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ABSTRACT

Title of Thesis: Synthesis of
Trimethylolpropane-Tolylene-2,4-diisocyanate Adduct
And Its Blocked Monomers

Farhad Forohar, Master of Science in Engineering Science, 1984

Thesis directed by: Professor W. H. Snyder and Professor David Kristol

A trimethylolpropane adduct of tolylene-2,4-diisocyanate (TMP-TDI) was prepared by reaction in a heterogeneous solvent system. The isocyanate functional groups of the TMP-TDI adduct were blocked with the following blocking agents: p-cresol, eugenol, o-chlorophenol, and one to one mole ratio of mixtures of 2-hydroxyethyl methacrylate (HEMA) and each of the three preceding blocking agents. A sample of TMP-TDI adduct blocked with only HEMA was also prepared. The products were characterized by melting point, infrared spectroscopy, and elemental analysis. Monomers of TMP-TDI blocked with 50% HEMA and 50% blocking agents may be very useful as dental restorative materials.

SYNTHESIS OF TRIMETHYLOLPROPANE-TOLYLENE-2,4-DIISOCYANATE ADDUCT AND ITS BLOCKED MONOMERS

by
Farhad Forohar

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 Engineering Science

1984

APPROVAL SHEET

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DEDICATION

This thesis is dedicated in memory of Dr. W. H. Snyder (1929-1983) a researcher and educator and my first research advisor. I shall always remember his kind and loving personality. His courageous fight against the dreaded disease of leukemia, although unsuccesful, was indeed admirable. He was not only a beloved professor but also a good and caring friend.

ACKNOWLEDGEMENT

I would like to express my indebtedness to professor William H. Snyder for his advice pertaining to this thesis while he was alive. I also wish to thank professor David Kristol for his invaluable guidance and kind assistances during the course of this thesis. I am very thankful to Mr. Mohammad Tajalli, Mr. Asghar Tajalli, and Mr. Abolfazl Tabatabaei for their support and encouragement that made this work possible. Special thanks to Dr. George Y. Lei and Dr. Howard Perlmutter for their final corrections of this thesis.

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I. Introduction

A) Objective: This thesis is part of an investigation to develop a polymeric dental adhesive material that would react with the dentin part of the tooth and form a strong covalent bond. A brief description of the constituents of the tooth can be helpful to the overall understanding of this project.

The outer covering of the part of the tooth that is exposed above the gum line is enamel. Enamel is the hardest substance in the human body[1]. The enamel has no blood supply and any decay in the tooth surface will be the result of the hard material-though not as hard as enamel-called dentin, which forms the bulk of the tooth (figure 1).

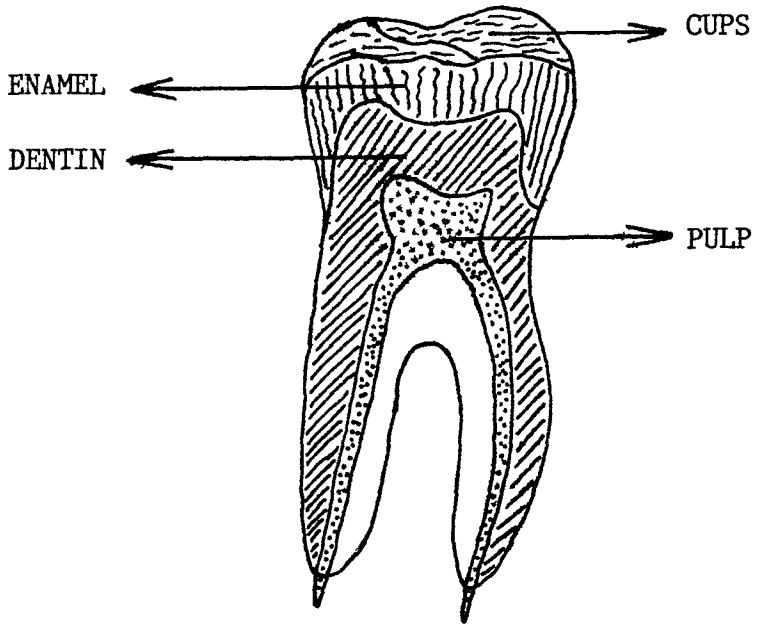


Figure 1. The Structure of A Tooth.

Once decay activity breaks through the hard enamel surface, the

bacteria can attack the dentin and advance more rapidly. If the tooth decay is not stopped at the dentin layer, the disease organisms can enter the pulp chamber where they will multiply quickly and produce an acute inflammation that can spread through the blood vessels to other parts of the body.

Dentin contains approximately 60% hydroxyapatite, 20% collagen fibrils and 20% water. Collagen is a triply stranded protein molecule with a molecular weight of about 300,000[2]. It has a large number of polar groups (OH and amine groups) capable of reacting with the isocyanate functioal groups (NCO) . The constituents of amino acid units of collagen protein which can react with isocyanates through their side chain functional groups are[3]:

Threonine (secondary OH) Hydroxylysine(primary amine and secondary OH)

Serine (primary OH) Arginine (primary amine)

Tyrosine (phenolic OH) Lysine (primary amine)

Hydroxyprolin (secondary OH)

B) Developing Isocyanate Adhesives: The idea behind this project is to prepare isocyanate based molecules that could react with the OH and amine functional groups of the collagen part of dentin and form strong and permanent bonding. Isocyanate molecules are very reactive toward OH and amine groups :

$$RNCO + HO\text{-}COLLAGEN \longrightarrow RNHC(=O)\text{-}O\text{-}COLLAGEN \quad (1)$$

and

$$RNCO + H_2N\text{-}COLLAGEN \longrightarrow RNHC(=O)\text{-}NH\text{-}COLLAGEN \quad (2)$$

A free isocyanate can also readily react with the water molecules present in the mouth and produce undesired products[4]:

$$RNCO + H_2O \longrightarrow RNH_2 + CO_2 \quad (3)$$

The newly formed NH2 can react with another molecule of NCO and produce urea.

$$RNCO + RNH_2 \longrightarrow RNH\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}R \qquad (4)$$

Therfore, one molecule of water can use up two molecules of NCO that were available for reaction with amine groups of dentin. To prevent the reaction of isocyanate with the water the NCO can first be reacted with weakly acidic proton donating substances such as phenols, alcohols, oximes, etc. to form what is known as the "blocked isocyanates". There are several patents and books describing the chemistry and properties of blocked isocyanates[5-9]; the most comperhensive one is a review articale by Zeno W. Wicks Jr[10].

The blocked isocyanates are less reactive toward alcohols and water than the parent isocyanates, and phenol blocked aromatic diisocyanates are reported to be unreactive toward hydroxyl containing materials but reactive toward aliphatic primary and secondary amines at room temparature[11].

The present thesis is directed toward preparing polymeric blocked isocyanate adhesives that can react with the collagen fibrils in dentin and at the same time remain relatively unreactivbe to water. The desired reaction would be :

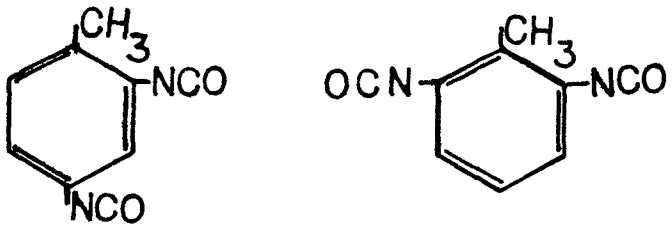
$$ADHESIVE\text{---}\overset{\overset{O}{\|}}{N}HCOR + H_2N\text{---}(Protein) \longrightarrow ADHESIVE\text{-}NHC\overset{\overset{O}{\|}}{N}H\text{---}(Protein) + R\text{-}OH \qquad (5)$$

Where R-OH is the blocking agent.

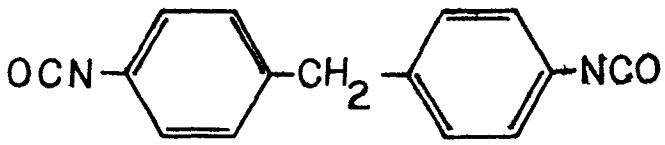
C) General Chemistry of Isocyanates: The isocyanates commonly used in industry are few in number. The most important isocyanates are :

$OCN\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NCO$

Hexamethylene diisocyanate (HDI)



Tolylene-2,4-and 2,6-diisocyantes (TDI)



Diphenylmethane-4,4-diisocyanate (MDI)

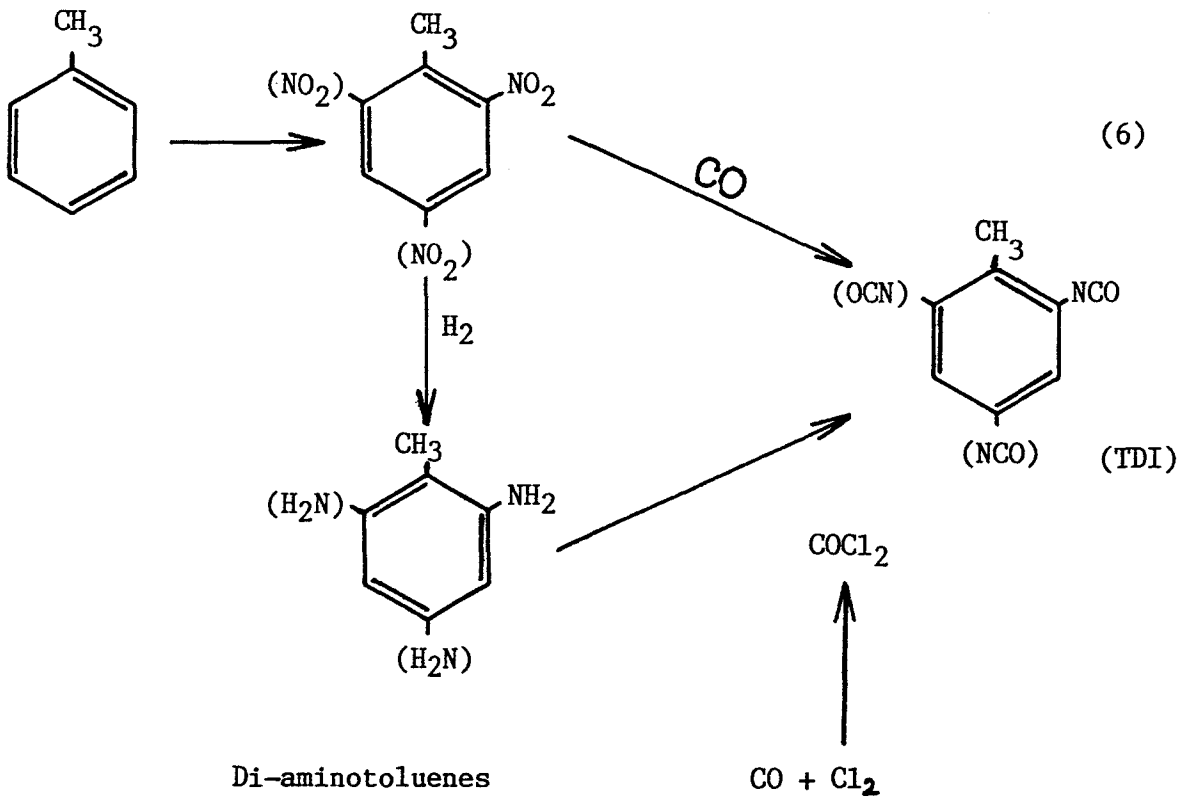
In addition to these well known isocyanates there are three other isocyanates which are worth mentioning. They are naphthylene-1, 5-diisocyanate, para and meta xylylene diisocyanates (XDI), and dicyclohexylmethane diisocyanate (PICM).

D) Tolylene Diisocyanate (TDI): Tolylene diisocyanate is the most widly used diisocyanate in polyurethane industry. It is usually used as a mixture of the 2,4 (80%) and 2,6 (20%) isomers; because this is the least expensive preparation. The -NCO group in the para or 4 position is 8 to 10 times more reactive than the -NCO group in the ortho or 2 position at room temperature[12,13]. At higher temperatures, however, this difference in reactivity decreases so that at about 93°C. the NCO groups in all positions exhibit the same reactivity[14].

There are many papers concerned with the toxic aspects of its use in industry[15-17]. Operators exposed to TDI develope irritation of the eyes, irritation or dryness of the throat, and tightness of the chest. However, Zapp has found the oral toxicity and the skin absorption

toxicity of TDI to be very low[18]. Many different techniques have been employed to determine the quantity of unreacted TDI in polyurethane products; these include gas chromatography and spectrometry[21,22]. There has been a new attempt to produce TDI through direct reaction of nitro compounds with carbon monoxide, in place of the normal conversion of HCl[23,24].

Figure 2. Comparison of Standard and New Routes to TDI



E) Reactions of Isocyanates: The isocyanates undergo two basic reactions:

1- The reaction of isocyanates with compounds containing reactive hydrogen to give addition products.

2- The polymerization of isocyanates,i.e. self-addition.

