisGMA (commercial)

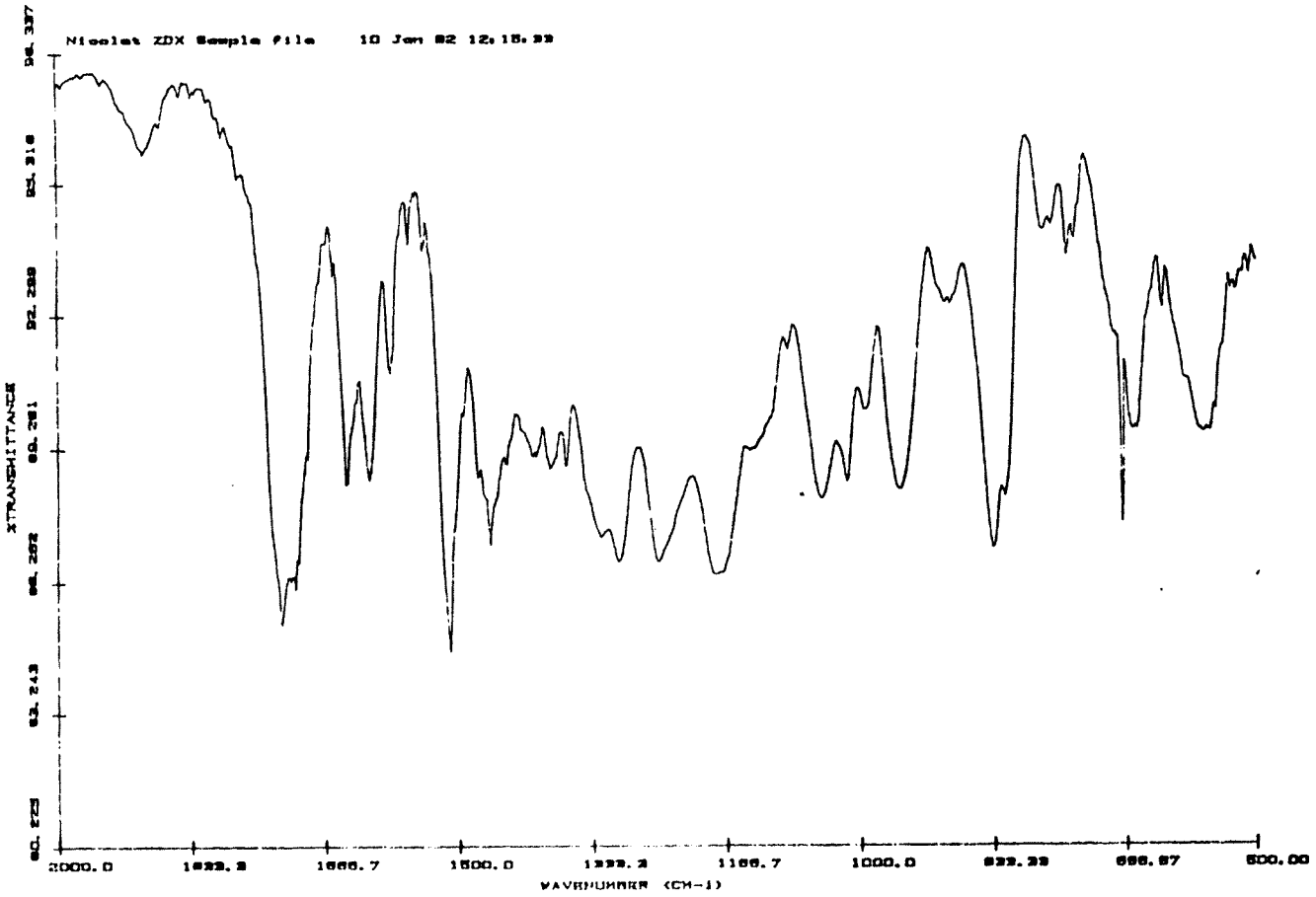


Fig.16 FTIR of BisGMA (commercial)

2.3.4 GC-MASS Spectra of BisGMA

The GC-Mass spectra of BisGMA were obtained by using a GC-Mass spectrometer with acetonitrile as a solvent. The retention time of GC spectra scanned was between 1000 to 2854. Three major peaks at 1856, 2368, and 2546 were detected in the mass spectrum. The GC column temperature was 280 - 300^{o}C. The detailed GC peaks and mass spectra are shown in Fig 17 through 20.

2.4 Bonding Strength Test

2.4.1 Preparation of Aluminum Rods

For the bonding strength test, the face of the aluminum rod to be placed on the dentin of the tooth was smoothed out with sandpaper and soaked in acetone for 60 minutes to remove grease. The face of the rod was further treated with a Na_2CrO_7/H_2SO_4 cleaning solution (the ratio of Na_2CrO_7 : H_2SO_4 : H_2O was 1 : 15 : 30) and etched for 4 min in the oven at 40^{o}C. After etching, the rod was rinsed with distilled water, petroleum ether and air blown dry before it was stored in a desiccator (The cross sectional area of the aluminum rod is about 0.196 square inch).

2.4.2 Tooth Treatment and Mounting of the Specimen

To provide a smooth bonding surface of dentin, the top of the tooth was cut off by using a low speed diamond saw. The cut surface of the tooth was polished with wet fine sand paper. After polishing, the surface was rinsed with aqueous methanol, wiped dry with a paper towel and blown dry with air. The specimen was then embedded in a resin housed in a plastic holder of 25 mm diameter, with the cut surface facing up. A hole was then drilled through the holder near its bottom which was used to attach to a metal rod fastened on the Instron. (see Fig. 21-22)

