ABSTRACT

Title of Thesis: PREPARATION AND TESTING OF NOVEL DENTAL ADHESIVES BASED ON BIS-GMA/TEGDMA MONOMER SYSTEM

Deyun Sun, Master of Science, Chemistry Department, 1991

Thesis directed by: Dr. George Y. Lei, Associate Professor

In this study, polymerizable phosphonate adhesives synthesized from Diethylchlorophosphate and 2-Hydroxyethylmethylacrylate and formulated with G-methacryloxypropyltrimethoxy silane is used in Bis-GMA/TEGDMA monomer system. All the raw materials and finished products are characterized with infrared spectra, vapor pressure osmometry, viscosity and gel test. The bonding strength to tooth materials is determined by Instron machine. The work emphasizes applying polymeric organic phosphonate adhesive to Bis-GMA/TEGDMA monomer system and investigates the appropriate conditions for the crosslinking of Bis-GMA/TEGDMA monomer system. Average bonding strength of 744 psi to enamel and 600 to dentine are obtained in comparision to 550 psi to enamel for phosphonate/silane/MMA/PMMA and 120 psi for the commercial product "Gluma".

PREPARATION AND TESTING OF NOVEL DENTAL ADHESIVES BASED ON BIS-GMA/TEGDMA MONOMER SYSTEM

by

Deyun Sun

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Title of Thesis: PREPARATIOM AND TESTING OF NOVEL DENTAL ADHESIVES BASED ON GIS-GMA/TEGDMA MONOMER SYSTEM

Name of Candidate: DEYUN SUN
Master of Science in Engineering Science(Chemistry), 1991

Thesis and Abstract Approved:

Dr. George Y. Lei — Date
Associate Professor
Chemistry Department

Dr. Barbara B. Kebbekus — Date
Professor
Chemistry Department

Dr. Richard Parker — Date
Professor
Chemistry Department

VITA

Name: Deyun Sun

Permanent address:

Degree and date to be conferred: MS in Eng. Sci.(Chemistry), May, 1991

Date of birth:

Place of birth:

Collegiate institutions attended	Dates	Degree	Date of Degree
East China University of Chemical Technology	1978-1982	B.S.	Feb. 1982
New Jersey Institute of Technology	1989-1991	M.S. Chem	May 1991

Major: Polymer Chemistry

To My Parents and Friends

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Chapter 1

Introduction

Dentistry has led the health-science field in taking advantage of the rapidly expanding family of polymeric materials, even though its usage is not significant compared with the total consumption of plastics[1]. Dental restoration is one of the most important aspects of dentistry. A dental restorative, ideally, should supply rapid, convenient and inexpensive manipulation and application; it should be hardened rapidly at or near mouth temperature with minimal shrinkage; should be chemically and dimensionally stable, insoluble both in oral fluids and in the corrosive oral environment, less conduction of heat, and be easy to handle. The material must also be nontoxic and well tolerated by adjacent and opposing tissue, either hard or soft. It is necessary for a restorative to produce a good chemical bond with enamel and dentine, and be physically and chemically compatible with the tooth structure as well[2][3] However, it is likely that no restorative can satisfy all these requirements. Probably the main defect of dental restoratives is the lack of true adhesive bonding between the currently used polymeric materials and the hard tooth tissues in this humid environment. Therefore, enhancement adhesion leads the way to a successful restorative material.

The objective of this thesis is to continue what has been done previously, synthesize the polymeric organic phosphonate adhesive and formulate a new dental adhesive emphasizing the increase of bonding strength between the tooth and the new restorative. Thermosetting resin Bis-GMA[4] as a composite matrix which has been proved to have significant potentials for clinical practice.

1.1 Tooth structure and chemical composition

The tooth is composed of the crown and the root. The crown is covered by enamel, a highly calcified substance covering the part of the tooth that is visible. Chemically, enamel is composed of small quantities of organic matter consisting of soluble proteins, peptides, insoluble protein, citric acid, and a mineral phase which has an apatite structure, principally hydroxy apatite. Beneath the enamel surface is the bulk of tooth substance dentine, resembling bone in many respects. The organic constituents of dentine are collane, small quantities of citric acid, insoluble protein, mucopolysaccharide and lipid[5]. The mineral part of dentine is hydroxyapatite. Fig.1 shows the tooth structure.

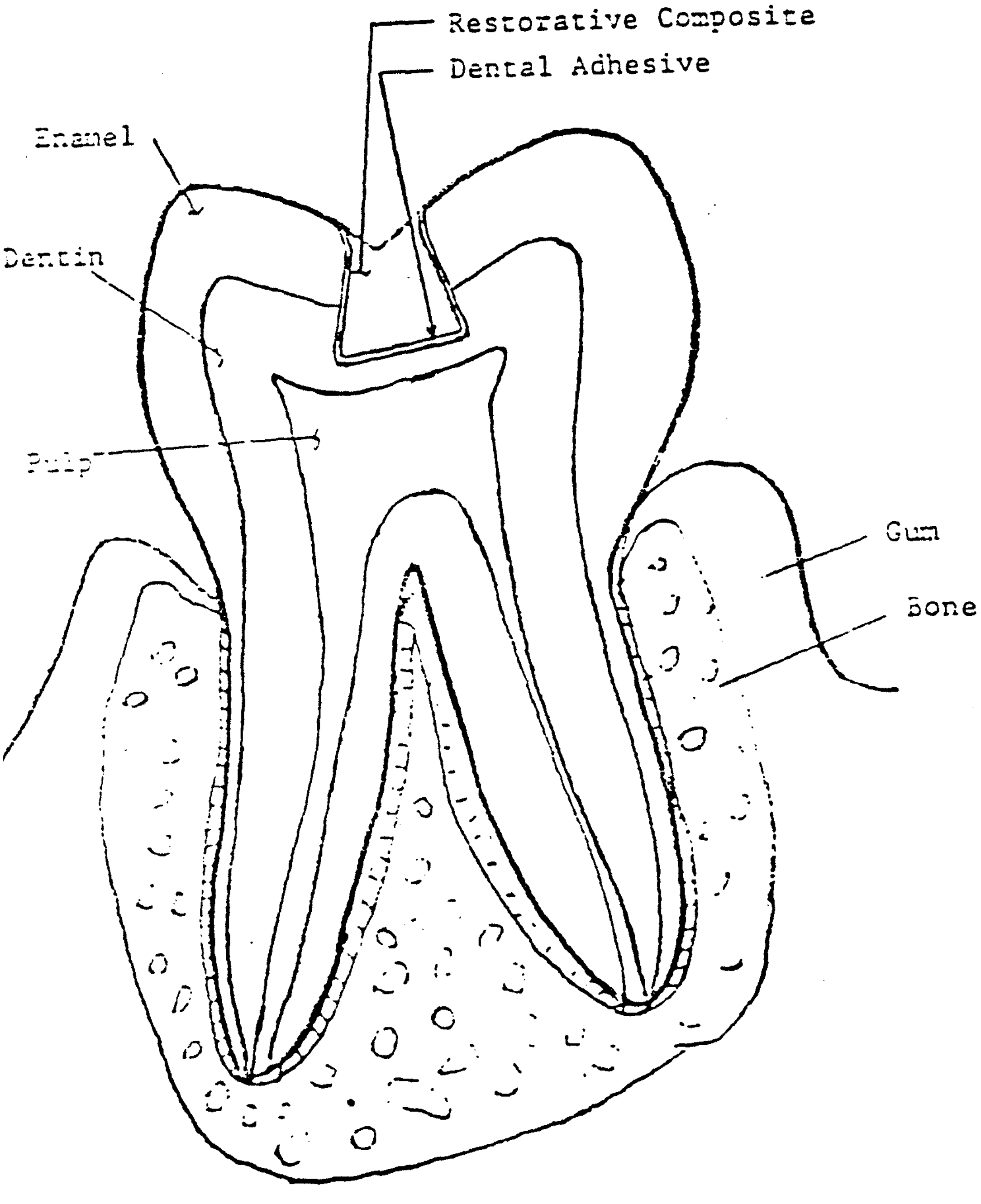


Fig.1. Tooth Structure[5]

The approximate chemical compositions of enamel and dentine[5] are shown in Table I.

	Mineral Phase		Organic Matter		water	
	Vol(%)	(Wt%)	Vol(%)	(Wt%)	Vol(%)	(Wt%)
enamel	92	(97)	2	(1)	6	(2)
dentine	48	(69)	29	(20)	23	(11)

The hydroxyapatite in enamel appears in the rod shape termed enamel prisms. These are approximately 4 to 5 um in diameter, and run from the interface between dentine and the enamel surface. Fig.2 shows hydroxyapatite shape in enamel[6]

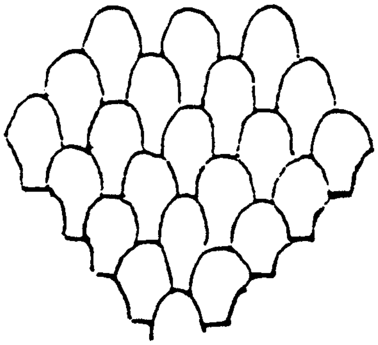


Fig.2 Hydroxyapatite shape in enamel

Fig.3 is a diagrammatic crosssection of dentine, cut perpendicular to the tubules. The tubules contain slender prolongations or processes of connective tissues. Peritubular dentine is highly calcified annular layer with each tubule, which surrounds the odontoblastic process. In the tubule, the space is filled with dentinal fluid, which is similar to tissue fluid in its composition. Fluid flows from tubules of freshly cut dentine. Between the tubules, the intercellular substance is composed of bundles of fibers of collagen, embedded in a calcified substance.[6][7]

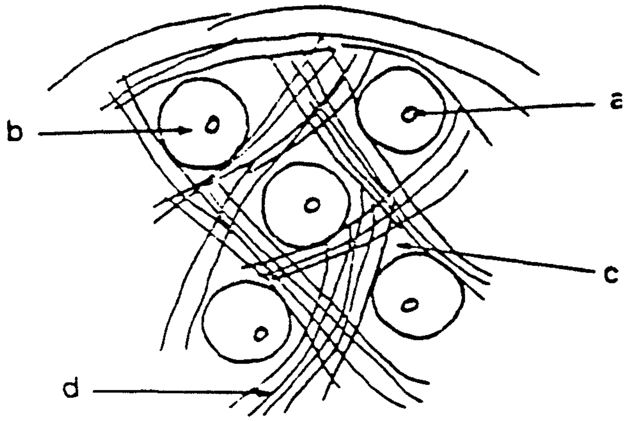


Fig.3 Section of dentine, cut perpendicular to the dentinal tubules. a. dentinal tubule; b. peritubular dentine; c. intertubular ddentine; d. collangen fibers.

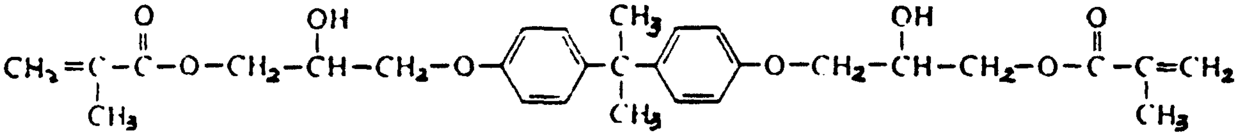
1.2 Constituents of Dental Composite[4]

1.2.1 a. Principal monomer

Like any other composite, the dental composites are mainly composed of a principal monomer, a diluent monomer, an inorganic filler,a silane coupling agent, an initiator and an activator[10]. For dental purposes the monomer must be polymerizable. The filler serves to reduce shrinkage and coefficient of thermal expansion. Some early composites used methyl methacrylate as a principal monomer. Because of its structure, several defects are found for this monomer, namely:

1. producing high volume shrinkage during polymerization
2. generating heat in the process of polymerization
3. easy to volatilize
4. highly irritating to pulp and soft tissue

A significant advancement was made by R Bowen who developed a new monomer based on bisphenol A and bis 2 hydroxy propyl methacrylate (2,2- bis[4(2- hydroxy- 3methacryloyloxy- propyloxy)-phenyl] propane). This new monomer has a structure as the follows and has been proven a most successful monomer for dental applications[8].



The bis-phenol unit in the monomer reinforces the strength of the

The bis-phenol unit in the monomer reinforces the strength of the polymer and the terminal methacrylate groups can be polymerized by free redicals resulting in a thermosetting resin. The advantages of this monomer over MMA are: [8][9]

1. Its volume shrinkage is much less during polymerization
2. It generates less heat of polymerization
3. It is nonvolatile

1.2.2 b. Diluent monomer

The functions of diluent monomers are to reduce the viscosity of the material to achieve good mixing with the inorganic constituents. There are two types of diluent monomer. Type I is monofunctional such as methyl methacrylate, and Type II is difunctional such as triethylene glycal dimethacrylate. Although diluent monomers can reduce viscosity of materials, they can also produce volume shrinkage during polymerization if the diluent monomer is used in large quantity[7].

Normally, a difunctional monomer is preferred as a diluent solvent. Reasons for this are:

1. Difunctional monomers produce less shrinkage than do

monofunctional monomers during polymerization

2. Difunctional monomers can produce a more cross-linked structure which is harder and stronger, and has a lower coefficient of thermal expansion

3. Difunctional monomers are less volatile

1.2.3 c. Fillers

A wide varity of fillers have been used in dental restorative materials. For the early composites, synthetic calcium phosphates and fused silica were used as inorganic fillers.

Current materials contain lithium aluminosilicates, crystalline quartz, barium aluminoborate silica glasses, strontium glass and microfine filler consisting of silica.

Effects of filler are to improve mechanical properties, reduce coefficient of thermal expansion, reduce contraction on setting and generate less heat in polymerization[4]. In this research no filler is used.

1.3 Principles of Adhesion

Adhesion takes place when two different substances join together on their contacting interface. Adhesion is the result of intermolecular attachment through either physical adsorption or chemical bonding, highly localized in the vicinity of each surface,but sometimes it may also be produced by mechanical interlocking.

