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## ABSTRACT

Title of Thesis: Preparation and Properties of Novel Dental Adhesives Based Upon Pentaerythritol

Yuan-Yuan Su,Master of Science in Chemical Engineering, 1985

Thesis directed by: Professor David S. Kristol

Urethane methacrylates were synthesized from pentaerythritol, TDI, HEMA and four phenolic blocking agents or from hydroxypropyl methacrylate, TDI and two phenolic blocking agents. All the products were characterized by melting point, infrared spectroscopy, NMR spectra, and elemental analysis. The bonding of these materials to dentin slices was also investigated. Such materials are supposed to not only react with the organic constituent of dentin but also polymerized with restorative resin. It was found that bond strength was enhanced by the use of the urethane methacrylates, resulting in best mean bonding strengths of 2400 psi.

# PREPARATION AND PROPERTIES

# OF

# NOVEL DENTAL ADHESIVES BASED UPON PENTAERYTHRITOL

by
YUAN-YUAN SU

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial fulfillment
of the requirements for the degree of
Master of Science in Chemical Engineering

APPROVAL SHEET

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# Introduction

I. Introduction : For more than a quarter of century, many investigators[1-15] have sought to obtain the bonding of restorative resin to dentin by means of an intermediary monomer. Although the acid-etch technique was introduced for the bonding of resins to enamel for the prevention of pit and fissure caries,[6-7] this technique does not give adequate bond strengths to the dentin surface. Further, the use of hypertonic solutions of phosphoric or citric acid on vital dentin is usually contraindicated because they can have harmful effects on the dental pulp.[8-9] Attemps to bond through a micromechanical mechanism by an enzymatic pretreatment have also been made.[10-15] For example, it was thought that limited treatment of the dentin with collagenase will cause pitting and result in greater surface contact with adhesive agents. However, these attempts were unsuccessful.

One approach[16] which had limited success was the use of bifunctional monomers, in which one part of the monomer molecule was designed to have a potential capability to react with either the inorganic or the organic constituent of the dentin, while another part of the molecule containing a polymerizable double bond caused a polymerization reaction with restorative resins. These monomers were 2,4-tolylene diisocyanate reacted with 2-hydroxyethyl methacrylate at one isocyanate. However, such monomers which might possibly react with the -OH or $-NH_2$ side chains of the dentin protein were found to give relatively low bonding strength. It was

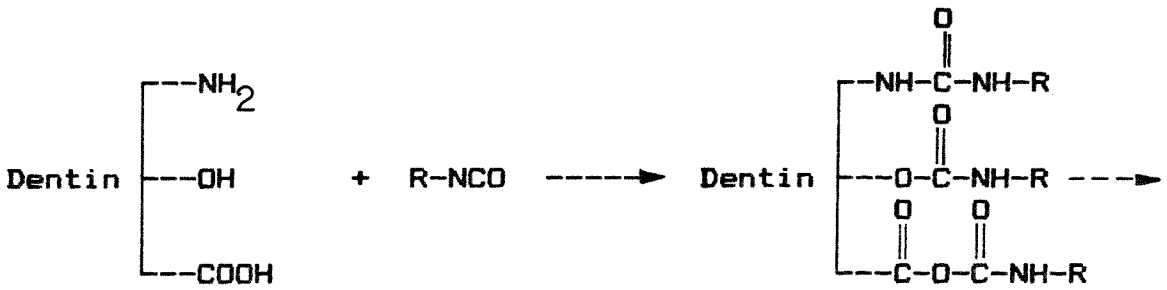
suggested that this result might be associated with the presence of water, which probably reacts with the free isocyanate in the bifunctional monomer, more readily than does with collagen. In order to avoid the reaction between isocyanate groups and water from occuring, our laboratory conceived the idea of the blocked isocyanates which were prepared by subsequent treatment of the second isocyanate group with phenols. Thus, the object of this research is to prepare, characterize and test bifunctional monomers containing blocked isocyanate groups for their ability to form chemical bonds to human dentin.

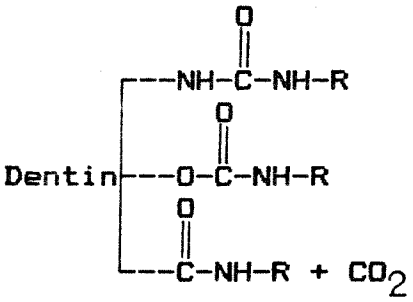
II. Principle

A. The Development of Adhesive Material : The human tooth basically consists of the crown and root. The crown is covered by a thin coating of enamel, while the root contains a coating called cementum. Beneath the enamel, which is the hardest substance in the human body and has no blood supply, is the composite dentin containing 60% hydroxyapatite, 20% organic matter and 20% water by weight. Organic matter called collagen [17-18] is a triply stranded protein molecule which contains a large number of polar groups with active hydrogen such as $-NH_2$, -OH, -COOH. In addition, the primary amide groups (-NH-C(=O)-) present in the backbone of collagen have much less active hydrogens.

The well-known reactions of organic isocyanates with active hydrogen compounds [19-20] and the potential availability of a large number of such active hydrogen sites in collagen

suggested the synthesis of monomers with isocyanate groups as potential adhesion-promoting agents for collagenous substrates. The chemcial mechanism for promoting adhesion to dentin via the isocyanate group is as follows:





In an oral environment, however, the competitive reaction of water present on the dentin surface with isocynate can be significant.

$$R\text{-}NCO + H_2O \longrightarrow R\text{-}NH_2 + CO_2$$

The amine group formed after the release of carbon dioxide can react with another isocyanate to form urea linkage,

$$R\text{-}NCO + R\text{-}NH_2 \longrightarrow R\text{-}NH\text{-}CO\text{-}NH\text{-}R$$

That means one water molecule can consume two isocyanate groups that are available for bonding to the dentin surface. Furthermore, carbon dioxide produced in the water-isocyanate reaction tends to form gas bubbles which will foam the

adhesive material and restorative material, possibly also resulting in the reduction of bonding strength.[21] Fortunately, Wick[22] described that one of the distinct advantages of blocked isocyanates is that they do not react with water at neutral PH at ambient temperature. In this way, it makes possible to develop a covalent bonding of the polymeric adhesive to dentin by reacting the blocked isocyanate functions to the hydroxyl or amino groups of collagen. The mechanism of the reaction along with the release of the blocking agent, R'-OH

$$R\text{-}NH\text{-}COO\text{-}R' + H_2N\text{----}Dentin \longrightarrow R\text{-}NH\text{-}CO\text{-}NH\text{----}Dentin + R'\text{-}OH$$

B. General Chemistry of Blocked Isocyanate : A blocked isocyanate[23] is an isocyanate which has been reacted with a material which will prevent its reaction at room temperature. with compounds that conventionally react with isocyanates but will permit that reaction to occur at higher temperature The formation mechanism of a blocked isocyanate is

$$R\text{-}NCO + BH \rightleftharpoons R\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}B$$

Where BH is a hydrogen donor molecule such as alcohol, phenol or amine.

The overall reaction with active hydrogen compounds is

$$R\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}B + HY \rightleftharpoons R\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}Y + HB$$

Williams[24-25] has studied the alcoholysis of phenyl N-phenyl urethanes and concluded that the mechanism of the deblocking reaction is an E1cB type involving two intermediates :

$$Ar\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}B + OH^- \overset{\text{fast}}{\lesssim\!=\!=\!=\gtrsim} Ar\text{-}\overset{(-)}{N}COB \pm H_2O \overset{\text{slow}}{\lesssim\!=\!=\!=\gtrsim} Ar\text{-}NCO + BH + OH^-$$

BH: Blocking Agents

Thus, the initial step is proton removal in a rapid equilibrium reaction followed by the slower expulsion of the phenolate or alkoxide ion.

Rand[26] has found that the course of the transesterification reactions is a rapid deblocking reaction to phenol (BH) and free isocyanate followed by a slower, rate-controlling reaction of the isocyanate with the alcohol (ROH).

$$Ar\text{-}NH\text{-}COB \underset{}{\overset{\text{fast}}{\rightleftharpoons}} Ar\text{-}NCO + BH$$

$$Ar\text{-}NCO + ROH \overset{\text{slow}}{\rightleftharpoons} Ar\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR$$

In constrast to the situation with alcohol, the reaction between a blocked isocyanate and primary or secondary amines is relatively rapid and not readily reversible. The rate-controlling step was the deblocking of the urethane to isocyanate, followed by the rapid reaction with the amine. It can be concluded that the free isocyanate site will largely react with $NH_2$ groups on the surface of dentin instead of OH groups.

C. Dissociation of blocked isocyanate : It can be assumed that the bonding strength of the adhesive material to dentin is mainly dependent on the number of free isocyanate sites which are available to react with amine groups in dentin. Thus, the rate and extent of the deblocking reaction are significant and , therefore, described in this section.

Due to its importance in industrial applications, several investigators have studied the deblocking reaction

for many years. Wicks[22] has summarized that the rate and extent of the deblocking reaction are affected by structure of blocking agents, catalyst, and solvent. Among the above three factors the choice of a compound to be used as a blocking agent is particularly crucial to the successful use of a blocked isocyanate. Frisch's[26] study showed that the thermal deblocking reaction of urethane in very general terms proceeds in the following order:

| | |
|---|---|
| Alkyl-NHCOO-Alkyl | 250°C |
| Aryl-NHCOO-Alkyl | 200°C |
| Alkyl-NHCOO-Aryl | 180°C |
| Aryl-NHCOO-Aryl | 120°C |

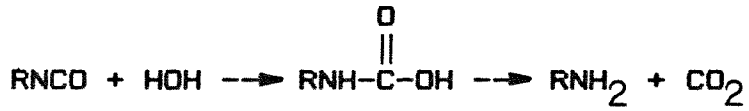
It was recognized that urethane derived from alkyl groups were more stable than those derived from aryl groups. Moreover, Fedoseev[27] reported that the stability of blocked isocyanates is significantly affected by substitution on the aromatic ring. The presence of electron-withdrawing groups decreases stability, and that of electron-releasing groups increases stability. Moreover, Ortho-substituted phenol will tend to deblock at lower temperatures than para-substituted ones.[28-30] According to the above guidelines, Kanaya tried p-cresol, while Chikazoe and Yamamoto tried phenol as blocking agents in their work. The choice of p-cresol, eugenol, ortho-methoxyphenol,and ortho-chlorophenol in this study are primarily based on a previous study by Dr. W.H. Snyder, Dr. D. Kristol, and colleagues.[31-33]

Like most reactions, catalyst also plays an important

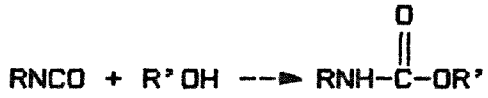
role in deblocking reactions. The deblocking temperature can be largely lowered by means of introducing a catalyst to the deblocking reaction. A patent[34] claims that calcium 2-ethyl-hexanoate is significantly more effective as a catalyst than tin compound. Also claimed are Mg, Ca, Sr, or Ba salts of hexanoic, octanoic, naphthenic or linoleic acid. Another patent[35] claims a marked synergistic effect with a combination of organotin compounds and quaternary ammonium salts, with not only a lower "release temperature" but also improved heat stability of the cured urethane coatings. Thus the combination of dibutyltin dilaurate and an alkyl ($C_{11}$ -$C_{18}$) dimethyl benzyl ammonium phthalimidate largely decreased the "release temperature". For the effect of solvent, Fedoseev[26] and co-workers studied the deblocking reaction in a series of solvent and found that the reaction rate increased with solvent polarity. Reilly and orchin[36] showed that dissociation proceeded more rapidly at 60°C in tetrahydrofuran than in benzene at 80°C.

D. Reaction of Isocyanates : In most reactions, especially with active hydrogen compounds, the aromatic isocyanates are more reactive than the aliphatic isocyanates. In addition, substitution of electronegative groups on the aromatic ring enchances the reactivity whereas electropositive groups reduce the reactivity of the isocyanate. As would be expected, steric hindrance on either the isocyanate or the active hydrogen compound will retard the reaction. All of the reactions are subject to catalysis by acid and, usually

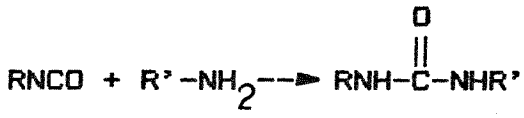
most strongly, by base. Typical reactions of isocyanates with active hydrogen compounds are shown as follows[37]:



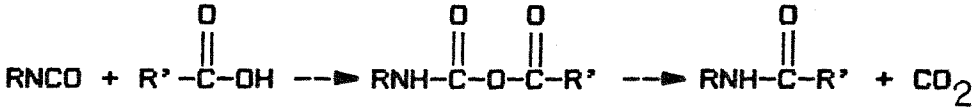
Carbamic Acid Amine



Urethane



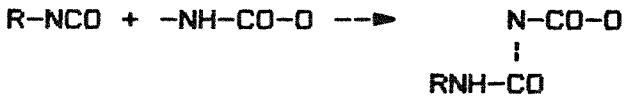
Urea



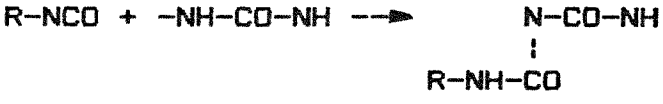
Mixed Anhydride Amide

The usual order of reactivity is $R'NH_2$ > R'OH > HOH > $C_6H_5OH$ > R'COOH. These reactions are considered to be the backbone of the polyurethane chemistry.

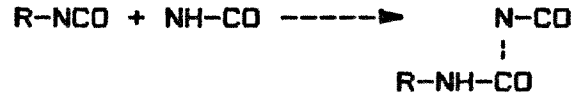
It is important to note that the further reaction between the primary product with an active hydrogen atom and another isocyanate group may also take place as follows:



Urethane Allophanate



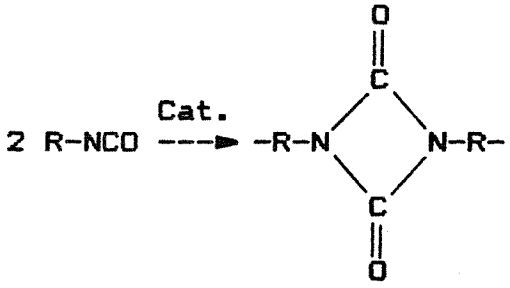
Urea Biruet



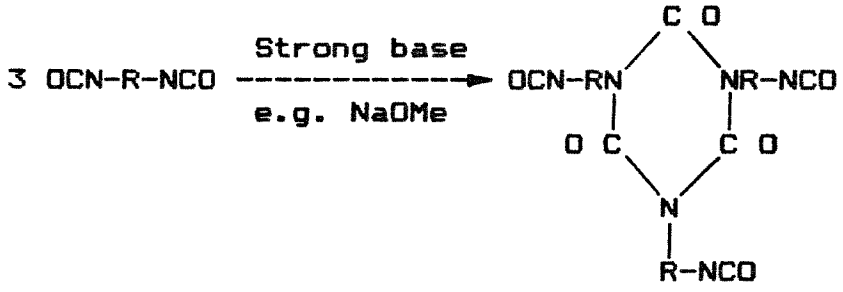

Amide Acyl Urea

These reactions[37] do not occur appreciably unless the reactant are heated or unless there is a catalyst present which will encourage the reaction. Some times these secondary reactions are desired for the formations of crossliking and branching which have an effect on polyurethane properties.

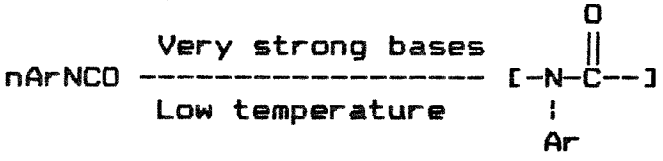
As a special case of the reaction with unsaturated compounds, isocyanates may react with themselves to form dimers, trimers, and even linear polymers.[37]




Isocyanate Dimer




Isocyanate Trimer



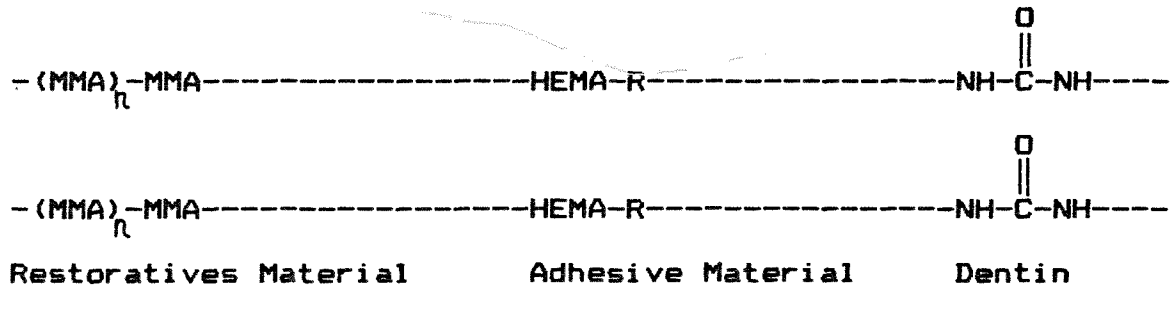

Linear Polymer

Isocyanate dimers at elevated temperatures react much as do isocyanates, sometimes by prior dissociation to the ioscyanate, sometimes by direct reaction between dimer and active hydrogen compound. Thus, dimers may give nearly the same reaction as the monomeric isocyanate. Trimerization is an important reaction in urethane polymer chemistry in that the trimer is relatively quite stable. In addition, trimerization is significant because it leads to branching of the polymer. For the linear polymer, its properties resemble nylon. So it is of importance in fiber industry.

E. Polymerization reaction:As noted before, the bifunctional monomers expected to come out of this study should both bond to the surface of the dentin and also polymerize with the restorative material. Currently, the most widely used restorative material is acrylic resin, poly methyl methacrylate. 38
In molding procedures, however, poly methyl methacrylate by itself is not used in dentistry to a great extent. Rather, the liquid monomer, methyl methacrylate, is mixed with the polymer at a ratio of 70% to 30% by weight. The monomer partially dissolves the polymer to form a plastic dough. this dough is packed into the mold, and the monomers are polymerized.

When the dough of MMA-PMMA is placed on the adhesive material, the polymerization reaction occurs not only between methyl methacrylate monomers themselves but also between methyl methacrylate monomers and 2-hydroxy ethyl methacrylates. The concept of dental adhesion by means of

diisocyanates can be generalized in the following Chemistry Scheme :




In this way it can be recognized that the interface of restorative material layer and adhesive material layer is a copolymer, and the restorative material layer itself is a homopolymer. Both of these reaction products are derived from vinyl radical polymerizations. The general chemistry for both homopolymerization and copolymerization will be discussed separately as follows:

F.Free radical Homopolymerization[39]: Initiation in the presence of an initiator, I , may be considered in two steps: first, the rate-determining decomposition of the initiator into free radicals, R· ,

$$I \xrightarrow{k_d} 2R\cdot$$ I: e.g., benzyl peroxide

and, second, the addition of a monomer unit to form a chain radical $M_1\cdot$

$$R\cdot + M \xrightarrow{k_a} M_1\cdot$$ M: e.g., methyl methacrylate monomer

The successive steps in propagation,

$$M_1\cdot + M \xrightarrow{k_p} M_2\cdot$$

$$M_2\cdot + M \xrightarrow{k_p} M_3\cdot$$

or, in general

$$M_X\cdot + M \xrightarrow{K_p} M_{X+1}\cdot$$

are assumed all to have the same rate constant $K_p$ because radical reactivity is presumed to be independent of chain length.