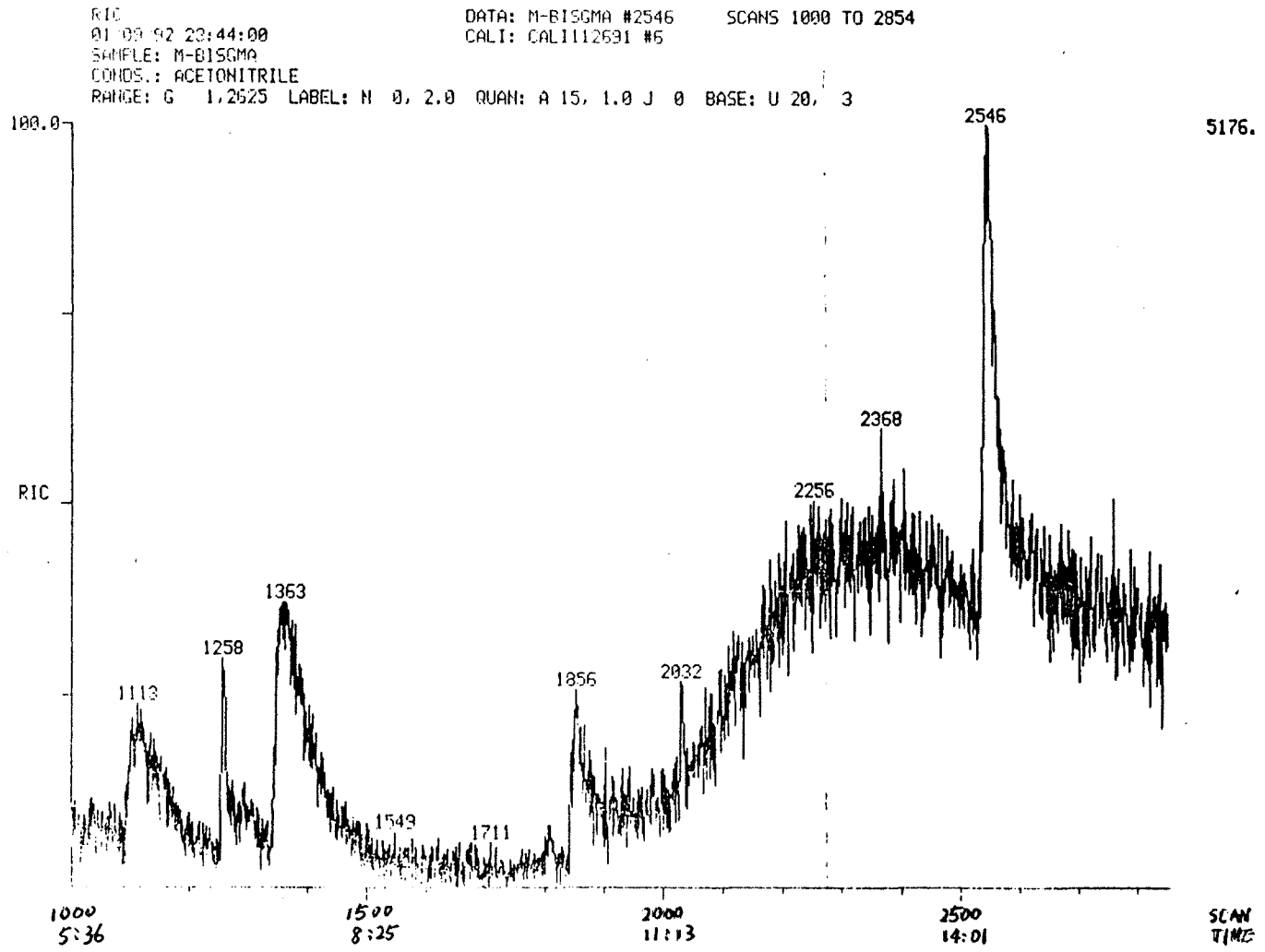


Fig.17 GC peaks of BisGMA (monomer)