1.3.1 a. Surface Properties and Bonding

Surface properties are important for a good adhesion. Basically, there are two factors affecting the surface properties and bonding. The first factor is surface roughness. The most of the surface to which adhesive bonding is required should be microscopically or macroscopically rough. If the rough surface is adquately wetted by an adhesive, the effective area of contact may be increased and the bond strength improved as well. The second factor is pockets of air trapped between the adhesive and the surface. Theese reduce the area of contact between adhesive and adherend, thus reduce the bonding stregnth[12][13].

Surface forces, such as Van der Waals forces, are appreciable although they are weaker than chemical bonds. However, Van der Waals forces between two bonded materials decrease rapidly with the distance of seperation. For a good adhesion, surface forces and surface roughness are both necessary. The adhesive must flow across the surface and fill all microscopic irregularities so that wetting of the both adherends is achieved[14].

1.3.2 b. Surface tension and wetting

The surface tension and wetting of a liquid is an important basic property that can be altered by a variety of factors. The ability of an adhesive to wet the surface of the adherend can be measured by the contact angle of a drop of liquid on the surface. The contact angle of a liquid on a reasonable smooth surface is inverse to the degree of wetting of the surface. Materials having low surface energy will not be easily wetted. When contact angle is large the surface wetting is poor. The greater the tendency to wet the surface, the lower the contact angle. Complete wetting occurs at a contact angle equal to zero[13][14].

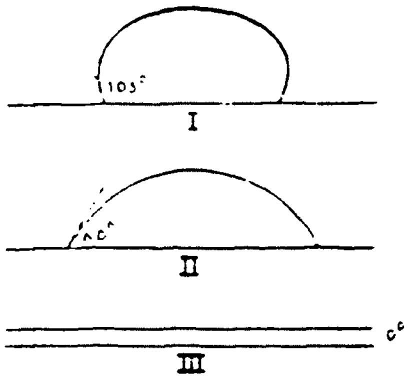


Fig.4 surface wetting I. contact angle 105 °C; II. contact angle 60°C; III. contact angle 0°C.

1.3.3 c. Requirements for setting adhesion system[7]

There are several requirements for setting adhesion systems, to obtain a good adhesion.

1. Adhesive must have good ability to wet the adherend
2. Adhesive should have suitable viscosity to make itself flow over the surface of adherend easily
3. Setting of the adhesive should take place without large dimensional changes.
4. Proper thickness of the adhesive layer

1.3.4 d. Type of adhesive bonding failure

For an adhesive bond being tested in tension, there are mainly three types of failure: failure of adhesive bonding; tensile failure of the adhesive; and tensile failure of either adherend[15][7]

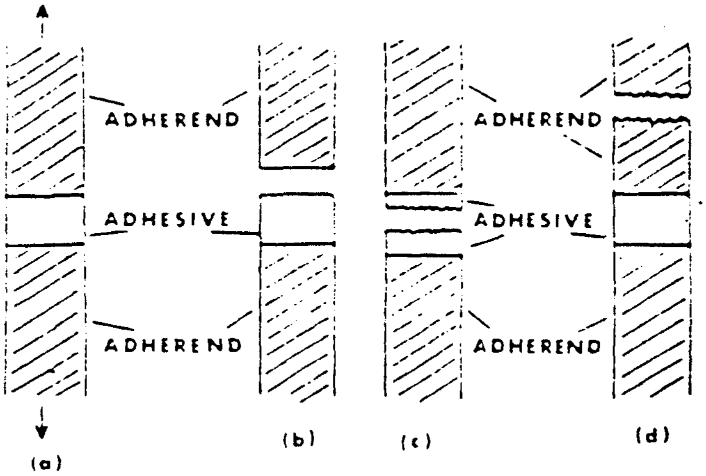


Fig.5 Adhesion bonding a. adhesion bond in tension; b. failure of adhesive bond; c. tensile failure of adhesive; d. tensile failure of adherend.

1.3.5 e. Dental considerations

For use in dental consideration, firstly, an adhesive should ideally react with both organic and inorganic constituents of the tooth. Secondly, the adhesive should ideallybe hydrophilic, not repelled by water existing in enamel and dentine. Thirdly,the the adhesive should be stable in the oral environment[7][2][16].

1.4 Adhesion system and each component's effect

1.4.1 Phosphonate adhesive[17][19]

As mentioned above enamel and dentine are principally composed of hydroxy apatite which is a calcium phosphate mineral. Phosphonate adhesive can adhere to the tooth by forming chemical bonds between calcium ion in hydroxyapatite and restorative polymer by taking part in the polymerizing reaction this can prevent seepage of fluids from the restorative- tissue interface[20][25]. Polymeric phosphonate can be indicated as M-R-X, where M is methylmethacrylate group, R is a spacer, and X is the group capable of bonding to the tooth by interacting with calcium ions in tooth(see Fig.6). The establishment of this bond leaves the dentine covered with a layer of adhering methacrylate group[17][24][18].

The phosphonate group is shown in Fig.6 in partly ionized form. The attraction between negatively charged oxygen atoms of the phosphate group and calcium ions in hydroxyapatite is shown by two arrows[21].

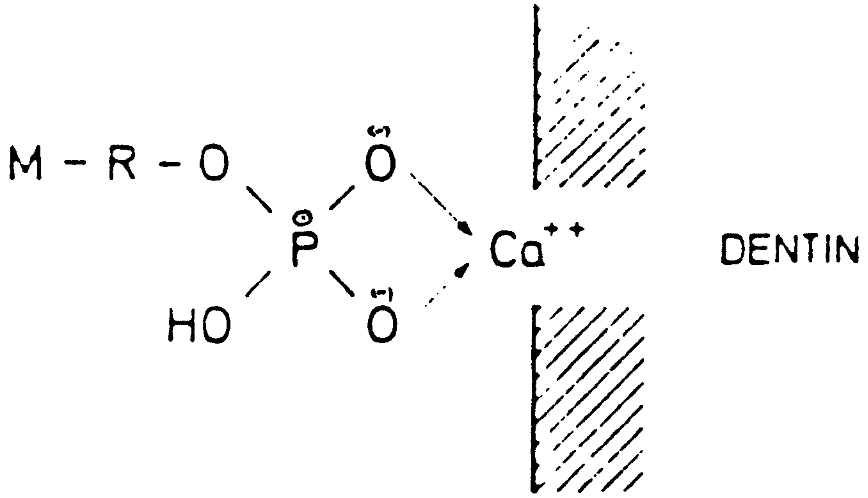
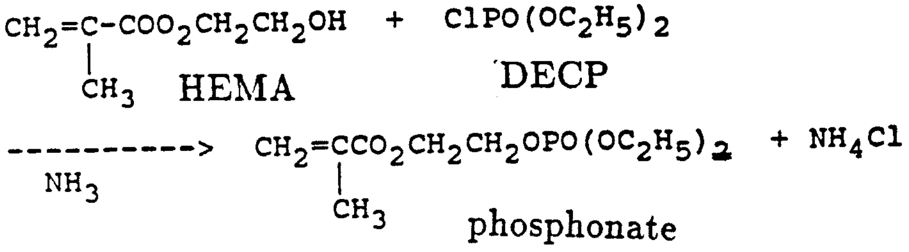


Fig.6 Bonding mechanism of phosphate.

1.4.2 Synthesis of polymeric organic phosphonate[26]

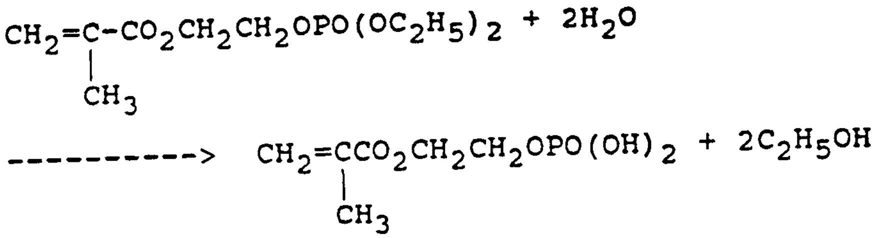
The polymeric organic phosphonate having one double bond end group and one functional end group was synthesized from 2-hydroxyl mechacrylate (HEMA) and diethylchlorophosphate (DECP) in this research. The reaction is:



$$\underset{\text{HEMA}}{CH_2{=}\underset{\displaystyle |\atop CH_3}{C}{-}COO_2CH_2CH_2OH} \quad + \quad \underset{\text{DECP}}{ClPO(OC_2H_5)_2}$$

$$\xrightarrow[NH_3]{} \underset{\text{phosphonate}}{CH_2{=}\underset{\displaystyle |\atop CH_3}{C}CO_2CH_2CH_2OPO(OC_2H_5)_2} \quad + \quad NH_4Cl$$

The reaction between tooth and polymeric phosphonate is based on the hydrolysis of the phosphonate which take place as soon as the monomer is applied to the tooth surface where water exits[26]. The process is shown as follows:



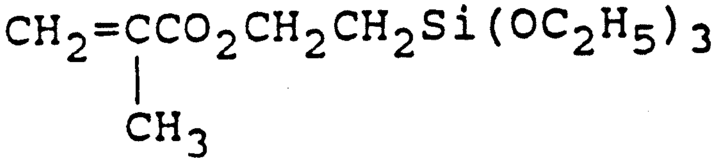
$$CH_2=\underset{\underset{CH_3}{|}}{C}-CO_2CH_2CH_2OPO(OC_2H_5)_2 + 2H_2O$$

$$\text{---------->}\ CH_2=\underset{\underset{CH_3}{|}}{C}CO_2CH_2CH_2OPO(OH)_2 + 2C_2H_5OH$$

The product of hydrolysis has two functional end groups. One of them can polymerize with double bonds in the basic resin BIS-GMA, silane and other substances containing double bonds. The other can react with calcium ion in tooth, so the adhesion is established between restorative materials and tooth.

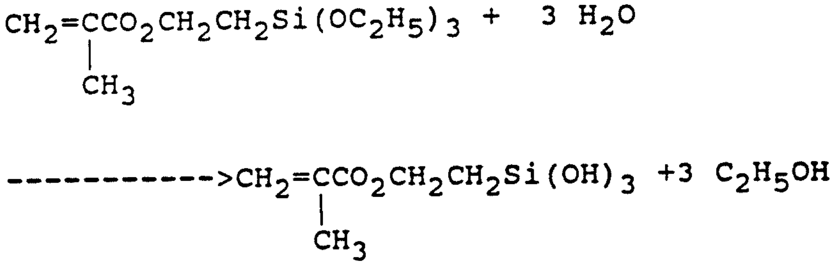
1.4.3 Silane coupling agent[23]

Silane coupling agent is usually used as a pretreatment agent for mineral filler to increase the adhesion between the organic and the inorganic. Gamma-methacryloxy-propyltriethoxysilane was used in the experiment. Its structure is



$$CH_2{=}\underset{\underset{CH_3}{|}}{C}CO_2CH_2CH_2Si(OC_2H_5)_3$$

Compound has a double bond which can polymerize with bis-GMA and TEGDMA(adiluent) and three hydrolyzable groups. The hydrolysis is shown as follows[26]



$$CH_2{=}\underset{\underset{CH_3}{|}}{C}CO_2CH_2CH_2Si(OC_2H_5)_3 + 3\ H_2O$$

$$\longrightarrow CH_2{=}\underset{\underset{CH_3}{|}}{C}CO_2CH_2CH_2Si(OH)_3 + 3\ C_2H_5OH$$

After hydrolysis, the mineral interface is then proposed in which silane coupling agent provides a bond at the interface capable of using hydrolytic intrusion of the surface, with self-healing as a means of stress relaxation without disrupting the overall bond between polymer and mineral surface[26]. Fig.7 shows the adhesion reaction between polymer-silane- tooth surface.

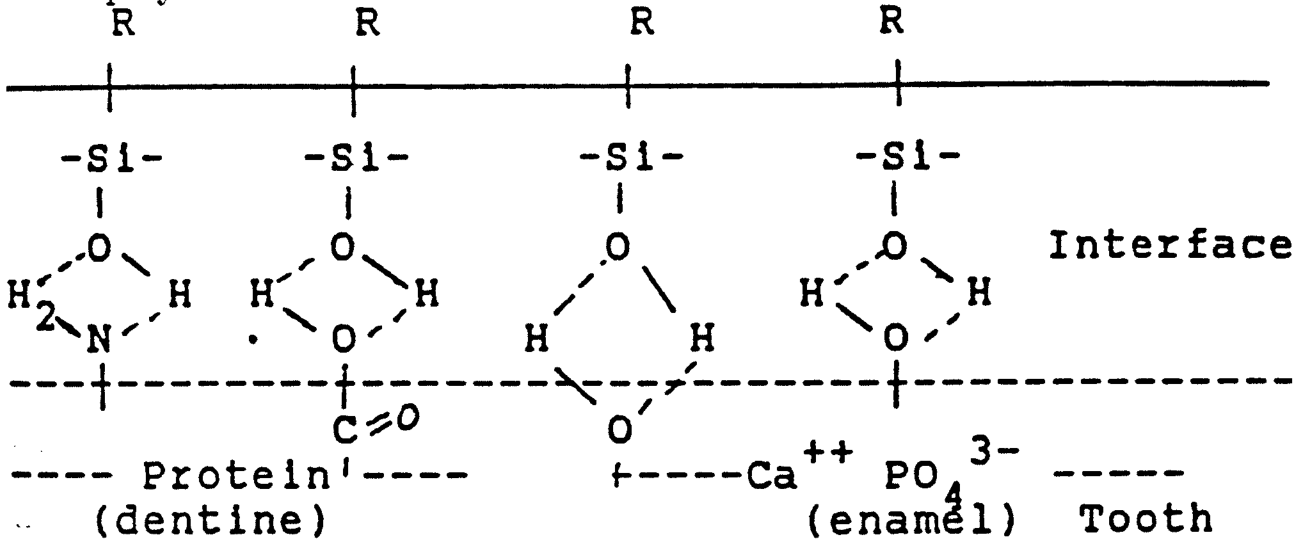
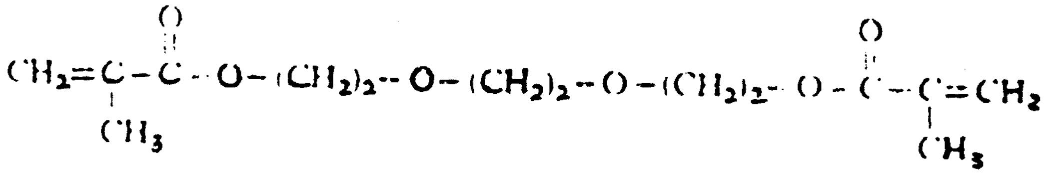


Fig.7 Bonding mechanism of adhesive

1.4.4 Diluent Monomer

Since the main component, bis-GMA. prepolymer, is a very viscous liquid it is difficut to use it directly without dilution. In this experiment, triethylene glycol dimethylacrylate is chosen as the diluent monomer.[7]



$$CH_2=\underset{\displaystyle CH_3}{\overset{}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle CH_3}{C}=CH_2$$

It has two double bonds thus it can also be used as a cross-linking agent for bis-GMA prepolymer, silane compound and phosphonate to form three dimensional network structure.