The termination step involves combination

$$M_X\cdot + M_Y\cdot \xrightarrow{k_{tc}} M_{X+Y}$$

or disproportionation, where $M_X$ and $M_Y$ are alkane and alkene.

$$M_X\cdot + M_Y\cdot \xrightarrow{k_{td}} M_X + M_Y$$

Only in the case where it is necessary to distinguish between the two mechanisms, the termination rate constant can be denoted $K_t$, a lumped parameter.

The rate of initiation is

$$V_i = \left(\frac{d\,[M\cdot]}{d\,t}\right)_i = 2\,f\,k_d\,[\,I\,]$$

where f = efficiency of the radical to initiate the monomer

The rate of termination is

$$V_t = -\left(\frac{d\,[M\cdot]}{d\,t}\right)_t = 2\,k_t\,[\,M\cdot\,]^2$$

At the steady-state, $V_i = V_t$

$$[\,M\cdot\,] = \left(\frac{f\,k_d\,[\,I\,]}{k_t}\right)^{1/2}$$

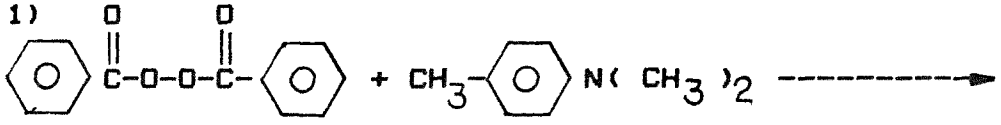
The rate of propagation,

$$V_p = -\frac{d\,[\,M\,]}{dt} = k_p\,[\,M\,]\,[\,M\cdot\,] = k_p\left(\frac{f\,k_d\,[\,I\,]}{k_t}\right)^{1/2}[\,M\,]$$

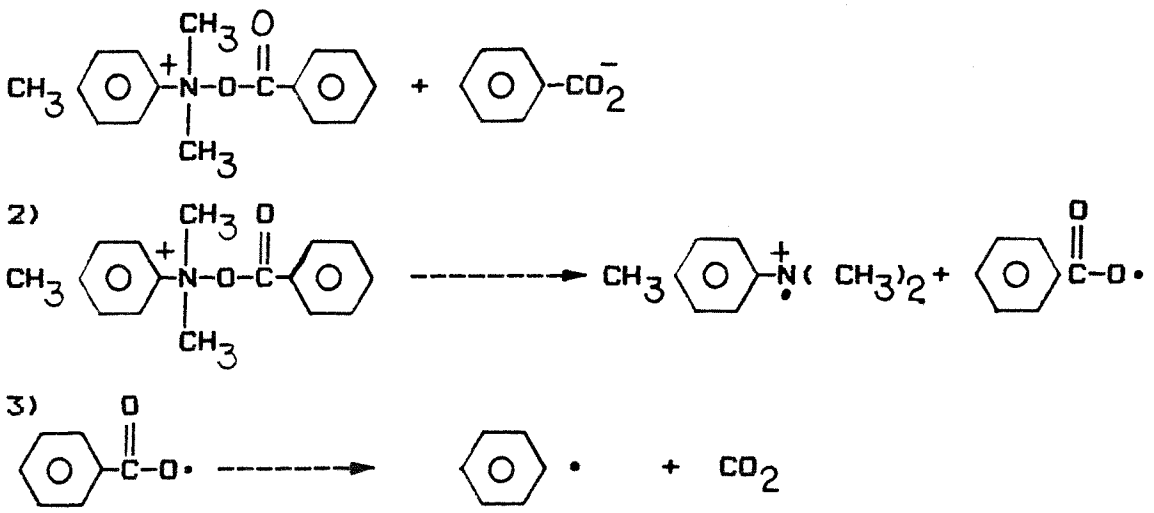
Thus the over-all rate of polymerization should be proportional to the sqaure root of the initiator concentration and to the first power of the monomer concentration. A number of substances which are capable of generating free radicals are potent initiators for the preparation of poly methyl methacrylate resins. The most commonly employed is benzoyl peroxide, which decomposes at relatively low temperature to release free radicals. In order to obtain good physical properties, a maximal useful concentration of the peroxide is 2.0 percent.[40] Hence, aside from increasing the concentration of monomer and initiator, the only way to increase the rate of polymerization is to find a good promoter which can activate the peroxide to decompose faster. This permits an increase in the rate of polymerization by increasing f, the efficiency of the radical, without increasing the initiator concentration. Meltzer and Tobolsky[41] showed that the propagation steps and termination steps of the chain reaction are not affected by a promoter in a peroxide-amine initiated system. It must, therefore, change the initiation step.

Steven's work[42] showed the decomposition step mechanism of initiator as follows:

1)



Benzoyl Peroxide N,N-dimethyl-p-Toluidine



Free Radical

According the above decomposition mechanism, the substitution of electron-repelling groups[43] in the para position of dimethylaniline will increase decomposition rate efficiency. But a methyl group substitution[43] in ortho position of dimethylaniline reduces the decomposition rate of benzoyl peroxide to such an extent that polymerization does not take place readily. As compared to the meta position, an aliphatic group in ortho position decreases peroxide decomposition. By using a modified ultrasonic viscometer, Brauer[43] and his coworkers concluded that polymerization with tertiary aromatic amines proceeds fastest. Furthermore, they showed that polymerization with N,N-dimethyl-p-toluidine or 2,2'- (m-tolylimino) diethanol gave products having the best physical properties. For the consideration of physical properties of material, however, a maximal useful concentration of the amine was found to be approximately 0.75 percent.[38]

G. Copolymerization[30] of Methyl Methacrylate and Hydroxyethyl Methacrylate : The initiation and termination steps are the

same as previously mentioned in homopolymerization. Dostal[44] made the first attack on the mechanism of copolymerization by assuming that the rate of addition of monomer to a growing free radical depends only on the nature of the end group on the radical chain. Thus monomers $M_1$ and $M_2$ lead to radical of types $M_1\cdot$ and $M_2\cdot$. There are four possible ways in which monomer can add:

$$M_1\cdot + M_1 \xrightarrow{K_{11}} M_1\cdot \qquad K_{11}\,[M_1\cdot]\,[M_1]$$

$$M_1\cdot + M_2 \xrightarrow{K_{12}} M_2\cdot \qquad K_{12}\,[M_1\cdot]\,[M_2]$$

$$M_2\cdot + M_1 \xrightarrow{K_{21}} M_1\cdot \qquad K_{21}\,[M_2\cdot]\,[M_1]$$

$$M_2\cdot + M_2 \xrightarrow{K_{21}} M_2\cdot \qquad K_{22}\,[M_2\cdot]\,[M_2]$$

If we assume that a steady state applies to each radical type separately,[45-48]

$$K_{21}\,[M_2\cdot]\,[M_1] = K_{12}\,[M_1\cdot]\,[M_2]$$

$$-\frac{d[M_1]}{dt} = K_{11}[M_1\cdot][M_1] + K_{21}[M_2\cdot][M_1]$$

$$-\frac{d[M_2]}{dt} = K_{12}[M_1\cdot][M_2] + K_{22}[M_2\cdot][M_2]$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\,\frac{r_1[M_1]+[M_2]}{[M_2][M_1]+r_2[M_2]}$$

$$r_1 = K_{11}/K_{12} \qquad r_2 = K_{22}/K_{21}$$

$M_1$ : Methyl Methacrylate monomer

$M_2$ : Hydroxyethyl Methacrylate monomer

$M_1\cdot$: living copolymer with Methyl Methacrylate terminers

$M_2\cdot$: living copolymer with Hydroxyethyl Methacrylate terminers

1) If $r_1 \cdot r_2 = 1$ then $\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]}$

In this case the end group on a growing chain has no influence on the rate of addition, and the two types of units are arranged at random along the chain in relative amounts determined by the composition of the feed and the relative reactivities of the two monomers. This copolymer system is said to be ideal.

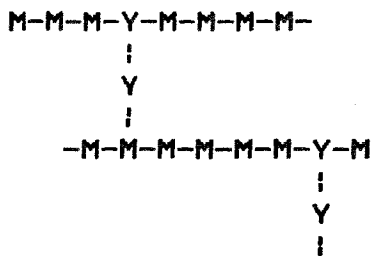
2) If $r_1 = r_2 = 0$, then $\frac{d[M_1]}{d[M_2]} = 1$

The monomers alternate regularly along the chain regardless of the composition of the monomer feed. This is so called alternative copolymer.

3) If $r_1$ , $r_2 > 1$, The system corresponds to the tendency to form block copolymer .

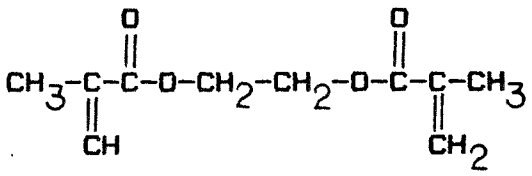
Most actual cases lie between the ideal and the alternating systems; $0 < r_1 r_2 < 1$ .

H. Effects of Cross Linking on Dental Material: Theoretically, cross-linkage[49] provides a sufficient number of bridges between the linear macromolecules to form a three-dimensional network that alters the strength, solubility, and water sorption of the resin. A general cross linking structure is as follow :




Most acrylic resin materials contain a cross-linking

agent such as ethylene glycol dimethacrylate :



This chemical contains two polymerizable bonds, and it can cross-link with other groups in at least two directions when it is polymerized. When it is used as a copolymer with methyl methacrylate, a more insoluble and in fusible resin results compared with the similar properties of poly methyl methacrylate alone.

For the investigation of the mechanical properties, investigations have been carried out in Japan by Masuhara and Hirasawa[50] which included the study of hardness, tensile and transverse strengths, abrasion resistance and water absorption of co-polymers of methyl methacrylate and a variety of cross-linking agents. Their results indicated that there was a small increase in tensile strength in some of the cross-linking specimens over that of linear poly-methyl methacrylate ones. All other tests displayed no significant difference.

I. Residual Monomer in Restorative Resins: Since the introduction of restorative homopolymerizing resins there has been a continuous effort to improve the properties of the material and the quality of the finished restoration. The shortcomings of resin restorations have been discussed fully and are well known. Some of the difficulties encountered in the past were the lack of color stability,

poor adaption, low strength and hardness, and an absence of anticarcinogenic characteristics. Investigations of the mechanical properties of resins have indicated that they are related, in general, to the residual monomer content. The modulus of elasticity, yield strength and hardness develop with time, and the rate of improvement exhibit a direct relationship to the decrease in the monomer content.[51-52] Generally, the more rapidly the residual monomer is reduced, the more rapidly the physical properties improve.

Our work is an attempt to improve the mechanical properties of methacrylate-based dental restorative resins.

# EXPERIMENTAL

## I. Synthesis

### A. HPMA-TDI-Blocking Agent Synthesis

1. Preparation of HPMA-TDI Adduct: This reactoin was carried out in a solution which contains TDI(2,4-toluene diisocyanate) and HPMA(2-hydroxy propyl methacrylate) in the molar ratio 3:1. The apparatus was set up as indicated in Appendix A.

120.0 grams(0.690 moles) of TDI was stirred with 500 mL of petroleum ether and 6 drops of DBTDL(dibutyltin dilaurate) as catalyst in a high shear stirring flask. The mixing was carried out for 15 minutes in a nitrogen atmosphere. HPMA, 33.0 grams(0.230 moles) was added dropwise to the solution by means of an addition funnel.

Under conditions of vigorous agitation and nitrogen circulation, the reaction was exothermic. A cooling water bath was used to maintain the temperature below 35$^{\circ}$C to prevent gel formation due to by-product reactions.

After one hour addition of HPMA, 250 mL of petroleum ether was added. Addition of fresh petroleum ether should turn the reacting solution cloudy. If this does not occur, the agitation is continued and the rate of HPMA is controlled until the desired cloudiness is obtained. Generally, the rate of HPMA is controlled at 1 drop/15 secs. The addition of fresh petroleum ether can also prevent HPMA-TDI adduct from sticking to the body of the flask. Therefore, it is necessary to keep adding fresh petroleum ether during

the reaction. The total amount of fresh petroleum ether being added in the adducting reaction should not be less than 1000 mL.

After all the HPMA has been added, the reaction was allowed to procede overnight under conditions of continuous agitation and nitrogen atmosphere.

2. Precipitation of HPMA-TDI Adduct: The stirrer was turned off, 100 mL of petroleum ether was added and the system was left undisturbed under nitrogen circulation for at least 6 hours. The colorless liquid at the top of the flask consisting of excess TDI and petroleum ether was suctioned off by means of a rubber bulb.

Another 1000 mL of fresh petroleum ether was added and the solution was continuously stirred for 20 minutes in order to remove the TDI residues adsorbed on HPMA-TDI adduct. This purification process was repeated twice more. Finally, the solid product at the bottom of the flask was collected by suction filtration. The filtered cake was washed with fresh petroleum ether to ensure the complete removal of TDI residues. The filtered cake was placed on a watch glass and vacuum dried at room temperature for one day to remove all traces of petroleum ether from the adducting product. A yield of 30 grams(41%) of HPMA-TDI adduct was obtained.

3. Blocking HPMA-TDI Adduct: The HPMA-TDI adduct from part 2 of section A was blocked with two blocking agents such as p-cresol, and m-methoxy phenol. However, in this section only the blocking reaction of p-cresol will be discussed in

detail. For the case where m-methoxyphenol is used as a blocking agent, the experimental procedure used is similar to the one discussed for p-cresol. Reaction conditions, such as required time for completion of the blocking reaction, amount of blocking agent, etc., are listed in Table I

12.0 grams (0.038 moles) of the HPMA-TDI adduct were dissolved in 150 mL of dry THF (tetrahydrofuran) in a 250 mL Erlenmeyer flask. [ one liter of THF solvent had been dried by the addition of lithium aluminum hydride, and a simple distillation of the resulting suspension was performed.] 5 drops of DBTDL as catalyst was added to the solution along with 4.9 grams (0.045 moles, 20% excess) of p-cresol. The solution was gently shaken to ensure that all reactants were mixed well and nitrogen gas was passed through it for about 1 to 2 minutes. The flask was now capped with a rubber stopper, which was wrapped in aluminum foil to prevent direct contact with the blocking solution. The blocking reaction was carried out in a hot oil bath maintained at 50$^{o}$C. A sample was checked for a free isocynate peak at 2250 cm$^{-1}$ by means of an infrared spectrophotometer. For the case of p-cresol, it took three days for the completion of the blocking reaction, as shown by the absence of a free isocyanate peak. The solution at this point became more viscous and its color changed from light to dark yellow.

4. The Precipitation of P-cresol Blocked HPMA-TDI Adduct:
The blocked solution from part 3 of section A was filtered to remove undissolved impurities. Before the precipitation

was performed, it was necessary to ensure that each drop of the blocked solution added to petroleum ether immediately precipitated as a fine solid material. Formation of large coalesced particles on contact of the blocked solution with petroleum ether would imply that the blocked solution had to be diluted with more dry THF solvent. On the other hand, too much dilution with dry THF solvent would cause the formation of a cloudy solution instead of fine powder precipitation and loss of product. A total of 100 mL of dry THF was added to the solution of HPMA-TDI-p-cresol and the contents of the flask was shaken gently. The diluted blocked solution was added dropwise to 1000 mL of petroleum ether in a flask under nitrogen atmosphere and vigorous agitation. Upon contact of the blocked HPMA-TDI solution with the petroleum ether, a well dispersed white solid was observed. After the addition of about half the blocked solution, 500 mL of petroleum ether was poured into the solution to prevent the precipitate from coalescing to each other or from sticking to the wall of flask. Once all the blocked HPMA-TDI solution was precipitated, the excess p-cresol, dry THF, and catalyst were removed by washing with petroleum ether. The washing procedure described in part 2 of section A would be applicable to the above case. Finally, 13.0 grams (81% yield ) of HPMA-TDI-p-cresol blocked adduct was obtained.

Table I Preparation of HPMA-TDI-m-methoxyphenol

The general procedure is the same that was described in parts 3,4 of section A with following quantities of the reactants and characteristics:

Weight of the HPMA-TDI Adduct : 14.0 grams (0.044moles)

THF solvent used in the blocking reaction : 150 mL

Weight of m-methoxyphenol : 8.19 grams (0.066 moles)

DBTDL as catalyst : 5 drops

Temperature of blocking reaction : 50°C

Time for completing the blocking reaction : 4-5 days

More THF solvent used for dilution : 100 mL

Total vol.of petroleum ether used for Precipitation :3500 mL

Weight of the product : 13.2 grams (68% yield)

B. Pentaerythritol-TDI-HEMA-Blocking Agent Synthesis:

1. Preparation of Pentaerythritol-TDI Adduct: In this case, the adducting reaction was carried out in a heterogeneous system. The same apparatus previous section were used.

34.0 grams (0.250 moles) of pentaerythritol was ground into a fine powder, and then dried in a vacuum oven at 40°C for one day. The dried powder was placed in a flask and 500 mL of distilled p-dioxane, 261 grams (1.5 moles, 50% excess) of TDI, and 5 drops of DBTDL were added to it. The reaction was now carried out under nitrogen circulation and vigorous agitation. It was found that pentaerythritol was insoluble in p-dioxane.

Since p-dioxane is a very good solvent for pentaerythritol-TDI adduct, once the adduct was formed, it dissolved in the p-dioxane immediately. In this way the adduct product was easily separated from the pentaerythritol. Similarly, The reaction of hydroxy group of pentaerythritol with isocyanate group of TDI occured exothermically. In order to avoid the formation of gel material due to by-product reactions, a cooling water bath had to be used.

As the reaction proceeded, the total amount of pentaerythritol was observed to gradually diminish. At the same time the colorless solution turned yellow and became more viscous. Generally, the fresh distilled p-dioxane had to be poured into the flask to prevent oversaturation at this time. In the case of oversaturation another 50 mL of distilled p-dioxane had to be added to the reacting solution every 2-3

hours. The reaction was continued until the amount of pentaerythritol was observed to remain constant.

2. Precipitation of Pentaerythritol-TDI Adduct: Upon completion of the reaction, the solution of pentaerythritol- TDI was filtered to remove the unreacted solid pentaerythritol in petroleum ether. The precipitating procedures described in part 4 of section A can be applied to this case. Finally, the milky solid material obtained was dried and found to weigh 128.5 grams (yield of 61.9%).

3. Blocking the Pentaerythritol-TDI Adduct: In the blocking reaction, the 1:1 molar ratio of HEMA (2-hydroxy ethyl methacrylate) and each of the four blocking agents were used to block the samples of pentaerythritol-TDI adduct. Although four different blocking agents were applied in the blocking reaction, only the blocking reaction of p-cresol will be described in detail in this section. For the remaining three blocking agents, the reaction conditions, such as temperature, required time for completion of the blocking reaction, and excess amount of blocking agents etc., are individually listed in Table II-IV.

8.0 grams of pentaerythritol-TDI adduct from part 2 of section B were placed in a 250 mL Erlenmeyer flask and 100 mL of dry THF were added to it dissolve the pentaerythritol -TDI adduct. Upon the addition of THF, the solution turned a reddish brown color. p-cresol, 2.2863 grams (0.021 moles or 20% excess), 2.576 grams (0.0198 moles or 60% excess) of HEMA, and 6 drops of DBTDL as catalyst were simultaneously

poured into the solution which was gently shaken to ensure that all reactants were thoroughly mixed. Nitrogen gas was passed through it for about 1 tO 2 minutes. The flask was capped with a rubber stopper, which was wrapped in aluminum foil. The blocking reaction proceeded in a oil bath, maintained at 50°C. Using the same procedure as described in the previous section, an Infrared Spectrometer was used to check for the free isocyanate peak. In the case of p-cresol blocking reaction, it was found that the free isocyanate peak had reached its minimum after seven days. In order to ensure completion of the blocking reaction, as indicated by the absence of free isocyanate peak, 0.4172 grams of p-cresol was added to the blocking solution. One day later, the free isocyanate peak was completely eliminated. The blocking solution was now diluted with 90 mL of dry THF to obtain a good precipitation.