The addition to the reactive hydrogen compounds are as follows :

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

$$R\text{-}NCO + \acute{R}OH \longrightarrow R\text{-}NH\text{-}CO\text{-}O\acute{R} \quad \text{(Urethane)} \qquad (7)$$

$$R\text{-}NCO + \acute{R}NH \longrightarrow R\text{-}NH\text{-}CO\text{-}NH\acute{R} \quad \text{(Urea)} \qquad (8)$$

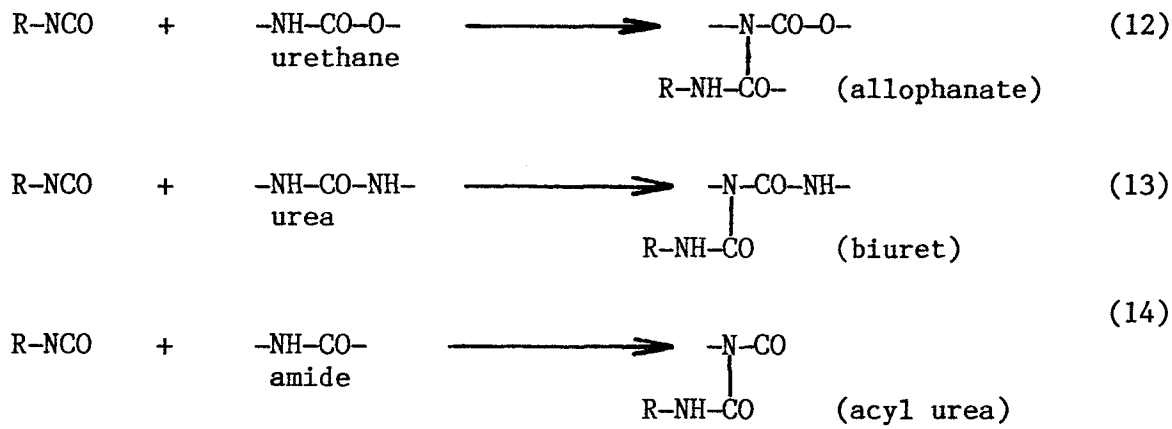
$$R\text{-}NCO + H_2O \longrightarrow R\text{-}NH\text{-}COOH \quad \text{(Carbamic acid)} \qquad (9)$$

Then

$$R\text{-}NH\text{-}COOH \longrightarrow R\text{-}NH_2 + CO_2 \xrightarrow{R\text{-}NCO} R\text{-}NH\text{-}CO\text{-}NHR \quad \text{(Urea)} \qquad (10)$$

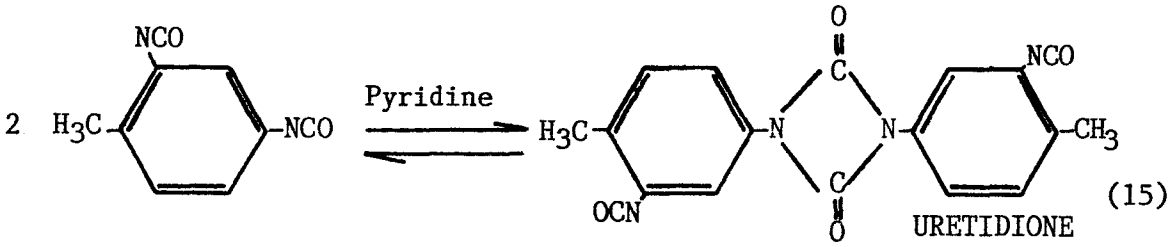
$$R\text{-}NCO + \acute{R}\text{-}COOH \longrightarrow R\text{-}NH\text{-}CO\text{-}O\text{-}CO\text{-}\acute{R} \longrightarrow R\text{-}NH\text{-}CO\text{-}\acute{R} + CO_2 \quad \text{(Amide)} \qquad (11)$$

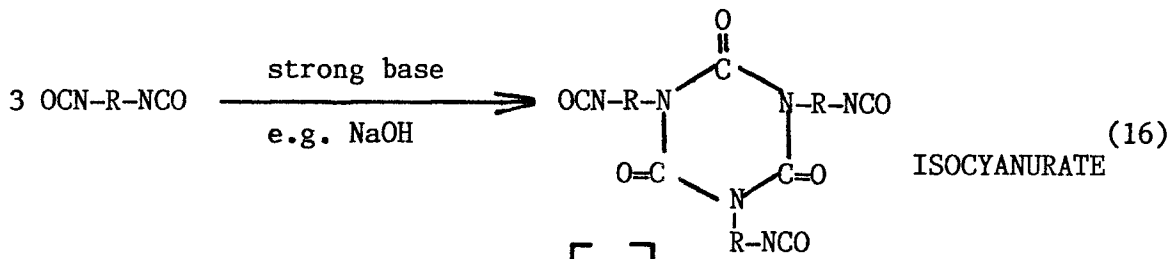
Isocyanates react with hydroxyl compounds to give urethanes and with amines to give ureas. Similar reactions occur with water and carboxylic acids, resulting in formation of carbamic acid and mixed acid anhydrides, respectively. However , in both of these cases the intermediates thus formed then break down and produce new compounds. In the case of water an amine is formed which further reacts with more isocyanates to give a urea. In the case of carboxylic acid the mixed anhydrides break down to form amide groups. These reactions are considered to be the backbone of the polyurethane chemistry. It is important to note that some secondary reactions may also take place. The secondary reactions are the reactions of the isocyanates with the active hydrogen of the primary products.

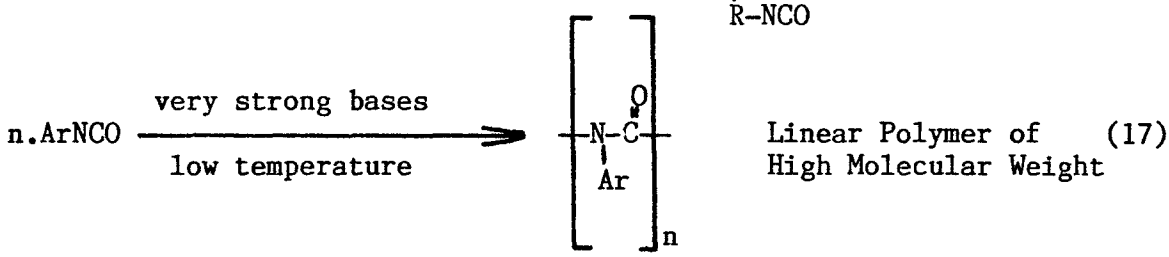


These secondary reactions are responsible for crosslinking and branching which have an important effect on polyurethane properties in many instances.

Another class of isocyanate reactions involve self-condensations which influence the branching and crosslinking during the building up of polyurethane structures. Three major types of such isocyanate reactions are:







These first type of polymerization is simple dimerization giving

rise to uretidione rings. This is a reversible reaction capable of breakdown to give two molecules of the original compounds. The second type is trimerization of isocyanates to give isocyanurate rings. These trimers are exceptionally stable. The third type of polymerization is the formation of substituted linear polyamides resembling nylon.

There is also a condensation polymerization between isocyanate molecules with elimination of CO_2. This reaction involves the formation of carbodiimides at high temperatures[25].

$$R\text{-}NCO + OCN\text{-}R \longrightarrow R\text{-}N{=}C{=}N\text{-}R + CO_2 \qquad (18)$$

$$n\ OCN\text{-}\acute{R}\text{-}NCO + n\ OCN\text{-}R\text{-}NCO \longrightarrow OCN\text{-}\acute{R}\text{-}\left[\text{-}N{=}C{=}N\text{-}R\text{-}\right]_{(2n-1)}NCO + (2n-1)CO_2 \qquad (19)$$

F) General Chemistry of Blocked Isocyanates: Wicks defines a blocked isocyanate as an " isocyanate which has been reacted with a material which will prevent its reaction at room temperature with compounds that conventionaly reacts with isocyanates but will permit that reaction to occur at higher temperature." The general scheme for the formation of a blocked isocyanate is:

$$RN{=}C{=}O + BH \longrightarrow RNHC(=O)\text{-}B \qquad (20)$$

Where BH is a hydrogen donor molecule such as an alcohol, phenol or amine. If the blocking agents are alcohols or phenols the adducts are urethanes. Equation (20) is an equilibrium reaction where free NCO is always present to a small extent which depends upon the nature of "R" and "B".

The dissociation of blocked isocyanates in presence of alcohols is reported by Williams[27,28] to follow equiations (21) and (22). Equation (21) shows the rapid dissociation of blocked isocyanate to form free

isocyanate. Equation (22) is the rate controlling step and indicates the slow reaction between the free NCO and the alcohol group.

$$RNHC(=O)-B \xrightarrow{\text{fast}} RNCO + BH \qquad (21)$$

$$RNCO + \acute{R}OH \xrightarrow{\text{slow}} RNHC(=O)-O\acute{R} \qquad (22)$$

If the B group represents an aromatic group, then the free NCO group in reaction (21) preferably reacts with the aliphatic alcohol, ROH in equation (22), rather than the aromatic blocking agent in equation (21) and the equilibrium of these equations will be shifted significantly to the right in (22).

Unlike the reaction with alcohols, the reaction between a blocked isocyanate and primary or secondary amines is rapid and not readily reversible. If the alcohol is replaced by an amine in equation (22) then the rate controlling step for the overall process would be equation (21) because amines react much more rapidly with free isocyanate molecules than do alcohols[29] .

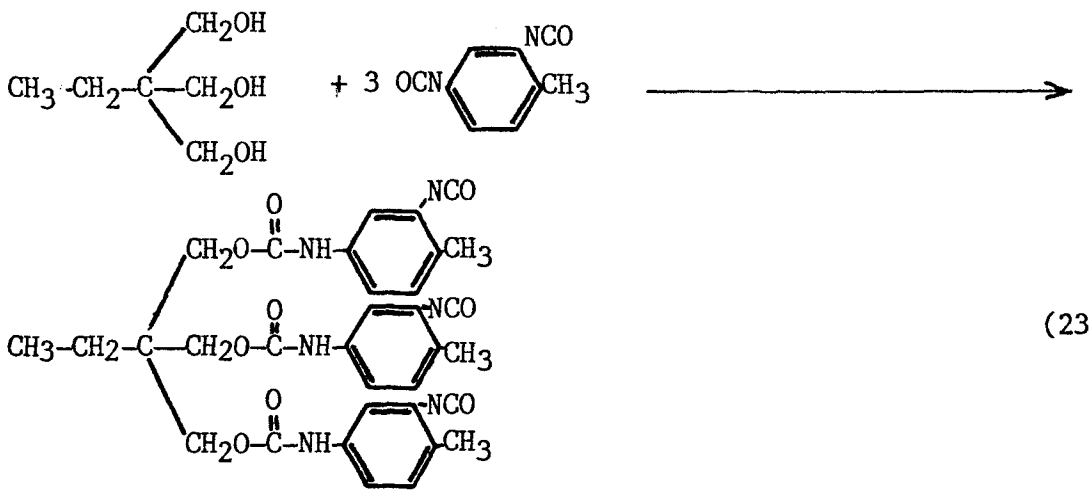
G) Decomposition of Blocked Isocyanates: At high temperatures thermal decomposition causes the blocking agent to detach from the blocked isocyanate. The minimum temperature at which free NCO could be detected from the decomposition of the blocked isocyanate (deblocking temperature) is reported by Griffin and Willwerth[30] . The thermal dissociation of urethanes is reported to have the following order[31] :

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

The substituents on the two aromatic rings have a strong effect on the stability of the molecules. In general, the presence of electron-releasing groups increase the stability while electron-withdrawing groups decrease the stability[32].

H) Preparation of TMP-TDI Adduct: This is the basic work of this thesis. Trimethylolpropane has three alcohol functional groups which can react with three molecules of TDI and form a TMP-TDI adduct. This adduct can be used as an intermediate in the preparation of polyurethanes when reacted to polyols and glycols.

Since the reactivity of para NCO is 8 to 10 times greater than that of the ortho NCO the predominant reaction would be:



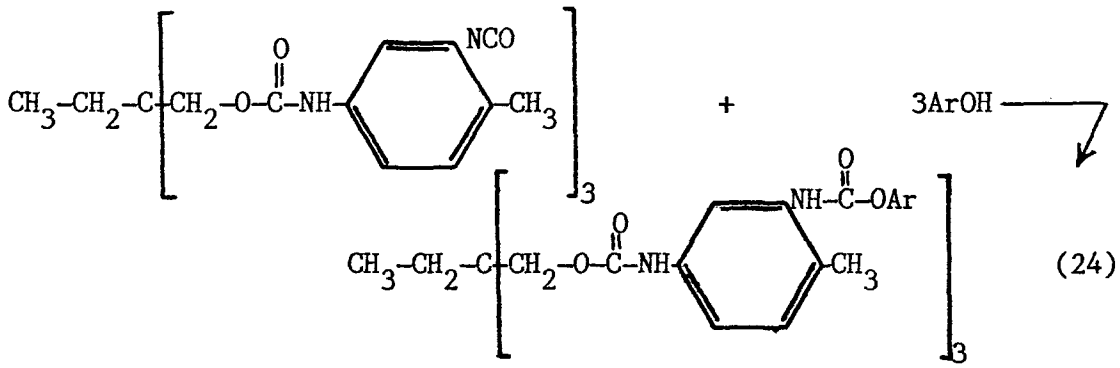
(23)

Some reaction may also occur at ortho position leaving the para NCO free.

Trimethylolpropane is an alcohol with three hydroxyl functional groups. It is used in the manufacturing of cross linked polymers and in heat activated oven cleaners[33]. It is synthesized by condensation of butyraldehyde with formaldehyde in aqueous alkalin solutions[34-37]. Purification of TMP is reported by Palmer using a countercurrent extraction method[38].