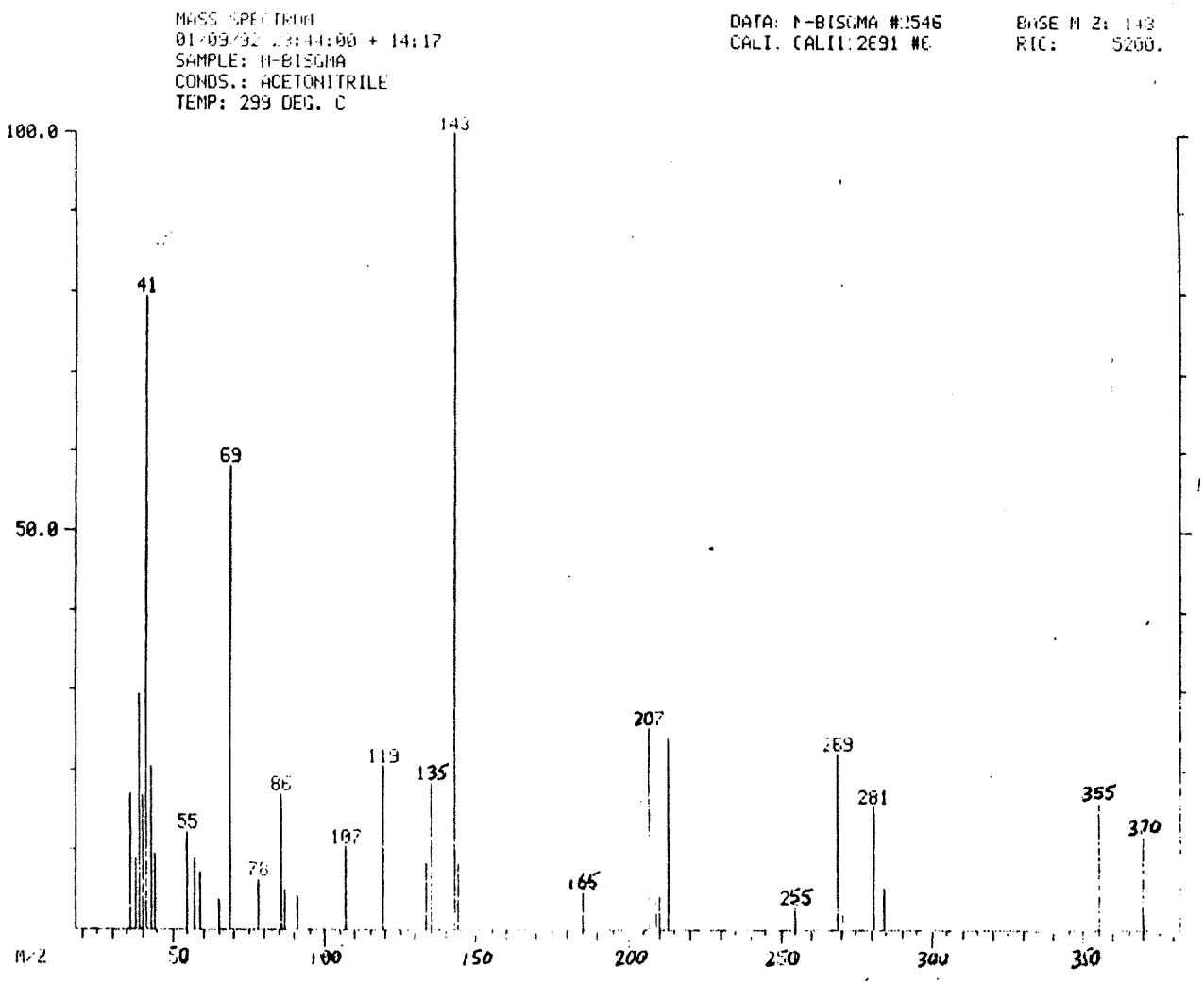


Fig.18 Mass spectra

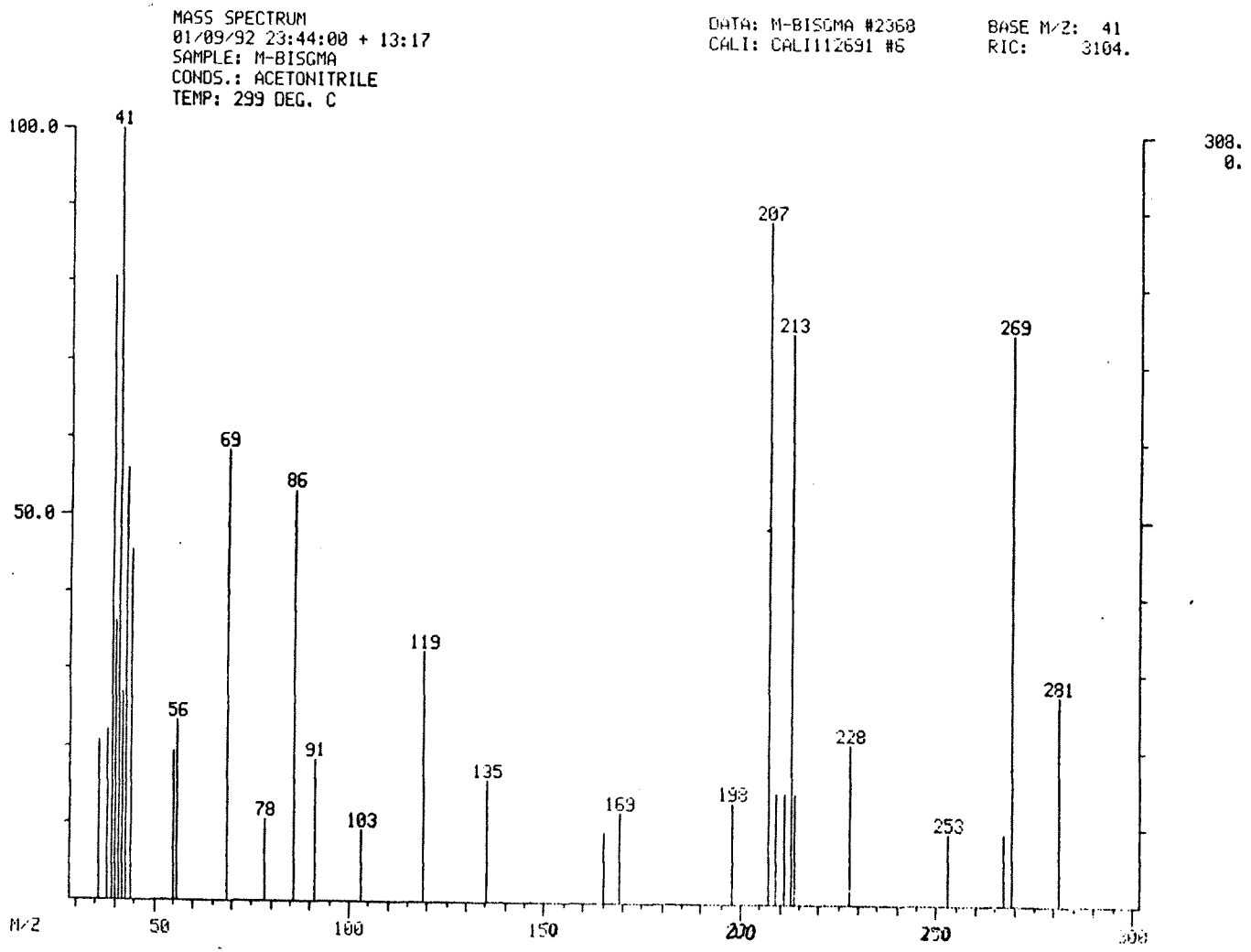


Fig. 19 Mass spectra

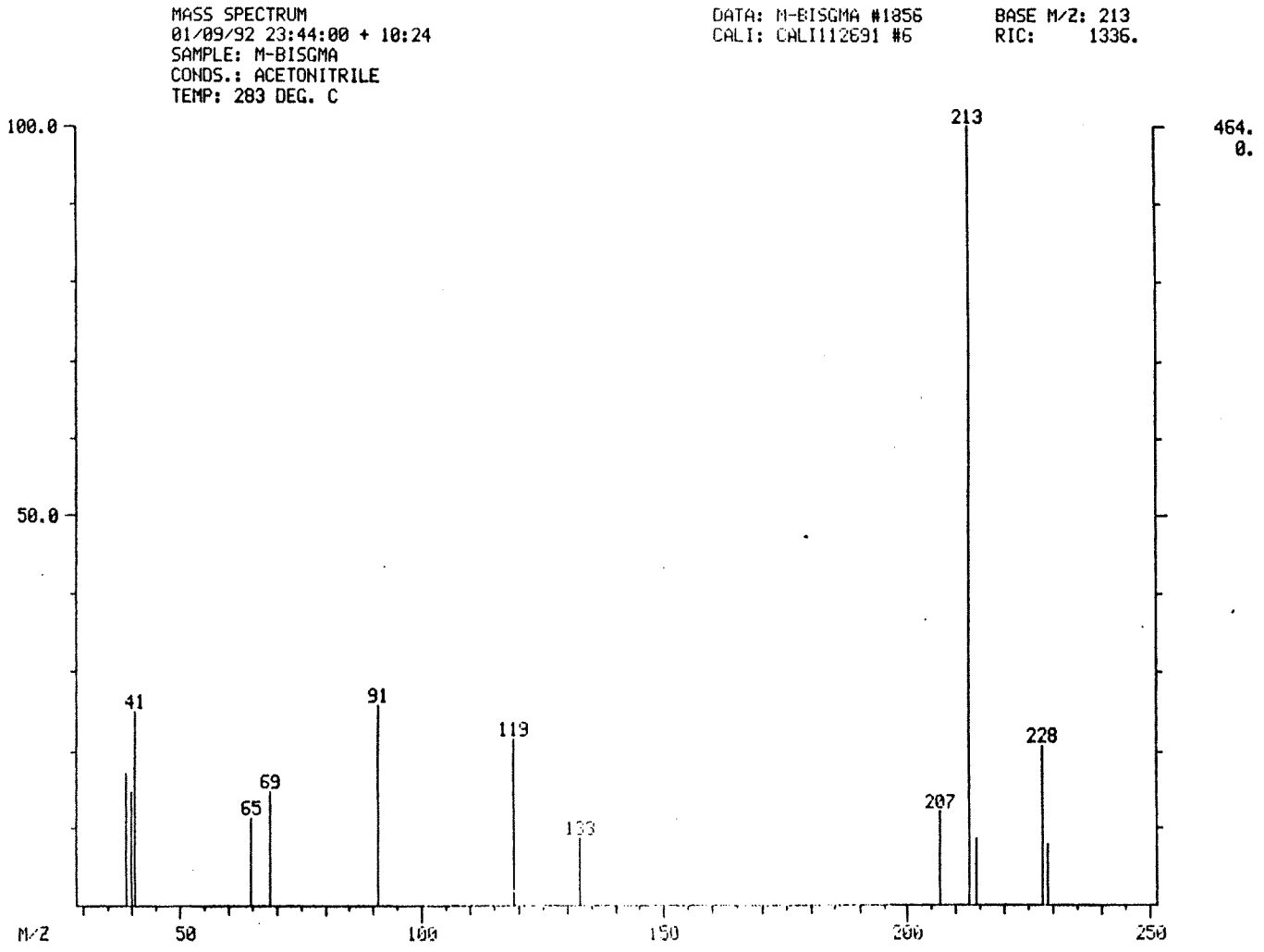


Fig. 20 Mass spectra

2.4.3 Formulation and Test of Adhesives

With the following chemicals:

BisGMA: (isopropylidene bis [p-phenoxy(2-hydroxytrimethylene)])

DECP-HEMA: (Diethylchlorophosphate 2-hydroxyethylmethylacrylate)

Organosilane: (3-(trimethoxysilyl) propyl methacrylate)

TEGDMA: (triethylglycol dimethacrylate), used as solvent for BisGMA

BPO: (benzoyl peroxide)

N, N - Dimethylaniline

Seven adhesives were formulated. In all seven formulations BPO was an initiator and N, N-dimethylaniline was a promotor. The seven formulations are listed below:

Formulation 1

BisGMA	1.0g
TEGDMA	0.008g
N, N - Dimethylaniline	0.02g
BPO	0.005g

Formulation 2

BisGMA	1.0g
TEGDMA	0.05g
*DECP-HEMA and Organosilane	0.05g
N, N-Dimethylaniline	0.04g
BPO	0.005g

*2 parts DECP-HEMA, 8 parts silane

Formulation 3

BisGMA	1.0g
DECP-HEMA and Organosilane	0.05g
N, N-Dimethylaniline	0.05g
BPO	0.005g

Formulation 4

BisGMA	1.0g
DECP-HEMA and Organosilane	0.08g
N, N-Dimethylaniline	0.02g
BPO	0.003g

Formulation 5*

BisGMA	1.0g
TEGDMA	0.05g
DECP-HEMA and Organosilane	0.08g
N, N Dimethylaniline	0.02g
BPO	0.003g

* The dentine surface was washed with 30% phosphoric acid several times.

Formulation 6 **

BisGMA	1.0g
TEGDMA	0.05g
DECP-HEMA and Silane	0.04g
N, N-Dimethylaniline	0.02g
BPO	0.003g