4. The Precipitation of Pentaerythritol-TDI-HEMA-p-cresol.

The solution from above was precipitated in petroleum ether. All precipitating procedures are similar to those described in part 4 of section A. Finally, 10.2 grams (84% yield) of pentaerythritol-TDI-HEMA-p-cresol was obtained.

Table II Preparation of Pentaerythritol-TDI-HEMA-Eugenol

The general procedure is the same that was described in parts 3,4 of section B with following quantities of the reactant and characteristics:

Weight of pentaerythritol-TDI adduct: 8.0 grams ($9.61\times10^{-3}$ moles)

THF solvent used in blocking reaction : 100 mL

Weight of HEMA : 2.576 grams (0.0198 moles)

Weight of Eugenol 3.47 grams (0.021 moles,18% excess)

DBTDL as catalyst : 5 drops

Temperature of the blocking reaction : 45°C

More Eugenol added for completing the blocking reaction after 7 days : 0.63 grams ($3.8\times10^{-4}$ moles,4% excess)

Time for completing blocking reaction : 13 days

More THF solvent used for dilution : 150 mL

Total volume of petroleum ether used for precipitation : 3500 mL

Weight of product :9.8 grams (72% yield)

Table III Preparation of Pentaerythritol-TDI-HEMA-o-Methoxy-phenol

The general procedure is the same that was described in parts 3,4 of section B with following quantities of the reactant and characteristics:

Weight of pentaerythritol-TDI Adduct: 8 grams

($9.61\times10^{-3}$ moles)

THF solvent used in the blocking reaction : 100 mL

Weight of HEMA : 2.576 grams (0.0198 moles)

Weight of o-methoxyphenol: 2.62 grams

(0.021 moles,18% excess)

DBTDL as catalyst : 5 drops

Temperature of blocking reaction :45$^{\circ}$C

More o-methoxyphenol added for completing blocking reaction after 7 days : 0.48 grams ($3.8\times10^{-4}$ moles,4% excess)

Time for completing the locking reaction : 11 days

More THF solvent used for dilution after 7-8 days :150 mL

Total volume of petroleum ether used for precipitation : 3500 mL

Weight of product : 8.7 grams (67.5% yield)

Table IV Preparation of Pentaerythritol-TDI-HEMA-o-Chlorophenol

The general procedure is the same that was described in parts 3,4 of section B with following quantities of the reactant and characteristics:

Weight of pentaerythritol-TDI adduct : 10 grams(0.012 moles)

THF solvent used in blocking reaction : 100 mL

Weight of HEMA : 3.23 grams(0.02484 moles, 7% excess)

Weight of o-chlorophenol : 3.47 grams

(0.027 moles, 25% excess)

DBTDL as catalyst : 5 drops

Temperature of blocking reaction : 37°C

More o-chlorophenol added for completing the blocking reaction after two weeks : 2.00 grams

($1.11\times10^{-3}$ moles, 9% excess)

Time for completing the blocking reaction : 19 days

More solvent used for dilution : 200 mL

Total volume of petroleum ether used for

Precipitation : 3500 mL

Weight of product : 11.4 grams (70.4% yield)

C. Hydroxyhexyl Monomethacrylates

1. Preparation of Hydroxyhexyl Monomethacrylates: the reaction of hydroxyl group of 1,6-hexanediol with the carboxyl group of methacrylic acid proceeded at 80°C and 100-150 mm Hg under an oxygen atmosphere. The apparatus was set up as indicated in Appendix B. The detailed experimental procedures are as follows:

137.7 grams(1.6 moles) of methacrylic acid, 189.1 grams (1.6 moles) of 1,6-hexanediol, 1.5 grams of p-Toluene sulfonic acid monohydrate (as catalyst), and 0.6 grams of di-tert-butyl -p-cresol (antioxidant) were poured into a 500 mL resin kettle and gently shaken to ensure proper mixing. The reactants were heated to 80°C and oxygen gas was carefully introduced. At the same time, a vacuum of 100-150 mmHg was developed by using a vacuum pump and controlled by using the regulator. As long as a temperature of 80°C and a pressure of 100-150 mmHg was maintained, water was observed to condense in the collecting flask and the trap. For this reaction, temperature and oxygen gas are the most important factors. In fact, the best reaction rate can be obtained at 80°C. Beyond this temperature, the polymerization reaction would occur at the double bond of methacrylic acid. The purpose of introducing oxygen gas was to inhibit the polymerization reaction, thereby obtaining a higher yield of the product. The reaction was continued until all the water, a by product, was removed. The final product was 190 mL.

2. Purification of 6-Hydroxyhexyl monomethacrylates: The

liquid from above part contained both monoester and diester. The monoester was separated from diester by extracting the diester with n-octane three times. Using 600 mL of n-octane each time. Finally,55.0 grams (16.8% yield) of yellow liquid was obtained.

II. Characterization

1. Melting Points of Monomers: In determining the melting points of the monomers, a light microscope with a hot stage and a crossed-polarized lens made by Bristoline Company was used. For each of the monomers, the melting point determinations were performed twice. A heating rate of approximately $1^{\circ}C$ / 1 min was used to obtain a precise melting point. The melting points for all of monomers are listed in Table V

2. IR Spectra :The samples except for the hydroxyhexyl monomethacrylates were KBr pellets. The monomer, $1.4 \times 10^{-3}$ grams, was mixed with 0.5 grams of KBr, and ground together using an agate mortar and pestle. The sample discs were made with a Carver press, and the IR instrument was the Perkin--Elemer Infrared Spectrophotometer model 1310. IR data are given in Tables VI-XIV. IR Spectra are shown in Figs 1-9.

3. NMR Spectra: Only proton NMR was used. Unisol or acetone was used as solvent, and TMS as reference. The samples were dissolved in the solvent and filtered through 0.45 micro nitro-cellulose filters. The instrument used was the Perkin-Elemer EM 360L. The NMR data are given in Tables XV-XXII. NMR Spectra for all of monomers are shown in Figs 10-17.

4. Elemental Analysis: This analyses were performed by Mic Anal Corporation of Tuscon, Arizona. The reported percentage of Carbon, Hydrogen, Nitrogen, and Chlorine are given in Tables XXIII-XXX.

5.Tensile Strength Test: The procedure for preparing the samples for tensile strength testing is as follows:

a. Preparation of Aluminum rods: The faces of the rods, which were sandblasted for better adhesion, were put into petroleum ether in an ultra sound machine for 5 minutes for degreasing. The $Na_2Cr_2O_7/H_2SO_4$ etching solution was used to etch the faces of the rods, which were then rinsed with tap water and followed by distilled water. Finally, the rods were set face up in a Jig with rubber sleeves around them to minimize the leakage of the adhesive.

b. Tooth Slices Treatment: Tooth slices were immersed in 5% citric acid for 2 minutes and then washed with distilled water for 1 minute. The etched tooth slices were soaked with DME (1,2-Dimethoxy ethane) for two minutes. The monomers made in section A and B were dissolved in DME to form an adhesive solution. The tooth slices which were previously soaked in DME were now placed in the adhesive soltion.

c. Sample Making: PMMA-MMA mixture (75% MMA, 25% PMMA) along with NNDMPT as catalyst and benzoyl peroxide as initiator was placed on the treated rods in the Jig. The treated tooth slices were now dipped in PMMA-MMA mixture and immediately placed on the faces of the rods. Finally, Six samples were subjected to a load of 1875 grams for about one hour. The bonded tooth slices were then measured for their tensile breaking strength in a SCOTT-CRE 1500 Tensile Testing Machine. The results of the testing for each of monomers are listed in Tables XXXI-XXXX.

Table V Melting Point of The Products

| Compound | Melting Point |
|---|---|
| HPMA-TDI Adduct | 185-187°C |
| HPMA-TDI-P-Cresol | 85-87°C |
| HPMA-TDI-m-Methoxy Phenol | 83-86°C |
| Pentaerythritol-TDI | 305-307°C |
| Pentaerythritol-TDI-HEMA-P-Cresol | 104-108°C |
| Pentaerythritol-TDI-HEMA-Eugenol | 103-105°C |
| Pentaerythritol-TDI-HEMA-o-Methoxy Phenol | 122-125°C |
| Pentaerythritol-TDI-HEMA-o-Cholorophenol | 119-122°C |

Table VI Selected IR Absorptions of HPMA - TDI

| Assignments | Wave number $cm^{-1}$ |
|---|---|
| N-H stretch | 3350 (s) |
| C-H aliphatic and arometic stretch | 2960 (s) |
| N=C=O | 2280 (s) |
| C=O carbonyl | 1740 (s) |
| C=C | 1640 (m) |
| C=H aromatic skeletal stretch | 1530 (s) |
| $CH_2$ bending | 1460 (s) |
| $CH_3$ bending | 1390 (s) |
| C-O | 1300 (s) |
| C-N stretch | 1230 (s) |
| C-N stretch | 1170 (s) |
| C-O | 1120 (m) |
| C-O | 1090 (s) |
| C-O | 1050 (m) |
| C-H out of plane deformation | 1000 (m) |
| C-H out of plane deformation | 950 (m) |
| C-H out of plane deformation | 870 (m) |
| C-H out of plane deformation | 820 (m) |
| C-H out of plane deformation | 760 (m) |

Table VII Selected IR Absorptions of HPMA-TDI-P-Cresol

| Assignments | Wave number $cm^{-1}$ |
|---|---|
| N-H stretch | 3320 (s) |
| C-H aliphatic stretch aromatic | 2880 & 2990 (s) |
| C=O carbonyl | 1720 (s) |
| C=C | 1600 (m) |
| C=H aromatic skeletal stretch | 1530 (s) |
| C=H aromatic skeletal stretch | 1510 (s) |
| $CH_2$ bending | 1450 (s) |
| $CH_3$ bending | 1360 (m) |
| $CH_3$ bending | 1330 (m) |
| C-N stretch | 1270 (m) |
| C-O | 1230 (s) |
| C-O | 1210 (s) |
| C-N stretch | 1190 (s) |
| C-H in plane bend | 1070 (s) |
| C-H out of plane deformation | 910 (s) |
| C-H out of plane deformation | 820 (m) |

Table VIII Selected IR Absorptions of HPMA-TDI-m-Methoxy-phenol

| Assignments | Wave number $cm^{-1}$ |
|---|---|
| N-H stretch | 3290 (s) |
| C-H aliphatic and aromatic stretch | 2880 & 2900 (s) |
| C=O carbonyl | 1720 (s) |
| C=C | 1600 (s) |
| C=H aromatic skeletal stretch | 1530 (s) |
| C=H aromatic skeletal stretch | 1490 (s) |
| $CH_2$bending | 1460 (s) |
| $CH_3$bending | 1360 (m) |
| C-O | 1290 (s) |
| C-N stretch | 1230 (s) |
| C-N stretch | 1190 (s) |
| C-O | 1170 (s) |
| C-O | 1150 (s) |
| C-H in plane | 1070 (s) |
| C-H out of plane deformation | 950 (m) |
| C-H out of plane deformation | 910 (s) |
| C-H out of plane deformation | 850 (m) |
| C-H out of plane deformation | 770 (m) |
| C-H out of plane deformation | 690 (m) |

Table IX Selected IR Absorptions of Pentarythritol-TDI

| Assignment | Wave Number $cm^{-1}$ |
|---|---|
| N-H stretch | 3320 (s) |
| C-H aliphatic and aromatic stretch | 2920 & 2960 (m) |
| N=C=O | 2270 (s) |
| C=O | 1720 (s) |
| C=H aromatic skeletal stretch | 1600 (s) |
| C=H aromatic skeletal stretch | 1520 (s) |
| $CH_2$ bend | 1390 (m) |
| C-O | 1270 (m) |
| C-N stretch | 1220 (s) |
| C-N stretch | 1160 (s) |
| C-H in plane | 1000 (m) |
| C-H out of plane deformation | 930 (m) |
| C-H out of plane deformation | 860 (m) |
| C-H out of plane deformation | 810 (m) |
| C-H out of plane deformation | 760 (m) |

Table X Selected IR Absorptions of Pentaerythritol-TDI-HEMA-P-Cresol

| Assignment | Wave Number $cm^{-1}$ |
|---|---|
| N-H | 3320 (s) |
| C-H aliphatic and aromatic stretch | 2920,2980 (m) |
| C=O | 1720 (s) |
| C=C | 1600 (s) |
| C=H aromatic skeletal stretch | 1530 (m) |
| C=H aromatic skeletal stretch | 1450 (m) |
| $CH_2$ bend | 1410 (s) |
| $CH_3$ bend | 1300 (s) |
| C-N | 1230 (s) |
| C-O | 1200 (s) |
| C-O | 1070 (s) |
| C-H in plane bend | 1000 (m) |
| C-H out of plane deformation | 950 (m) |
| C-H out of plane deformation | 870 (m) |
| C-H out of plane deformation | 820 (m) |
| C-H out of plane deformation | 760 (m) |

Table XI Selected IR Absorptions of Pentaerythritol-TDI-HEMA-Eugenol

| Assignment | Wave Number $cm^{-1}$ |
|---|---|
| N-H | 3330 (s) |
| C-H aliphatic and aromatic stretch | 2900 (m) |
| C=O | 1730 (s) |
| C=C | 1610 (s) |
| C=H aromatic skeletal stretch | 1540 (s) |
| C=H aromatic skeletal stretch | 1460 (m) |
| $CH_2$ bend | 1430 (m) |
| $CH_3$bend | 1330 (m) |
| C-N | 1240 (s) |
| C-N | 1210 (s) |
| C-O | 1200 (s) |
| C-O | 1150 (s) |
| C-O | 1080 (s) |
| C-H in plane bend | 1010 (m) |
| C-H out of plane deformation | 960 (m) |
| C-H out of plane deformation | 880 (m) |
| C-H out of plane deformation | 830 (m) |
| C-H out of plane deformation | 770 (m) |

Table XII Selected IR Absorptions of Pentaerethritol-TDI-HEMA-o-Methoxyphenol

| Assignment | Wave Number $cm^{-1}$ |
|---|---|
| N-H stretch | 3380 (s) |
| C-H aliphatic and aromatic stretch | 2920 & 2960 (m) |
| C=O | 1710 (s) |
| C=C | 1600 (s) |
| C=H aromatic skeletal stretch | 1530 (s) |
| C=H aromatic skeletal stretch | 1440 (m) |
| $CH_2$ bend | 1410 (m) |
| $CH_3$bend | 1310 (m) |
| C-N stretch | 1290 (m) |
| C-O | 1220 (m) |
| C-N stretch | 1170 (s) |
| C-O | 1130 (m) |
| C-O | 1060 (s) |
| C-H in plane | 1000 (m) |
| C-H out of plane deformation | 940 (m) |
| C-H out of plane deformation | 870 (m) |
| C-H out of plane deformation | 810 (m) |
| C-H out of plane deformation | 760 (m) |

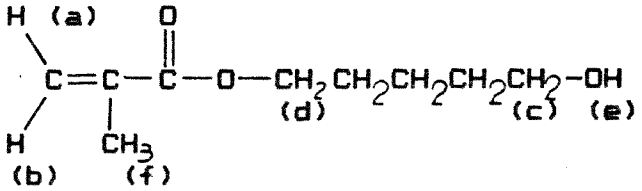
Table XIII Selected IR Absorptions of Pentaerythritol-TDI-HEMA-o-Chlorophenol

| Assignment | Wave Number cm |
|---|---|
| N-H stretch | 3400 (s) |
| C-H aliphatic and aromatic stretch | 2920 & 2940 (m) |
| C=O | 1700 (s) |
| C=C | 1600 (s) |
| C=H aromatic skeletal stretch | 1530 (s) |
| C=H aromatic skeletal stretch | 1440 (s) |
| $CH_2$ bend | 1410 (m) |
| $CH_3$ bend | 1310 (m) |
| C-N stretch | 1290 (m) |
| C-O | 1220 (s) |
| C-N | 1170 (s) |
| C-O | 1130 (m) |
| C-O | 1060 (s) |
| C-H in plane bend | 1000 (m) |
| C-H out of plane deformation | 950 (m) |
| C-H out of plane deformation | 870 (m) |
| C-H out of plane deformation | 810 (m) |
| C-H out of plane deformation | 760 (m) |

Table XIV Selected IR Absorptions of Hydroxyhexyl-methacrylate

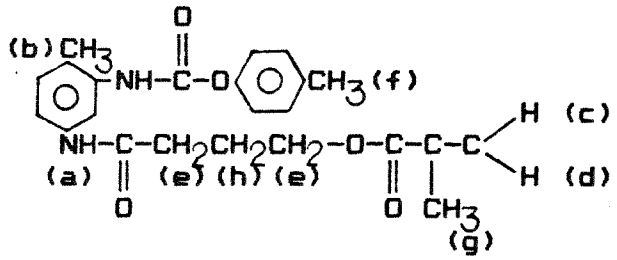
| Assignment | Wave Number $cm^{-1}$ |
|---|---|
| O-H stretch | 3330 |
| C-H Aliphatic stretch | 2880 & 2920 |
| C=O | 1710 |
| C=C | 1640 |
| CH (alkane) bend | 1450 |
| CH (alkane) bend | 1430 |
| CH (alkene) bend | 1410 |
| O-H bend | 1300 |
| C-O stretch | 1170 |
| C-O-C | 1020 & 1060 |
| OH bend | 950 |
| C-H out of plane deformation | 820 |

Table XV NMR Signals of Hydroxyhexylmethacrylate



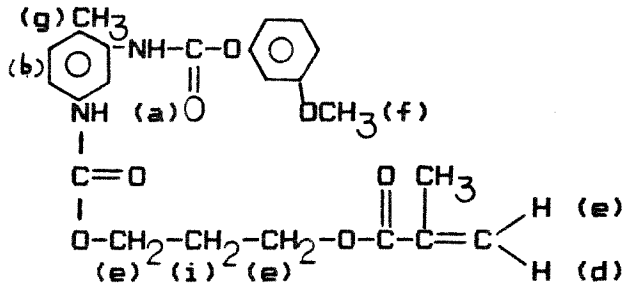

| | | | |
|---|---|---|---|
| a. | 6.10 δ | (s) | (1H) |
| b. | 5.50 δ | (s) | (1H) |
| c. | 4.10 δ | (t) | (2H) |
| d. | 3.60 δ | (t) | (4H) |
| e. | 3.30 δ | (s) | (3H) |
| f. | 1.90 δ | (s) | (3H) |
| g. | 0.9-1.8 δ | (?) | |

Table XVI NMR Signals of HPMA-TDI-p-Cresol



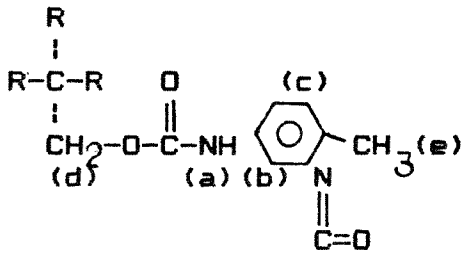

| | |
|---|---|
| a. | ? |
| b. | 7.0-8.0 δ (?) (6H) |
| c. | 6.10 δ (s) (1H) |
| d. | 5.60 δ (s) (1H) |
| e. | 4.30 δ (d) (3H) |
| f. | 2.20 δ (d) (?) |
| g. | 1.90 δ (s) (4H) |
| h. | 1.30 δ (d) (5H) |