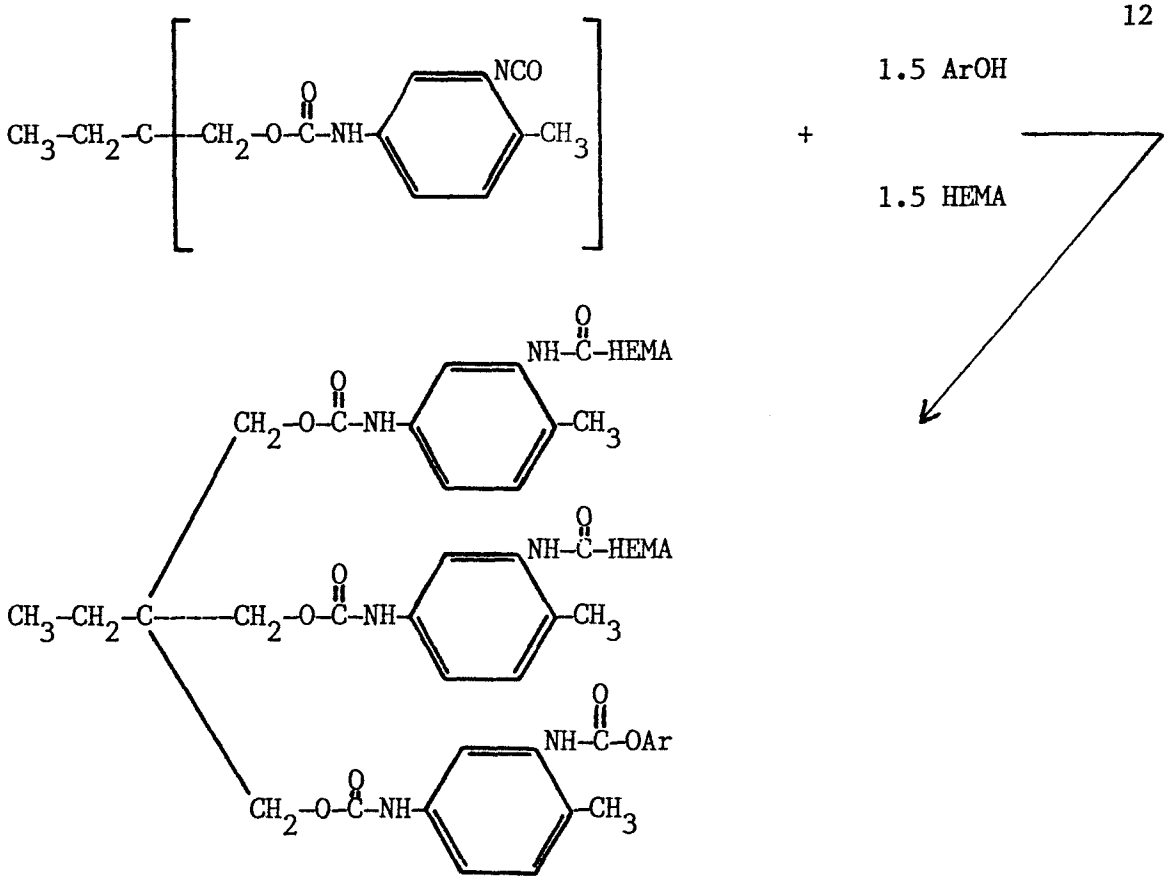
extraction method[38].

I) Blocking The TMP-TDI Adduct: The TMP-TDI cannot be applied directly on dentin because the free NCO would immediately react with water around the tooth (equation 3). Therfore, the free NCO of the adduct must be blocked with blocking agents such as different phenols. These blocked isocyanates are assumed to be unreactive toward water,while, in the presence of amine functional groups of dentin would immediatly deblock and produce free NCO which would react with the available amines.

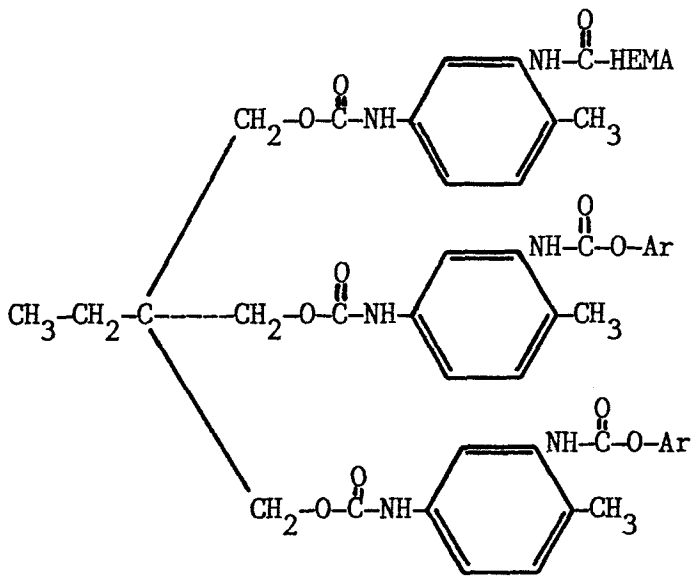


(24)

Since these compound are to be used as dental adhesives and dentin has single OH or amine groups in it (rather than polyols or diamines) the product of reaction (24) cannot form a polymer with dentin. The blocked adducts would react with amine of dentin forming only a monomolecular layer because the blocked adducts are not connected to any other molecule to form a polymer. Therefore, if in equation (24) instead of three moles of blocking agent an average of 1.5 moles of blocking agent and 1.5 moles of a double bond containing aliphatic alcohol, e.g. 2-hydroxyethyl methacrylate(HEMA) , is used the double bond can later be copolymerized with methylmethacrylate so that the molecules that bond to dentin can also be polymerized. The reaction of TMP-TDI adduct with equal amounts of blocking agent and HEMA would result in two predominent products:



or



(25)

These molecules can then easily be polymerized by traditional methods.

II. EXPERIMENTAL

A) Preparation of TMP-TDI Adduct Using A Homogeneous Solution Containing About 10 Moles of TDI For One Mole of TMP: The apparatus consisted of a 3000 ml high shear stirring flask with three necks, a high speed stirrer, a water condenser, one thermometer, a 250 ml addition funnel, nitrogen inlet, a variac and a gas bubbler. The set up is shown in figure 3.

About 21 grams trimethylolpropane (TMP) was dried in a vacuum oven at 30 C for about 12 hours. 234.0 grams (1.344 moles) of 2,4-tolylene-diisocyanate (TDI) were placed in a flask and about 550 ml petroleum ether and 14 drops of dibutyltindilaurate (DBTDL) catalyst[39] were added. This solution was mixed for about 30 minutes with the whole system being kept under nitrogen. Meanwhile, 18.3 grams (0.1363 moles) of dry TMP were dissolved in 135 ml of tetrahydrofuran (THF) and transferred to the addition funnel. The solvent had been dried by adding lithium aluminum hydride to it, then dry THF was recovered by simple distillation. Next, the TMP solution was added dropwise (§18 ml/hour) to the TDI-petroleum ether solution at room temperature (19°C) and the variac was set at 15,000 RPM. After one hour of addition of the TMP solution the temperature reached to 22°C; the stirrer was stopped and 450 ml of fresh petroleum ether was added. The colorless solution turned cloudy immediately after addition of the new portion of petroleum ether. The stirrer was turned on again and more TMP solution was added; white solid particles began to appear in the flask. More petroleum ether was added at different intervals to ease the precipitation of the TMP-TDI product and prevent them from sticking to the body of the

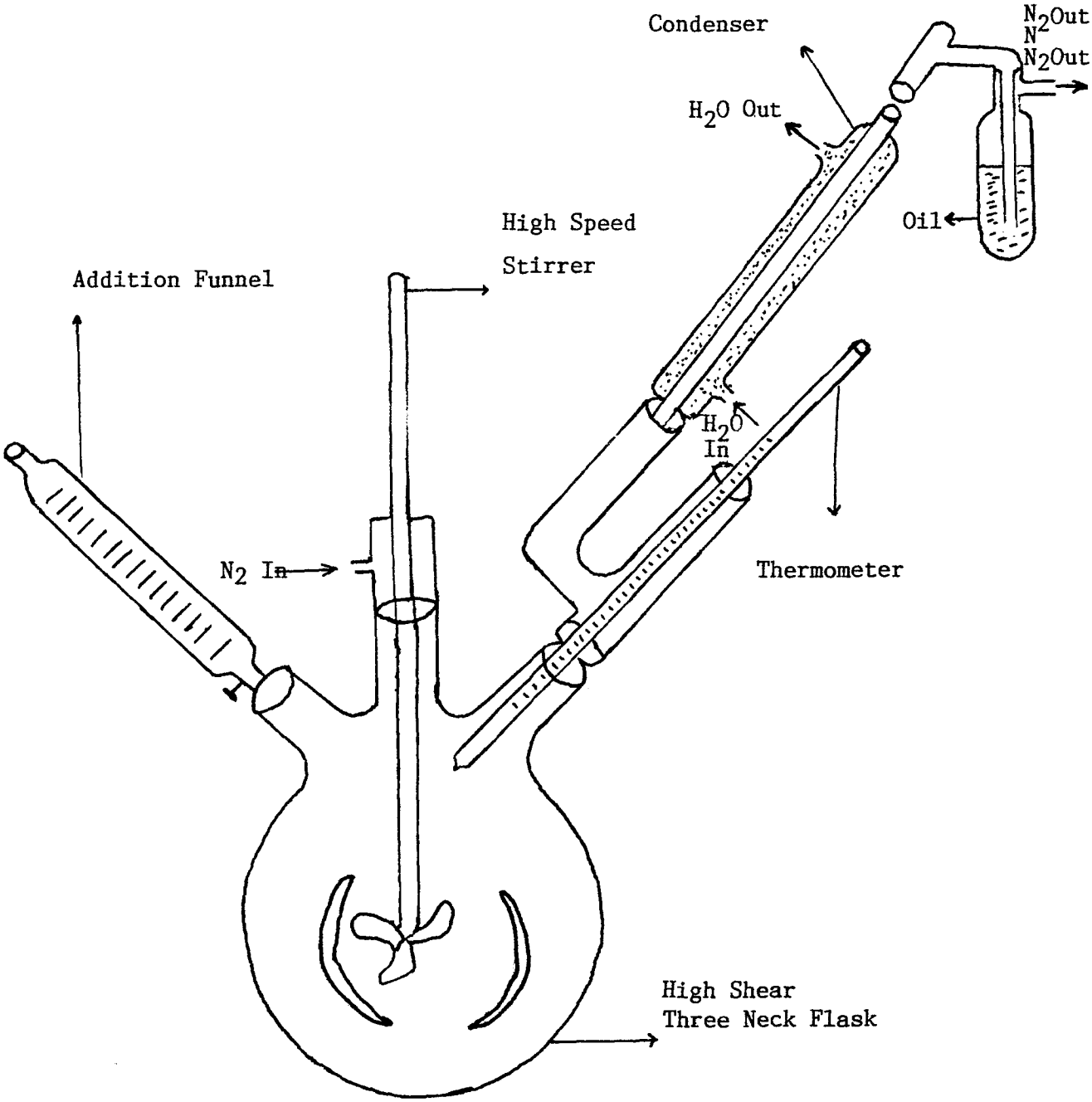


Figure . The Equipment Set Up For Preparation of The TMP-TDI Adduct

flask. Table 1 shows the addition of petroleum ether at different intervals.

Table I- Sequence of Addition of Pet-Ether and TMP Solution For Synthesis of TMP-TDI Adduct:

Time After The Initial Addition of TMP Solution (hour)	Volume of TMP solution Added (ml)	Pet-ether Added (ml)
1	15	450
3	50	300
6	95	100
7	118	150
8	135	100
		Total= 1100

The above intervals need not be followed exactly, but the total amount of petroleum ether added should not be less than 1100 ml. Because the reaction of TDI to TMP is exothermic and the high speed stirring itself also generates some heat the temperature of the system tends to rise as high as 40° C if not controlled. Thus, the temperature was kept below 25° C by using a water bath. At temperatures higher than 35 C sticky materials, which could be oligomers or polymers, formed around the glass.

In the course of the reaction whenever the stirrer was stopped, the TMP-TDI product precipitated as a white solid material while the petroleum ether remained a colorless liquid.

After addition of the TMP solution, which took about 8 hours, the reaction was allowed to go on for another hour with the stirrer still on. Then the stirrer was turned off, another 100 ml petroleum ether was added and the system was left undisturbed under nitrogen overnight.

After about 12 hours the clear, colorless liquid at top of the flask which consists of petroleum ether and excess TDI was drained out and 600 ml more fresh petroleum ether was added. The stirrer was turned on again for five minutes, then the solution was filtered by suction filtration. The filtered cake was again transffered to the flask and 500 ml petroleum ether was added to it; the solution was mixed for about five minutes. It was filtered again and the process of filteration and washing was repeated two more times. The last filtered cake was sprayed with about 500 ml petroleum ether to make sure that all of the excess TDI was washed out.

The white solid product was kept in the vacuum oven at 25 ^{o}C for 18 hours. The dry TMP-TDI product thus obtained weighed 76.4 grams (85.4% yield).

B) Blocking The TMP-TDI Adduct: Samples of TMP-TDI adducts synthesized in section A were separately blocked with the following blocking agents: p-cresol, eugenol, o-chlorophenol, and one to one mole ratio mixtures of 2-hydroxyethyl methacrylate (HEMA) and each of the three preceding blocking agents. For different blocking agents different conditions, such as temperature,necessary time for complete blocking,and excess amount of blocking agent, had to be employed. Tables II-VIII list all the details for each blocking procedure. In all these cases, first the TMP-TDI adduct was completely dissolved in the appropriate amount of dry THF (about 10 ml THF for each gram of TMP-TDI) in 100 ml Erlenmeyer flasks, then a few drops of DBTDL catalyst was added. Finally, the blocking agent was added and nitrogen gas was run through the solution for about one minute. The flasks were immediately capped with rubber stoppers wrapped in aluminum foil (the

solutions never came in contact with the stoppers) and they were put in a water bath for a number of days depending upon the nature of the blocking agent (see tables II-VIII). Also, in all these cases excess amount of blocking agents were used (more than 3 moles of blocking agent per mole of TMP-TDI adduct).

Section D represents the complete procedure for blocking the TMP-TDI adduct by eugenol as a typical blocking procedure.