** The dentine surface was washed with 50% surfuric acid several times.

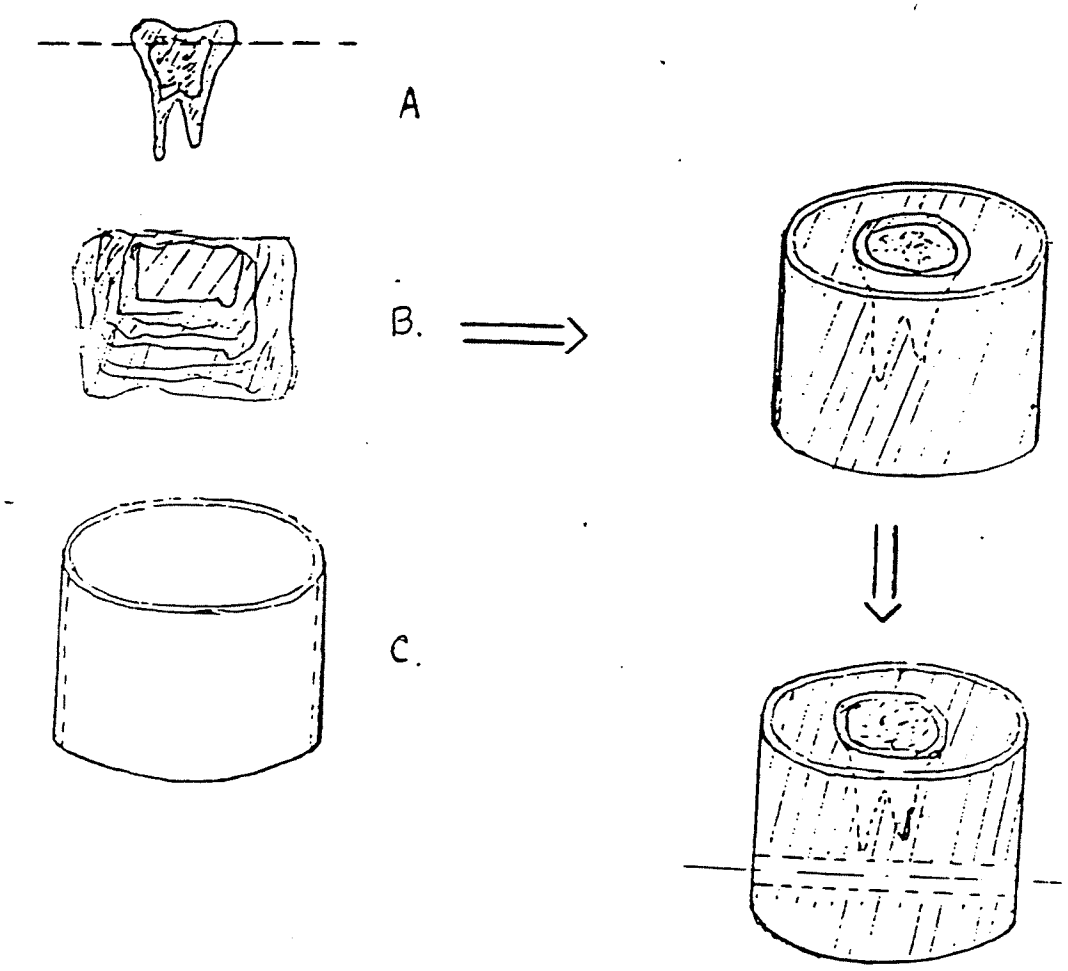
Formulation 7

BisGMA(m)	1.0g
TEGDMA	0.01g
N, N-Dimethylaniline	0.02g
BPO	0.005g

The detailed formulation was as follows: BisGMA, BPO and if used, TEGDMA were mixed together in a small glass vial. N, N-Dimethylaniline was mixed with a mixture of DECP-HEMA and organosilane (2 parts DECP-HEMA, 8 parts organosilane) in another small glass vial. The contents of the two vials were then mixed thoroughly and several drops of the solution were applied to the cut surface of the tooth. One drop of TEGDMA, DECP - HEMA - Organosilane, and N, N - Dimethylaniline was about 0.02g. The amount of each conponent is shown above. The aluminum rod was then placed lightly on the adhesives. Curing of the adhesives was about 30-60 seconds at room temperature. After curing, the tensile strength of the adhesives was measured on the instron. Table 8 is a list of the test results.

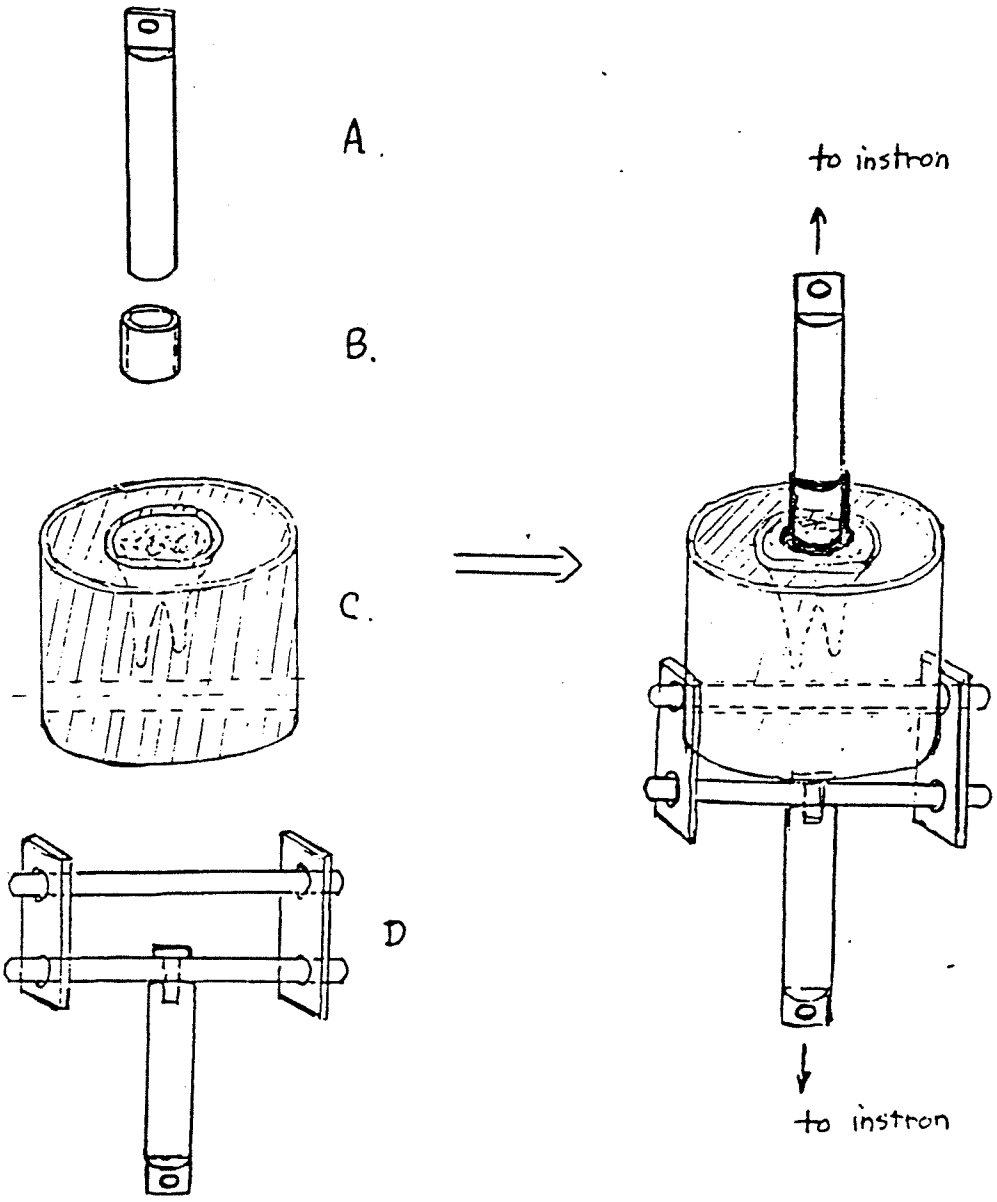
Table 8 Formulation and Test Bonding Strength

Formulation	Tensile Strength(psi)
1	6.73
2	14.39
3	89.18
4	118.24
5	62.86
6	4.61
7	<1.00



A. Tooth
B. Mounting material
C. Plastic adapter

Fig. 21 Sample preparation for testile strength testing



A. Aluminum Bar
B. Mounting material
C. Mounted tooth sample
D. Fixer

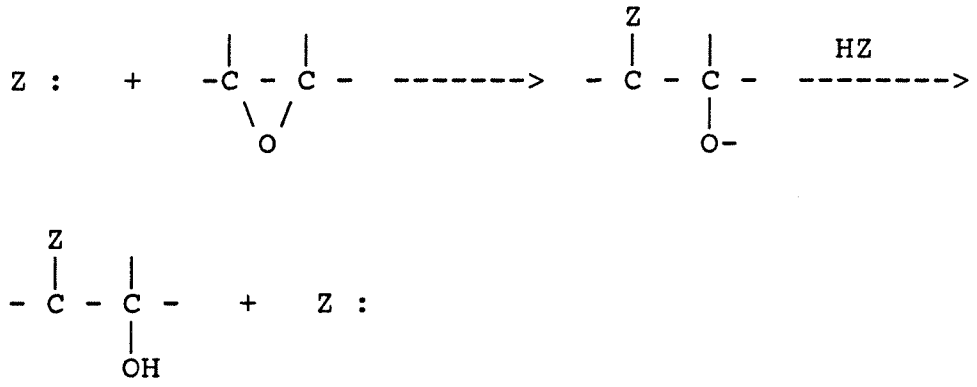
Fig. 22 Sample made for instron testile strength testing