Table XVII NMR Signals of HPMA-TDI-m-Methoxyphenol



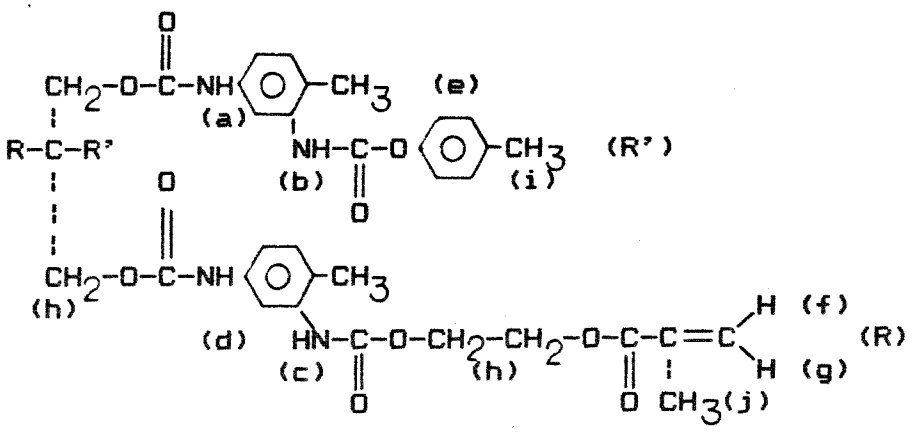

| | | | |
|---|---|---|---|
| a. | 8.50-9.00 δ | (t) | (?) |
| b. | 6.60-8.00 δ | (?) | (7H) |
| c. | 6.10 δ | (s) | (1H) |
| d. | 5.50 δ | (s) | (1H) |
| e. | 4.30 δ | (d) | (3H) |
| f. | 3.80 δ | (d) | (2H) |
| g. | 2.20 δ | (d) | (4H) |
| h. | 1.90 δ | (s) | (3H) |
| i. | 1.30 δ | (d) | (?) |

Table XVIII NMR Signals of Pentaerythritol-TDI



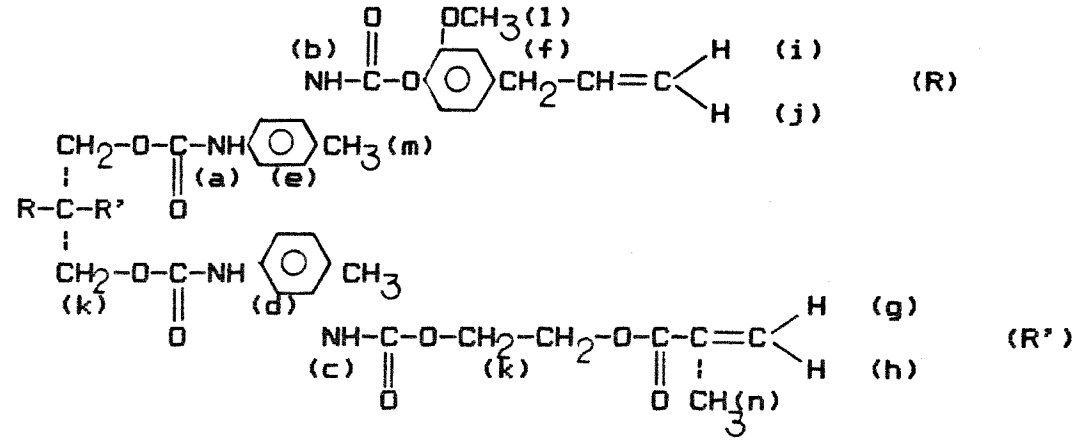

| | | | |
|---|---|---|---|
| a. | 9.25 δ | (s) | (4H) |
| b. | 7.30 δ | (s) | (4H) |
| c. | 7.10 δ | (d) | (9H) |
| d. | 4.30 δ | (s) | (7H) |
| e. | 2.20 δ | (s) | (13H) |

Table XIX NMR Signals of Pentaerythritol-TDI-HEMA-p-Cresol



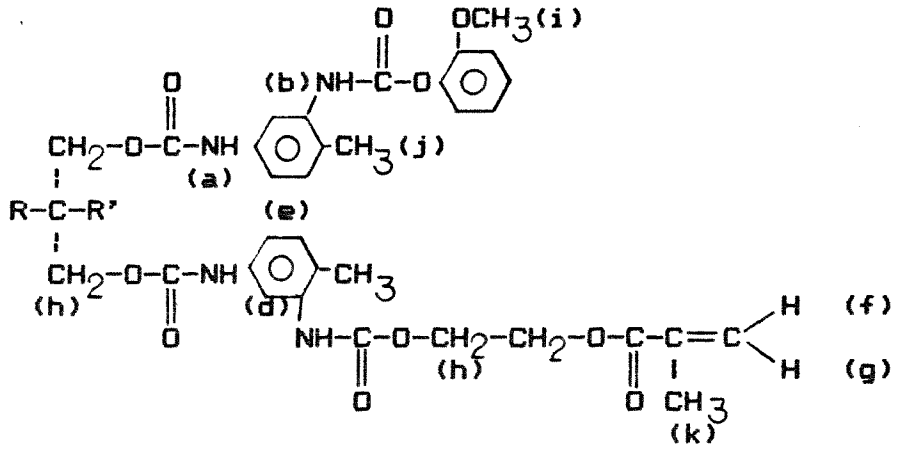
| | | | |
|---|---|---|---|
| a. | 9.25 δ | (s) | (4H) |
| b. | 8.65 δ | (s) | (1.3H) |
| c. | 8.10 δ | (s) | (2.7H) |
| d. | 7.75 δ | (s) | (4H) |
| e. | 7.10 δ | (t) | (14H) |
| f. | 6.10 δ | (s) | (2H) |
| g. | 5.60 δ | (s) | (2H) |
| h. | 4.35 δ | (s) | (18H) |
| i. | 2.30 δ | (d) | (18H) |
| j. | 1.90 δ | (s) | (8H) |

Table XX NMR Signals of Pentaerythritol-TDI-HEMA-Eugenol



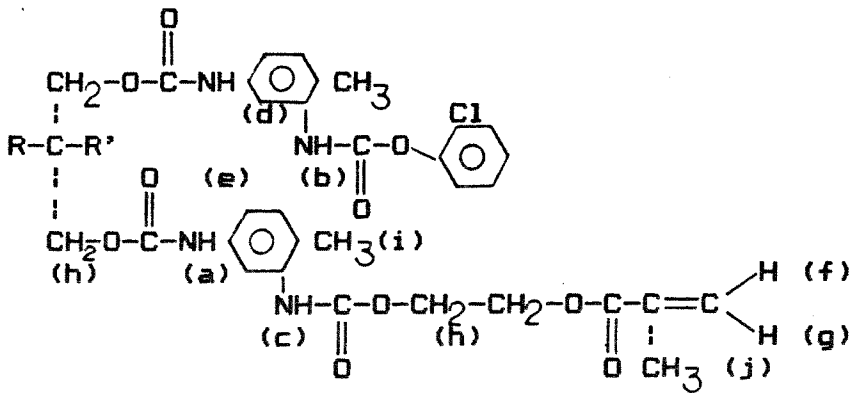
| | | | |
|---|---|---|---|
| a. | 9.20 δ | (s) | (4H) |
| b. | 8.70 δ | (s) | (1.6H) |
| c. | 8.10 δ | (s) | (2.4H) |
| d. | 7.60 δ | (s) | (4H) |
| e. | 7.10 δ | (t) | (13H) |
| f. | 6.80 δ | (s) | (2H) |
| g. | 6.10 δ | (s) | (2.4H) |
| h. | 5.60 δ | (s) | (2.4H) |
| i. | 5.20 δ | (s) | (1.6H) |
| j. | 5.00 δ | (s) | (1.6H) |
| k. | 4.40 δ | (s) | (16H) |
| l. | 3.80 δ | (s) | (6H) |
| m. | 2.20 δ | (d) | (16H) |
| n. | 1.90 δ | (s) | (9H) |

Table XXI NMR Signals of Pentaerythritol-TDI-HEMA-o-Methoxyphenol



| | | | |
|---|---|---|---|
| a. | 9.30 δ | (s) | (4H) |
| b. | 8.80 δ | (s) | (1H) |
| c. | 8.20 δ | (s) | (3H) |
| d. | 7.60 δ | (s) | (5H) |
| e. | 7.00 δ | (d) | (18H) |
| f. | 6.10 δ | (s) | (3H) |
| g. | 5.60 δ | (s) | (3H) |
| h. | 4.30 δ | (s) | (24H) |
| i. | 3.80 δ | (s) | (5H) |
| j. | 2.20 δ | (s) | (20H) |
| k. | 1.90 δ | (s) | (15H) |

Table XXII NMR Signals of Pentaerythritol-TDI-HEMA-o-Chlorophenol



| | | | |
|---|---|---|---|
| a. | 9.30 δ | (s) | (4H) |
| b. | 9.10 δ | (s) | (1H) |
| c. | 8.30 δ | (s) | (3H) |
| d. | 7.70 δ | (s) | (5H) |
| e. | 7.10 δ | (d) | (25H) |
| f. | 6.10 δ | (s) | (3H) |
| g. | 5.60 δ | (s) | (3H) |
| h. | 4.35 δ | (s) | (24H) |
| i. | 2.20 δ | (s) | (20H) |
| j. | 1.90 δ | (s) | (12H) |

Table XXIII Elemental Analysis of Hydroxyhexylmethacrylate :

| | Observed (%) | Theoretical (%) |
|---|---|---|
| C | 63.45 | 64.5 |
| H | 10.09 | 9.67 |

Table XXIV Elemental Analysis of HPMA-TDI-p-Cresol :

| | Observed (%) | Theoretical (%) |
|---|---|---|
| C | 64.76 | 64.77 |
| H | 6.03 | 6.15 |
| N | 9.21 | 6.57 |

Table XXV Elemental Analysis of HPMA-TDI-m-Methoxyphenol :

| | Observed (%) | Theoretical (%) |
|---|---|---|
| C | 62.11 | 62.43 |
| H | 5.97 | 5.92 |
| N | 8.00 | 6.33 |

Table XXVI Elemental Analysis of Pentaerythritol-TDI :

| | Observed (%) | Theoretical (%) |
|---|---|---|
| C | 59.06 | 59.13 |
| H | 4.52 | 4.36 |
| N | 13.73 | 13.46 |

Table XXVII Elemental Analysis of Pentaerythritol-TDI-HEMA-p-Cresol (In four free isocyanate position, 30% being substituted by p-cresol, 70% by HEMA) :

| | Observed (%) | Theoretical (%) |
|---|---|---|
| C | 59.92 | 59.20 |
| H | 5.60 | 5.40 |
| N | 8.44 | 9.22 |

Table XXVIII Elemental Analysis of Pentaerythritol-TDI-HEMA-Eugenol ( In four free isocyanates, 30% being substituted by Eugenol, 70% by HEMA )

| | Observed (%) | Theoretical (%) |
|---|---|---|
| C | 60.04 | 60.10 |
| H | 5.56 | 5.67 |
| N | 8.59 | 8.04 |

Table XXIX Elemental Analysis of Pentaerythritol-TDI-HEMA-o-Methoxyphenol ( In four free isocyanates, 25% being substituted by o-methoxyphenol, 75% by HEMA)

| | Observed (%) | Theoretical (%) |
|---|---|---|
| C | 58.02 | 58.83 |
| H | 5.36 | 5.54 |
| N | 9.90 | 8.32 |

Table XXX Elemental Analysis of Pentaerythritol-TDI-HEMA-o-Chlorophenol ( In four free isocyanates, 20% being substituted by o-Chlorophenol, 80% by HEMA )

| | Observed (%) | Theoretical (%) |
|---|---|---|
| C | 57.77 | 57.74 |
| H | 5.04 | 5.38 |
| N | 9.70 | 8.29 |
| Cl | 1.36 | 2.09 |

Table XXXI Bonding Strength of Pentaerythritol-TDI-HEMA-P-cresol

Filling Material: 75% MMA- 25% PMMA

Setting Time : 48 hours

Period of Storage in Water : 0

Promoter: New NNDMPT

| Sample Number | Boinding Strength (psi) |
|---|---|
| 1 | 1273 |
| 2 | 1160 |
| 3 | 953 |
| 4 | 2277 |
| 5 | 1382 |
| 6 | 1193 |
| 7 | 1783 |
| 8 | 1630 |
| 9 | 2139 |
| 10 | 1288 |
| Average Bonding Strength (psi) = | 1508 |

Table XXXII Bonding Strength of Pentaerythritol-TDI-HEMA-P-cresol

Filling Materia: 75% MMA- 25% PMMA

Setting Time : 48 hours

Period of Storage in Water : 168 hours

Promoter: New NNDMPT

| Sample Number | Bonding Strengdth (psi) |
|---|---|
| 1 | 327 |
| 2 | 233 |
| 3 | 284 |
| 4 | 502 |
| 5 | 364 |
| Average Bonding Strength (psi) = | 342 |

Table XXXIII Bonding Strength of Pentaerythritol-TDI-HEMA-P-cresol

Filling Material: 75% MMA- 25% PMMA

Setting Time : 48 hours

Period of Storage in Water : 240 hours

Promoter: New NNDMPT

| Sample Number | Bonding Strength |
|---|---|
| 1 | 335 |
| 2 | 167 |
| 3 | 175 |
| 4 | 218 |
| Average Bonding Strength (psi) = | 224 |

Table XXXIV Bonding Strength of Pentaerythritol-TDI-HEMA-P-cresol

Filling Material: 75% MMA-25% PMMA

Setting Time : 96 hours

Period of Storage in Water : 168 hours

Promoter: Old NNDMPT

| Sample Number | Bonding Strength |
|---|---|
| 1 | 357 |
| 2 | 371 |
| 3 | 335 |
| 4 | 895 |
| 5 | 327 |
| 6 | 400 |
| Average Bonding Strength (psi) = | 448 |

Table XXXV Bonding Strength of Pentaerythritol-TDI-HEMA-P-cresol

Filling Material: 75% MMA-25% PMMA

Setting Time : 0

Period of Storage in Water : 48 hours

Promoter: Old NNDMPT

| Sample Number | Bonding Strength |
|---|---|
| 1 | 1783 |
| 2 | 1273 |
| 3 | 1288 |
| 4 | 1281 |
| 5 | 2270 |
| 6 | 1302 |
| 7 | 1426 |
| Average Bonding Strength (psi) = | 1518 |

Table XXXVI Bonding Strength of Pentaerythritol-TDI-HEMA-P-cresol

Filling Material: 75% MMA-25% PMMA

Setting Time : 48 hours

Period of Storage in Water : 336 hours

Promoter: Old NNDMPT

| Sample Number | Bonding Strength |
|---|---|
| 1 | 982 |
| 2 | 1921 |
| 3 | 895 |
| Average Bonding Strength (psi) = | 1266 |

Table XXXVII Bonding Strength of Pentaerythritol-TDI-HEMA-o-MethoxyPhenol

Filling Material: 75% MMA- 25% PMMA

Setting Time : 0

Period of Storage kin Water : 960 hours

Promoter: Old NNDMPT

| Sample Number | Bonding Strength (psi) |
|---|---|
| 1 | 815 |
| 2 | 880 |
| 3 | 407 |
| 4 | 233 |
| Average Bonding Strength (psi) = | 584 |

Table XXXVIII Bonding Strength of Pentaerythritol-TDI-HEMA-o-Methoxyphenol

Filling Material: 75% MMA-25% PMMA

Setting Time : 0

Period of Storage in Water : 984 Hours

Promoter: Old NNDMPT

| Sample Number | Bonding Strength (psi) |
|---|---|
| 1 | 102 |
| 2 | 160 |
| 3 | 306 |
| 4 | 153 |
| 5 | 182 |
| Average Bonding Strength (psi) = | 181 |

Table XXXIX Bonding Strength of Pentaerythritol-TDI-HEMA-o-Chlorophenol

Filling Material: 75% MMA-25% PMMA

Setting Time : 0

Period of Storage in Water : 24 hours

Promoter: Old NNDMPT

| Sample Number | Bonding Strength (psi) |
|---|---|
| 1 | 1499 |
| 2 | 2619 |
| 3 | 2466 |
| 4 | 2648 |
| 5 | 2474 |
| average Bonding Strength (psi) = | 2341 |

Table XXXX Bonding Strength of Pentaerythritol-TDI-HEMA-o-Chlorophenol

filling Material: 75% MMA-25% PMMA

Setting Time : 0

Period of Storage in Water : 48 hours

SPromoter: Old NNDMPT

| Sample Number | Bonding Strength (psi) |
|---|---|
| 1 | 2081 |
| 2 | 888 |
| 3 | 1593 |
| Average Bonding Strength (psi) = | 1521 |