C) Precipitation of The Blocked Isocyanate: The precipitation process for all of these blocked isocyanates was basically the same. First, the blocked isocyanate solution must be diluted with dry THF; three to four times of the original volume of THF is needed. The original volume of the THF is the volume of THF that the TMP-TDI sample has been dissolved in. Then, the dilute solution is filtered to remove the foreign particles. The next step is very crucial. A large beaker of petroleum ether (about two to three liters) was prepared. Then the blocked adduct solution was slowly (dropwise) added to the petroleum ether while the petroleum ether was stirred vigorously to disperse the solid product as much as possible. Each drop of the blocked solution that falls into the petroleum ether must immediately precipitate as fine solid materials. If the drop forms a chuncky solid (rather than a powder) upon entering into the petroleum ether, the blocked adduct solution must be diluted with more THF solvent until it precipitates as fine powdery particles in petroleum ether. Too much dilution with THF must also be avoided because in that case the blocked adduct would not precipitate in petroleum ether; instead it forms a cloudy solution upon contact with petroleum ether. Only the right degree of dilution of the blocked adduct solution results in

formation of the fine solid product. Also, care must be taken that not too much blocked adduct be precipitated in a single beaker. More petroleum ether and a larger beaker (or another beaker) must be used if the fine precipitates begin to stick to the bottom of the flask. The large volume of the petroleum ether and its vigorous stirring are of prime importance.

Once all the blocked adduct is precipitated liquid which consists of petroleum ether, catalyst, and excess blocking agent, must be flushed away and fresh petroleum ether must be added. The solution is well stirred again. When stirring is stopped the solid product remains in the bottom again and the liquid phase is a clear solution. Again, the liquid is discarded and fresh petroleum ether is added. This purification process is repeated a total of three times. Finally, the solid product is filtered by suction filtration and the filtered cake is washed with fresh petroleum ether to get rid of any remaining blocking agent. The filtered cake is then dried in the vacuume oven. The dry solid product was always produced in good yield.

A complete precipitation process for separating the eugenol blocked adduct is described in section E.

D) Blocking The TMP-TDI Adduct With Eugenol: In a 250 ml Erlenmeyer flask 10.0 grams (0.0152 moles) TMP-TDI adduct was dissolved in 50 ml of dry THF. It took about five minutes to dissolve the adduct completely. To this clear, colorless solution five drops of DBTDL catalyst and 9.28 grams of eugenol (0.0565 moles, or 23.7% excess) was added. The solution turned yellow. The flask was flushed with nitrogen gas for one minute and was capped and put in a 50^{o}C water bath.

Every 24 hours a sample was taken out and precipitated in petroleum

ether (precipitation procedure in section C) and its IR was run to check for free isocyanate peak at 2250 cm^{-1}. After 10 days the isocyanate peak still existed, therefore another 1.49 grams of eugenol was added to have about 43% excess eugenol. Four days after addition of the second portion of eugenol the infrared spectrum showed no peak for the isocyanate functional group (see Figure 4) indicating that all of the isocyanate functional groups of the TMP-TDI adduct were completley blocked by the blocking agent. The blocked adduct solution was slightly more viscous than the original TMP-TDI solution. Next, the blocked adduct was precipitated out of the solution by a specific precipitation process.

E) Precipitation of Eugenol blocked TMP-TDI Adduct: Once the IR showed complete blocking of the TMP-TDI adduct by eugenol, the solution was diluted with 150 ml of dry THF. The solution was then run through a filter paper to remove undissolved impurities.

To a 4000 ml beaker 2200 ml petroleum ether was added. The eugenol blocked solution was added to the beaker dropwise while the petroleum ether solution was stirred vigorously. The eugenol blocked product precipitated at the bottom of the beaker as a fine white solid material. After all the blocked product was precipitated the stirring was stopped and the product could be seen as white solid in the bottom of the beaker.

The liquid phase, which was cloudy and contained petroleum ether and excess blocking agent, was discarded. Next, 700 ml of fresh petroleum ether was added and the mixture was stirred well. Once the mixing is stopped the liquid phase appeared as a clear and colorless liquid; this was also drained and fresh petroleum ether was added. This

purification process was repeated two more times using a total of 1000 ml petroleum ether. Finally the solid product was filtered by suction filtration and the filtered cake was washed with 300 ml of petroleum ether. The white solid product was kept in the vacuum oven at 25°C to remove the petroleum ether from it. After 20 hours in the vacuum oven the dry product which was collected weighed 14.0 grams (80.0% yield).

F) Blocking The TMP-TDI Adduct With A Mixture of HEMA and Eugenol: In a 250 ml Erlenmeyer flask 25 grams of TMP-TDI adduct (prepared in part A of the experimental section) was dissolved in 100 ml dry THF. After about 5 minutes the adduct was completely dissolved and a colorless solution resulted. Then, 11.19 grams (0.0682 moles or 19.3% excess) eugenol and 7.84 grams (0.0602 moles or 5.5% excess) HEMA and 7 drops of DBTDL catalyst were added to have a mixture of approximately 50% HEMA / 50% eugenol. The light yellow solution was flushed with nitrogen and was capped and kept in a 50°C water bath. Every 24 hours a sample was taken out and precipitated in petroleum ether (part C of the experimental section) its IR was run and was checked for the isocyanate peak at 2250 cm^{-1}. After nine days the isocyanate peak still existed. Therefore, another 2.61 grams (0.0158 moles or a total of 47.1% excess eugenol) eugenol was added to the mixture to accelerate the blocking process. Four days after addition of the new portion of eugenol the IR spectrum (figure 8) showed no peak at 2250 cm^{-1} indicating that all isocyanate functional groups of the TMP-TDI adduct were blocked with either eugenol or HEMA. The blocked adduct solution was slightly more viscous than the original solution. Next, the blocked adduct was recoverd by a precipitation process.

G) Precipitation of The HEMA-Eugenol Blocked Adduct: As soon as the IR spectrum of the HEMA-eugenol blocked adduct showed no peak at 2250 cm the blocked solution was diluted with 200 ml of dry THF. The solution was then filtered through a filter paper to remove the impurities. The clear solution was precipitated in a total of 4500 ml petroleum ether the same way that eugenol blocked adduct had been precipitated in section E. The white solid material was dried and weighed 36.1 grams or a yield of 86.3 percent.

III. RESULTS

A) Elemental analysis: The percentage of carbon, hydrogen, nitrogen, and chlorine present in each monomer were determined by elemental analysis which was performed by the Mic Anal Organic Microanalysis of Tucson, Arisona. Tables XVII and XVIII contain the theoretical and observed values of each element in each monomer product. The theoretical values are based upon the predicted chemistry, e.g. three moles of eugenol are supposed to attach to one mole of the TMP-TDI adduct and give 65.84% carbon, 5.96% hydrogen, and 7.31% nitrogen. The observed values are those reported by the testing company, e.g. for the same eugenol blocked adduct the observed values are reported to be 64.96% carbon, 5.80% hydrogen, and 7.99% nitrogen. In tables XVIII the percentages of probable deblocking along with the corresponding theoretical values (after deblocking) are reported. Theoretical values based on the deblockings are explained in discussion section.

B) IR Spectra: The infrared spectra of all eight products were obtained using a Perkin-Elmer infrared Spectrometer modle 457. The samples were prepared using KBr as the window material. About 0.002 to 0.003 grams of the monomer was mixed with approximately 0.3 grams of KBr and the mixture was ground using an agate mortar and pestle. The sample pellets were prepared with a Carver press. Tables IX to XVI list the major absorptions for each compound while figures 3 to 10 are the IR spectra of the products.

C) Melting Point Determinations of The Products: A light microscope with a hot stage and a crossed-polarized lens system made by Bristoline Company was used to determine the melting points of the products. The monomers were placed on glass microscope slides and four melting points

were taken for each monomer. The first trial used a very fast heating rate to obtain the approximate melting point. The other three trials were measured with new samples and heating rates of about one degree per thirty seconds. The average of these three were taken as the melting point of the monomer. The melting point values of the products are reported in table XIX.

IV. DISCUSSION

Previous attempts to prepare TMP-TDI adduct as a pure monomer had failed[40]. This was found to be mainly due to the polar solvents used in preparation of the adduct. In the beginning of this thesis considerable amount of time was spent In preparation of the adduct using different polar solvents such as ethyl acetate, 2-methoxyethyl acetate, and 1,2-dimethoxyethane. In all these cases stoichiometric amounts of TMP and TDI were used. First the solvent and a few drops of DBTDL were added to the TDI. Then, the solid TMP (which was dried in a vacuum oven at 30 C) was slowly added to the mixture. The whole system was kept under nitrogen and the high speed stirrer was used to mix the solution. The equipment and set up are shown in figure 3, except that instead of the addition funnel a special spherical glass container was used to add the solid TMP periodically in a closed system. After all the TMP was added a viscous solution was obtained which became very hard after keeping it in a closed jar for 2 to 3 months. Since all possible efforts were made to make the system free of water, e.g. drying the solvent and TMP and working under nitrogen gas, the viscosity of the solution and its subsequent hardening must be due only to the kind of reaction that takes place. Under these conditions the TDI may participate its ortho as well as its para isocyanates in the reaction. Therefore, one TDI could have two molecules of TMP attached to it, the other four branches of TMP molecules could react with different TDIs at ortho, para, or both sites. This sequence could go on and produce oligomers and/or polymers.

Dr. W. H. Snyder[41] recommended a new approach: replacing the polar solvent by a non polar one (e.g. petroleum ether) so that once the

adduct was formed it would precipitate out in the bottom of the flask and reduces the possibility of formation of oligomers. This "heterogeneous system" had already been used successfully by Kirti Kamdar in preparing a TDI-HEMA monomer[42]. This new heterogeneous system was tried using stoichiometric amounts of solid TMP and liquid TDI in the presence of petroleum ether. This method also failed to produce the desired adduct because solid TMP would not readily react with TDI in presence of a non polar solvent such as petroleum ether. Thus, TMP was first dissolved in a minimum amount of dry THF. Then this TMP solution was slowly added to the TDI-petroleum ether mixture. Although by this method some solid product was obtained, the elemental analysis showed that not all three hydroxyl groups of TMP have reacted with TDI. From this information Dr. Kristol[43] recommended that an excess amount of TDI is necessary to help all the hydroxyl groups of TMP to react with TDI molecules. Therefore, about 10 moles of TDI was used for each mole of TMP, or 3.3 moles of TDI for each hydroxyl group of TMP. Actually using excess TDI may have two advantages: 1) when a drop of TMP solution falls into the TDI-petroleum ether solution it would encounter so many TDI molecules that the probability of each TDI to react with more than one TMP molecule decreases drastically. 2) A drop of TMP solution is surrounded by so many TDI molecules. Therefore, the reaction takes place preferably with the para isocyanate of TDI molecules (para isocyanate is 8-10 times more reactive than otho-isocyanate at room temperature) without permitting a significant opportunity for isocyanate to participate in the reaction. This of course, does not mean that there would be no reaction between TMP and TDI at the ortho position; it is only suggested that because there

is an excess of TDI the TMP is not forced to react at less faverable ortho isocyanate position. In other words, if there are not adequate amounts of TDI available to react with TMP molecules, a TDI may use both of its isocyanates in reaction with TMPs resulting in oligomers or even polymers. Using excess TDI only ensures that there is at least one TDI molecule available for each hydroxyl group of a TMP molecule and there is no need for a single TDI to contribute both of its isocyanates at once and form undesired dimer or oligomer. As it was explained in part A of the experimental section the new procedure finally gave rise to the desired TMP-TDI monomer.

In short one must realize that in synthesis of TMP-TDI adduct six factors are essential:

1) The system must be kept free of water as much as possible. Even a few molecules of water can prove very destructive because, a molecule of water would react with the isocyanate and produce amine which would subsequently react with another molecule of isocyanate and produce a urea. In other words, one molecule of water would waste two molecules of isocyanates. Therefore it is essential to dry TMP and THF before using them.

2) A heterogeneous system must be used (i.e. using TDI-petroleum ether solution). Polar solvents such as ethyl acetate, 1,2 dimethoxyethane, and 2-methoxyethylacetate repeatedly failed to give the desired TMP-TDI monomer; they produced gels or oligomers.

3) Solid TMP should be dissolved in a polar solvent such as THF. This would not only facilitate the addition of TMP to the TDI-petroleum ether solution but also helps the TMP molecules to become more dispersed in

the solution and have more encounter with TDI molecules.

4) Use excess TDI. This is absolutely necessary because, if there are excess TDI molecules in the solution they would replace any possible isocyanate sites that were lost due to the reaction with water or any other foreign materials. As it was mentioned earlier, it may also help to have more reaction at para position by not forcing the ortho isocyanate to participate in the reaction with TMP. Once the reaction is complete the excess TDI would easily be extracted along with petroleum ether (see part A of experimental section).

5) Use high speed stirrer. The high speed stirrer undoubtedly plays an important role in this system. It mainly disperses the incoming TMP solution and increases the encounter of TMP molecules with TDI. It also prevents accumulation of TMP molecules in one spot and diminishes the chances of formation of oligomers.

6) Maintain the temperature below 25^{o} C. Although the reactivity ratio of para isocyanate to ortho isocyanate in TDI is 8-10 to one in favor of para isocyanate at room temperature, at higher temperatures this ratio no longer holds. Actually it is known that at 93^{o} C para and ortho isocyanates of TDI have the same reactivity. Due to the exothermic behavior of the reaction and the heat evolved by high speed stirrer the temperature tends to rise as high as 40^{o} C. Thus, it is absolutely important to keep the temperature below 25^{o}C by a cold water bath. Although it was not tried by this auther, Lower temperatures such as 10^{o}C or 15^{o}C may perhaps shift the reactivity more in favor of the para isocyanate.

Since TMP has three hydroxyl functional groups there are four possible structures for the TMP-TDI adduct. 1) All three hydroxyl groups

of TMP react with para isocyanate groups of three different TDI molecules. 2) All three hydroxyl groups may react with ortho isocyanate groups of three different TDI molecules; this is very unlikely because of the low reactivity of ortho isocyanate groups at room temperature. 3,4) Two hydroxyl groups of a TMP molecule may react with para isocyanates of two different TDI molecules while the third hydroxyl functional group reacts with ortho isocyanate of a third TDI molecule,or vice versa.