CHAPTER 3
DISCUSSION

3.1 The BisGMA Reaction Mechanism

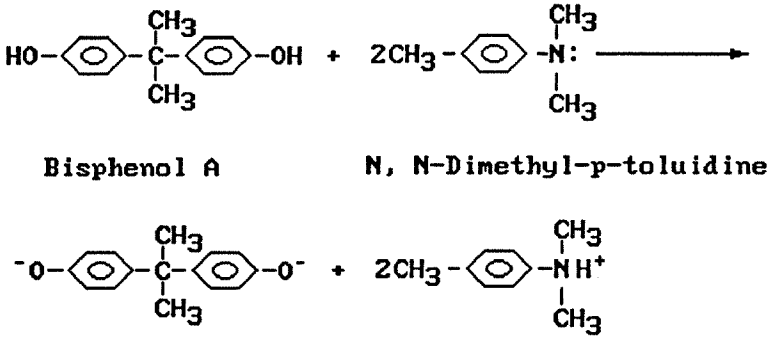
The high reactivity of epoxy compounds is due to the ease of opening of the highly strained three-membered ring. Since the oxygen atom cannot be located to permit maximum overlap of orbitals, the bonds are weaker than those in an ordinary ether bond, and hence the molecule is less stable.

Epoxides can be cleaved under alkaline conditions. Unlike in the acid condition, the epoxide itself, not the protonated epoxide, undergoes nucleophilic attack through the following mechnism[23].



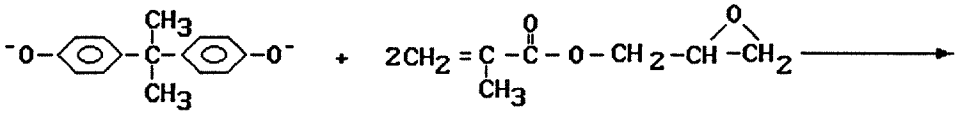
In the base catalyzed cleavage, the leaving group is a strongly basic alkoxide oxygen and the nucleophile is phenoxide (z). The lower reactivity of the non-protonated epoxide is compensated for by the more basic, more strongly nucleophilic reagents that are compatible with the alkalines such as phenoxides, ammonia, etc.

In the Bisphenol A and DMPT (N, N-dimethy-p-toluidine) reaction, the DMPT captures the proton from the Bisphenol A, leaving the Bisphenol A nucleophillic and the DMPT protonated:

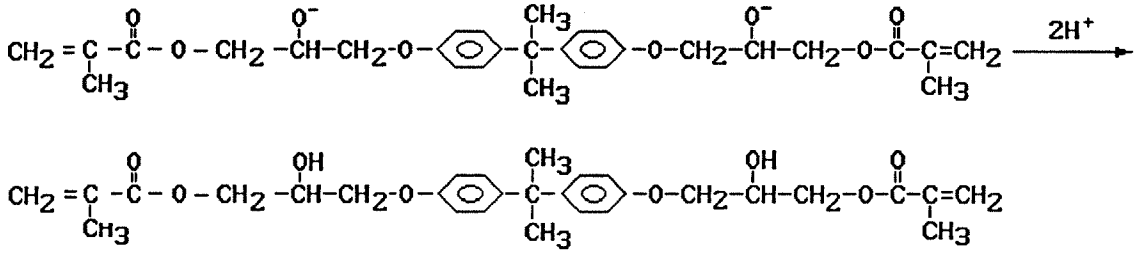


Bisphenol A N, N-Dimethyl-p-toluidine

Then the strongly nucleophillic Bisphenol A can react with the non - protonated GMA as follows:



Strong Nucleophile (Bisphenol A) Non-ProtonatedEpoxide (GMA)

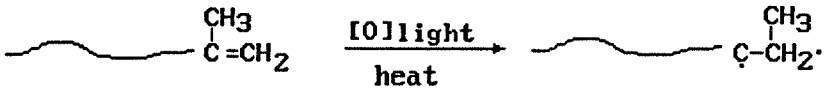


Here the proton came from the protonated catalyst DMPT.

3.2 The Influence of the Inhibitor on the Synthesis of BisGMA [24]

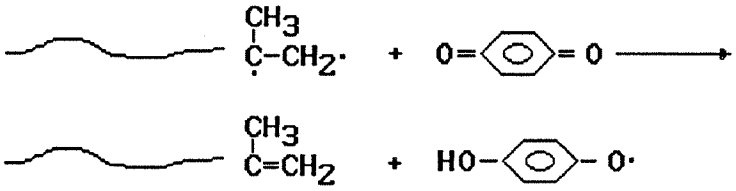
Heat, light or O_2 can generate free radicals in polymerizable monomers.

In GMA:

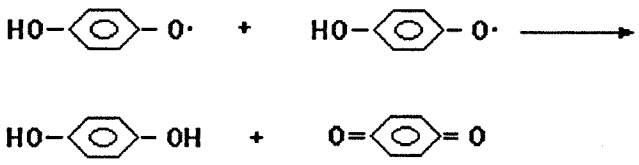


These free radicals can propagate as a side reaction during the Bisphenol A and GMA reaction. In order to scavenge any free radicals, quinone can be used as an inhibitor. Since quinone comes as hydroquinone, quinone must be generated. The hydroquinone is easily oxidized by exposing it to the O_2 in air:

Quinone can then react with the radical chain, eliminating the free radical:



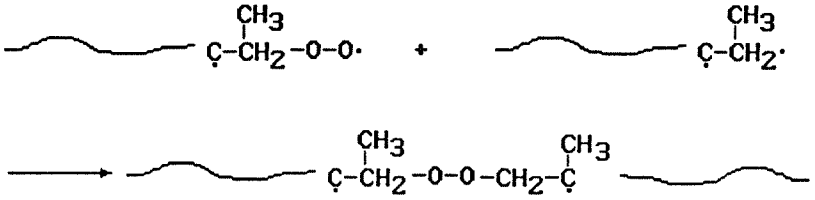
The aryloxy radical can terminate by coupling (disproportioning) with another propagating radical or with itself:



The hydroquinone/quinone can continue this reaction, inhibiting chain propagation.