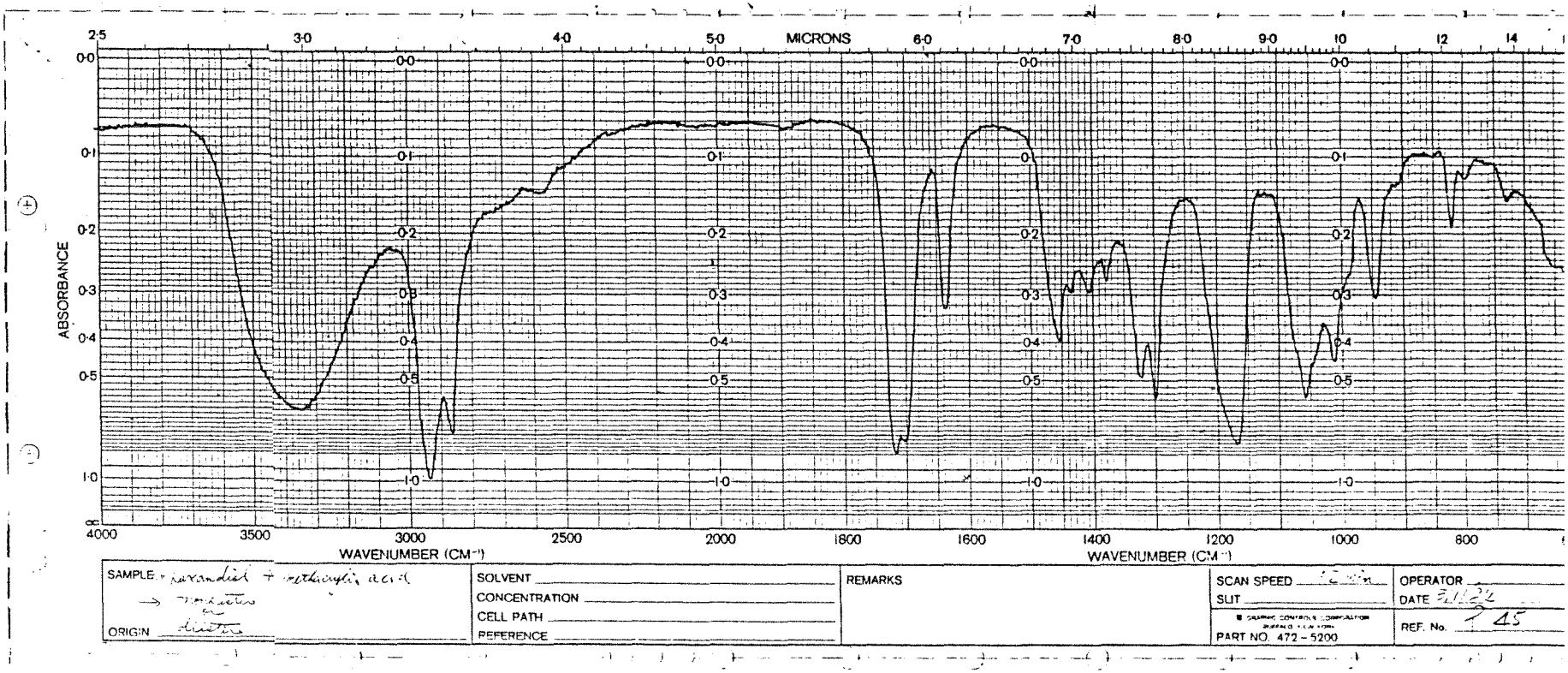



Fig.1 IR Spectra of Hydroxyhexylmethacrylate

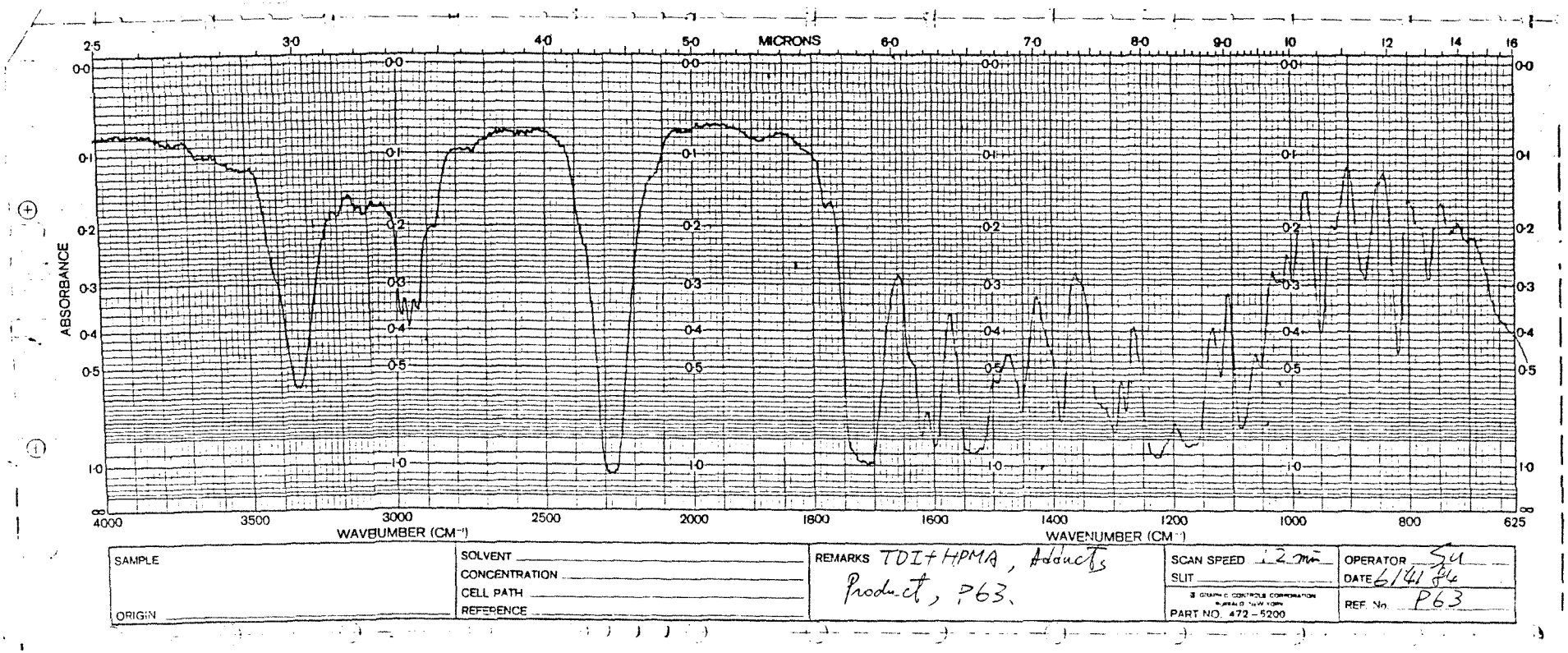



Fig. 2 IR Spectra of HPMA-TDI

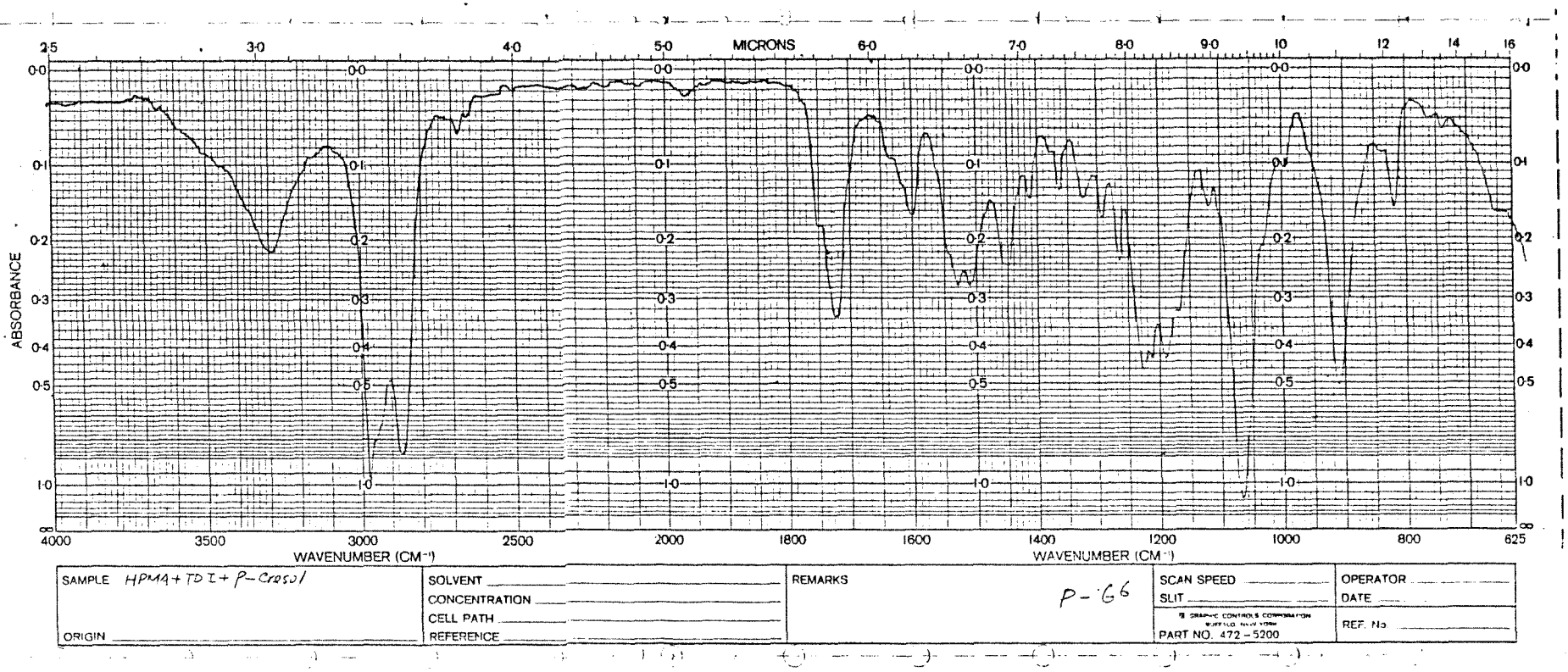



Fig. 3 IR Spectra of HPMA-TDI-p-Cresol

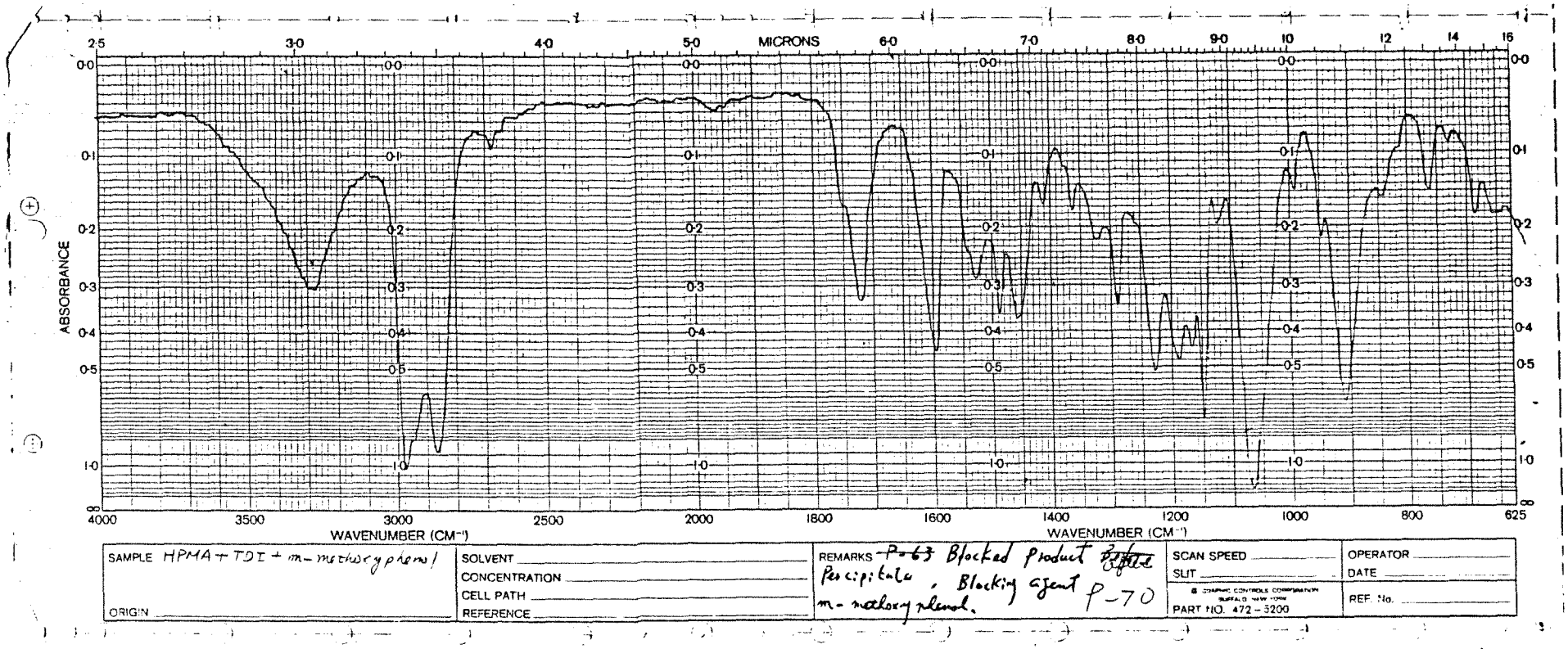



Fig. 4 IR Spectra of HPMA-TDI-m-Methoxyphenol

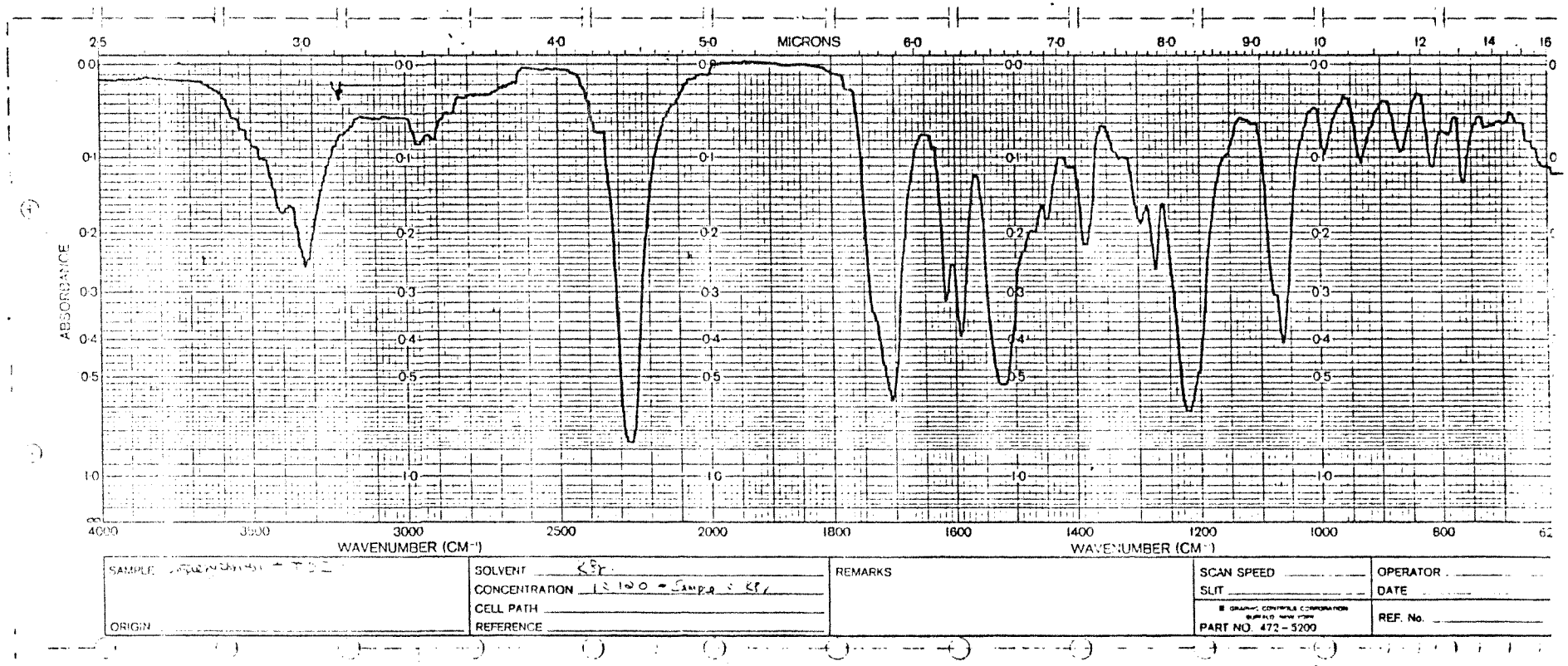



Fig. 5 IR Spectra of Pentaerythritol-TDI

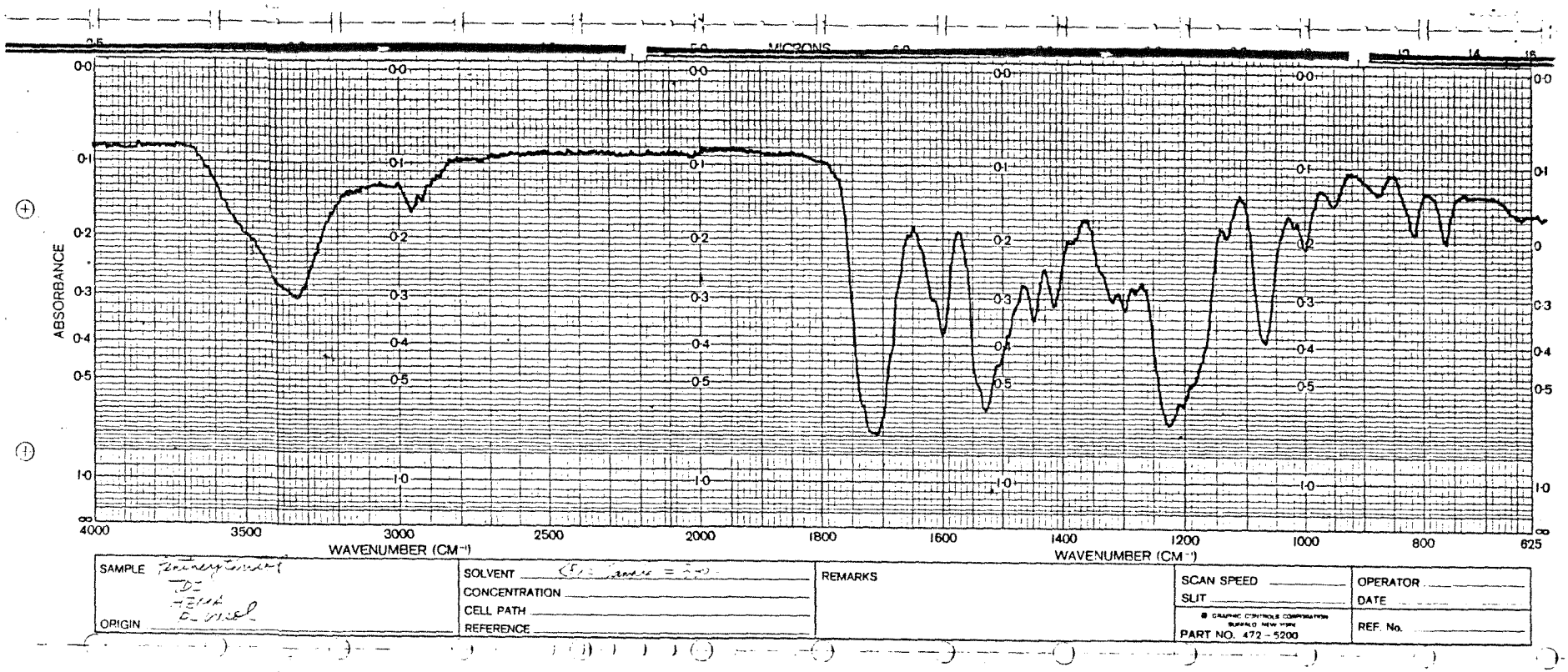



Fig. 6 IR Spectra of Pentaerythritol-TDI-HEMA-p-Cresol

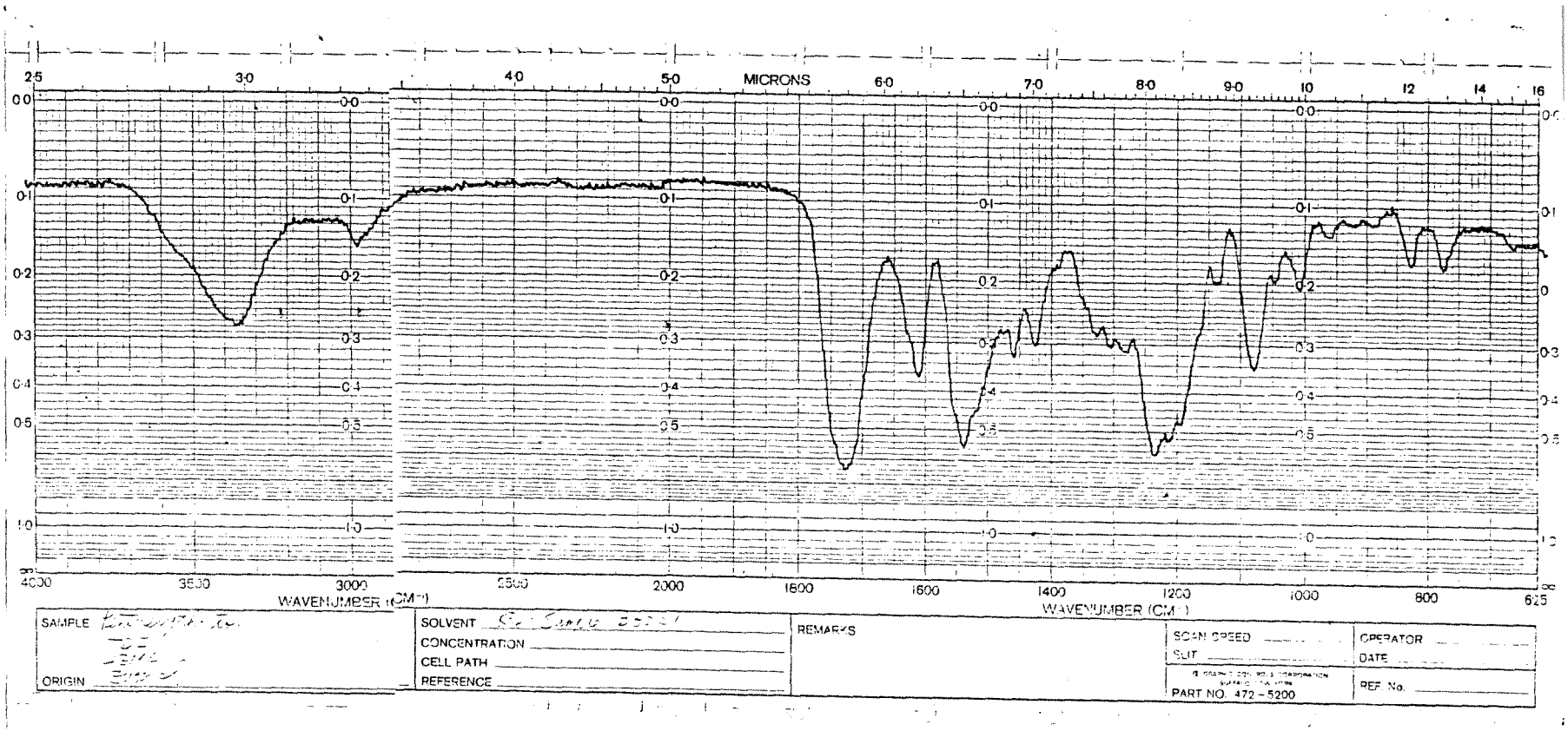