All four structures, however, have the same molecular weights and their quantities have no effect on the elemental analysis results. Table XVII indicates that the result of the elemental analysis of the TMP-TDI adduct shows excellent agreement between the theoretical and the actual values. The infrared spectrum is also shown in figure 3. The presence of a strong peak at 2250 cm^{-1}, indicates that free isocyanates are available in the adduct. This free isocyanate is mostly ortho NCO which can latter be blocked with different blocking agents.

Since the ultimate goal of this project is to apply these new products as dental adhesives, these monomers must not only react with dentin but should also fill the cavities. Therefore, the TMP-TDI adduct was blocked with both HEMA and different phenolic blocking agents at the same time. The reason that HEMA must be used is that it contains a double bond which can subsequently be copolymerized with some other molecules such as methylmethacrylate. This copolymerization will produce a strong material that could fill the cavity. Thus, each TMP-TDI molecule, which has 3 isocyanate functional groups , must be blocked with at least one molecule of HEMA (for later copolymerization) and

one molecule of the phenolic blocking agent (for deblocking in presence of amine and subsequent reaction with dentin). The third isocyanate of the adduct could react with either HEMA or phenolic blocking agent. The idea is that because HEMA is an aliphatic hydroxyl containing molecule it would not easily deblock once it has reacted with an isocyanate. The phenolic blocking agents, on the other hand, are aromatic hydroxyl containing molecules and after reaction with isocyanates they easily deblock in presence of amines. Consequently, if each TMP-TDI adduct is blocked with at least one phenolic blocking agent and one HEMA molecule, once this blocked monomer comes in contact with dentin the phenolic blocking agent would easily deblock and the corresponding freed isocyanate would immediately react with the amine functional groups of dentin while the HEMA blocked branch of the adduct remains untouched. The HEMA site of the blocked monomer can then be copolymerized with a mixture of methylmethacrylate and poly methylmethacrylate and form a strong polymer that could fill the cavity. Thus, there is a molecule that is attached to the dentin at one site and connected to a strong polymer at another site. This is why the TMP-TDI adduct has been blocked with 50% HEMA and 50% phenolic blocking agents. It is important to note that regardless of what the third isocyanate branch of the TMP-TDI reacts with (HEMA or phenolic blocking agent) it only improves the quality of the blocked monomer either by attaching to dentin (if blocked with phenolic blocking agent) or by coplolymerization with the methylmethacrylate (if blocked with HEMA).

Blocking the TMP-TDI adduct with HEMA and a phenolic blocking agent at the same time could result in four different products:

1- All three isocyanates of the TMP-TDI adduct react with HEMA molecules.

2- All three isocyanates of the adduct react with the phenolic blocking agent molecules.

3- Two isocyanates of the adduct react with HEMA molecules while the third isocyanate reacts with the phenolic blocking agent.

4- Two isocyanates of a TMP-TDI molecule react with the phenolic blocking agent and the third isocyanate reacts with a HEMA molecule.

Blocking the TMP-TDI adduct with equal molar quantities of HEMA and phenolic blocking agent could have two advantages: a) It makes the three isocyanate functional groups of the adduct equally available to both HEMA and the phenolic blocking agent molecules and diminishes the possibility (or the quantity) of all three isocyanates being blocked with only one of them. As a matter of fact the reason that both HEMA and the blocking agent are added at the same time is to prevent the three isocyanates being blocked by only one of the two blocking agents. b) Assuming that each TMP-TDI adduct is blocked with at least one HEMA and one phenolic blocking agent molecules, addition of one to one mole ratio of the two blocking agents may produce equal quantities of monomers with two isocyanates blocked with HEMA and the third blocked with the phenolic blocking agent and, monomers with two isocyanates blocked with the phenolic blocking agent and the third blocked with HEMA.

Blocking the TMP-TDI adduct is described in parts B through G of the experimental section. It is absolutely essential to use excess amounts of blocking agent to have all the free isocyanates of the adduct blocked in a reasonable time. Tables II-VIII present the excess amount of each blocking agent used. From these tables it can be concluded

that, in general, increasing the percentage of excess blocking agent results in shorter time for completion of the reaction. The best example would be the blocking with ortho chlorophenol. When about 20% excess ortho- chlorophenol was used to block a sample of TMP-TDI adduct the blocked product always showed a peak for free isocyanate, indicating that the blocking was never complete. However, when 103% excess ortho-chlorophenol was used (table V) the IR showed no peak for isocyanate functional group after eight days. For the mixture of 50% ortho chlorophenol and 50% HEMA, only 23.4% excess ortho chlorophenol was first added . After nine days there was still a considerable peak for isocyanate functional group. Knowing that only 6.1% excess HEMA is enough to block a TMP-TDI sample in seven days (table III), and the fact that 6.58% excess HEMA had already been used in the 50% ortho chlorophenol 50% HEMA solution, the delay in blocking could be only due to insufficient amount of ortho chlorophenol. Thus, after nine days more ortho chlorophenol blocking agent was added for a total excess of 48.87%. It took only four more days to have complete blocking of the adduct with ortho chlorophenol and HEMA.

Blocking by para cresol (50% excess) and 50% para cresol 50% HEMA (total of 25.1% excess) took nine days in both cases. For eugenol (43.5% excess) and 50% HEMA 50% eugenol (total of 52.6% excess) comlete blocking took 14 and 13 days, respectively. All of these data support the assumption that increasing the amount of the blocking agent decreases the time of the reaction. It must also be noted that aliphatic blocking agents (e.g. HEMA) react faster with isocyanate functional groups than aromatic ones. For instance, with only 6.1 %

excess HEMA it took 7 days to block a TMP-TDI sample completely whereas, in the case of other blocking agents, which were aromatic, and using much more than 6.1% excess of them it took more than 7 days for complete blocking to take place (tables II-VIII).

Since the purpose of this thesis was the preparation of specific blocked isocyanates rather than comparison between different experimental procedures, the times of reactions reported in tables II-VIII indicate only approximate values. For example in the case of eugenol, 50% HEMA /50% ortho chlorophenol, and 50% eugenol/50% HEMA additional quantities of the blocking agents were added only when the reactions took more than nine days to complete (see tables II,VIII,VI). It is, therefore, safe to say that if more excess blocking agents were used initially, it would take less time for reactions to go to completion.

It took a considerable amount of time to determine the best procedure to precipitate the blocked product out of the solution. First, the petroleum ether (as the non solvent) was added to the blocked TMP-TDI solution in the hope of having the product precipitate. No precipitation took place; instead an oily sticky material was formed in the bottom of the beaker which became very hard upon exposure to air. When this oily material was taken out of the solution and placed in a vacuum oven to evaporate the petroleum ether a foam like material was obtained. No matter how much petroleum ether was added the oily product would always form in the bottom of the beaker. In other trials samples of blocked isocyanate with different quantities of petroleum ether were put in the refrigerator for as long as one week with no crystallization or precipitation happening. After a

great deal of experimentation it was discovered that if the blocked isocyanate solution was added slowly to a large volume of petroleum ether chunky materials would immediately form and precipitate down the beaker. By diluting the blocked isocyanate solution with extra volume of dry THF the problem of formation of chunky pieces was also solved. When the blocked isocyanate solution was adequately diluted with THF and was added dropwise to a large volume of petroleum ether, which was vigorously stirred, fine solid products precipitated down.

When all of the blocked product was precipitated the liquid phase was discarded and the solid product was washed a few times with large quantities of fresh petroleum ether (see part E of the experimental section). It should also be noted that if too much THF is added to the blocked isocyanate solution no precipitation would take place, instead, a cloudy mixture results. Therefore, having the proper amount of THF in the blocked solution is very important. In summary, in precipitating the blocked product three important points must be followed: a) The blocked isocyanate solution must be adequately diluted with THF. b) Large volumes of petroleum ether should be used. c) While adding the blocked isocyanate solution to petroleum ether the petroleum ether solution must be stirred vigorously to help dispersion of the solid products.

Tables XVII and XVIII refer to the elemental analysis calculations. It can be seen from table XVII that the observed values of the elements sometimes do not exactly match the theoretical values. Using these observed and theoretical values it was found that some deblocking or non-blocking takes place for each monomer. For example for eugenol

blocked monomer the following calculations were performed to find the theoretical percentages of each element in this monomer.

	33	carbons	3 molecules of	3x10=30 carbons
	32	hydrogens	eugenol has:	3x12=36 hydrogens
TMP-TDI has:	9	oxygens		3x2=6 oxygens
	6	nitrogens		

For a TMP-TDI adduct blocked with three eugenols:

Number of carbons: 33+30=63 or 63x12.011= 756.693 grams

Number of hydrogens: 32+36=68 or 68x1.008= 68.544 grams

Number of oxygens: 9+6= 15 or 15x15.9994= 239.991 grams

Number of nitrogens: 6 or 6x14.007= 84.042 grams

Total weight of a eugenol blocked adduct = 1149.29 grams

This means 65.84% carbon ($\frac{756.693}{1149.29}$ x100= 65.84), 5.96% hydrogen, 20.88% oxygen, and 7.31% nitrogen. Whereas, the observed values are 64.96% carbon, 5.80% hydrogen, 21.25% oxygen, and 7.99% nitrogen.

No matter how much deblocking (or unblocking) takes place the weight of nitrogen remains constant at 84.042 grams because eugenol has no nitrogen in it, nitrogen exists only in the TMP-TDI adduct. Therefore, the percentage of dissociation of the blocking agent (or the non-blocking percentage) can be calculated as follows:

$$\frac{84.042}{1149.29 - M} \times 100 = 7.99$$

Where 84.042 is the weight of the nitrogen in the monomer, 1149.29 is the weight of the eugenol blocked monomer, 7.99 is the observed percentage of nitrogen in the monomer, and M is the weight of the blocking agent lost due to deblocking. From the above equation the value of M was found to be 97.4727 grams.

Since a molecule of eugenol blocked adduct has three eugenols

attached to it, the percentage of deblocking would be:

$$3 \text{ moles of eugenol } \left(\frac{164.12}{\text{mole eugenol}}\right) = 492.36 \text{ grams}$$

$$\frac{97.4727 \text{ gr}}{492.36 \text{ gr}} \times 100 = 19.8\ \%$$

or 19.8% of the eugenol has deblocked or not reacted at all.

Based on 19.8% deblocking the weight of each element in this partially blocked monomer would be:

$$\frac{(100 - 19.8) \text{ moles eugenol left}}{100 \text{ moles eugenol}} \times 3 \text{ moles eugenol} = 2.406 \text{ moles of eugenol reacted}$$

$$\frac{10 \text{ carbons}}{1 \text{ mole eugenol}} \times 2.406 \text{ moles eugenol} = 24.06 \text{ carbons}$$

$$\frac{12 \text{ hydrogen}}{1 \text{ mole eugenol}} \times 2.406 \text{ moles eugenol} = 28.872 \text{ hydrogens}$$

$$\frac{2 \text{ oxygens}}{1 \text{ mole eugenol}} \times 2.406 \text{ moles eugenol} = 4.812 \text{ oxygens}$$

The molecular weight of the 19.8% deblocked monomer would be:

(24.06 + 33) x 12.011 = 685.347 grams carbon

(28.872 + 32) x 1.008 = 61.359 grams hydrogen

(4.812 + 9) x 15.9994 = 220.9837 grams oxygen

6 x 14.007 = 84.042 grams nitrogen

Total weight (molecular weight) = 1051.7324grams.

The difference between the molecular weights of completely blocked and partially blocked monomer is:

1149.29 - 1051.7324 = 97.55 or almost equal to M (97.47).

The percentage of each element in the 19.8% deblocked monomer are calculated below and compared with the observed values reported by the

Mic Anal Testing Company.

		Calculated Values	observed Values
% of C	$\frac{685.347}{1051.7324} \times 100 =$	65.16	64.59
% of H	$\frac{61.359}{1051.7324} \times 100 =$	5.83	5.80
% of O	$\frac{220.983}{1051.7324} \times 100 =$	21.01	21.25
% of N	$\frac{84.042}{1051.7324} \times 100 =$	7.99	7.99

From the above comparison it is obvious that the calculated values based on 19.8% deblocking are very close to the reported values by the testing company. Table XVIII shows the calculated values based on the corresponding deblocking percentage for different monomers. The only problem is that if there is 19.8% deblocking it would mean that 19.8% of the isocyanate functional groups of the adduct remain intact. If so, why there is no isocyanate peak in the IR spectrum of the blocked adducts? A possible answer would be that the blocking agents have efficiently reacted with the isocyanate functional groups of the adduct (Hence, no peak at 2250 cm^{-1}) but the blocked products may deblock in the course of the elemental analysis in such a way that a significant fraction of the phenol is lost. The monomers prepared through this work however, are suitable and useful for the present adhesive tests. These products are now being studied at the New Jersey Dental School for their adhesive properties. This work may lead to a significant improvement in dental restorative practice in the future.

V. CONCLUSIONS AND SUGGESTIONS

This thesis was directed toward synthesis of blocked diisocyanate compounds that could be used as dental restorative materials. Synthesis of the TMP-TDI adduct was the major achievement of this work. Once this adduct was made its subsequent blocking with different blocking agents was easily performed. Synthesis of eight new materials made this thesis a very successful work.

The parent structure of these products, the TMP-TDI adduct, has three isocyanate functional groups which are able to react with the dentin part of the teeth. Preparing molecules with more than three isocyanate functional groups could increase the adehesion to dentin, significantly.

Table II. Preparation of Eugenol Blocked Adduct

The general procedure is the same as that described in parts D-E of the experimental section with the following quantities of the reactants used and characteristics:

Weight of the TMP-TDI adduct was 10.01 grams.

The adduct was dissolved in 50 ml of THF.