The N_2 atmosphere is used in the setup to drive out oxygen, since the oxygen forms peroxide radicals, causing another undesirable side reaction:

Because of the double radical property of oxygen, the peroxide radical can then combine with another GMA radical to form a peroxide compound:



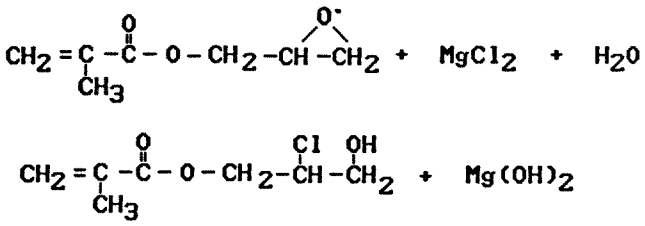
3.3 Epoxy Value [17]

3.3.1 The Importance of Epoxy Value in Evaluating the Reaction:

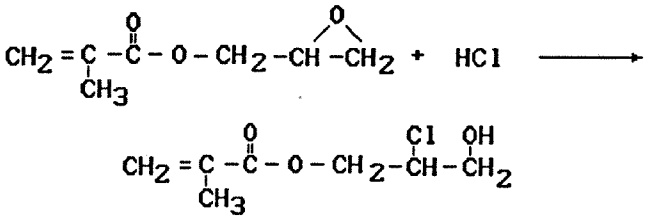
The epoxy value is very important in evaluating the reaction of Bisphenol A with GMA. A high epoxy value means many GMA epoxy groups did not react with Bisphenol A. These unreacted GMA monomers contain epoxy groups and their number can be determined as discussed below in section 3.3.2. So the lower the epoxy value, the more complete the GMA reaction with Bisphenol A.

3.3.2 The Calculation of Epoxy Value

To measure the epoxide content of the sample, the following reaction is carried out:



Here the epoxy groups and the magnesium chloride solution (containing hydrochloric acid) react to form chlorohydrin. The reaction is only quantitative in the presence of hydrochloric acid, which is wholly responsible for the reaction according to the equation:



The number of moles of epoxide in the sample can be calculated through the equation,

$$\frac{V_1N_1 - V_2N_2}{1000} = \text{epoxide mole number content of sample}$$

V_1 = the volume (ml) of blank salt saturated acid solution

N_1 = the equivalent concentration of blank salt saturated acid solution.

V_2 = the volume(ml) of saturated acid solution

containing the sample.

N_2 = the equivalent concentration of saturated acid solution containing the sample.

For example, if 12ml of 0.1N NaOH is used to titrate 20ml $MgCl_2$ acid solution, the equivalent concentration of the blank salt saturated acid solution, N_1, is then

$$N_1 = \frac{N_2V_2}{V_1} = \frac{0.1(12.00)}{20} = 0.06N$$

Now, suppose a 0.081g sample of the BisGMA product is added to 20ml of a saturated acid solution and the solution is then titrated with 10.65ml of 0.1N NaOH.

The equivalent concentration of the saturated acid solution containing the sample will be

$$N_2 = \frac{N_1V_1}{V_2} = \frac{0.1(10.65)}{20} = 0.0533M$$

and the mole of epoxide in the 0.081g sample is:

$$\frac{V_1N_1 - V_2N_2}{1000} = \frac{20(0.06) - 20(0.0533)}{1000} = 0.000135moles$$

So baesd on a sample of 0.081g for the experiment listed in Table 6 where 0.5 moles of GMA (117.5g) is used, there is therefore 0.1958 moles of epoxide groups left

in the residue, which amounts to 0.5 - 0.1958 = 0.30412 moles of epoxy groups consumed in the reaction.

3.4 Discussion of the Synthesis of BisGMA

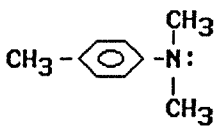
3.4.1 Bisphenol A - GMA Ratio (Table 1)

If there is more than one mole of Bisphenol A for every two moles of GMA, the product will contain excess Bisphenol A, a difunctional compound.

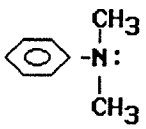
One may note from Table 1, as the Bisphenol A : GMA ratio is reduced, the time to gel increased. However changing the ratio alone is not sufficient to insure a gel free product. It is assumed that there must be some other factor(s) involved. Therefore, the ratio was set at 1 : 2.5 while other variables were investigated.

3.4.2 DMPT Catalyst

It is seen that from Table 2 for a decrease in the amount of the catalyst DMPT, the time to gel increases. In fact in the third experiment, no gel appeared after one hour and it was possible to make an epoxy determination. DMPT is a catalyst in the reaction of Bisphenol A and GMA (discussed in 3.1). It is also used as a catalyst in the formulation (see 3.5). The molecular structure of DMPT is similar to N, N dimethylaniline. Both contain a tertiary amine:

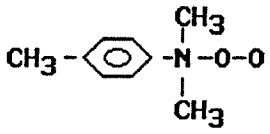


N, N Dimethy-para-toluidene



N, N Dimethyaniline

DMPT can also react with oxygen, to form peroxide radicals:



This peroxide radical can initiate the polymerization of GMA or BisGMA. Therefore with a large amount of DMPT, gel has been resulted.

3.4.3 Temperature

In all of the previous experiments, the reaction temperature was 60°C. In table 3, it is seen that the product quickly became a gel at 70°C (too high a temperature can initiate the monomer activity). At 50°C the epoxy value is higher than that of at 60°C, indicating that a slower reaction of GMA at lower temperatures.

3.4.4 Time

In Table 4, we see that the longer the reaction time, the lower is the epoxy value when both catalyst (DMPT) and inhibitor (hydroquine) are present in the reaction. The effects of DMPT and hydroquine on reaction are totally different, but the present of both is useful in the formation of a gel free BisGMA. The amount of DMPT was added to the reaction mixture at several intervals. Therefore, the rate of reaction was reduced.

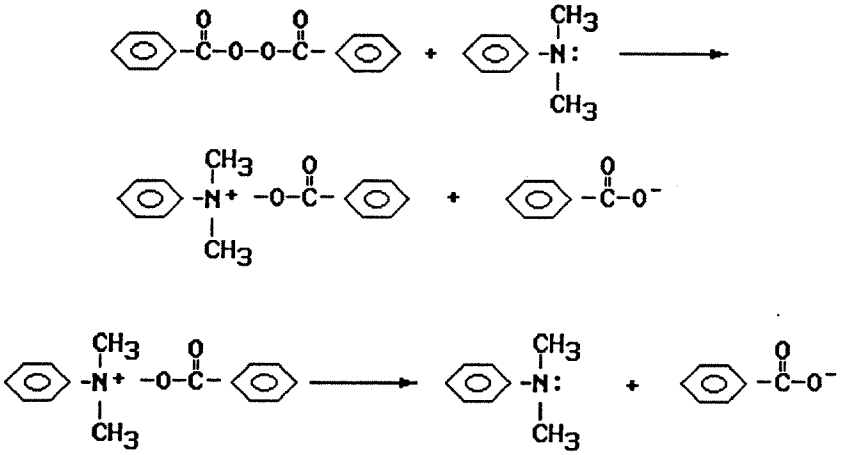
3.4.5 Type of Inhibitor

In Table 5, we tried two kinds of inhibitors were tried to find which yield a better result (lower epoxy value). Hydroquinone was clearly superior to chloranil.