Fig. 7 IR Spectra of Pentaerythritol-TDI-HEMA-Eugenol

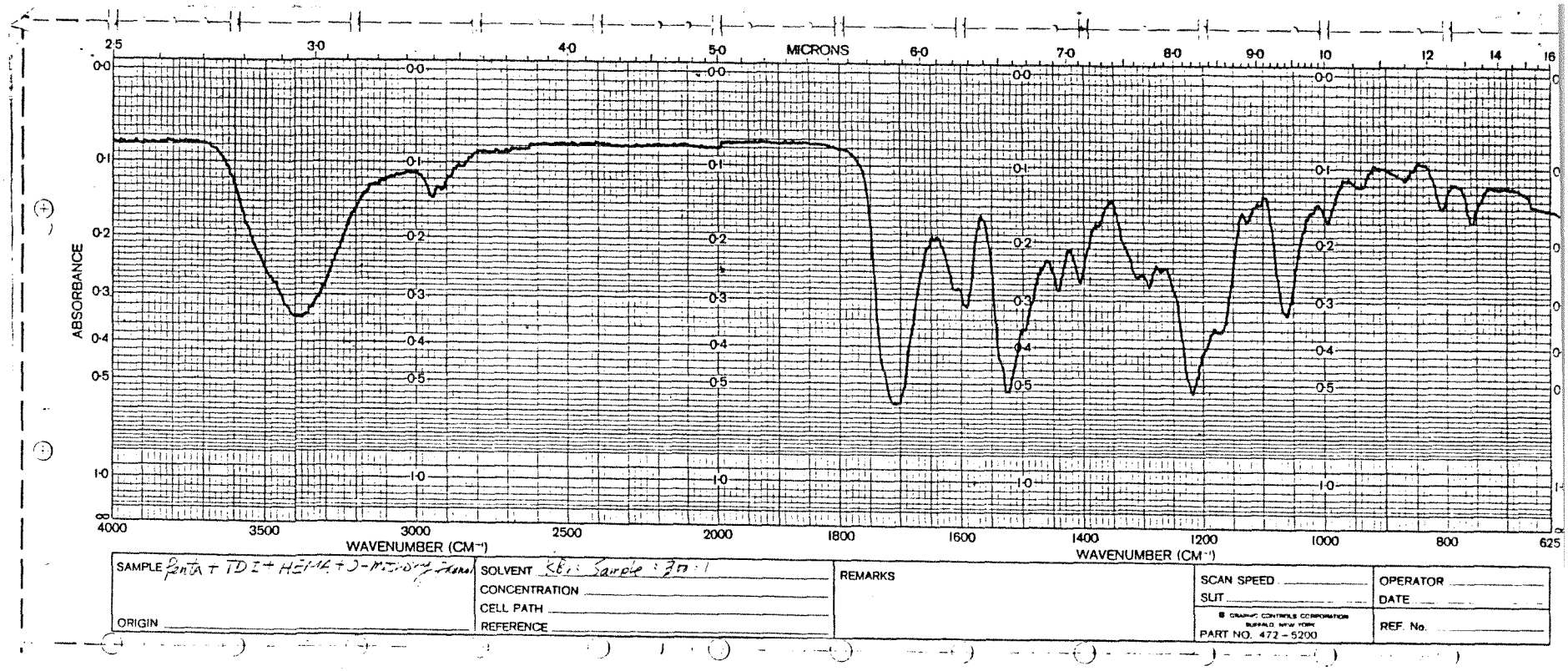



Fig. 8 IR Spectra of Pentaerythritol-TDI-HEMA-o-Methoxyphenol

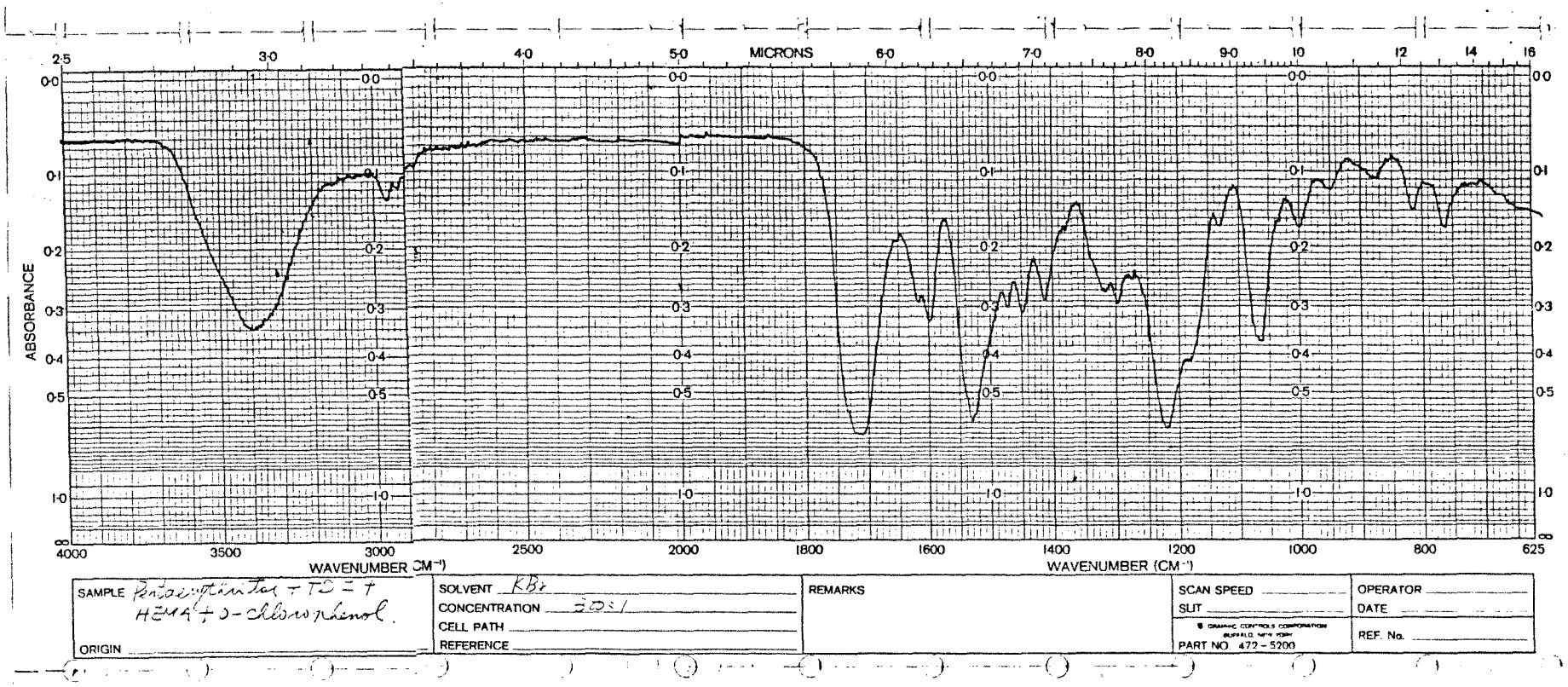



Fig. 9 IR Spectra of Pentaerythritol-TDI-HEMA-o-Chlorophenol

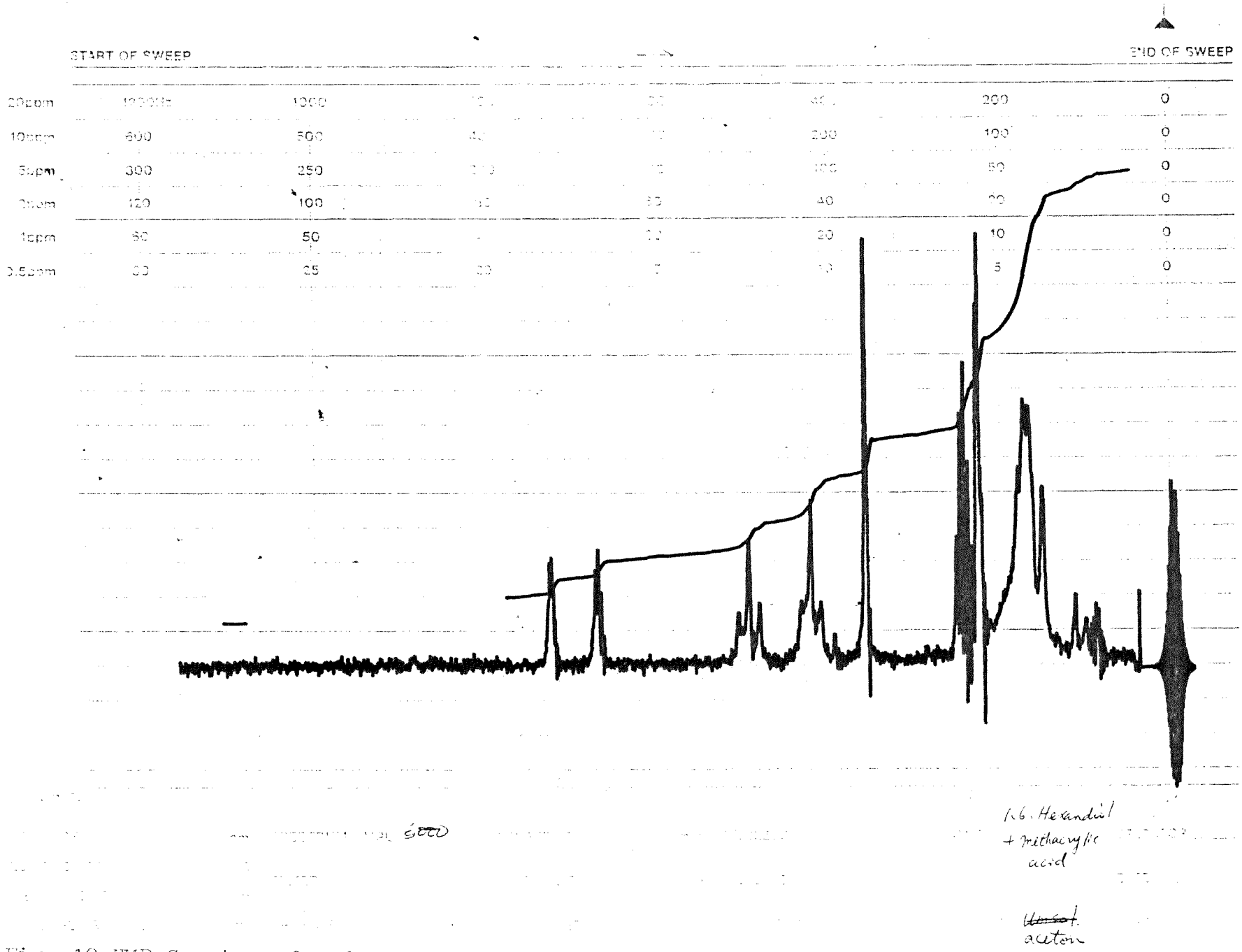



Fig. 10 NMR Spectra of Hydroxyhexylmethacrylate

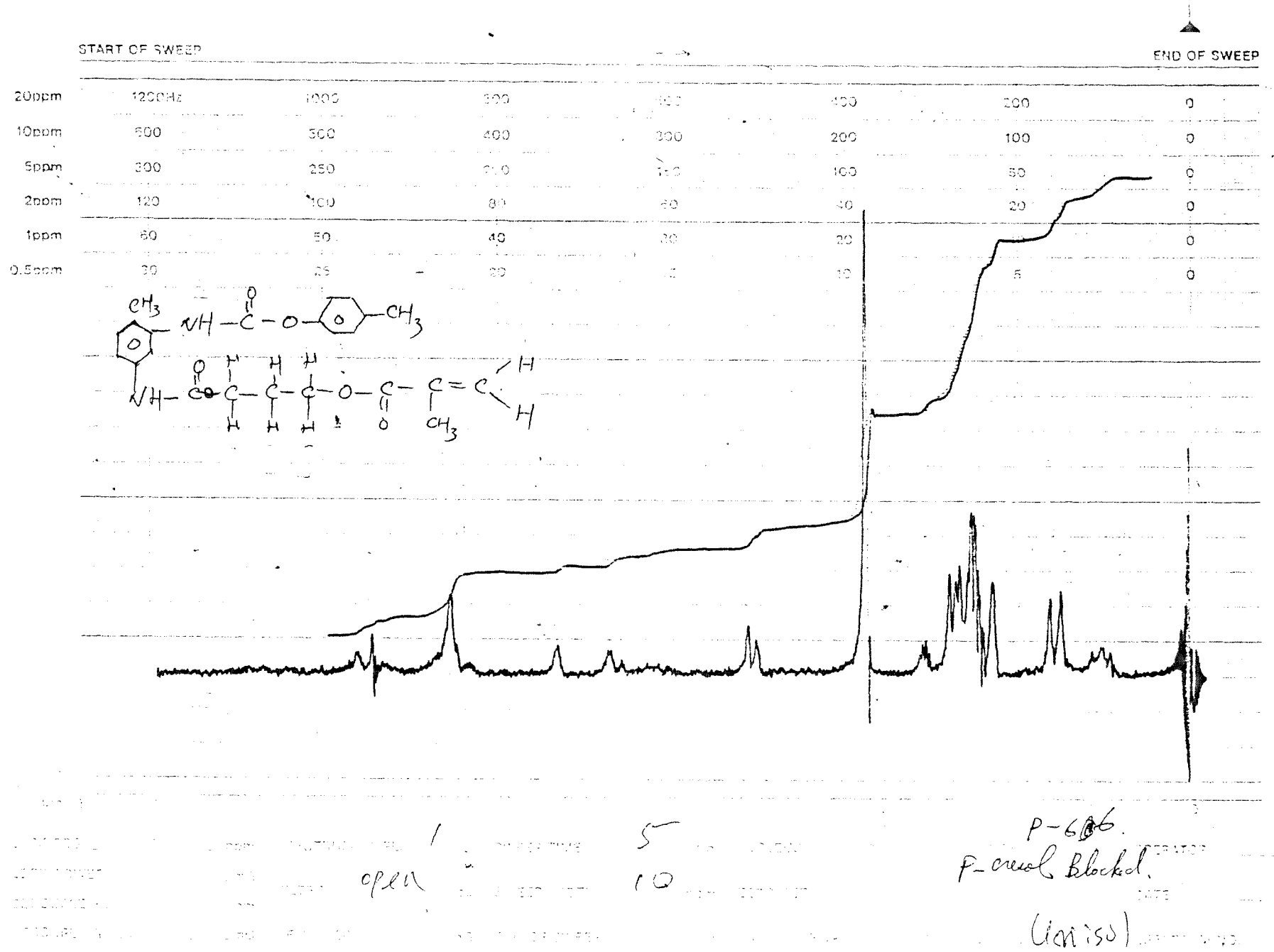



Fig. 11 NMR Spectra of HPMA-TDI-p-Cresol

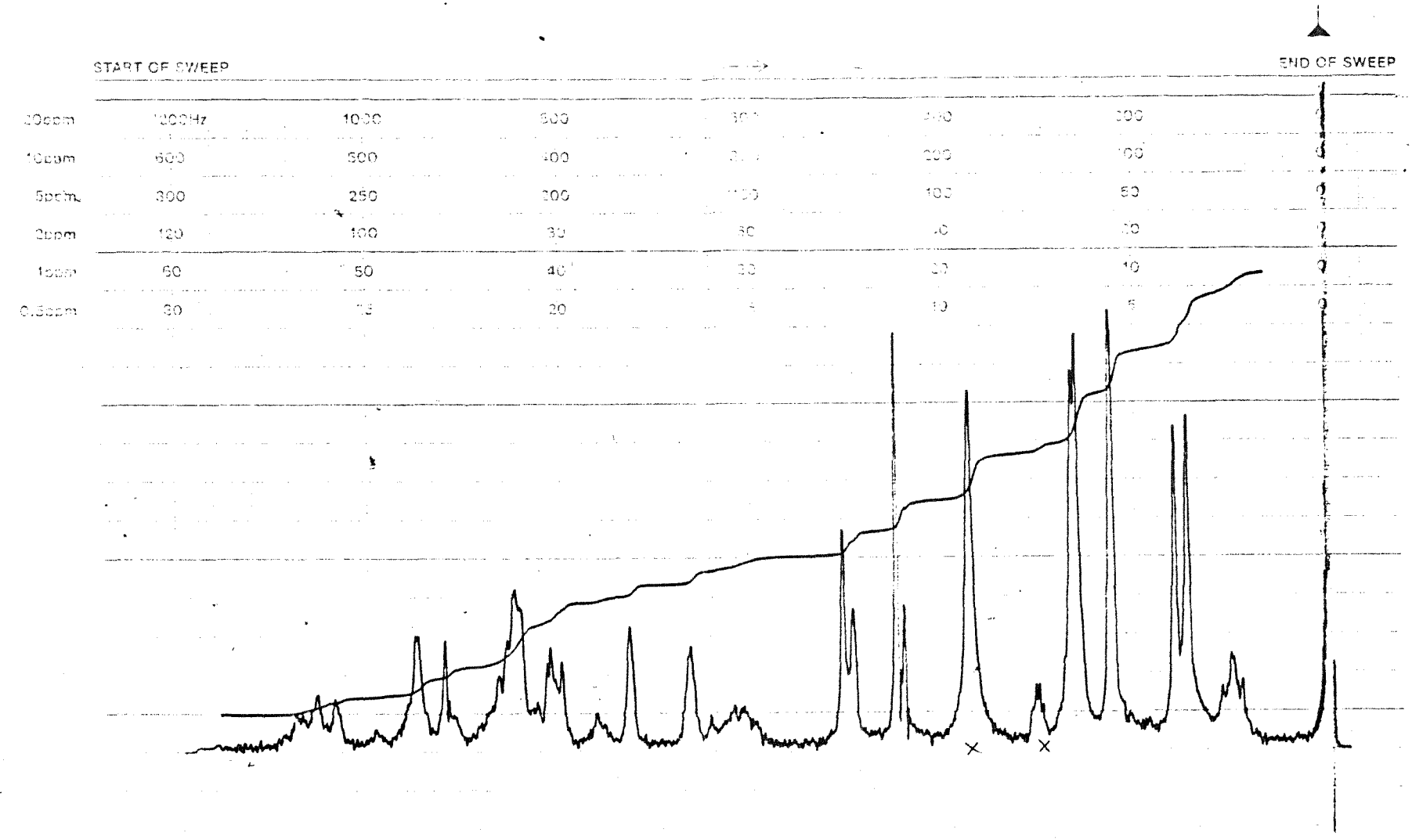
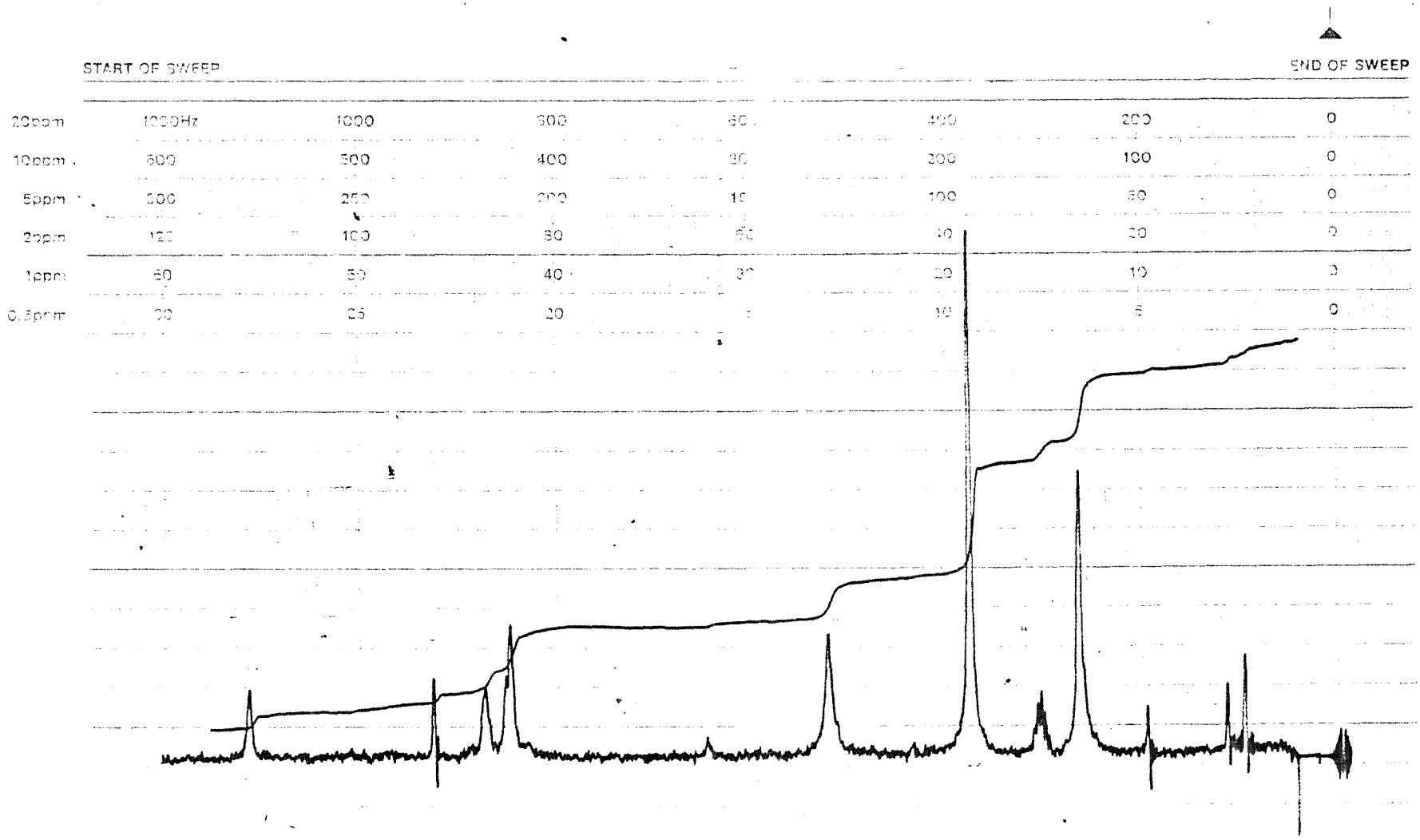