Weight of the eugenol was 9.28 grams (23.7% excess). After 10 days another 1.49 grams of eugenol was added (a total of 43.5% excess).

Five drops of DBTDL catalyst was added.

Color of the solution immediately after addition of the blocking agent was slightly yellow.

The solution was kept at 50^{o} C water bath.

It took 14 days for complete blocking (no peak at 2250 cm^{-1}, see Figure 4).

Precipitation of The Blocked Solution:

The blocked solution was diluted by 150 ml THF.

Total volume of petroleum ether used for precipitation was 4200 ml.

Weight of the product was 14.0 grams (80% yield).

Table III. Preparation of HEMA Blocked Adduct

The general procedure is the same as that described in parts D-E of the experimental section with the following quantities of the reactants used and characteristics:

Weight of the TMP-TDI adduct was 10.00 grams.

The adduct was dissolved in 70 ml of THF.

Weight of the HEMA added was 6.31 grams (6.1 excess).

Five drops of DBTDL catalyst was added.

About 0.065 grams of chloranil inhibitor was added to prevent polymerization.

Color of the solution turned red because of the inhibitor.

The solution was kept at 37°C water bath.

It took 7 days for complete blocking (no peak at 2250 cm^{-1}, see Figure 5).

Precipitation of The Blocked Solution:

The blocked solution was diluted by 100 ml THF.

Total volume of petroleum ether used for precipitation was 3500 ml.

Weight of the product was 14.5 grams (91% yield).

Table IV. Preparation of P-cresol Blocked Adduct

The general procedure is the same as that described in parts D-E of the experimental section with the following quantities of the reactants used and characteristics:

Weight of the TMP-TDI adduct = 10.01 grams.

The adduct was dissolved in 50 ml of THF.

Weight of the P-cresol = 6.17 grams (25% excess)

Five drops of DBTDL catalyst was added.

Color of the solution immediatly after addition of the blocking agent was slightly yellow.

The solution was kept at 50^{o} C water bath.

After 5 days the solution became a little viscous and another 50 ml THF was added.

It took 9 days for complete blocking (i.e. no peak at 2250 cm^{-1}. see figure 6)

Precipitation of The Blocked Solution:

The blocked solution was diluted by 100 ml THF.

Total volume of petroleum ether used for precipitation was 3200 ml

Weight of the product was 13.0 grams (87% yield).

Table V. Preparation of O-chlorophenol Blocked Adduct

The general procedure is the same as that described in parts D-E of the experimental section with the following quantities of the reactants used and characteristics:

Weight of the TMP-TDI adduct was 10.00 grams.

The adduct was dissolved in 35 ml of THF.

Weight of the O-chlorophenol was 11.96 grams (103% excess).

Five drops of DBTDL catalyst was added.

Color of the solution immediately after addition of the blocking agent was slightly yellow.

The solution was kept at 37 ^{o}C water bath.

It took 8 days for complete blocking (no peak at 2250 cm^{-1}, see Figure 7).

The solution turned red after 8 days.

Precipitation of The Blocked Solution:

The blocked solution was diluted by 100 ml THF.

Total volume of petroleum ether used for precipitation was 3500 ml.

Weight of the product was 13.5 grams (85% yield).

Note: After the blocked adduct was precipitated it was redissolved in 80 ml THF, filtered and reprecipitated in 2500 ml petroleum ether to remove some broken glasses from it.

Table VI. Preparation of HEMA-Eugenol Blocked Adduct

The general procedure is the same as that described in parts F-G of the experimental section with the following quantities of the reactants used and characteristics:

Weight of the TMP-TDI adduct was 25.01 grams.

The adduct was dissolved in 100 ml of THF.

Weight of the eugenol initially used was 11.19 grams (19.3% excess).

After 9 days another 2.61 grams of eugenol was added (total of 47.1% excess).

Weight of HEMA used was 7.84 grams (5.5% excess).

Eight drops of DBTDL catalyst was added.

Color of the solution immediately after addition of the blocking agents was slightly yellow.

The solution was kept at 50° C water bath.

It took 13 days for complete blocking (no peak at 2250 cm^{-1}, see Figure 8).

Precipitation of The Blocked Solution:

The blocked solution was diluted by 200 ml THF.

Total volume of petroleum ether used for precipitation was 4500 ml.

Weight of the product was 36.1 grams (86.3% yield).

Table VII. Preparation of HEMA-Para-cresol Blocked Adduct

The general procedure is the same as that described in parts F-G of the experimental section with the following quantities of the reactants used and characteristics:

Weight of the TMP-TDI adduct was 25.02 grams.

The adduct was dissolved in 100 ml of THF.

Weight of the P-cresol used was 7.26 grams (17.6% excess).

Weight of HEMA used was 7.99 grams (7.5% excess).

Eight drops of DBTDL catalyst was added.

The solution immediately after addition of the blocking agents was colorless. The final solution was slightly yellow.

The solution was kept at 50^{o} C water bath.

It took 9 days for complete blocking (no peak at 2250 cm^{-1}, see Figure 9).

Precipitation of The Blocked Solution:

The blocked solution was diluted by 150 ml THF.

Total volume of petroleum ether used for precipitation was 4000 ml.

Weight of the product was 37.0 grams (95.8% yield).

Table VIII. Preparation of HEMA-Ortho-chlorophenol Blocked Adduct

The general procedure is the same as that described in parts F-G of the experimental section with the following quantities of the reactants used and characteristics:

Weight of the TMP-TDI adduct was 25.02 grams.

The adduct was dissolved in 100 ml of THF.

Weight of the O-chlorophenol initially used was 9.06 grams (23.4% excess). After 9 days another 1.87 grams of O-chlorophenol was added (total of 48.8% excess).

Weight of HEMA used was 7.92 grams (6.58% excess).

Eight drops of DBTDL catalyst was added.

Color of the solution immediately after addition of the blocking agents was slightly yellow.

The solution was kept at 37^{o}C water bath.

It took 13 days for complete blocking (no peak at 2250 cm^{-1}, see Figure 10).

The solution slowly turned red in 13 days.

Precipitation of The Blocked Solution:

The blocked solution was diluted by 150 ml THF.

Total volume of petroleum ether used for precipitation was 4000 ml.

Weight of the product was 37.5 grams (94.2% yield).

Table IX. Selected IR Absorptions of TMP-TDI Adduct

Assignments	Wave Number cm^{-1}
N-H stretch	3320 (s)
C-H aliphatic stretch	2960 (m)
-N=C=O	2250 (s)
C=O carbonyl	1700 (s)
C=C aromatic, skeletal stretch	1580 (s)
" " " "	1500 (s)
" " " "	1375 (m)
C-N stretch	1275 (s)
C-O stretch	1220 (s)
" "	1060 (s)
" "	980 (m)
C-H out of plane deformation	860 (m)
" " " " "	810 (m)
" " " " "	750 (m)

Table X. Selected IR Absorption of TMP-TDI Adduct Blocked With Eugenol

Assignment	Wave Number cm^{-1}
N-H stretch	3300 (s)
C-H aliphatic stretch	2950 (m)
C=O carbonyl	1700 (s)
C=C aromatic, skeletal stretch	1600 (s)
" " " "	1500 (s)
" " " "	1440 (s)
" " " "	1410 (s)
C-N stretch	1270 (s)
C-O stretch	1200 (s)
" "	1050 (s)
" "	980 M)
C-H out of plane deformation	810 (w)
" " " " "	750 (w)

Table XI. Selected IR Absorption of TMP-TDI Adduct Blocked With HEMA

Assignment	Wav Number cm^{-1}
N-H stretch	3300 (s)
C-H aliphatic stretch	2960 (m)
C=O carbonyl	1700 (s)
C C aromatic, skeletal stretch	1580 (s)
" " " "	1520 (s)
" " " "	1430 (m)
" " " "	1400 (m)
C-N stretch	1290 (m)
C-O stretch	1210 (s)
" "	1050 (s)
" "	980 (m)
C-H out of plane deformation (Alkene)	940 (m)
C-H out of plane deformation	860 (w)
" " " " "	800 (m)
" " " " "	750 (m)

Table XII. Selected IR Absorptions of The TMP-TDI Blocked With Para-Cresol

Assignment	Wave Number cm^{-1}
N-H stretch	3300 (s)
C-H aliphatic stretch	2960 (w)
C=O carbonyl	1700 (s)
C=C aromatic, skeletal stretch	1590 (s)
" " " "	1500 (s)
" " " "	1440 (m)
" " " "	1400 (m)
C-N stretch	1310 (m)
C-O stretch	1200 (s)
" "	1050 (m)
" "	980 (w)
C-H out of plane deformation	860 (W)
" " " " "	810 (W)
" " " " "	750 (W)

Table XIII. Selected IR Absorptions of The TMP-TDI Adduct Blocked With O-chlorophenol

Assignment	Wave Number cm^{-1}
N-H stretch	3300 (s)
C-H aliphatic stretch	2970 (w)
C=O carbonyl	1700 (s)
C=C aromatic, skeletal stretch	1590 (m)
" " " "	1510 (s)
" " " "	1460 (s)
" " " "	1400 (m)
C-N stretch	1310 (m)
C-O stretch	1210 (s)
" "	1050 (s)
" "	980 (m)
C-H out of plane deformation	860 (w)
" " " " "	790 (w)
" " " " "	730 (m)

Table XIV. Selected IR Absorptions of The TMP-TDI Blocked With HEMA And Eugenol

Assignment	Wave Number cm^{-1}
N-H stretch	3300 (s)
C-H aliphatic stretch	2970 (m)
C=O carbonyl	1700 (s)
C=C aromatic, skeletal stretch	1590 (s)
" " " "	1520 (s)
" " " "	1440 (s)
" " " "	1400 (s)
C-N stretch	1270 (m)
C-O stretch	1200 (s)
" "	1050 (s)
" "	980 (m)
C-H out of plane deformation (alkene)	940 (w)
C-H out of plane deformation	800 (m)
" " " " "	750 (m)

Table XV. Selected IR Absorptions of The TMP-TDI Adduct Blocked With HEMA And Para-cresol

Assignment	Wave Number cm^{-1}
N-H stretch	3300 (s)
C-H aliphatic stretch	2965 (m)
C=O carbonyl	1700 (s)
C=C aromatic, skeletal stretch	1590 (s)
" " " "	1510 (s)
" " " "	1440 (s)
" " " "	1400 (s)
C-N stretch	1290 (s)
C-O stretch	1200 (s)
" "	1060 (s)
" "	980 (m)
C-H out of plane deformation (alkene)	940 (w)
C-H out of plane deformation	860 (w)
" " " " "	810 (m)
" " " " "	750 (m)

Table XVI. Selected IR Absorptions of The TMP-TDI Adduct Blocked With HEMA And Ortho-chlorophenol

Assignments	Wave Number cm^{-1}
N-H stretch	3300 (s)
C-H aliphatic stretch	2960 (m)
C=O carbonyl	1700 (s)
C=C aromatic, skeletal stretch	1580 (s)
" " " "	1510 (s)
" " " "	1430 (s)
" " " "	1400 (s)
C-N stretch	1285 (m)
C-O stretch	1200 (s)
" "	1050 (s)
" "	980 (m)
C-H out of plane deformation (alkene)	940 (m)
C-H out of plane deformation	860 (w)
" " " " "	750 (m)

Table XVII. The Elemental Analysis Results

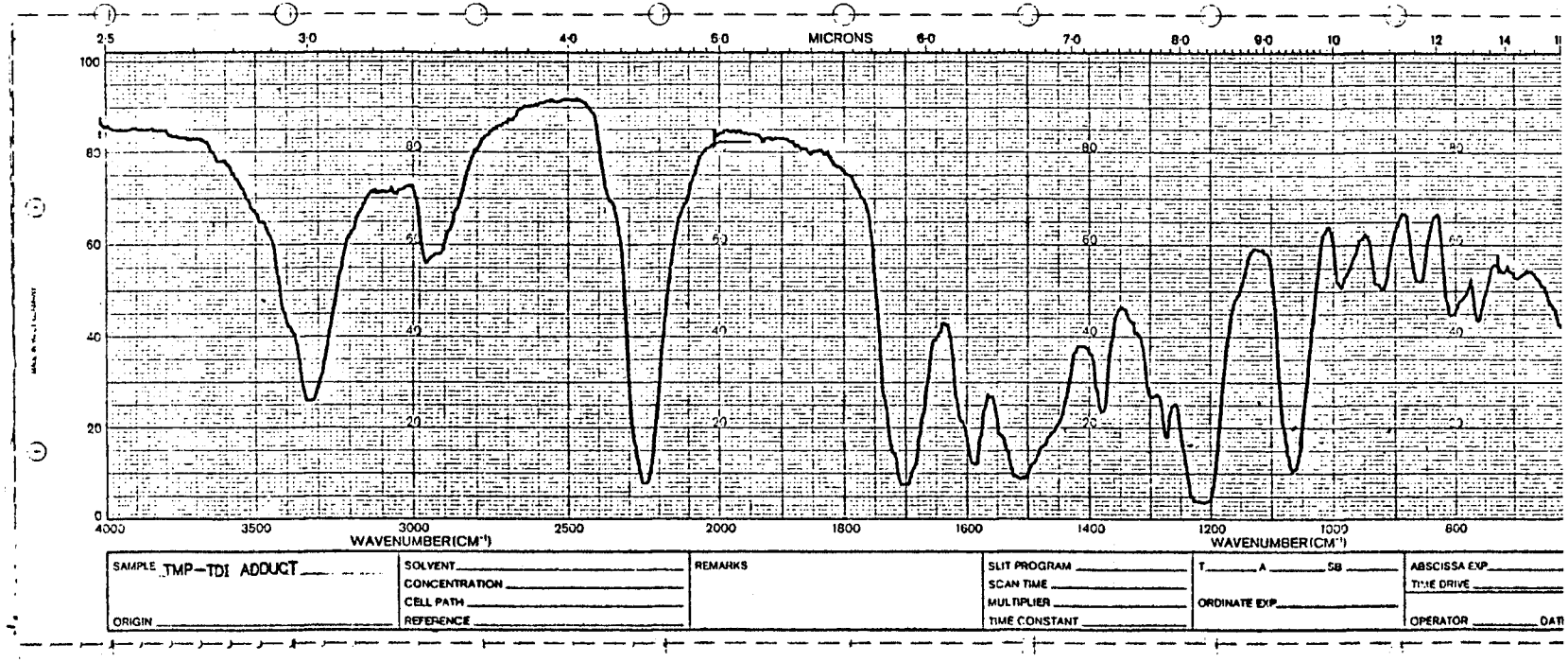
Compound		Carbon%	Hydrogen%	Nitrogen%	Chlorine
TMP-TDI Adduct	Theoretical	60.36	4.91	12.79	-
	Observed	60.52	5.10	12.63	-
Eugenol Blocked	Theoretical	65.84	5.96	7.31	-
Adduct	Observed	64.96	5.80	7.99	-
P-cresol Blocked	Theoretical	66.11	5.75	8.56	-
Adduct	Observed	65.29	5.70	9.15	-
O-chlorophenol	Theoretical	58.76	4.54	8.06	10.2
Blocked Adduct	Observed	58.77	4.60	8.62	8.57
HEMA Blocked	Theoretical	59.07	5.05	8.10	-
Adduct	Observed	58.41	5.68	8.24	-
HEMA-Eugenol	Theoretical	62.14	5.97	7.65	-
Blocked Monomer	Observed	61.75	5.97	7.95	-
HEMA-P-cresol	Theoretical	62.18	5.86	8.29	-
Blocked Monomer	Observed	62.60	6.37	8.17	-
HEMA-O-chlorophenol	Theoretical	58.63	5.26	8.05	5.09
Blocked Monomer	Observed	59.92	6.02	7.98	2.97