1.4.5 Glutaradehyde[24][22]

Glutaradehyde is usually used as a protein crosslinking agent in biochemistry. Tt can react with the amine group of protein(-NH_2). In this research, glutaradehyde was also used to react with protein of the tooth and the small amount of HEMA residue left over during synthsis of polymeric phosphonate.

1.4.6 Adhesion Through Bis- GMA- Phosphonate- Silane- TEGDMA System

Since bis-GMA prepolymer is a thermosetting plastic, it can form a three-dimentional network with cross-linking agent or with heat. The degree of curing depends on the double bonds which have reacted with the cross-linking agent. Double bonds of the prepolymer can also react with the double bonds of phosphonate and silane coupling agent, as well as the curing agent TEGDMA to form a solid. Fig.8 shows the reaction between adhesion interfaces.

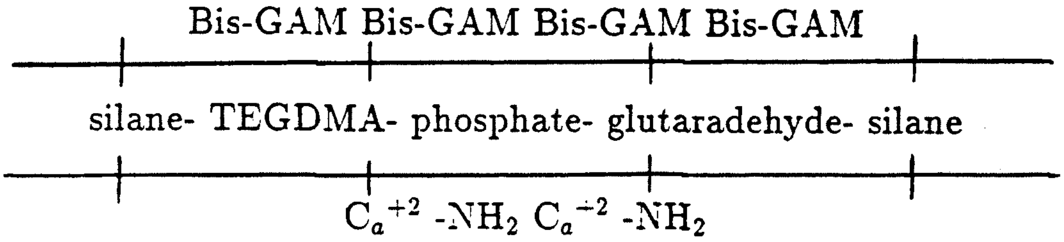


Fig.8 reaction between adhesion interfaces

1.5 Pretreatment technique[24]

In order to enhance the bonding of an adhesive to enamel and dentine, it is important to pretreat the surface of the substrate for better results. Enamel Acid-etch can remove about 5 um of the enamel and selectively decalcify the enamel to a depth of 15 to 120 μm. The etched enamel surface has an increased surface area for bonding, a high surface energy to enhance wetting, and a porous structure for resin to penetrate.

Dentine acid-etch is not recommended because of the dentine tubules which extend to the dental pulp and contain tissue fluid[7]. In the experiment, phosphoric acid (50% wt) and ferric oxalate (5% wt) were tried to treat enamel and dentine surface. There is further work to be done.

Chapter 2

Experimental

2.1 Synthesis of Phosphonate

2.1.1 Reagents

Diethylchlorophosphate(DECP),$C_4H_{10}POCl$, F.W.=172.55, Aldrich Chemical Co.
2-Hydroxylmethylacrylate(HEMA), $C_6H_{10}O_3$ F.W=135.2, Fluka Co.
Pyridine C_5H_5N, F.W.=79.10, Aldrich Chemical Co.
Chloronil $C_6Cl_4(=O)_2$, Aldrich Chemical Co.
Ammonia gas NH_3

2.1.2 Apparatus

500 ml three-necked flask
Thermometers -10 – 150° C
250 ml two-necked distillation flasks(2)
Condensor with two 105° adapters
250 ml Erlemeyer flask

250 ml heating mantles
250 ml separation funnel
Magnetic stirrer

2.1.3 Procedure[26]

1. Purification of DECP and HEMA by distillation

100ml Diethylchlorophosphate(DECP) was placed into a 250 ml flask equipped with two thermometers, a magnetic stirrer and a condensor /receiver and a vacuum pump system. The flask was heated slowly to 74°C by a heating mantle. The distillation was maintained under a vacuum of about 5 mm Hg between 74 to 80° C, and the initial portion of the distillate was discarded. A total of 70 ml distillate was collected. The distillate was stored in a desiccator.

100 ml Hydroxyethylmethacrylate(HEMA)was placed into a 250 ml flask along with 2 to 3 drops of chloranil as inhibitor. The flask was equipped with necessary accessories as above for distillation. The distillation was carried out under 5 mm Hg vacuum between 60 to 65°C. Finally 60 ml distillate was collected. The distillate was then stored in a refrigerator at about 5 °C to avoid self-polymerization.(for apparatus see Fig.9.)

2. Reaction

51.77g freshly distilled DECP and 38.75g freshly distilled HEMA were placed into a 500 ml three-necked flask equipped with a thermometer, a magnetic stirrer and a inlet glass tube for introducing NH_3 gas to react with the by-product HCl to form a white precipitate . In addition 5 drops of pyridine were also introduced to the flask as catalyst. The reaction mixture was stirred for about 5 minutes before the flask was placed into an ice-bath. As the temperature of the reactants dropped down to 8 - 5°C, the reactants were stirred again, and meanwhile from a gas cylinder NH_3 gas was also introduced to the flask and bubbled through the reactants. During the introduction of NH_3, the system was kept stirred. After 5 to 10 minutes the white precipitate NH_4Cl was formed in the flask. Since the formation of NH_4Cl was an exothermic reaction, the temperature of the flask tended to rise. However, the temperature of the reactants was kept between 10 to 15°C by addition of ice and salt to the cooling bath from time to time. 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 indicator paper. (for apparatus see Fig. 10.)

3. Collection of product

The reaction mixture was left to stand at room temperature for about one hour without stirring. 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 Formulation of Adhesive and Bonding Agent

2.2.1 Chemicals

Bis-GMA (Bisphenol A Bis 2 Hydroxy Propyl methacrylate prepolymer), Freeman Co.
TEGDMA (Triethylene Glycol Dimethacrylate), Fluka Co.
G-methacryloxypropyltriethoxysilane, RCP Inc.
Benzoyl peroxide, Aldrich Chemical Co.
N,N-Dimethylaniline, Aldrich Chemical Co.
N,N-Dimethyl-p-toluidine, PFALTZ and BAUER Inc.
Divinylbenzene, Fluka Chemical Co.
Methylmethacrylate, PFALTZ and BAUER Inc.

2.2.2 Formulation of Phosphonate Adhesive

The adhesive was formulated by adding 2 ml of DECP-HEMA adduct (phosphonate) to 10 ml G-methacryloxypropyltriethoxy silane. The mixture was then thoroughly mixed with 0.125 g N,N-Dimethylaniline. Five minutes later, the pH of the mixture was measured and adjusted to 4 to 6 with citraconic acid. The adhesive was kept in the refrigerator for further use.

2.2.3 Formulation of Bonding Solutions A and B

Solution A

14 g Bis-GMA viscous prepolymer was diluted with 6 g TEGDMA. In order to avoid air bubble formation, stirring was very gentle. After Bis-GMA was completely dissolved, 140 mg benzoyl peroxide was added to the mixture to form a homogenous system through gentle stirring.

Solution B

In the similar manner another 14 g Bis-GMA prepolymer in 6 g TEGDMA was prepared. In this case 0.648g N,N-Dimethylaniline activator was added to the solution.

(Note: Different proportions of Bis-GMA, TEGDMA, peroxide, and activator were tried in this research for optimum formulation).

2.3 Characterization

2.3.1 IR Spectra

Using the salt plate smear method, the IR spectra of DECP, HEMA, Phosphonate and TEGDMA were obtained through Infrared spectrophotometer, Perkin Elmer, model 1310. The spectra were scanned over the wave numbers between 650- 4000 cm-1. The spectra are collected in Fig. 11 to 14.

2.3.2 The Number Average Molecular Weight($\overline{M}n$) of Bis-GMA Prepolymer by Vapor Pressure Osmometer

Following the instruction manual of the Wescon vapor pressure osmometer, using benzil (molecular weight 210.24) as standard and toluene as solvent, five standard solutions of different concentrations along with five Bis-GMA solutions of different concentrations were measured at room temperature (21°C). The results are shown in Fig.15 and 16.

2.3.3 Intrinsic Viscosity[n] of Bis-GMA

A 100 ml stock solution was prepared by dissolving 8.776 g Bis-GMA in acetone. The flow time of the stock solution, diluted solution and the solvent were separately measured in the Ubbelohde viscometer. The results are summarized in Table 15.

2.3.4 Gel Test

The gel test is to measure the polymerization time, and subsequently, to determine whether the initiator/promotor system is suitable. In this experiment, the gel test was done by noting the time required for a certain amount of Bis-GMA/TEGDMA to gel upon addition of a certain amount of the initiator, benzoyl peroxide and promoter, N,N-Dimethylniline. The results of the gel test are listed in Table 14.

2.3.5 Degree of Curing

0.6779 g cured Bis-GMA sample (cured at room temperature and under inert atmosphere N_2 gas for 30 minutes), was dipped in the acetone solvent for seven days at room temperature. The weight loss of the sample was then determined and the degree of curing was calculated from to the weight loss.

2.3.6 Effect of O_2 Effect on Curing

The effect of O_2 on curing Bis-GMA/TEGDMA with initiator and promotor was checked under the following 3 conditions:

a. Curing in open air for one hour.

b. Curing in a small pan and covered with a piece of polyester film for 1 hour.

c. Curing in a desiccator filled with N_2 gas.

After the specified curing time, the specimen was examined for its physical appearance. Best curing is acheived where the liquid becomes a dry solid.

2.4 Bonding Strength Test

2.4.1 Preparation of Aluminum Rods

For bonding strength test, the face of the aluminum rod to be placed on the dentine or enamel of tooth was first smoothed with sandpaper and soaked in acetone for 30 min to remove grease. The face of the aluminum rod was further treated with Na_2CrO_7/H_2SO_4 solution(the ratio of $Na_2CrO_7/H_2SO_4/H_2O$ is 1/15/30) and was allowed to etch for 4 minutes in the oven at 40° C. After etching, the rod was rinsed with distilled water, followed by petroleum ether and air blown dry before it was stored in a desiccator.

2.4.2 Tooth Treatment and Mount of The Specimen in Test Holder

Teeth were cut respectively along the dentine face or the enamel face by a low speed diamond cutting saw to provide a smooth bonding surface. The cut surfaces of teeth were polished with a wetted fine sandpaper (wetted by a few drops of water). After polishing the surfaces were rinsed with aqueous methanol, wiped dry with paper towel and blown dry with air. The specimen was then mounted in a holder of 25 mm in diameter and 30 mm in length containing self-curing and hardening resin with the cut surface facing up, a hole was drilled through near the bottom of the plastic holder which was used to attach a metal rod for the grip of Instron.

2.4.3 Formulation and test of Adhesives

Different compositions of adhesives were tried in the research. First, a thin layer of adhesive was put on the surface of the cut tooth specimen, then the aluminum rod was placed lightly on the surface of the treated specimen. The specimen was cured in different conditions such as in N_2 gas or in air. After the specimens were cured, half of the specimens were taken to measure the dry state tensile strength and the other half were dipped in water for 72 hours before the wet state tensile strength was measured.

Group 1 Tensile strength of Bis-GMA/TEGDMA (70/30)

a. Bonding strength of Bis-GMA/TEGDMA (70/30) to dentine and enamel

Eight dentine samples and eight enamel samples were chosen. 15 drops of solution A containing benzoyl peroxide and 1 drop of solution B containing promotor N,N-dimethyl aniline, were mixed throughly. Now the mixture was contained 0.66 % benzoyl peroxide and 0.12 % N,N-dimethylaniline. 1 drop of the mixture (about 36 mg) was applied on the treated cut surface of each sample. Then the aluminum rods were placed on the surfaces of the test samples lightly to fix the sample to the Instron machine. Curing was accomplished under room temperature and with N_2 gas for 30 min. Then they were left in the air for four hours. Half of the samples (4 pieces) were taken to measure the tensile strength and the other half were soaked in water for 72 hours before testing their water resistance (see Table 1 and tooth specimen setting see appendix III and IV).

b. Testing water resistance of bonding

The other half of samples preparedly the above procedure were dipped into water at room temperature for 72 hours before they were taken out of the water to be tested for their tensile strength(see Table 1).

Group 2 Adhesion tensile strength of silane

a. Bonding strength of Bis-GMA/TEGDMA to dentine and enamel

Eight dentine and eight enamel cut tooth samples were coated with G-methacryloxypropyltrimethoxy silane. Three minutes later, a drop of about 36 mg mixture of solution A and B (ratio 15/1) which contained 0.66 % BPO and 0.12each sample. Then the aluminum rod was set up to fix the sample to the Instron. The curing was done at room temperature under N_2 gas environment for 30 minutes. After 4 hours in the air half of the samples were taken to measure tensile strength, the other half were dipped into water for water resistance test(Table 2).

b. Testing water resistance of bonding

The remaining eight samples (4 dentine and 4 enamels) kept in the water for 72 hours at room temperature were taken to measure tensile strength (Table 2).