Fig. 12 NMR Spectra of HPMA-TDI-m-Methoxyphenol




0 4000 5
.01 1.0
105 10
.05 0
TMS
Pentaerythritol + TDI
Unisol
7/10/74

Fig. 13 NMR Spectra of Pentaerythritol-TDI

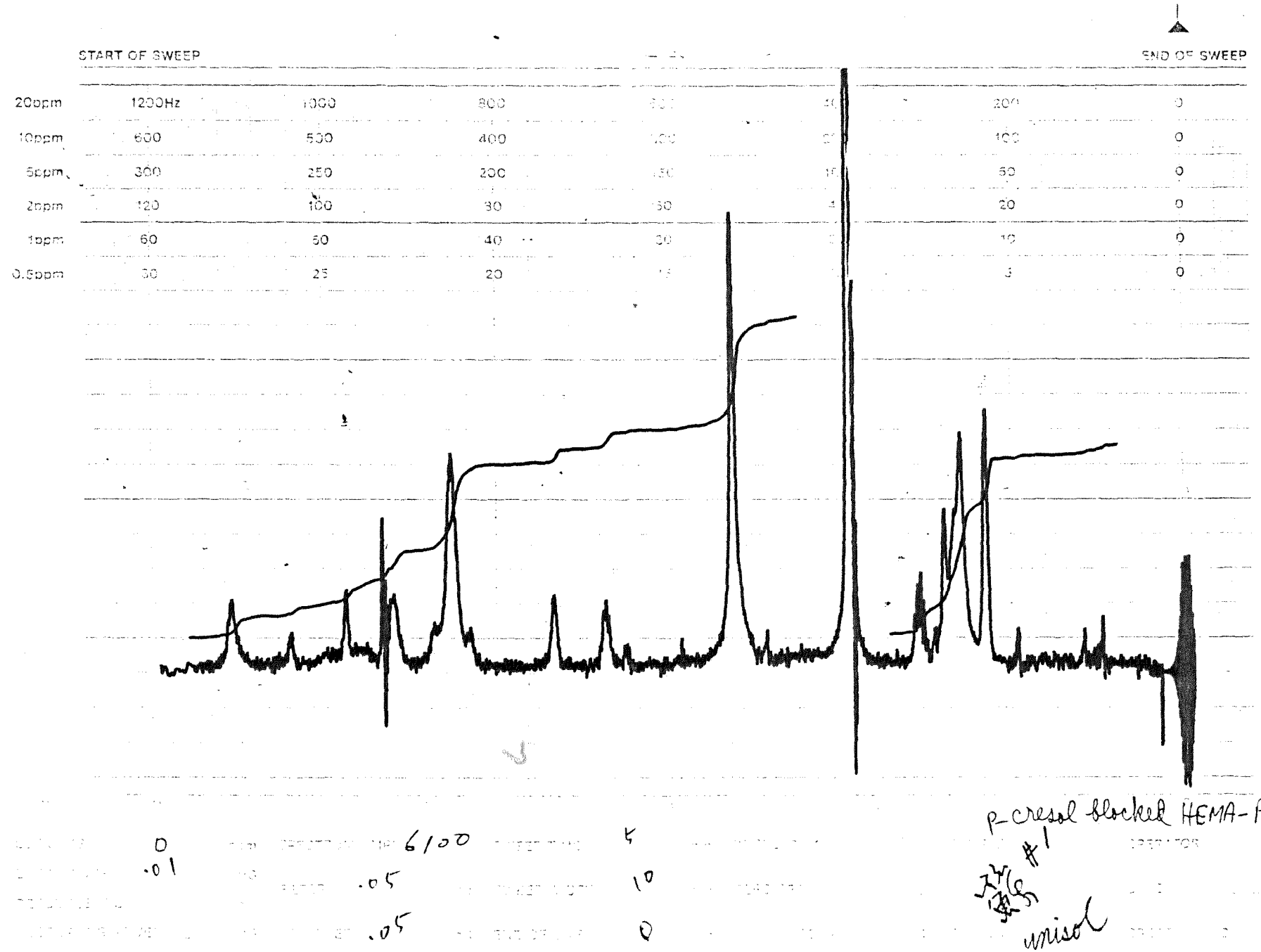



Fig. 14 NMR Spectra of Pentaerythritol-TDI-HEMA-p-Cresol

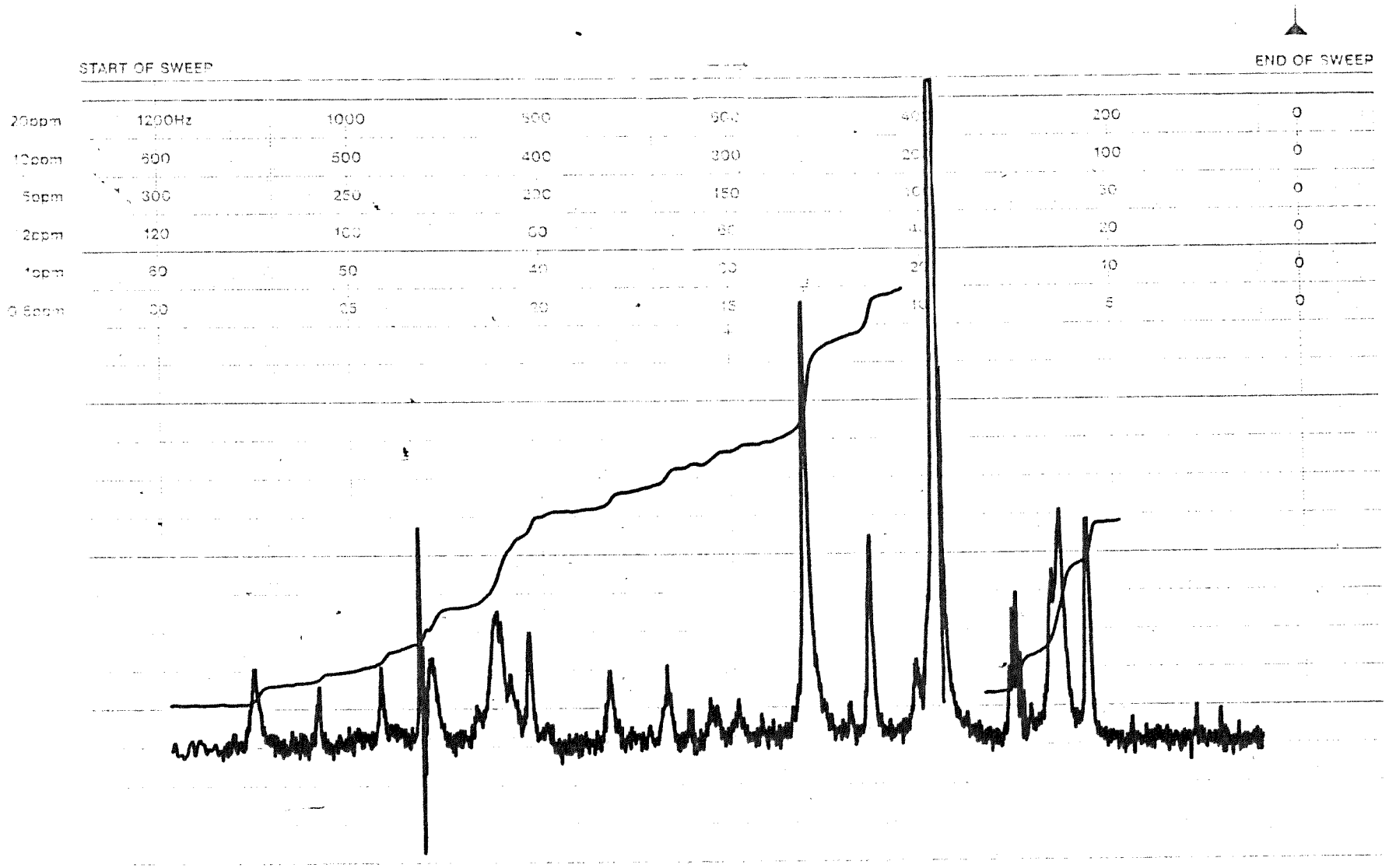



Fig. 15 NMR Spectra of Pentaerythritol-TDI-HEMA-Eugenol

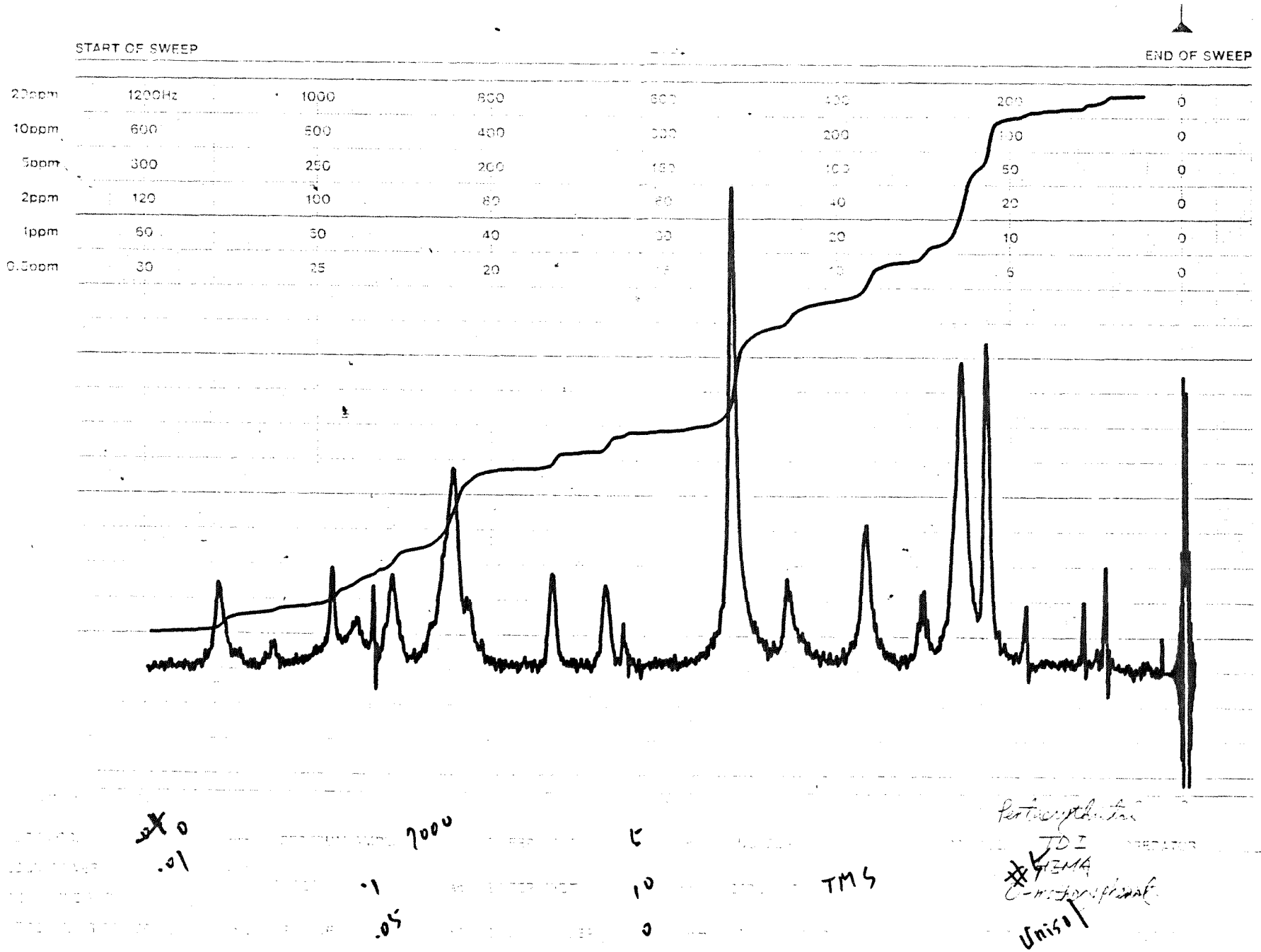



Fig. 16 NMR Spectra of Pentaerythritol-TDI-HEMA-o-Methoxyphenol

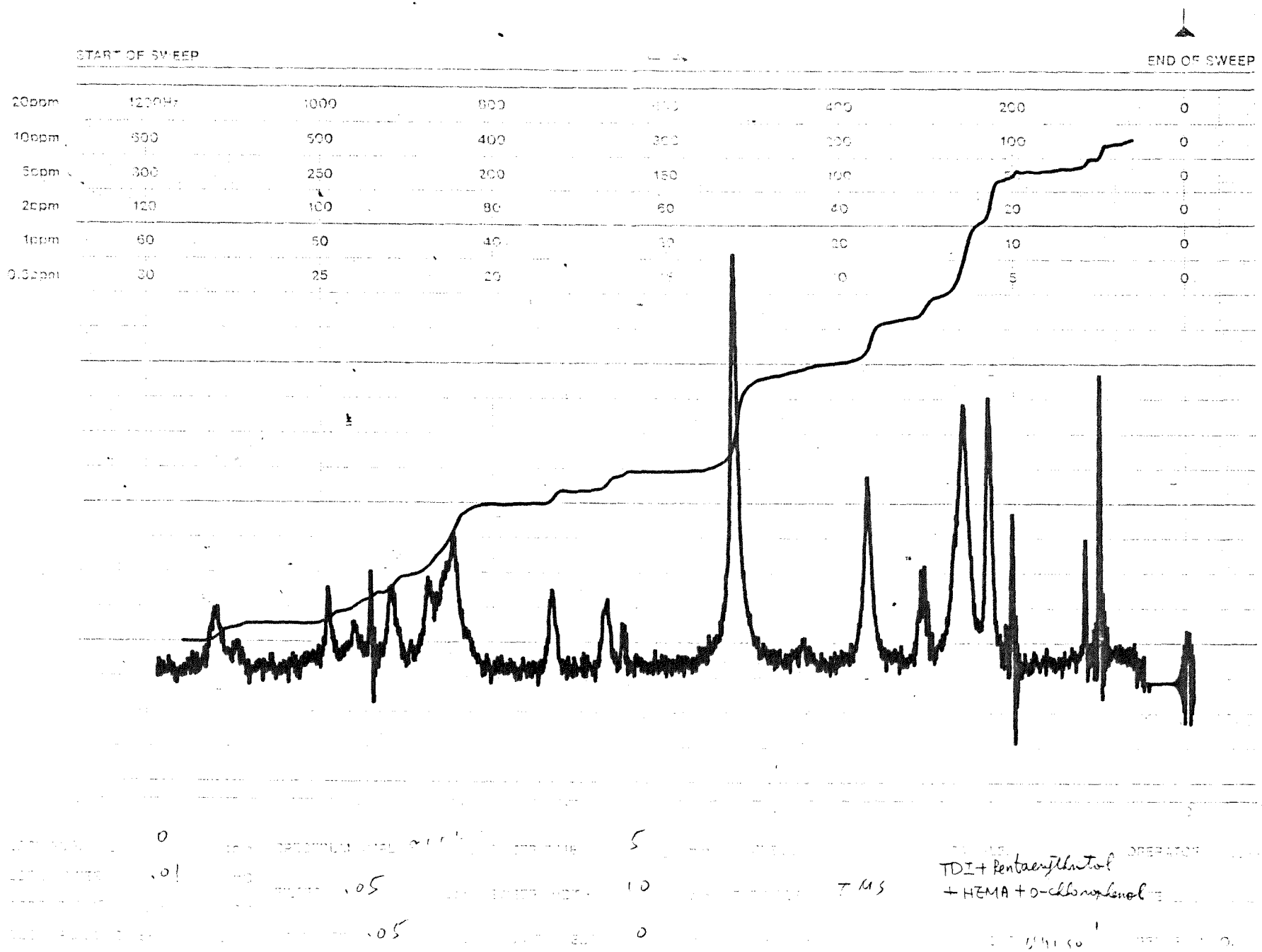



Fig. 17 NMR Spectra of Pentaerythritol-TDI-HEMA-o-Chlorophenol

## RESULT AND DISCUSSION

The use of TMP-TDI adduct as the main body of dental adhesives had been developed completely in previous attempts. There are three hydroxyl groups in TMP available for reaction with isocyanate groups in TDI. After reacting with hydroxyl groups in TMP, it was expected that an unreacted isocyanate group was left on each TDI for the next step, the reaction with blocking agent or HEMA. Therefore, three opportunities for bonding exist in the dental adhesive molecules, most probably two bonds to dentin and one to filling material or vice versa.

In order to maximize both the bonding to dentin and copolymerization to the resin, a compound with four hydroxyl groups, pentaerythritol, was selected in this study as the main body of the dental adhesives.