Table XVIII The Elemental Analysis Results Based on Partial Dissociation

Compound	% Of Probable Dissociation		Weight % C	H	N	Cl
Eugenol Blocked Adduct	19.8	Theoretical	65.16	5.83	7.99	-
		Observed	64.96	5.80	7.99	-
P-cresol Blocked Adduct	19.3	Theoretical	65.32	5.64	9.15	-
		Observed	65.29	5.70	9.15	-
O-chlorophenol	17.4	Theoretical	58.96	4.59	8.62	9.01
		Observed				

Table XIX Melting Points of The Products

Compound	Melting Point (°C)
TMP-TDI Adduct	108-110
Eugenol Blocked Adduct	115-118
P-Cresol Blocked Adduct	135-138
O-Chlorophenol Blocked Adduct	132-135
HEMA Blocked Adduct	72-73
HEMA-Eugenol Blocked Adduct	93-95
HEMA-P-Cresol Blocked Adduct	96-98
HEMA-O-Chlorophenol Blocked Adduct	94-96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REMARKS
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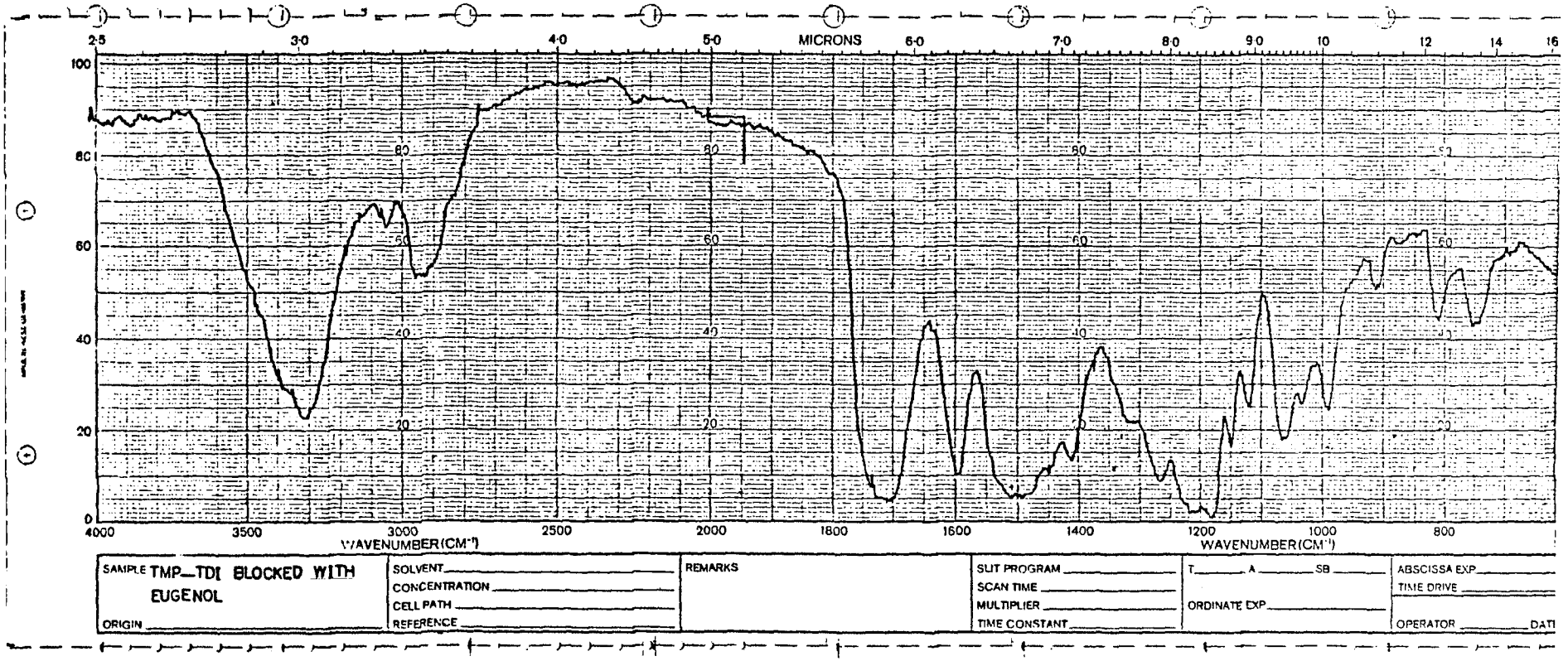
TIME DRIVE
OPERATOR
ORIGIN

Figure 4.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WAVENUMBER(CM⁻¹)
SAMPLE TMP—TDI BLOCKED WITH EUGENOL
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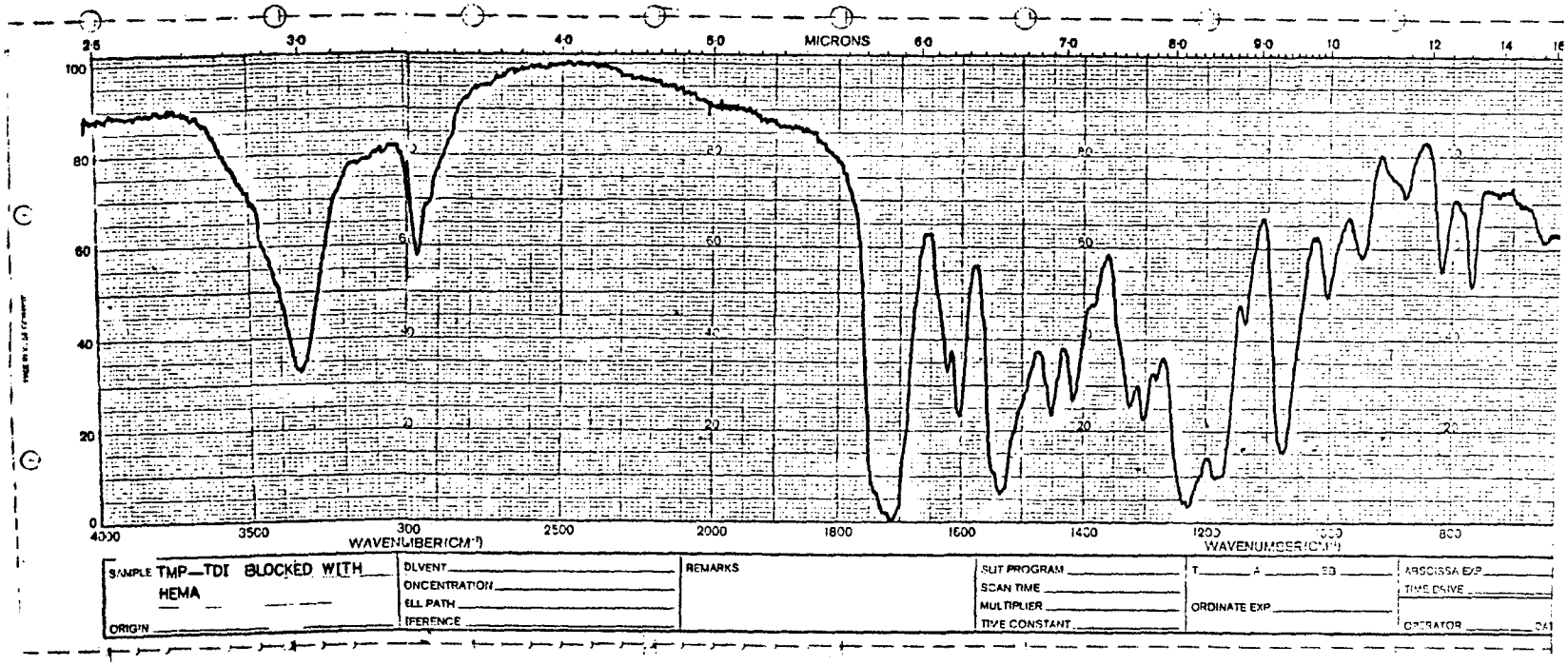
Figure 5.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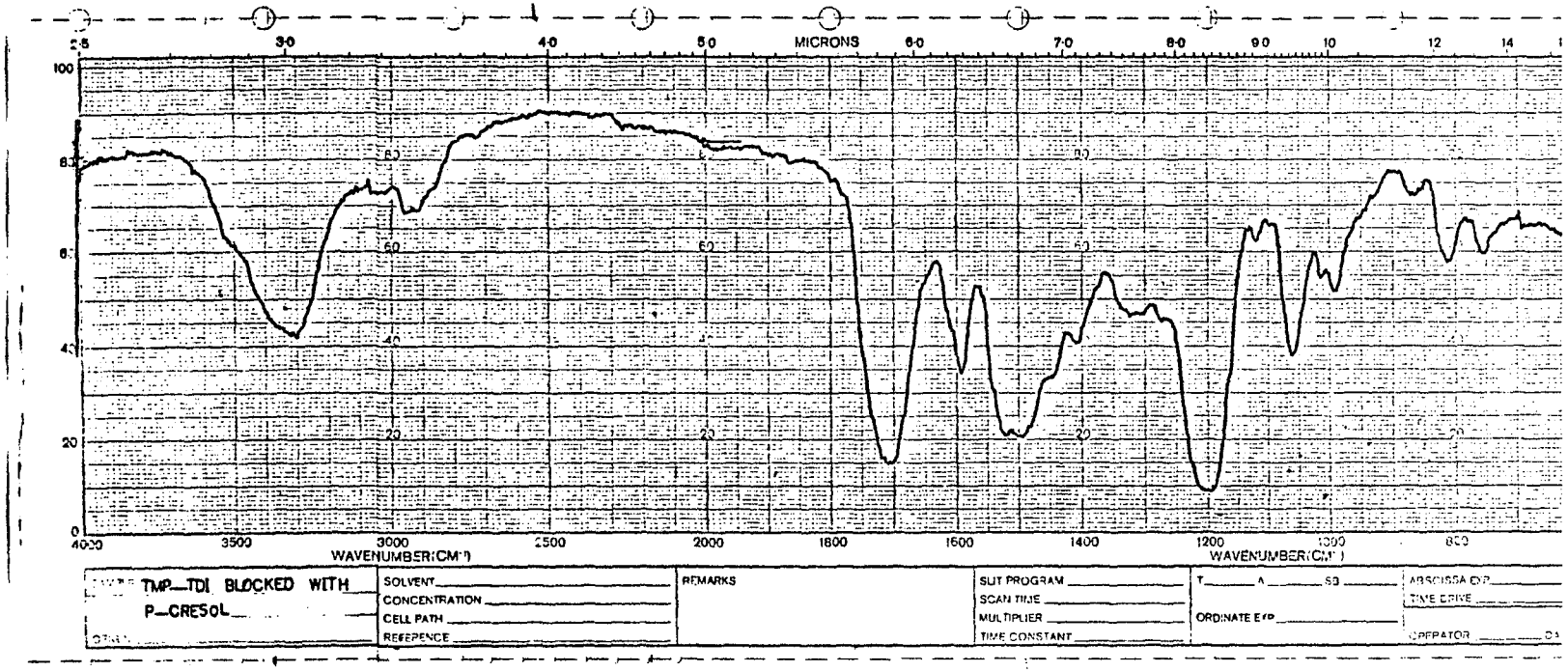
REMARKS