Group 3 Adhesion tensile strength of phosphonate

a. Bonding strength of Bis-GMA/TEGDMA(70/30) to dentine and enamel

Eight dentine and eight enamel cut tooth samples were coated with a thin layer of phosphonate/silane(ratio 2/10) by a tiny brush. Three minutes later,a drop of mixture of solution A and solution B(ratio of A/B was 15/1) was applied to the treated cut tooth surface of each sample, then the aluminum rod was set up to fix the sample to the Instron machine. The polymerization took place at room temperature under N_2 gas for 30 minutes and then 4 hours in air. Half of the samples were taken to measure tensile strength, the other half were placed in water for the water resistance test(Table 3).

b. Testing water resistance of bonding

Four dentine samples and four enamel samples were kept in the water at room temperature for 72 hours and taken out to measure the tensile strength.(Table 3)

Group 4 Adhesion tensile strength of silane-phosphonate

a. Bonding strength of Bis-GMA/TEGDMA (70/30) to dentine and enamel

Eight dentine samples and eight enamel samples were coated with a thin layer of mixture of silane and phosphonate which had a ratio of 10/2 by volume and did not contain BPO and promotor in it. Then a drop of mixture of solution A and B (ratio 15/1) was applied on the surface of the cut tooth. The procedure was the same as described before for testing tensile strength in the dry or wet state.

Group 5 Adhesion tensile strength of glutaradehyde-phosphonate-Silane

Eight dentine samples and eight enamel samples were coated with a thin layer of glutaradehyde by brushing on 50 % water solution, 5 minutes later,they coated with the mixture of phosphonate-Silane (ratio 2/10), 3 minutes later, a drop of mixture of solution A and solution B(ratio was 15/1) was applied on the treated cut tooth surface, then the aluminium rod was set up to fix the sample to the Instron machine. Curing took place at room temperature under N_2 gas for 30 minutes, then the samples were taken out for four hours. Half of the samples were taken to measure the tensile strength, and the other half were kept in the air for another 24 hours, and then their tensile strength was measured.

Group 6 to group 10 were tested with different compositions and in different curing conditions. Group 11 were the results of repeating group 5 and with the addition of the wet tensile strength measurement. Group 12 were results of repeating previous work in which crosslinking PMMA*(polymethyl methacrylate) was used as bonding matrix. The compositions and curing conditions of group 6 to group 12 are shown in the following Table. The tensile strengths of group 6 to 12 are shown in Table 6 to Table 12.

group No.	composition	curing condition
6	Bis-GMA/TEGDMA (60/40)	room temp. in air 4 hrs
7	Bis-GMA/TEGDMA (70/30)	room temp. in air 4hrs,etching
8	Bis-GMA/TEGDMA (60/40)	room temp. in air 4 hrs
9	Bis-GMA/TEGDMA (70/30)	room temp. N_2 10min
10	Bis-GMA/TEGDMA (75/25)	room temp. in air 4 hrs

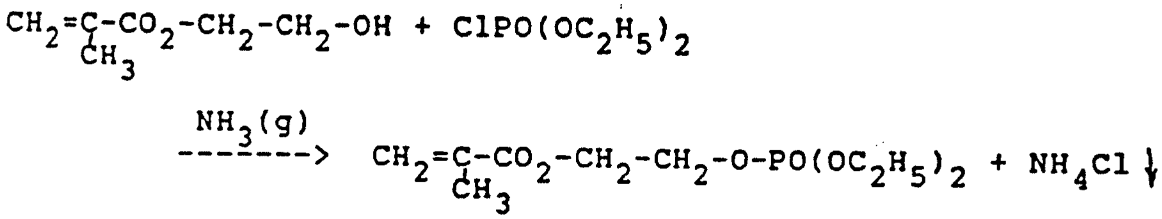
Chapter 3

Results and Discussion

3.1 Synthesis of Polymeric Organic Phosphonate from HEMA and DECP

By comparision of IR spectra the synthesized polymeric organic phosphonate, has the same structure, $CH_2=C(CH_3)CO_2C_2H_4OPO(C_2H_5)_2$ as that obtained by the previously by Wu[26]. As shown in Fig.15 the IR spectra shows an strong absorption peak at 1500 - 1600 cm^{-1} which is found neither in DECP nor in HEMA. This absorption can be attributed to -O-P=O streching vibration [26],[27],[28].

Several factors affect the synthesis. The first one is the purity of the reagents. For purification of the monomer, attention must be paid to the temperature control and the vacuum system especially for HEMA. HEMA has a double bond in its structure. If the distillation temperature is too high, it may cause the monomer to be partially polymerized, and thus reduce its ability to form phosphonate adduct with DECP. If the vacuum is too low, it is then difficult to distill. The second factor is the temperature. Because the synthesis of phosphonate is an exothermic reaction, proper temperature is vitally important. With pyridine as catalyst, the reaction can be carried out effectively in the temperature range 5 to 15 °C. The reaction rate can be controlled by the amount of NH_3 gas introduced to the reaction. If too much NH_3 is added, the reaction would take place violently causing the temperature a sharp rise to ruin the synthesis. If the amount of NH_3 gas is too little, the reaction would take a very long time to complete and make the synthesis impractical. The last factor is moisture, which must be avoided. Otherwise , the precipitate, NH_4Cl, would dissolve in it and makes the separation of HCl very difficult. The chemical reactions for the synthesis can be represented by the following equation:



$$CH_2{=}\underset{CH_3}{C}{-}CO_2{-}CH_2{-}CH_2{-}OH + ClPO(OC_2H_5)_2 \xrightarrow{NH_3(g)} CH_2{=}\underset{CH_3}{C}{-}CO_2{-}CH_2{-}CH_2{-}O{-}PO(OC_2H_5)_2 + NH_4Cl\downarrow$$

3.2 Formulation of Adhesive and Bonding Agent

The ratio of phosphonate (DECP-HEMA adduct)to silane coupling agent affects the final bonding strength. The optimum ratio found by

Wu is 2/10. At this ratio, the tensile strength is doubled as compared to the ratio 1/10. If the ratio increases to 3.5/10 the tensile strength decreases.[26]

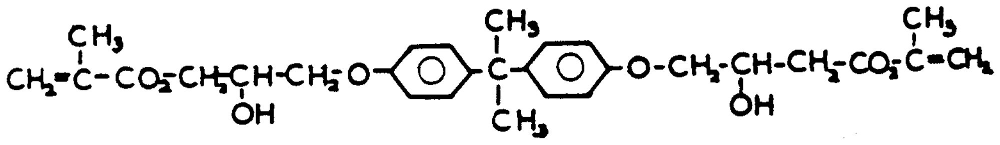
The ratio of Bis-GMA/TEGDMA is another factor affecting the bonding tensile strength. When the ratio is high, the viscosity of the mixture is high, and it is difficult to wet the tooth surface well thus resulting in low tensile strength. When the ratio is low, the flow property is good, but the tensile strength decreases as a result of the higher concentration of TEGDMA in the cured mass. The higher the amount of TEGDMA, the lower the tensile strength. The results of bonding strength tests have proved that the optimum ratio is at 70/30. Comparing the results in Table 10 with that in Table 6 and 7 at the same conditions, the tensile strength at ratio 70/30 is 100 psi more than that of at ratios 60/40 and 75/25.

3.3 Copolymerization of Bis-GMA/TEGDMA

Crosslinking of Bis-GMA with TEGDMA is actually a process of copolymerization of the two components, which is affected by the type and amounts of initiator/promotor system, and the environment in which the copolymerization takes place.

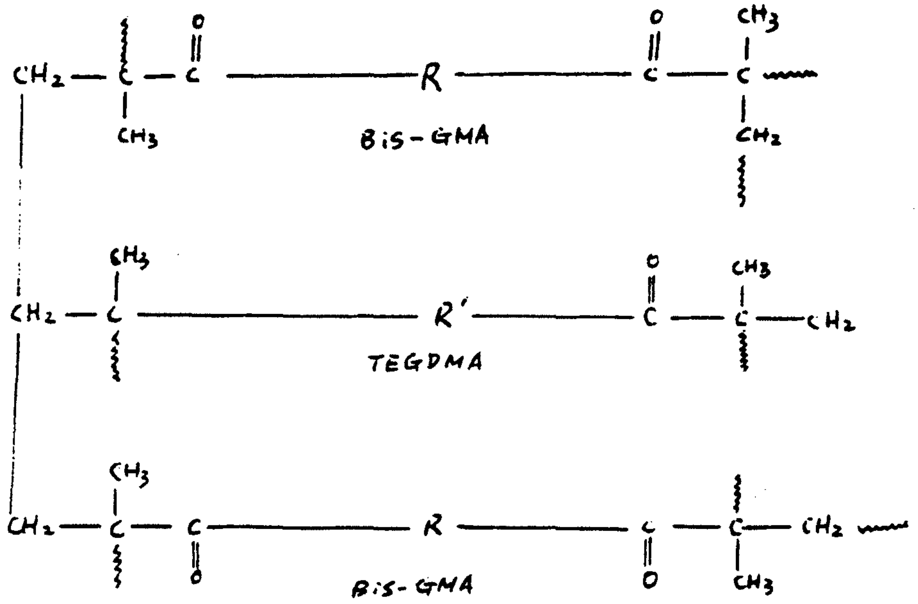
3.3.1 Structure of Bis-GMA

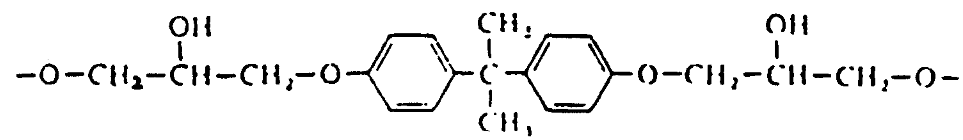
Bis-GMA is a thermosetting unsaturated viscous prepolymer. It is a product of condensation reaction, in which 1 molecule of bis-phenl A reacts with 2 molecules of Diglycidyl methacrylate, with a release of 2 molecules of water[24],[29]. The product contains the same end groups as the raw material monomer. In the condensation reaction the average degree of polymerization is dependent on how much the original molecules have been changed into polymer, the mole ratio of reacting groups, and the equilibrium of the condensation reaction. Because Bis-GMA has two pairs of double bonds in its structure it can form a three dimensional network structure by crosslinking with a crosslinking agent.



3.3.2 Crosslinking Process of Bis-GMA

As mentioned above, Bis-GMA is an unsaturated polyester which can be crosslinked with a crosslinker. After the final three dimensional structure is formed it can no longer be melted or dissolved even in a strong organic solvent. The crosslinking reaction can be initiated by ions or free radicals. In this experiment TEGDMA serves as dilution monomer but also serves as crosslinking agent. Part of the crosslinked structure of the copolymerization product is shown as the following



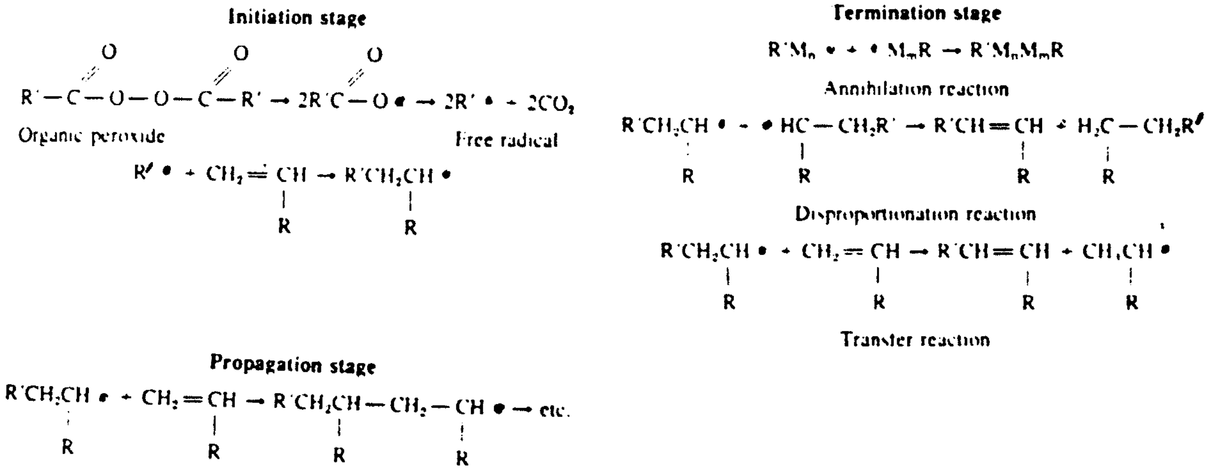
R represents 

R'represents $-O-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-O-$

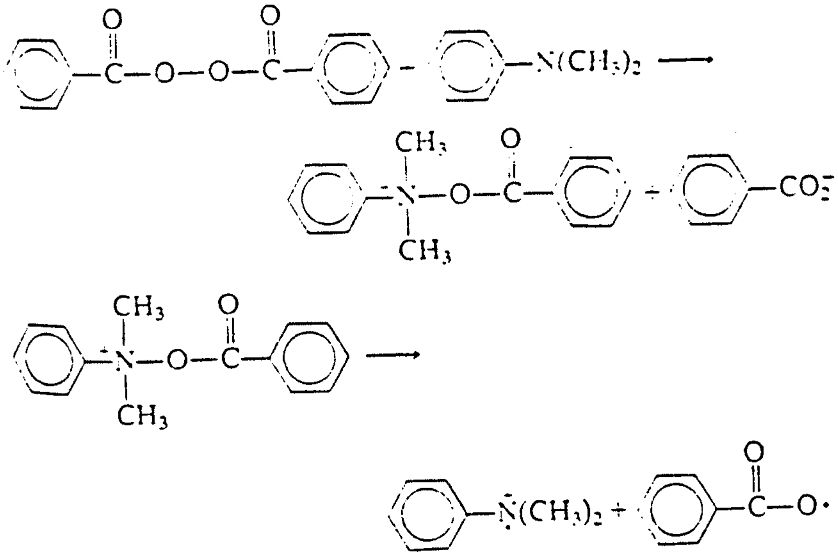
The crosslinked polymer is a solid.