The chemical principle for the reaction of pentaerythritol and TDI is the same as that of TMP-TDI, but the system for preparing pentaerythritol-TDI adduct is quite different from that of TMP-TDI. In the case of pentaerythritol-TDI adduct, the powdered pentaerythritol was directly added to the solution of TDI and p-dioxane instead of dissolving into dry THF solvent. Moreover, a polar solvent, p-dioxane, was used to dissolve the pentaerythritol-TDI adduct.



As the previous study found, the TDI may participate in the reaction of the ortho as well as the para isocyanate group even though the reactivity ratio of para isocyanate

to ortho isocyanate in TDI is about twelve to one in favor of para isocyanate at room temperature. In this way one TDI could attach to two molecules of pentaerythritol; the other branches pentaerythritol could react with different TDIs at ortho, para, or both sites. This sequence could go on and produce oligomers and/or polymers. Hence the tendency to increase the ortho position reactivity should be reduced as much as possible so that the formation of oligomers and /or polymers can be reduced drastically.

First, the reaction should be maintained below room temperature. It was known[37] that at 90°C para and ortho isocyanate of TDI have the same reactivity. In other words, the relative reactivity of ortho isocyanate would be increased at elevated temperatures. Due to the exothermic behavior of the reaction and the heat evolved by the high speed stirrer the temperature of the reaction tended to rise as high as 45°C. Thus, it is essential to maintain the temperature below room temperature by using a cooling system to depress the tendency of ortho isocyanate reaction.

Secondly, an excess amount of TDI is necessary to permit all the hydroxyl groups in pentaerythritol to react with para isocyanates on TDI molecules. When a molecule of pentaerythritol in contact with the TDI-dioxane solution it would be surrounded by many TDI molecules. Therefore, the hydroxyl groups would have a low probability of reacting with ortho isocyanates in TDI. Certainly, there are still some reactions between pentaerythritol and TDI at ortho

positions; Using an excess of TDI is to minimize the pentaerythritol reaction with the less favorable ortho isocyanates.

In Table XXVI we reported that the result of the element analyses of the pentaerythritol-TDI adduct shows excellent agreement between the theoretical and observed values. Also , the infrared spectrum shows in Fig 5 the presence of a strong peak at 2250 $cm^{-1}$, which indicates that free isocyanates are still available on the pentaerythritol-TDI adduct.

For the use of dental adhesives, the monomers must not only react with dentin but also with the filling material. The desired dental adhesives in this study are that in which two of the four isocyanate groups in pentaerythritol-TDI are reacted with HEMA,the other two with blocking agents Therefore, equal molar quantities of HEMA and blocking agent, were used to react the pentaerythritol-TDI adduct; both compounds were introduced simultaneously. HEMA contains aliphatic hydroxyl group, therefore, reacts more rapidly with the free isocyanate groups than do the phenolic blocking agents such as p-cresol, o-chlorophenol etc. Thus, an even larger amount of phenolic blocking agent was used in the reaction in order to increase the chance of blocking agents reacting with pentaerythritol-TDI adduct. At the beginning, 6% excess of HEMA and about 20% excess of phenolic blocking agents were added to the blocking reaction. After 7 days, the IR showed a peak for isocyanate functional group indica-

ting that the reaction was incomplete. Farfhad's[33] study showed that only 6% excess HEMA is sufficient to block a TMP-TDI in seven days. Therefore, the delay in our blocking reaction could be due only to the insufficient reactivity of blocking agents. Thus, after seven days more phenolic blocking agents were added, which resulted in complete reaction.

Blocking by para cresol and HEMA took nine days. For o-methoxyphenol-HEMA, eugenol-HEMA and o-chlorophenol-HEMA the reaction took 11, 13, and 19 days, respectively. It can be concluded that, in general, increasing the percentage of excess blocking agent results in shorter time for the complete blocking reaction.

Temperature is also a very important factor in the blocking reactions. The experiment shows that the blocking temperature for p-cresol-HEMA is 50°C. However, if this temperature is applied to each of the preparations o-methoxyphenol-HEMA, eugenol-HEMA and o-chlorophenol-HEMA, there were still observed considerable peaks for the isocyanate functional group at 2250 $cm^{-1}$ even after 20 days. In fact, it is well known that the blocking reaction is a reversible reaction; the forward reaction is a blocking reaction and reverse one is a deblocking reaction.

$$ArN{=}C{=}O \; + \; BH \underset{k2}{\overset{k1}{\rightleftharpoons}} ArNH{-}C{-}B \quad (\text{with } \| \text{ O})$$

According to the kinectics, the rate of reaction is

proportional to rate constant and concentration. At the beginning, the concentration of blocked product was almost equal to zero, the net reaction is favorable the forward reaction. But after the reaction proceeds for some time, the concentration of blocked product increases, the tendency in favor of forward reaction would gradually change to equilibrium between the forward and reverse reaction. At equilibrium the forward and reverse reaction rates are equal.

At lower temperatures the forward reaction was much faster than the reverse one , $k_1 >> k_2$. As temperature rises, however, the rate constant of reverse reaction would gradually approach that of forward reaction. Therefore, the equilibrium constant, K, becomes smaller and smaller. That is, there is no improvement in the yield of the blocking reaction. Thus, the reverse reaction becomes more obvious so that the absence of free isocyanate peak at 2250 $cm^{-1}$ would never be obtained. In this study, much of time was spent on the search of optimum blocking temperatures. For o-chlorophenol, in general, the blocking reaction must be below 40°C. for the other two cases, eugenol-HEMA and o-methoxyphenol-HEMA, the best temperature was found to be 45°C.

From the temperature data, it is learned that the order of the blocked product stability is p-cresol > eugenol , o-methoxyphenol > o-chlorophenol. If required time for completing blocking reaction is taken into consideration, it would be found that o-methoxyphenol adduct is more stable than eugenol adduct.

All these data support the theory that the required time and temperature for completing the blocking reaction largely depend upon steric and electronic effects in the phenol.

There is no doubt that p-cresol is more reactive to isocyanate groups than o-chlorophenol is, because the methyl group in p-cresol is an electron-releasing factor, unlike the case of electron-withdrawing chlorine in o-chlorophenol. For the methyl group in p-cresol and the methoxy group in o-methoxyphenol from the view point of electron releasing effect, there is no significant difference between both components. But if the steric effect is taken into consideration, it becomes obvious that the para-position substituted compound is more reactive than the ortho-position. Theoretically, the alkene group in eugenol decreases the reactivity of eugenol, but the alkane group can make up for the reduction of reactivity due to alkene group. Hence, it was expected that the reactivity of eugenol and o-methoxyphenol would be almost the same. In fact, the o-methoxyphenol blocked the pentaerythritol-TDI adduct more easily than eugenol did.

Tables XXIII-XXX refer to the elemental analysis for each monomer being made in this study. It can be seen from these tables that the observed values do not agree perfectly with the theoretical values for 50% HEMA and 50% blocking agent. Instead, the observed values match the theoretical values, e.g. for p-cresol, 70% HEMA and 30% p-cresol. In

addition, the NMR spectrum (Fig 10-17) also support the elemental calculations in Table XXIII and XXX. For example, in the case of o-methoxyphenol, the result of the integration of methoxy peak in o-methoxy phenol is about one third of the integration of methyl peak in HEMA. This proves the substitution of o-methoxyphenol is one third of the substitution of HEMA, 25% o-methoxyphenol and 75% HEMA as shown on Table XXIX.

A dental adhesive with 70% HEMA and 30% p-cresol attached to four isocyanate groups, for example, means 2.8 positions were attacked by HEMA and 1.2 positions were attacked by p-cresol. From these numbers, it can be assumed that the final monomers being obtained in this study could be a mixture of the following five monomers.

1. all four isocyanates of the adduct react with HEMA molecules.
2. all four isocyanates of the adduct react with the phenolic blocking agent molecules.
3. Three isocyanates of the adduct react with HEMA molecule and the fourth isocyanate reacts with the phenolic blocking agent.
4. Three isocyanates of the adduct react with phenolic blocking agents while the fourth isocyanate reacts with HEMA molecules.
5. Two isocyanates of the adduct react with HEMA molecules while the other two isocyanates react with phenolic blocking agent.

The monomers prepared through this work are intended for suitable adhesive tests. Slices of human teeth were obtained from the clinics of the New Jersey Dental School. As the distance from the tooth surface to the pulp increases the protein content increases. The slices of teeth cutted from the same tooth may have different protein contents. Generally, the tooth slices with a larger amount of protein would have a stronger bonding strength. In our testing, samples were prepared without considering the factor of different protein contents. The testing results are shown in Table XXXI-XXXX. The result on each table indicates a range of values in bonding strength decreases with the increase in reacting time of the sample in water. It suggests that these results may be due to the lack of strength of the dental collagen or the presence of water that reacts with the deblocked isocyanate groups. Samples having longer setting times show a stronger bonding strength by evidenced in the results shown on Table XXXII and XXXIV. However, the bonding strengths shown on Table XXXIII and XXXVI seem unrealistic because the bonding strength of the sample stored in water for 336 hours is stronger than that of stored for 240 hour. In fact, the testing results shown in Table XXXI-XXXIII were obtained from the specimen that were via a new batch of NNDMPT. As expected, the monomer blocked by o-chlorophenol has a stronger bonding strength than of blocked by p-cresol and the o-chlorophenol blocking monomers are easier to be deblocked to release more free isocyanate groups.

In fact, we found that there are two main influencing factors on bonding strength. One is the freshness of PMMA-MMA dough. the other is the homogenity of the dough. The PMMA-MMA must keep under nitrogen atmosphere and stored in refrigerator before use it; otherwise it will turn hard due to polymerization and becomes impossible to be applied to the dental adhesive layer coated on the dentin. Even if the dough prepared from partially polymerized PMMA-MMA, the bonding strength are still low. Therefore, we think the freshness and through mixing of the dough in a short time are very important. The degree of polymerization is a function of reaction time. At longer time there is less doubles bonds in PMMA-MMA mixture to react with the HEMA double bonds in the adhesives. As a result, the bonding is weakened. Furthermore, as the degree of polymerization of PMMA-MMA mixture increases, the viscosity of the mixture also increases. the increase in viscosity makes it rather diffcult to stir and consequently results in a non uniform mixture.

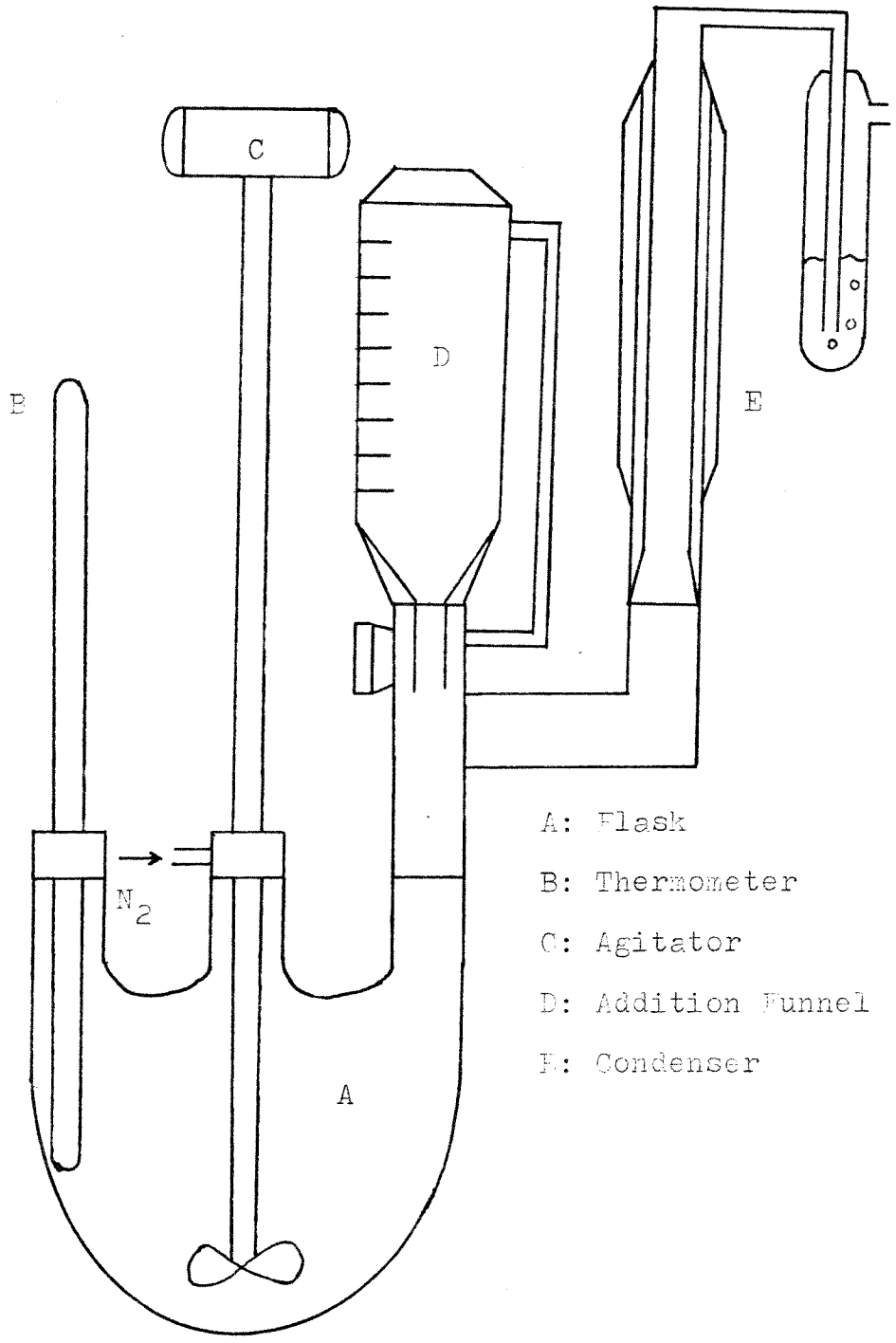
The increase in bonding strength for o-chlorophenol and p-cresol is a significant improvement over the previous studies. It believed that a more hydrophobic adhesive would be less resistant to degradation by water. Therefore, we prepared hydroxyhexylmethacrylate in order to eventually prepare blocked isocyanates containing phenols and a more hydrophobic vinyl monomer

# CONCLUSION

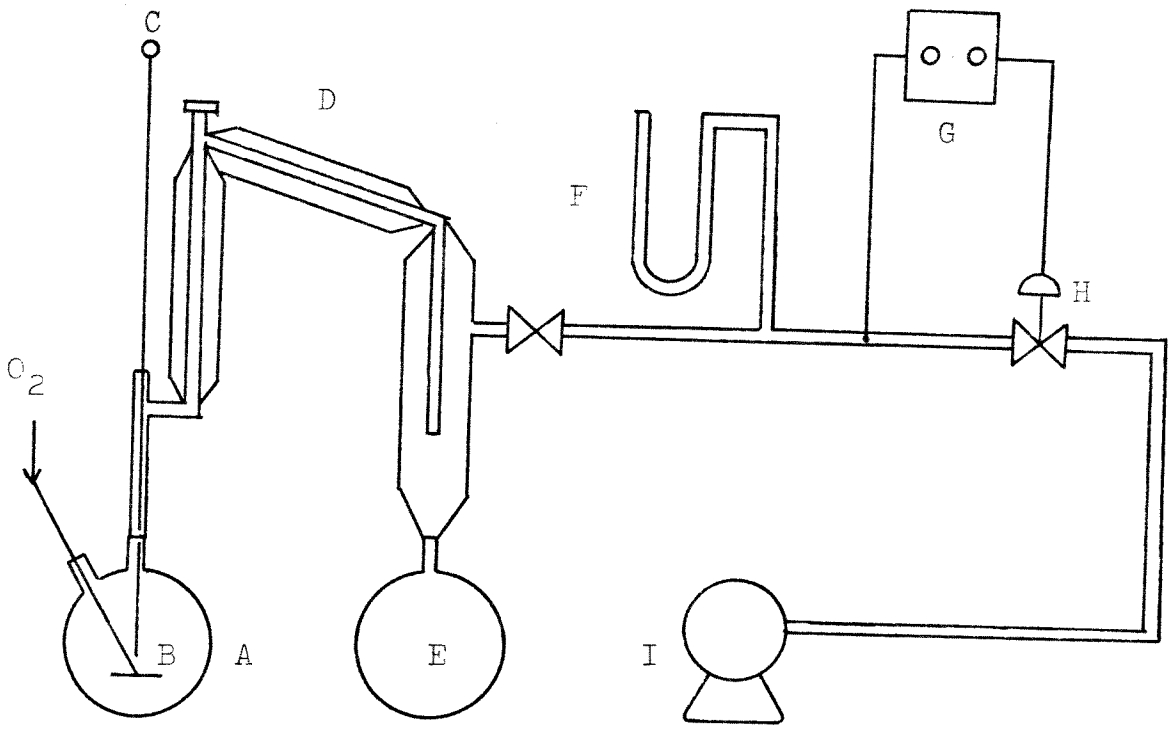
Although the dental adhesive made in this study was only with 20% o-chlorophenol, rather than the expected 50% o-chlorophenol, an impressive mean bonding strength of 2400 psi was obtained. It is believed that a dental adhesive with 50% o-chlorophenol substitution will greatly increase the bonding strength, because it increases the chance of adhension by a factor of two. In the future study, a dental adhesives with 50% o-chlorophenol would be very desirable. After the bonded specimens were stored in water, tensile loads decreased significantly. As Braden's work[53] stated, water can diffuse into acrylic resin and react with isocyanate groups in the dental adhesive to destory dimensional stability and reduce the bonding strength. Although the application of ethylene glycol dimethacrylate as cross linking agent was not successful, it is worth trying to find other cross linking agents, which will creat a three-dimensional polymer.

The significant accomplishments of this research should be followed by a methodical research to establish the mechanism and limits of the capability of these new dental adhesives.

## APPENDIX A. The Equipment Set Up For Preparation of The Pentaerythritol-TDI Adduct



## APPENDIX B. The Equipment Set Up For Preparation of The Hydroxyhexyl Methacrylate




A: Resin Kettle

B: Gas Bubbler

C: Thermometer

D: Condenser

E: Water Collecting Flask

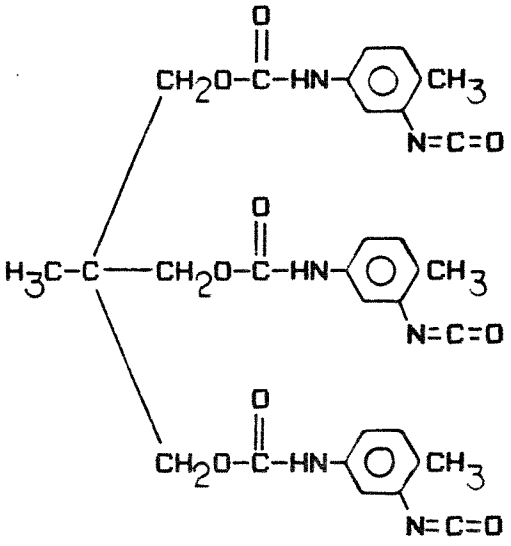
F: Vacuum Indicator

G: Regulator

H: Control Valve

I: Vacuum Pump

APPENDIX C. The Structure of TMP-TDI



# ABBREVIATION

DBTDL: Dibutyltin Dilaurate

HEMA: 2-Hydroxy Ethyl Methacrylate

HPMA: 2-Hydroxy Propyl Methacrylate

KBr: Potassium Bromide

MMA: Methyl Methacrylate

NNDMPT: N,N-dimethyl-p-Toluidine

PMMA: Poly Methyl Methacrylate

TDI: 2,4 Toluene Diisocyanate

THF: Tetrahydrofuran

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