Figure 6.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WAVENUMBER(CM⁻¹)
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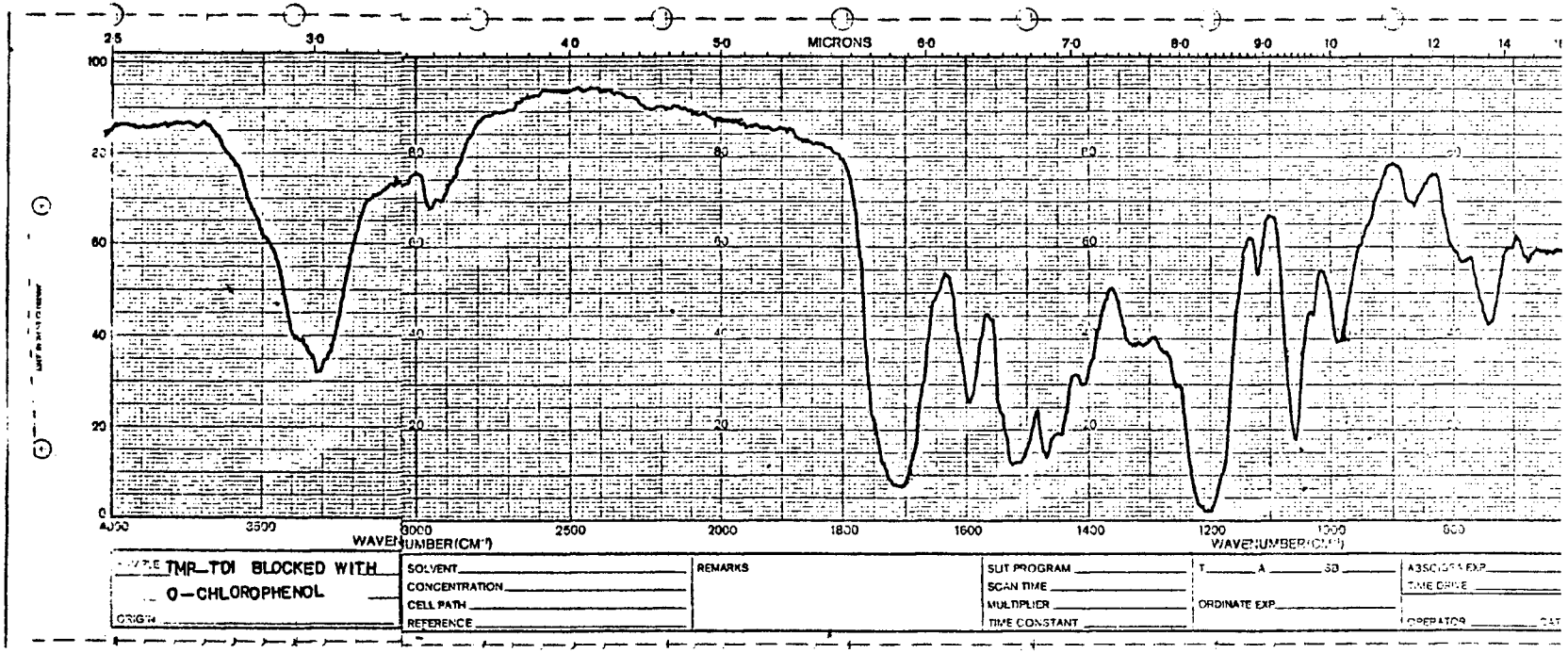
Figure 7.

58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SCAN TIME
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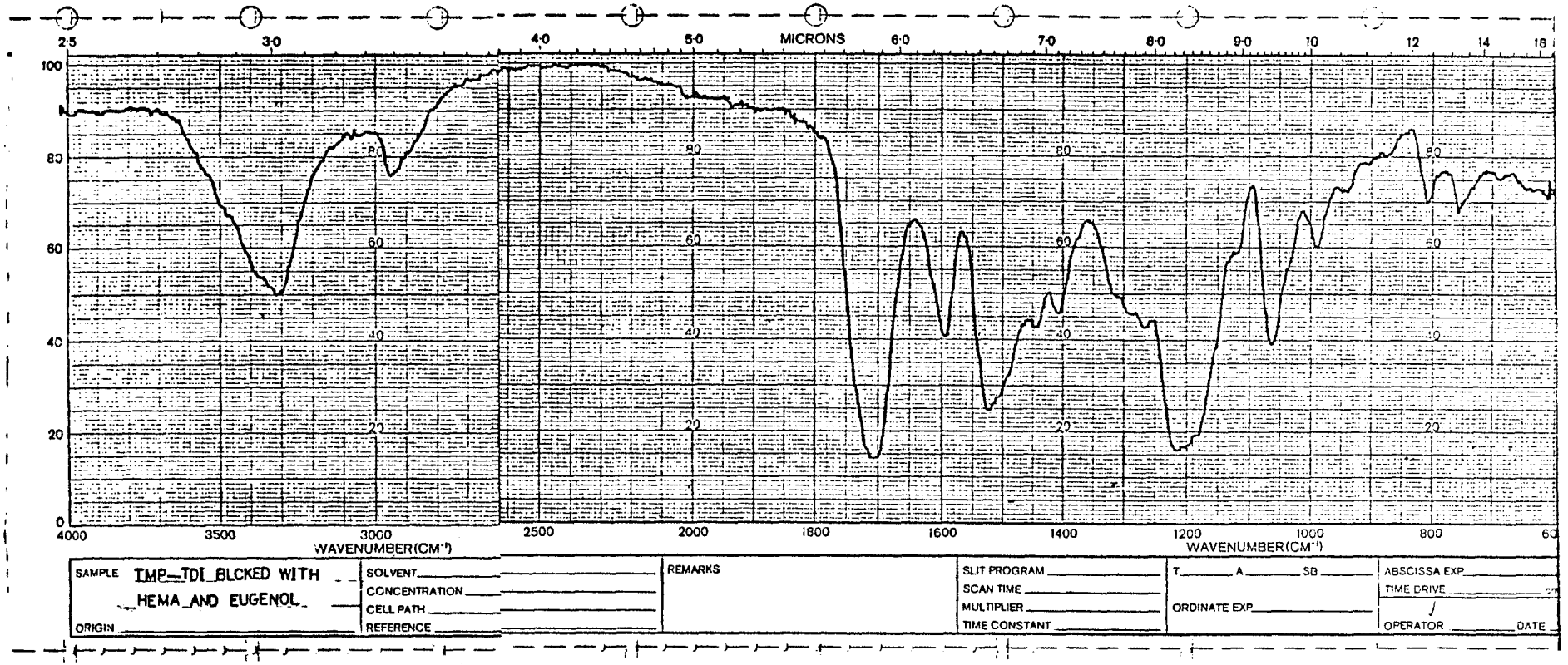
TIME CONSTANT
ORDINATE EXP
OPERATOR

Figure 8.

59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CONCENTRATION
CELL PATH
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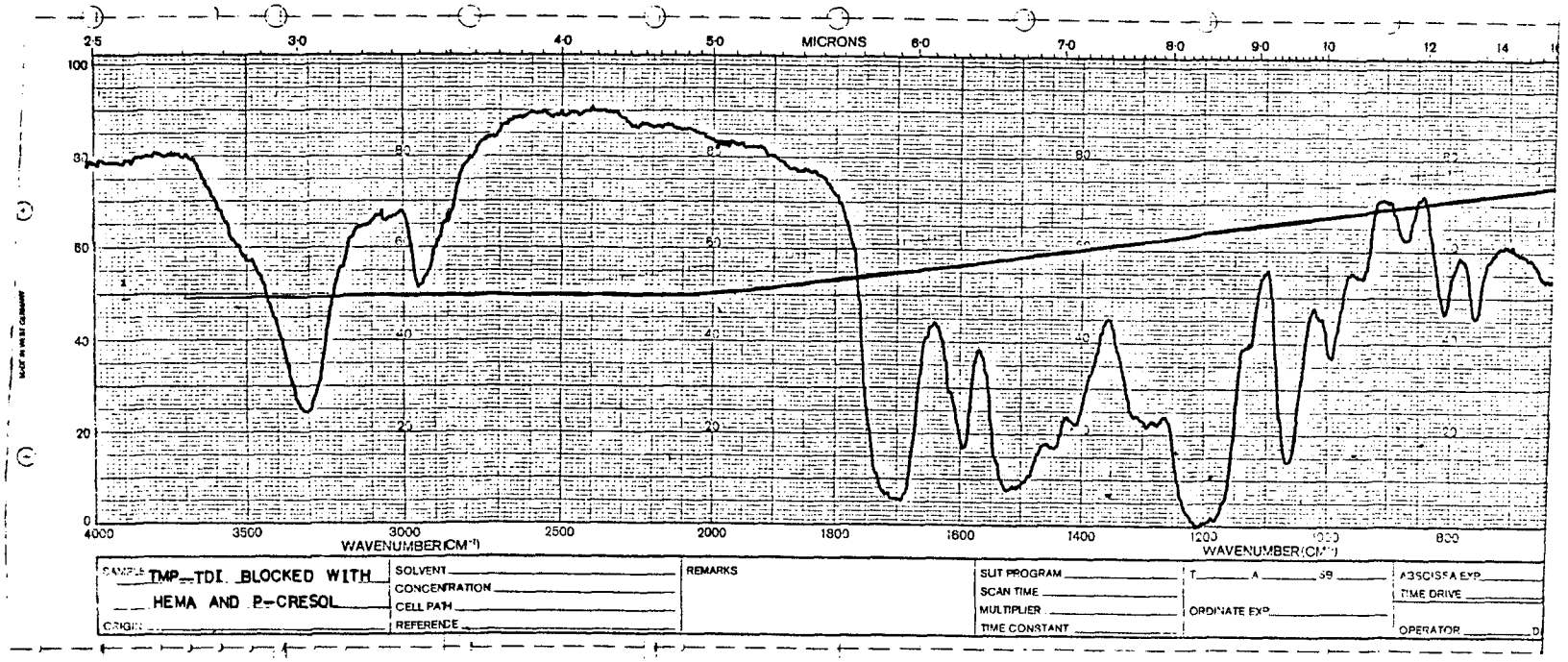
Figure 9.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WAVENUMBER(CM⁻¹)
TMP-TDI BLOCKED WITH
HEMA AND P-CRESOL
SOLVENT
CONCENTRATION
CELL PATH
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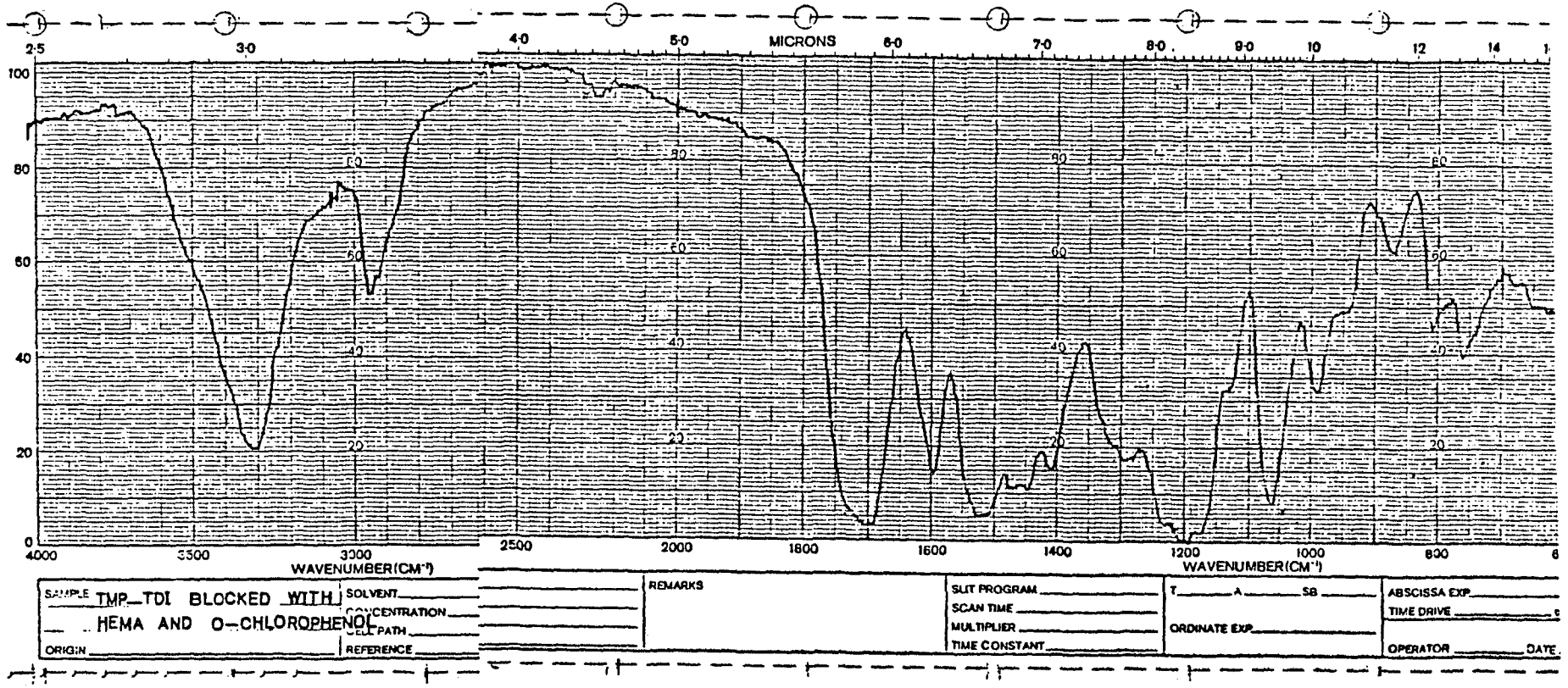
MULTIPLIER
TIME CONSTANT
ORDINATE EXP
ABSCISSA EXP
TIME DRIVE
OPERATOR

Figure 10.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1400
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1000
800
WAVENUMBER(CM⁻¹)
WAVENUMBER(CM⁻¹)
SAMPLE TMP-TDI BLOCKED WITH HEMA AND O-CHLOROPHENOL
SOLVENT
CONCENTRATION
CELL PATH
ORIGIN
REFERENCE
REMARKS
SLIT PROGRAM
SCAN TIME
MULTIPLIER
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ABSCISSA EXP
TIME DRIVE
OPERATOR
DATE

Figure 11.

ABBREVIATIONS

TMP	Trimethylolpropane or 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol
TDI	Tolylene-2,4-diisocyanate
THF	Tetrahydrofuran
HEMA	2-Hydroxyethyl methacrylate
DBTDL	Dibutyltin dilaurate

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