3.3.3 Free Radical Redox System for Bis-GMA Crosslinking

It is known that free radical polymerization can be undergone in three steps: the first step is to produce a free radical, the second step is chain growth and the third is chain termination:



The crosslinking process is a graft copolymerization which can be initiated by ions or free radicals[30],[31]. In a free radical initiating process there are two ways. One is just to use a free radical to initiate the reaction. The reaction is carred out at a temperature at which peroxide can be decomposed to produce enough free radicals to ensure crosslinking. Another method is to use a redox system which can make the crosslinking process proceed at room temperature. In this experiment, the redox system benzoyl peroxide /dimethylaniline is used. Benzoyl peroxide is activated by tertiary amine dimethylaniline which decomposes the peroxide into free radicals. The optimum temperature for this redox system is 0 to 25°C[32] between which it is very easy to operate. The mechanism of redox is shown in the following reaction equation:



Benzoyl peroxide which has a half life of 30 minutes at 100° C[32] can be rapidly decomposed by dimethylaniline into an unstable ionic intermediate at room temperature, which reacts further to produce benzoyloxy radical and a radical cation. The radical cation apparently undergoes reactions other than addition to monomer, since polymers formed by this method contain no nitrogen.

3.3.4 Rate of Crosslinking

The rate of reaction is controlled by the nature of the initiator/promotor and the ratio of initiator to promotor. In this experiment, N,N-dimethylaniline and N,N-dimethyl-p- toludine were tested as promotors. The different ratios of BPO/dimethyl toludine and BPO/dimethylaniline were used to cure Bis-GMA/TEGDMA samples by measuring the gel time. From the results of gel tests, it is found that N,N-dimethyl toludine is not very suitable for Bis-GMA/TEGDMA system because the reaction so quickly cures the sample in several seconds that it is difficult to operate. For BPO/dimethylaniline the reaction rate is lower than that of BPO/dimethyltoludine. This can be handled in a reasonable time when the ratio of initiator and promotor is adjusted to a suitable range. According to the results of gel tests the optimum ratio of BPO/dimethylaniline is at 0.66/0.12(wt% respectively in Bis-GMA/TEGDMA) at which the gel time can be controlled in the range of 3 to 6 minutes. In this time range, the operation of setting samples can be finished. (For gel test results see Table 14)

3.3.5 Oxygen Effect on Crosslinking

Oxygen is a complex factor in the polymerization process. In some cases it can work as promotor to speed the reaction, and in others it has the opposite effect. The free radical reaction involving unsaturated polyester is suppressed by oxygen which lowers the crosslinking activity at the exposed surface of gelling mass[30].

Molecular oxygen plays the role of an inhibitor in Bis-GMA/TEGDMA crosslinking process. Moleculer oxygen can react with carbon free radical rapidly to produce peroxide free radical R-O-O [30]. Although activity of peroxide free radical is less than that of carbon free radical, it can react with monomer to form a new carbon free radical which subsequently reacts with moleculer oxygen again. In comparing with the case where no oxygen present, this polymerization reaction is obviously inhibited. Actually, this process is the addition process of monomer with molecular oxygen alternatively resulting in polyperoxide[30,31] and the real monomer polymerization reaction does not take place in the normal way.

The effects of oxygen on Bis-GMA/TEGDMA is verified in the experiment. The tests have been already described in the experiment part of this paper. The results show that those samples placed in air have a sticky surface even after several weeks, while samples covered with polyester film and put in the desiccator filled with nitrogen gas have dry surfaces.

3.3.6 Degree of Crosslinking

The test of degree of crosslinking was done by dipping the cured Bis-GMA/TEGDMA sample in acetone for 7 days before the dissolved portion was determined. The degree of crosslinking can be calculated by the following equition:

Degree of Crosslinking= (W1-W2)/W1= (0.6779 - 0.1543)/0.6779=77.2%

Where W1 is the weight of original sample, W2 is the weight of the dessolved portion. As a result, the degree of crosslinking is high and the initiator/promotor system is suitable.

3.4 Bonding Test

For better bonding strength, attention should be paid to the following:

1. The cross-section surface of aluminum rod must be parallel to the flat surface of the sample which contains the thin layer of the adhesive.

2. The aluminum rod surface should be roughened.

3. The rod surface must be cleaned with petroleum ether before use.

4. Since the tooth samples are real teeth, they never have the same shape and the same size. Attention must be paid to embedding the cut tooth sample in the center of the plastic holder, so that the cut tooth surface is in the mounting compound horizontally.

3.5 Adhesion

Phosphonate can increase the adhesion between the tooth and the polymer bonding agent by forming chemical bonds. The bonding agent Bis-GMA/TEGDMA has been used in the research. Comparing it with the commercial product Gluma, its tensile strength is significantly greater. It produces adhesion to enamel and dentine as high as 744 and 600 psi of tensile strength respectively, while Gluma justs 120 psi and 80 psi (see Table 13). Comparing the data of group 1 containing no Phosphonate with those in group 11 containing phosphonate in Table 13, it is obvous that phosphonate works more effectively as an adhesive to connect tooth and bonding agent.

Oxygen is an important factor affecting the crosslinking process. In this experiment, several group tests were done to examine the effect of N_2 gas on the crosslinking process. Comparing the results in group 1 with group 7, it is clear that crosslinking in the presence of N_2 can achieve higher tensile strength, especially for dentine. Comparing the data in Table 9 with those in Table 1, introducing nitrogen gas for different lengths of time can produce different results. In group 9, when nitrogen purging is reduced to 10 minutes, the tensile strength of dentine is much lower. The reason for that is that the crosslinking process of Bis-GMA/TEGDMA needs time to complete even if the gel is formed in a short time. As long as the Bis-GMA/TEGDMA is exposed to the air, it is difficult to continue the further copolymerization because air has inhibition to Bis-GMA/TEGDMA.

In an experiment, one group of tests were done by treating the tooth surface with Glutaradehyde, (group 5) in order to react with the protein in tooth. Comparing it with results in group 2, group 3, and group 11, there is no obvious increase in its tensile strength in the dry state, but it seems to produce a higher wet tensile strength.

The failure of adhesion mostly occured in the interface between the cut tooth surface and the adhesive, and, in a few cases, occured in the interface between the aluminum surface and bonding agent. Therefore, the measured tensile strengths reflect the adhesion to the tooth surface.

Table 1. Tensile strength of Bis.GMA/TEGDMA (70/30)

No.	bonding to dentine (psi)		bonding to enamel (psi)	
1	567		536	
2	539		427	
3	468		668	
4	668		482	
5		187*		418*
6		392*		119*
7		101*		252*
8		225*		368*
mean	563	225	528	309

* samples were kept in water for 72 hrs. before tests

** curing condition: room temperature, N_2 30min

Table 2. Tensile strength of silane

No.	bonding to dentine (psi)		bonding to enamel (psi)	
1	353		487	
2	444		953	
3	353		694	
4	348		778	
5		306*		364*
6		73*		150*
7		199*		247*
8		139*		170*
mean	376	179	728	233

* samples were kept in water for 72 hrs. before tests

** curing condition: room temperature, N_2 30min.

Table 3. Tensile strength of Phosphonate (0.5% BPO)

No.	bonding to dentine (psi)		bonding to enamel (psi)	
1	610		814	
2	668		553	
3	779		711	
4	501		672	
5		401*		317*
6		348*		235*
7		441*		377*
8		307*		353*
mean	640	374	688	321

* samples were kept in water for 72 hrs. before test

** curing condition: room temperature, N_2 30min.

Table 4. Tensile strength of siland - Phosphonate (without BPO)

No.	bonding to dentine (psi)		bonding to enamel (psi)	
1	432		522	
2	542		596	
3	377		683	
4	679		435	
5		130*		320*
6		77*		187*
7		209*		130*
8		38*		55*
mean	508	114	559	173

* samples were kept in water for 72 hrs. before tests

** no BPO and promotor in the mixture of silane and Phosphonate

*** curing condition: room temperature, N_2 30min.

Table 5. Tensile strength of Glutaradehyde – silane – Phosphonate

No.	bonding to dentine (psi)		bonding to enamel (psi)	
1	608		810	
2	479		662	
3	564		1065	
4	550		405	
5		552**		702**
6		452**		851**
7		560**		714**
8		643**		631**
mean	550	552	736	725

* curing condition: room temperature, N_2 30min.

** these groups were kept in air 24 hrs, then measure tensile strength

Table 6. Adhesion tensile strength of Bis.GMA/TEGMA (60/40)

No.	bonding to dentine (psi)		bonding to enamel (psi)	
1	346		294	
2	446		501	
3	313		416	
4	371		503	
5		145*		97*
6		212*		376*
7		131*		165*
8				296*
mean	369	163	428	233

* samples were kept in water for 72 hrs. before tests

** curing condition: room temperature, no N_2

Table 7. Adhesion tensile strength of Bis.GMA/TEGDMA (70/30)

No.	bonding to dentine (psi)		bonding to enamel (psi)	
1	367		451	
2	355		536	
3	489		646	
4	360		296	
5		415*		209*
6		234*		346*
7		291*		130*
8		302*		432*
mean	393	310	482	279

* samples were kept in water for 72 hrs. before tests

** curing condition: room temperature, no N_2

Table 8. Tensile strength of Bis.GMA/TEGMA**
(60/40 etching)

No.	bonding to dentine (psi)		bonding to enamel (psi)	
1	441		411	
2	528		595	
3	597		506	
4	359		478	
5		207*		245*
6		312*		347*
7		339*		211*
8		161*		387*
mean	481	255	498	298

* samples were kept in water for 72 hrs. before tests

** etching procedure

a. put a drop 5% Ferric Oxalate solution on the dentine surface. wait 60 seconds, then wash the wet dentine surface by distillation water, then dry them by blown air.

b. put a drop 39% phosphoric acid solution on the enamel surfaces, wait 60 seconds, then wash them by distillation water, then dry the tooth samples by blown air.

*** curing condition: room temperature, no N_2

Table 9. Tensile strength of Phosphonate

No.	bonding to dentine (psi)		bonding to enamel (psi)	
1	293		583	
2	255		397	
3	133		674	
4	407		365	
5		138*		1152*
6		166*		105*
7		222*		180*
8		116		162*
mean	272	161	505	399

* samples were kept in water for 72 hrs. before tests

** curing condition: room temperature, N_2 10min.

Table 10. Tensile strength of Bis-GMA/TEGDMA(75/25)

No.	bonding to dentine (psi)		bonding to enamel (psi)	
1	367		451	
2	355		536	
3	487		646	
4	359		296	
5		209*		415*
6		346*		233*
7		130*		291*
8		432*		302*
mean	392	279	482	310

* samples were kept in water for 72 hrs. before test

** curing condition: room temperature, N_2 10min.

Table 11. Tensile strength of Bis-GMA/TEGDMA(70/30)-Silane-Phosphonate

No.	bonding to dentine (psi)		bonding to enamel (psi)	
1	694		658	
2	446		634	
3	538		785	
4	732		900	
5		355*		559*
6		420*		486*
7		408*		378*
8		370*		420*
mean	601	388	744	460

* samples were kept in water for 72 hrs. before tests

** curing condition: room temperature, N_2 30min.

Table 12. Tensile strength of PMMA*-Phosphonate-Silane

No.	bonding to dentine (psi)		bonding to enamel (psi)	
1	550		600	
2	489		432	
3	365		468	
4	431		520	
5		436		504
6		464		302
7		321		326
8		483		346
mean	459	408	550	367

* PMMA crosslinking with MMA by Divinyl benzine

** curing condiiton: first 40°C 30min. then room temperature 4 hrs.

Table 13 Summary

No.	Composite	Condition	Enamel (psi)		Dentine (psi)		Table No.
			dry	wet	dry	wet	
1	Bis-GMA/TEGDMA(70/30)	rm temp. N_2 30min	528	309	563	225	1
2	Silane-Bis-GMA/TEGDMA(70/30)	rm temp. N_2 30min	728	233	376	179	2
3	Phosphonate-Bis-GMA/TEGDMA(70/30)	rm temp. N_2 30min	688	327	640	374	3
4	Silane-Phosphonate-Bis-GMA/TEGDMA(70/30)	rm temp. N_2 30min	559	173	508	114	4
5	Glu-Phosphonate-Silane-Bis-GMA/TEGDMA(70/30)	rm temp. N_2 30min	736	725	550	552	5
6	Bis-GMA/TEGDMA(60/40)	rm temp. no N_2	428	233	369	163	6
7	Bis-GMA/TEGDMA(70/30)	rm temp. no N_2	482	279	393	310	7
8	Bis-GMA/TEGDMA(60/40)*	rm temp. no N_2	498	298	481	255	8
9	Bis-GMA/TEGDMA(70/30)	rm temp. N_2 10min	505	399	272	161	9
10	Bis-GMA/TEGDMA(75/25)	rm temp.	482	310	392	279	10
11	Silane-Phosphonate-Bis-GMA/TEGDMA(70/30)	rm temp. N_2 30min	744	460	601	338	11
12	Phosphonate-Silane-PMMA Δ	rm temp 4 hrs	550	369	459	401	12
13	Gluma #		120	00	80	00	

Phosphonate——HEMA-DECP adduct
PMMA——poly(methyl methacrylate) as bonding agent
Glu——glutaradehyde
* ——etching by H_3PO_4 solution
Δ ——repeat former student's work
#——data from former Wu's work

Table 14 Gel test

No.	Bis-GMA/ (WT) TEGDMA	BPO (wt%)	Aniline (wt%)	Gel time
1	70/30	0.21	0.18	10 min.
2	70/30	0.45	0.28	1 min.
3	70/30	0.60	0.28	1 min.
4	70/30	0.46	0.28	2 min.
5	70/30	0.30	0.28	8 min.
6	70/30	0.66	0.12	4 min.
7	75/25	1.20	0.70	40sec.
8	75/25	1.00	0.14	1.5 min.
9	75/25	0.66	0.12	3 min.
10	75/25			
11	75/25			
12	75/25			