3.5 Free Radical Redox System for BisGMA Crosslinking

The crosslinking process is a graft copolymerization which can be initiated by ions or free radicals. There are two ways to carry out a free radical initiated process. One is just to use a free radical producing agent alone. In tiis case the reaction must be carried out at a temperature that peroxide can decompose the initiator into free radicals free radicals. The other method is to use a redox system that can produce the radicals at loewr temperature such as room temperature.

In this experiment, the redox system is benzoyl peroxide and a tertiary amine such as dimethylaniline. The redox system decomposes to yield radicals between 0 to 25°C between which it is very easy to operate. The mechanism of the redox can be described by the following equation:[25, 26, 27]



Benzoyl peroxide, which has a half life of 30 min at 100°C can be rapidly decomposed by dimethylaniline into an unstable ionic intermediate at room temperature, which reacts further to produce a benzoyloxy radical and a radical cation.

3.6 Discussion of IR, FTIR and GC-Mass

1). DECP-HEMA IR Spectra

The IR spectra of DECP and HEMA are shown in Figure 6-7. The spectra of DECP-HEMA adduct is shown in Fig.8. In DECP, the covalent phosphate(-P=O) fall in the region between 1290-1280 cm^{-1}, while in HEMA spectra, there is no such as absorption. By comparing the IR spectra of the HEMA, DECP and HEMA-DECP, there is no any peaks at 1500-1600 cm^{-1} in the adduct HEMA-DECP. The peak can be attributed to be stretching vibration absorption.[28]

2). BisGMA IR and FTIR spectra

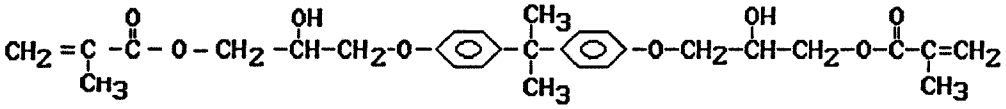
Comparing IR spectra of BisGMA(commercial) and BisGMA(made), both of them are almost consistant. Epoxy ring peaks 850-750 cm^{-1} fall in both spectra,which mean that the epoxide was not comsumed completely[29].

Comparing FTIR spectra of BisGMA (synthesized) (Fig 11-13) and commmercial BisGMA(Fig 14-16). One finds a strong absorption of the commercial product at about 2300cm^{-1}. The couse for this strong absortion can not be explained. There is no such as absorption in their regular IR spectra. (Note: The synthesized sample was applicated to the IR salt plate through its THF solution while the commercial product was directly smeared on the salt plate). The sharp absorption at 750 cm^{-1} of the synthesized sample is due to the residue Toluene, which was not removed compltely during the synthesis of the sample[30].

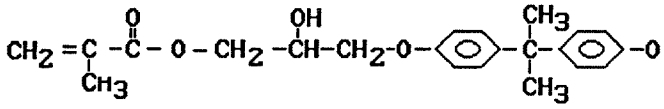
3) GC-Mass spectra

The scan time reange of GC-Mass spectra of BisGMA falls in between 1000-2854 seconds. Three peaks at time 2546, 2368 and 1856 were identified by mass spectra.

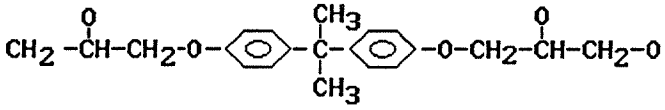
The biggest peak at 2546 represents the main product (BisGMA) of the sample. Its detailed mass spectra is shown in Fig. 18. The theoritical BisGMA molecule weight is 544 and its stracture is analized as follows:



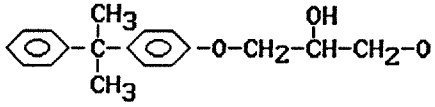
Mass 370 represents:



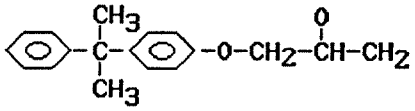
Mass 355 represents:



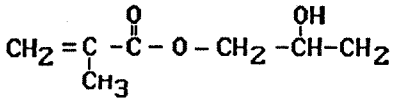
Mass 281 represents:



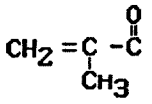
Mass 269 represents:



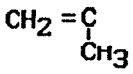
Mass 143 (main component):



Mass 69 represents:



Mass 41 represents:



In general, the stability of molecular ions of various types decrease in the following order: aromatic, conjugated olefins, unbrancked hydrocarbons, ketones esters, ethers, carboxylic acid, branched hydrocarbons and alcohols.[30] There are a lot of -OH, ethers, esters in the BisGMA molecule structure. They are not stable under electronics bomb so that many fragments were formed. The structure of these fragments are shown as above.

3.7 The Formulation and Bonding Strength of BisGma Adhesive

With BisGMA as main component of the adhesive, seven formulation has been prepared. The composition of each formulation is summerized in Table 7 along with bond strength of the adhesive to tooth dentin. Comparing it to the results 744 psi, or enamel and 601 psi on dentine by previous worker, Sun, Denyun, is much lower. However, the previous worker has applied N_2 gas to blow dry the sample after the adhesive is applied to the interface of the dentin or enamel and the testing aluminum. Where as this work has not used N_2 gas at all. In the research, the emphasis is primarily on the synthesis of BisGMA. May be more work is need on the formulation of the adhesive to improve bonding strength.

CHAPTER 4
CONCLUSION

The prepolymer of BisGMA has been synthezied by reacting Bisphenol A and glycidyl mathacrylate. The monomer of BisGMA has been achieved by seperating the prepolymer BisGMA using Chromatograph column. The properties of the dental adhesive containing prepolymer BisGMA with organophosphonate DECP-HEMA adduct and silane is better than the one containing monomer BisGMA with organophosphonate DECP-HEMA and Silane.

The tensile strength of this dental adhesive is rather low. but the properties of this dental adhesive basically satisfy the needs of clinic practice at room temperature rapidly without adhesives drying gas N_2 solidity the adhesives.

Although many works have been done in synthesis BisGMA and formulation of the adhesive, there is much work to do in choicing suitable monomer and pretreatment interface between teeth surface and adhesive. It is necessary to take further steps to improve and modify the formulation of the adhesive in order to enhance the tensil strength of the adhesive.

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