Table 15 Viscosity of Bis-GMA Solution

VISCOSITY (sec) / No	C_1	C_2	C_3	C_4	C_5
1	54.30	52.35	51.05	49.15	48.30
2	54.25	52.35	51.05	49.15	48.30
3	54.25	52.20	51.10	49.10	48.25
4	54.25	52.20	51.05	49.10	48.30
5	54.15	52.30	51.00	49.15	48.30
MEAN	54.24	52.28	51.06	49.13	48.29

5 $C_1 = 0.008176$ g/ml

7 $C_2 = 0.00584$ g/ml

9 $C_3 = 0.00454$ g/ml

11 $C_4 = 0.00372$ g/ml

13 $C_5 = 0.00314$ g/ml

```
   POINT              X                           Y
 ----------------------------------------------------------
     1             .00314                       .114
     2             .00372                       .1333
     3             .00454                       .1779
     4             .00584                       .2064
     5             .008176                      .2512
 ----------------------------------------------------------
 Slope =  26.96366  +/-  3.429149
Intercept =  3.949832E-02  -/-  1.374552E-02
Correlation =  .9765881
```

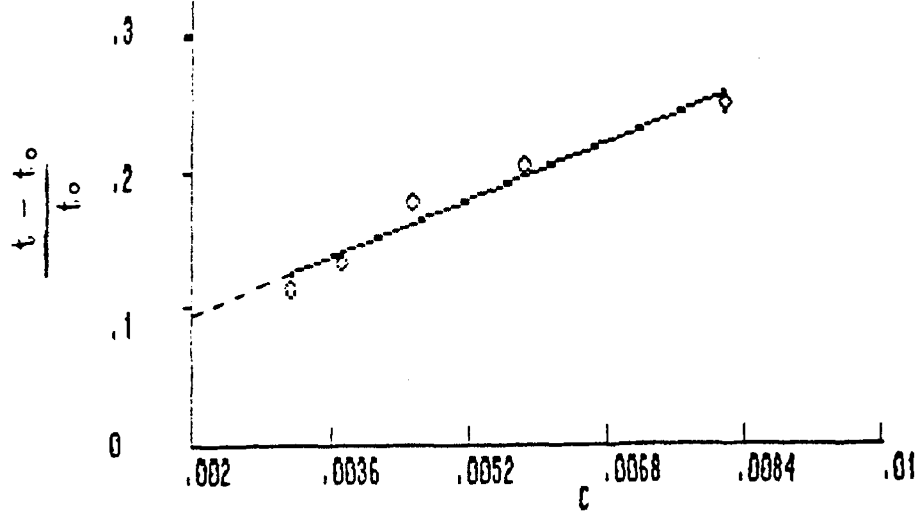
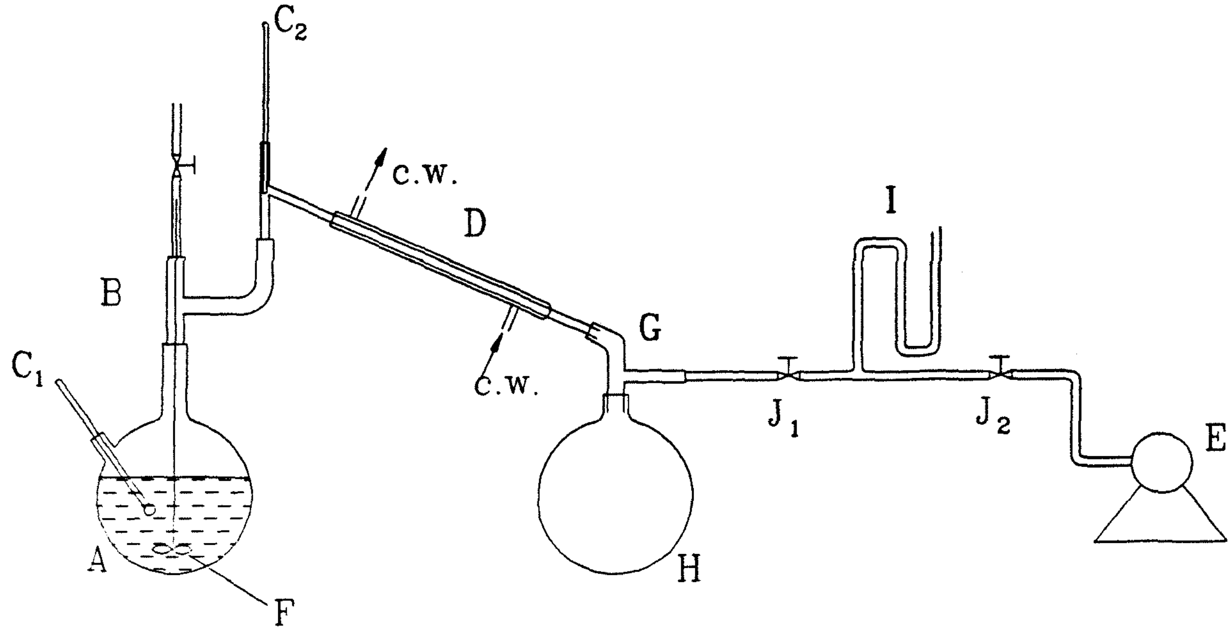


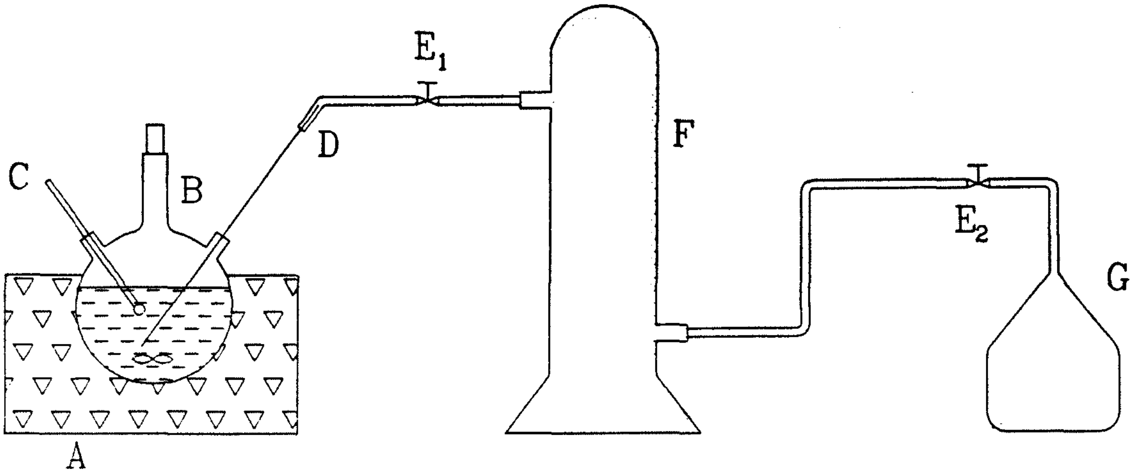
Fig. 9



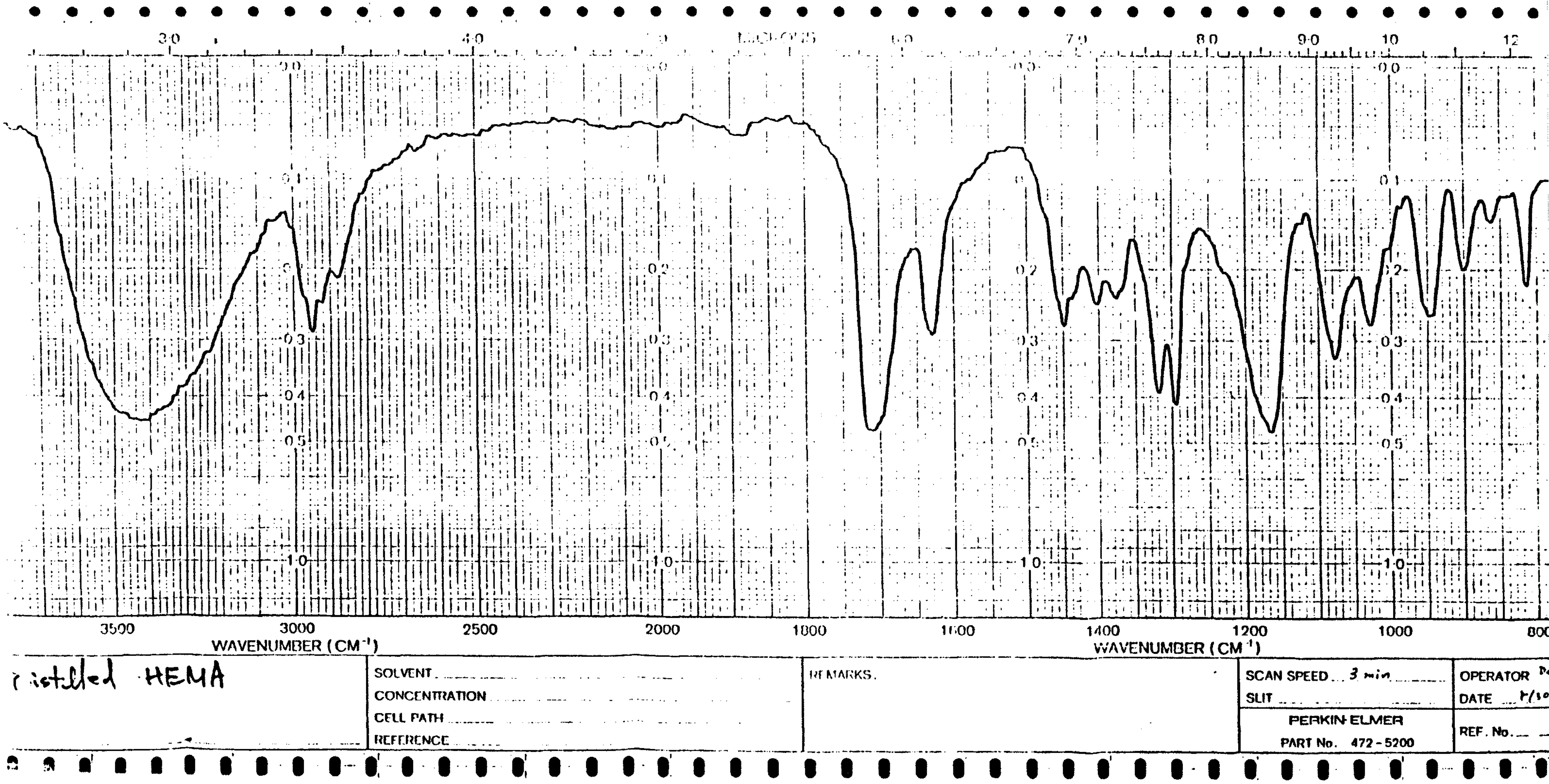
A – flask
B – adapter
C_1 & C_2 – thermometers
D – condenser
E – vacuum pump
F – magnetic stirring bar

G – adapter
H – collecting flask
I – manometer
J_1 & J_2 – valves

Fig. 10



A – ice bath
B – flask
C – thermometer
D – NH_3 gas introducing tube
E_1 & E_2 – valves
F – gas dryer
G – NH_3 gas tank



istilled HEMA

SOLVENT
CONCENTRATION
CELL PATH
REFERENCE

REMARKS.

SCAN SPEED 3 min
SLIT

PERKIN-ELMER
PART No. 472-5200

OPERATOR
DATE
REF. No.

Fig. 11

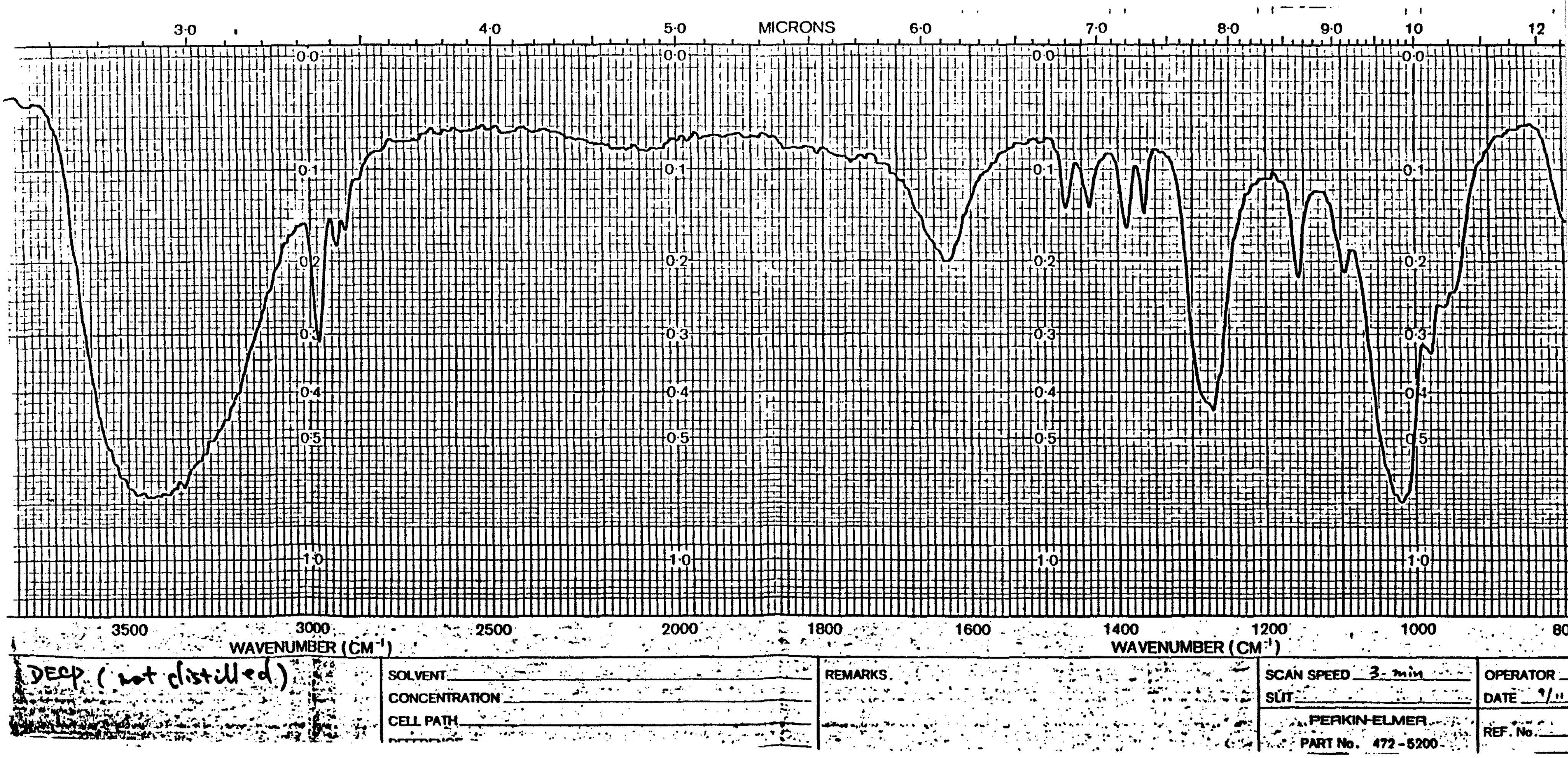
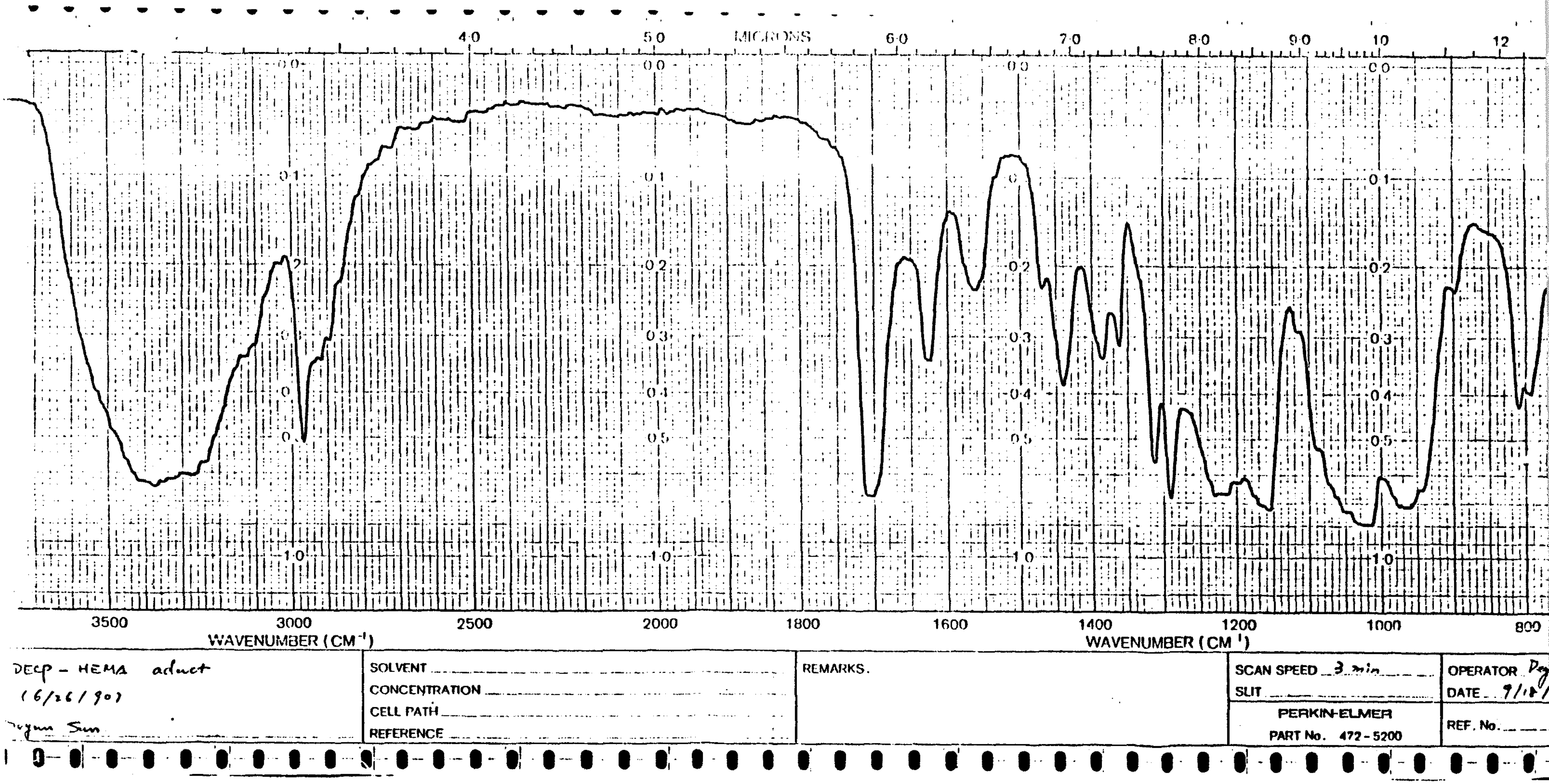

MICRONS
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
0·0
0·1
0·2
0·3
0·4
0·5
1·0
3500
3000
2500
2000
1800
1600
1400
1200
1000
WAVENUMBER (CM⁻¹)
DECP (not distilled)
SOLVENT
CONCENTRATION
CELL PATH
REMARKS
SCAN SPEED 3-min
SLIT
PERKIN-ELMER
PART No. 472-5200
OPERATOR
DATE 9/11
REF. No.

Fig. 12



DECP - HEMA adduct
(6/26/90)
yun Sun

SOLVENT
CONCENTRATION
CELL PATH
REFERENCE

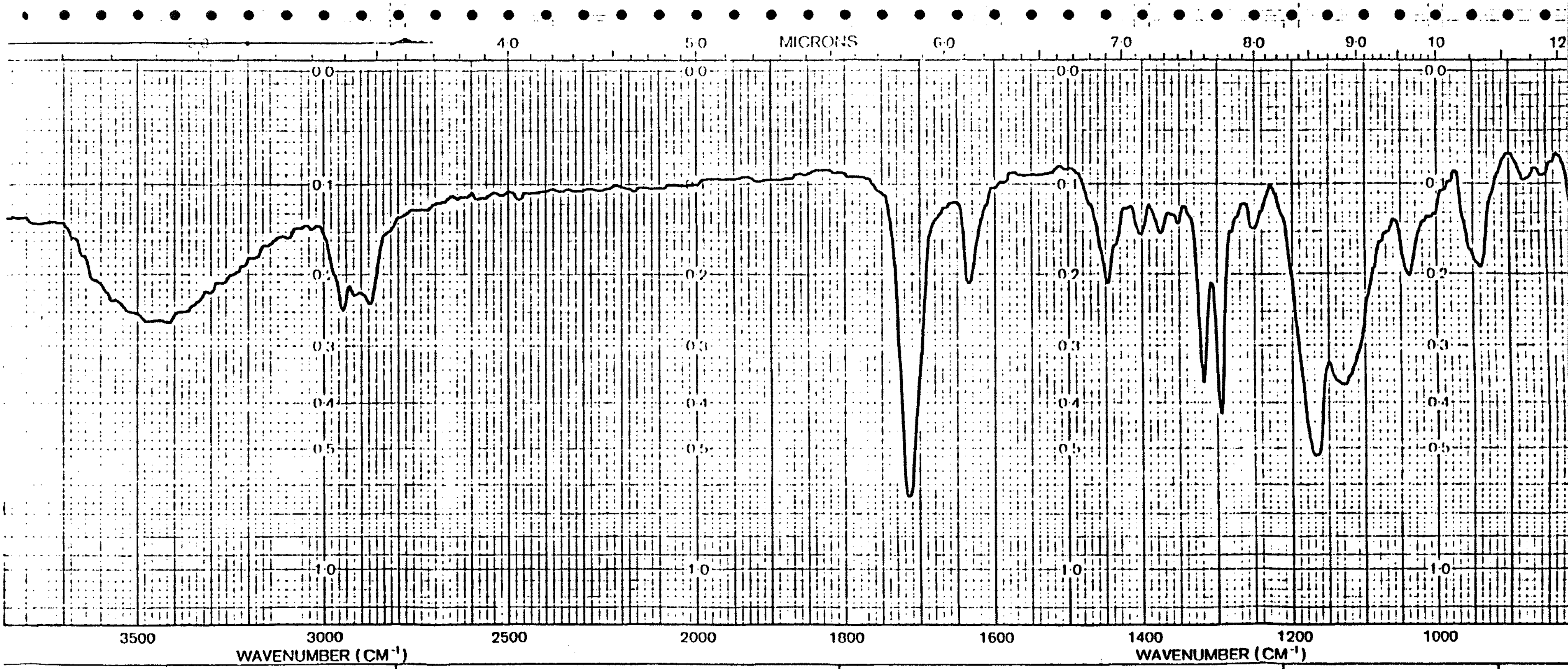
REMARKS.

SCAN SPEED 3 min
SLIT

PERKIN-ELMER
PART No. 472-5200

OPERATOR
DATE 9/1
REF. No.

Fig. 13



TEGDMA

SOLVENT

CONCENTRATION

CELL PATH

REFERENCE

REMARKS.

SCAN SPEED 3 min

SLIT

PERKIN-ELMER

PART No. 472-5200

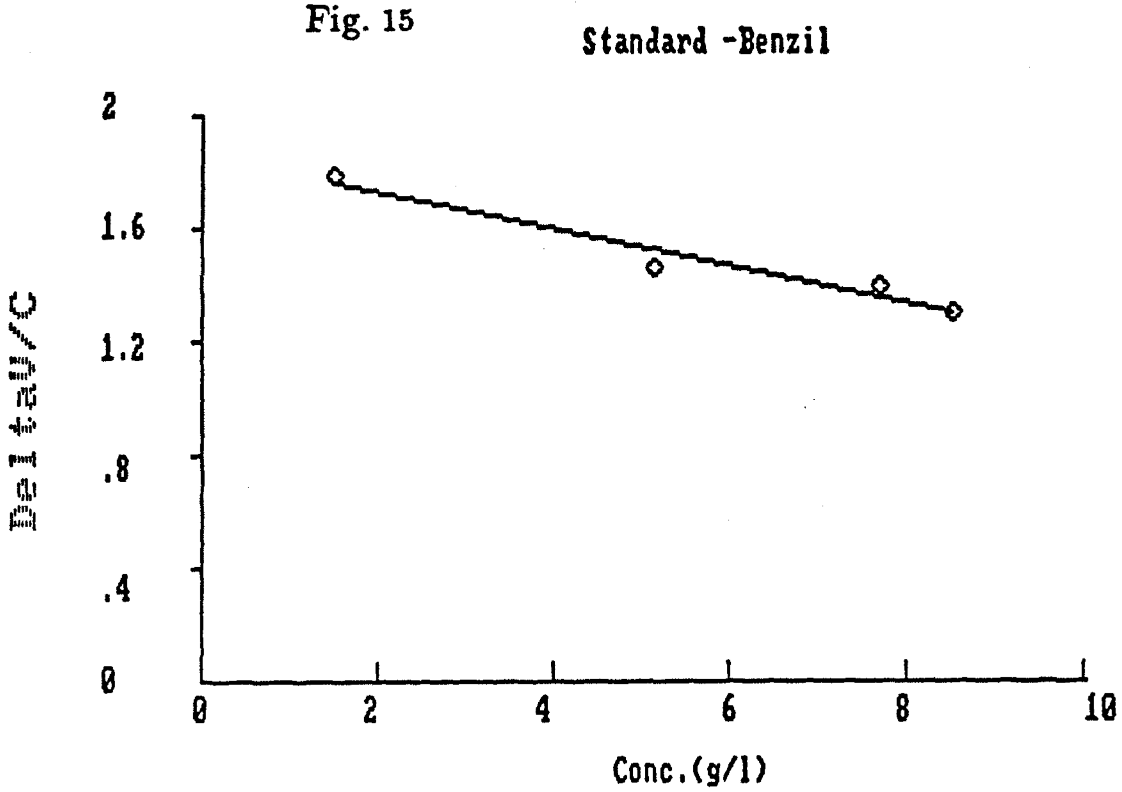
OPERATO

DATE

REF. No.

Fig. 14

Fig. 15



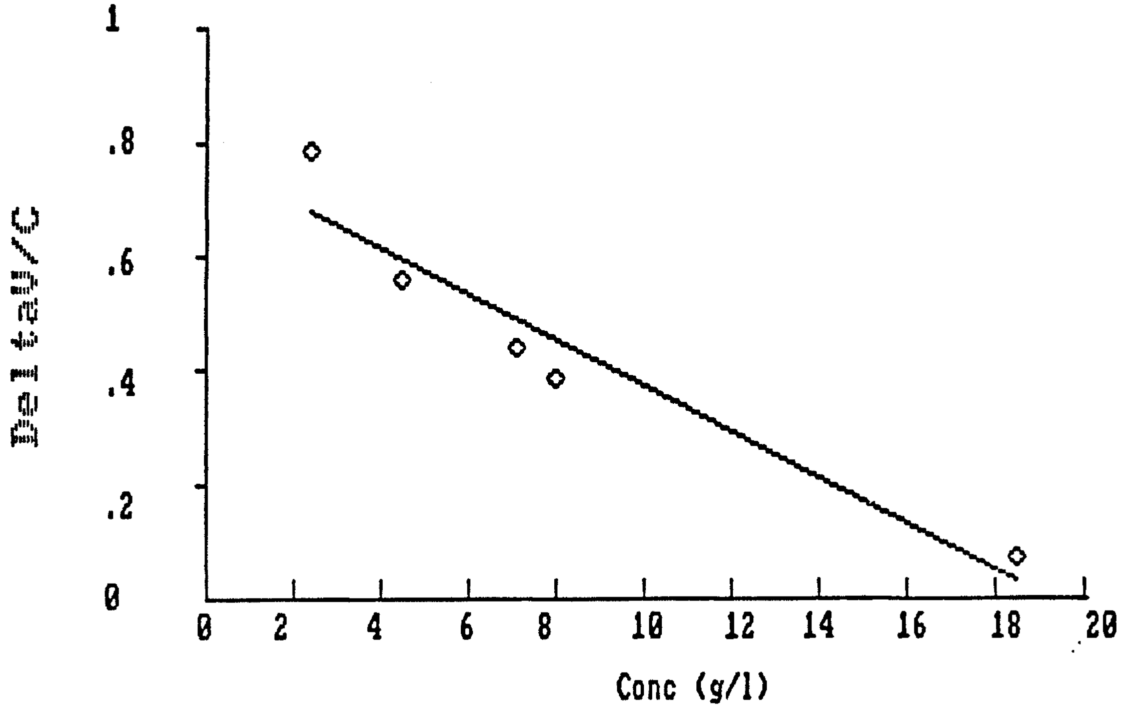
```
 Standard -Benzil


   POINT               X                          Y
_____________________________________________________________________
        1           1.5208                     1.7856
        2           5.163                      1.4506
        3           7.702                      1.3857
        4           8.54                       1.2998
______________________________________________________________________
 Slope = -6.578596E-02  +/-  1.047925E-02
Intercept =  1.857474  +/-  5.722835E-02
Correlation =  .9755524
Calculated on points  1  TO  4
```

$$\text{Intercept} = K/M_{standard} = 1.8575$$

$$K = 1.8575 \times M_{standard} = 1.8575 \times 210.3 \doteq 391$$

$$\text{Slop} = -0.06579 = K \times A' \quad A' = 0.000168$$

Fig. 16



```
  POINT               X                        Y
------------------------------------------------------------------
      1               2.418                    .784
      2               4.47                     .563
      3               7.11                     .4368
      4               8                        .3878
      5               18.486                   .07348
-------------------------------------------------------------------
 Slope = -4.017108E-02   +/-   6.751041E-03
Intercept =   .7742732  +/-   .0838655
Correlation =   .9601504
Calculated on points  1  TO  5
```

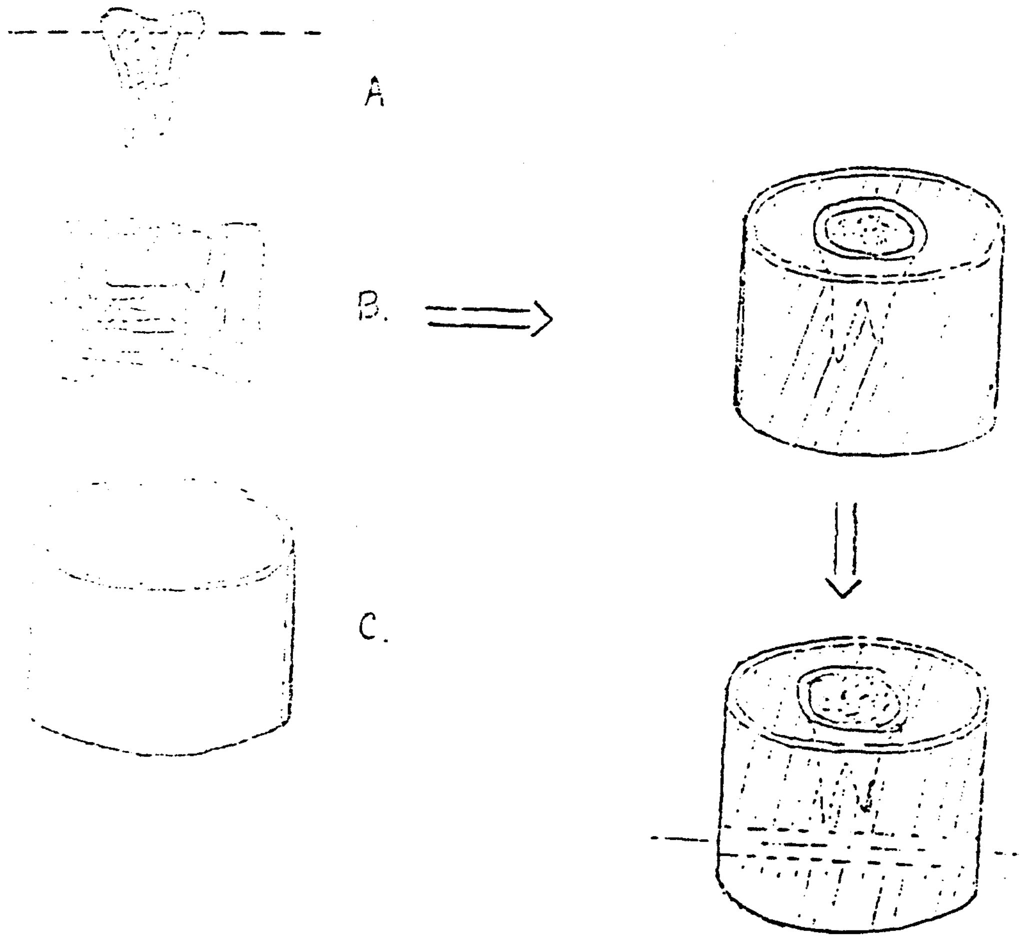
Intercept= 0.7743

$M_{unknow} = \frac{K}{Intercept} = \frac{391}{0.7743} = 505$

So, Bis-GMA $\bar{M}n$ is 505

Fig. 17

Sample preparation for tensile strength testing:



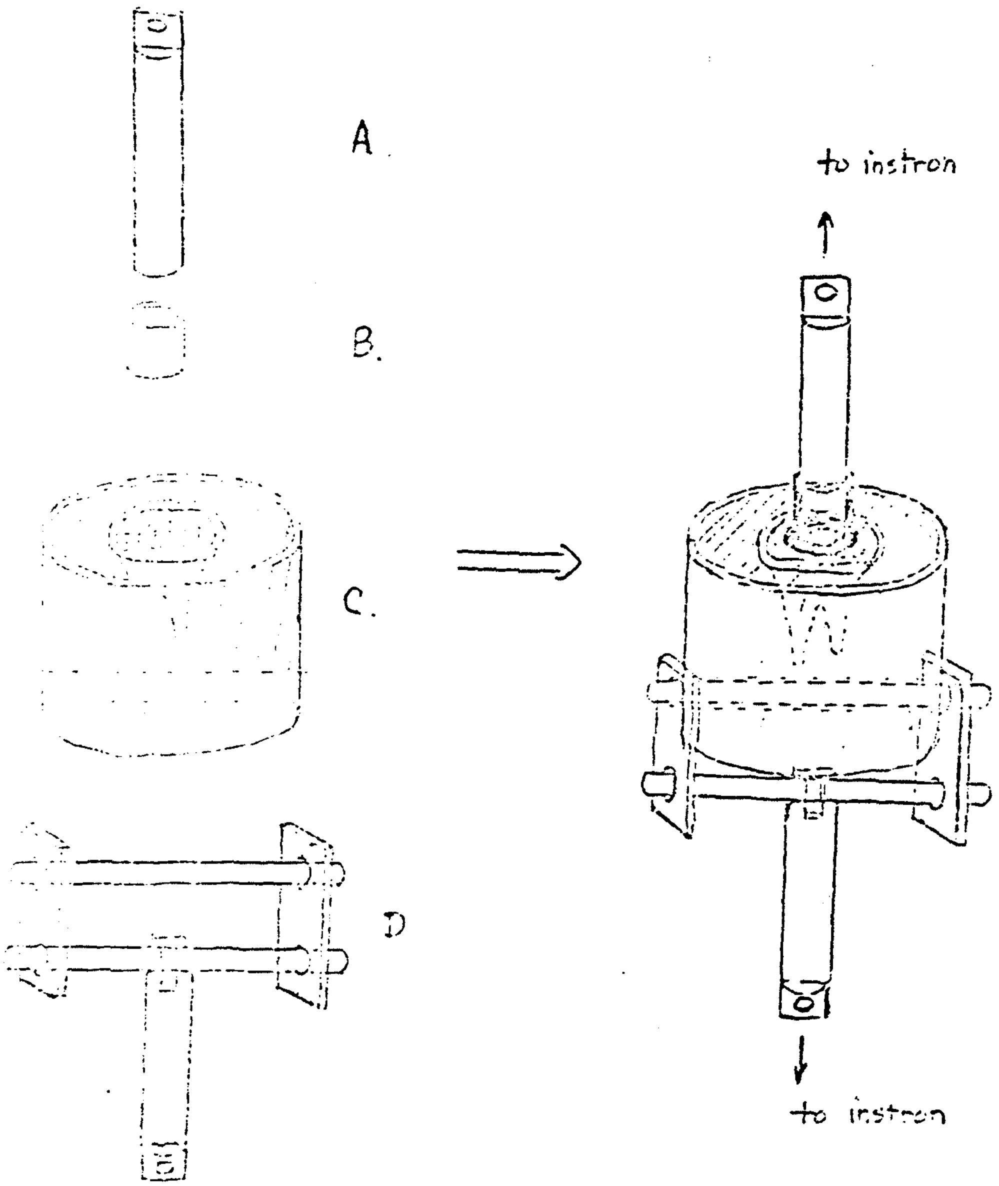
A. Tooth

B. Mounting material (Polymer)

C. Plastic adapter ring

Fig. 18

Sample made for instron tensile strength testing: _



A. Aluminum bar B. Rubber sleeves

C. Mounted tooth sample D. Fixer

Chapter 4

Conclusion

It is believed that a satisfactory progress has been achieved by applying polymeric organic phosphonate, silane and Bis-GMA/TEGDMA system. Adhesion effect of phosphonate has been verified by the increase of tensile strength which is as high as 744 psi to enamel and 600 psi to dentine. Therefore, the chemical bonds formed between phosphonate and tooth are proved to exist. The present research supplies of fundamental experimental data and suggests some important points for the further investigation in this field. There is no doubt that it will serve as a useful guide for future work and be helpful to the those interested.

Although organic phosphonate has been proved an effective adhesive by this experiment, more work needs to be done on increasing and enhancing the interface adhesion for the results of the experiment show that interface adhesion is a weakpoint and that adhesion failure mostly occurs in the interface between tooth and polymer. This experiment mainly deals with the chemical part of the material. Future work should lay emphasis on photoinitiating the process of polymerization, so as to enhance the material for clinical practice.

Bibliography

1. B. David Halpern EPST Vol. 14, "Dental application"

2. Nobuo Nalabayashi "Biocompatibility and promotion of adhesion to tooth subtaates" CRC Critical Reviews in Biocompatibility Vol.1 Issue 1, 1983

5. A.E.W. Miles "Structural and chemical organization of teeth" Vol. II, Academic Press, N.Y. and London 1967

6. Scott J H Symons NBB 1982, 9th edition section III, "Dental anatomy" Churchill livingston, Edinburgh.

7. E.C. Combe "Notes on dental materials"

8. Bowen R.L. 1979 "The components in composite restorations" J. of Dent. Res. 58:1493

9. Bowen R. L., Cobb E. N. and Rapson J. E., "Adhesion bonding of various materials to hard tissue: improvement in bond strength of dentine" J. Dent. Res. 61(9), 1982

10. Lutz F., Setcos J. C., Phillips R. W., Roulet J. F. 1983 "Dental restorative resins", Dental Clinical of North America 27: 697

11. Combe E. C.,1985 "Creating successful composite restorations" in: Derrick DD The Dental Annua; Wright, Bristal p34-42

12. Retief D. H. 1975 "The priciples of adhesion" J. of The Dental Association of South Africa 25: 285

13. Brauer G. M. 1975 "Adhesion and adhesives" In Von Fraunhofer, Butterworth London Ch2

14. A. J. Kinloch "The science of adhesion" Part II, J. Materials Science Vol.17, 1982 p617

15. Kinloch A. J. "The science of adhesion" Part I, J. Materials Science Vol.15, Aug. 1980 p2141

16. Ibsen R. S., Neville K. 1974 "Adhesive restorative dentistry" Saunders, Philadephia.

17. Council on dental materials, Instruments and equipment 1984, Resin dentine bonding systems. J. of American Dental Association 108: 240

18. M. Anbar, E. P. Farley "Potential use of organic polyphosphonates as adhesives in the restoration of teeth" J. Dent. Res., Vol.53 No.4 1974

19. Council on dental materials, Instruments and equipment: Dentine bonding systems: an update, J. American Dental Assoc. 114:91, 1987

20. E. Asmussin and E. C. Munksgaard " Adhesion of restorative resin to dentinal tissues" J. Dent. Res. 1985

21. Hansen, E. K. and Asmussen E. "Comparative study of dentine adhesives" J. Dent. Res. 93:280, 1985

22. Munksgaard, E. C., Hansen, E. K., and Asmussen, E. "Deffect of five adhesives on adaptation of resin in dentine cavities" Scand. J. Dent. Res. 95:544, 1984

23. Ediwin P. Plueddemann "Adhesion through silane coupling agent" J. Adhesion Vol.2, July 1970 p184

24. Dental Restorative 1985, Section "Direct esthetiv restorative materials" p269

25. Council on Dental Materials, Instruments and Equipment 1984, " Resin dentine bonding system" J. of the American Dent. Asso. 108:240

26. Wu, Yuning "Preparation and formulation of novel dental adhesives based on polyphosphonate and silane compound", M.S. thesis in Department of Che./Chemical Eng, NJIT 1988

27. Kohlrausch, "Raman Spectra" Edwards Bros. Amm Arbor, 1943, p314

28. Herzberg "Infrared and Raman Spectra" Van Nostr. and N.Y. 1945, p314

29. Product Description from Freeman Co.

30. D. Brann, H. Cherdron, W. Kern "Techniques of polymers syntheses and characterization" John Wiley, 1972

31. Encyclopedia of Polymer Science and Engineering Vol. 12 p268

32. Polymer chemistry, section III, "Free radical vinyl polymerization" p191

33. VPO instruction manual, Model 233, Wescan Instruments Inc.