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ABSTRACT

Title of Thesis: Approaches to the Synthesis of Dentin Bonding Agents Containing Vinyl and Carbamate Functional Groups

Steven W. Amato, Master of Science in Engineering Science, 1987

Thesis directed by: Professor W.H. Snyder and Professor D.S. Kristol

The synthesis of four new monomers containing vinyl and carbamate functional groups was attempted. The desired products were N-m-methacryloxyphenyl-O-phenyl carbamate, N-p-methacryloxy-O-phenyl carbamate, m-N-phenylcarbamato-2-methacryloxyethoxy benzoate, and p-N-phenylcarbamato-2-methacryloxyethoxy benzoate. The carbamate functional group was derived by the Lewis Acid catalyzed reaction of meta-aminophenol, para-aminophenol, meta-aminobenzoic acid, and para-aminobenzoic acid with diphenyl carbonate. The vinyl function was derived, in the case of the aminophenols, by reaction with methacrylyl chloride, and in the case of the aminobenzoic acids, with 2-hydroxyethyl methacrylate.

Partial products only were prepared, these being the two carbamate functional phenols, the two carbamate functional benzoic acids, the two methacryloxy functional derivatives of the aminophenols, and the two 2-methacryloxyethoxy

aminobenzoates. The products were characterized by elemental analysis and infrared spectroscopy.

It is believed that the desired products may be useful as dentin bonding agents for restorative purposes. Additionally, the reaction products of both meta- and para-aminobenzoic acid with 2-hydroxyethyl methacrylate were highly viscous, resinous fluids exhibiting properties which may prove these substances to be useful as contact- or pressure-sensitive adhesives.

APPROACHES TO THE SYNTHESIS OF DENTIN BONDING AGENTS CONTAINING VINYL AND CARBAMATE FUNCTIONAL GROUPS

by

Steven W. Amato

Submitted to the Faculty of the Graduate School of
the New Jersey Insititute of Technology in
partial fulfillment of the requirements
for the degree of Master of Science
in Engineering Science
1987

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DEDICATION

This thesis is dedicated to my wife, Ora C. Amato, without whose unending support this project would not have been completed.

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INTRODUCTION

A. Objective

This research was undertaken in an attempt to produce and characterize four new monomers which may be useful as dentin bonding agents. Each monomer contains a vinyl functional group which is intended to polymerize via a free-radical mechanism and a carbamate functional group, or blocked isocyanate, which is intended to deblock at the polymerization temperature. The deblocked isocyanate is then available for further reaction with functional groups contained in the chemical constituents of teeth. Due to the chemical similarities of teeth and bone, these monomers may also be useful for bonding bone tissue.

The use of chemical bonding agents for dentin is desired as a more permanent means of attaching bridgework, crowns, and other dental devices, thereby eliminating such devices as wire hooks and loops. The use of adhesives is also desired for purposes of comfort and esthetics for the recipient of the restorative device.

In order to gain a more complete understanding of the objective of this research, it is useful to discuss the historical aspect of dental restorative materials, the nature of adhesion and bioadhesion, the biochemistry of the tooth, and

the reaction mechanisms of the desired products of this research.

B. A Brief History of the Development of Synthetic Resins For Use in Dental Applications

Humankind has long been interested in dental restoration. Restorative materials historically parallels the development of the creative arts as evidenced by archeological findings. Etruscans and Phoenicians prepared restorative fixtures by holding human or animal teeth in place by metal wires or bands[1]. Similar techniques are still being utilized today. Circa 1700, skillfully carved dental structures of wood, bone, and ivory were developed[2]. This was the beginning of attempts to match restorative materials to the con- figuration of the individual mouth.

Dubois deChemant of Paris received a patent in 1789[3] for fused porcelain restorative devices, and this became the state of the art until the development of Vulcanite (hard rubber) in 1839 by Charles Goodyear. Nelson Goodyear, Charles' brother, received a patent for the dental applications of Vulcanite, and in 1853 Charles published "Gum Elastic and Its Varieties," wherein he described its dental applications in detail[4,5].

Two other synthetic resins were developed shortly thereafter. In 1868, John Wesley Hyatt described molding applications of cellulose nitrate (celluloid) for dental applications, and in 1870, the Albany Dental Company was formed[6]. In 1924, Doctor Stryker described dental applications of Bakelite, which is a phenol-formaldehyde resin developed by Leo Baekeland, in 1919[6].

Since 1930, various synthetic resins have been produced, and most have been applied to dental restoration. Some of these are: glycene, a reaction product of glycerine and phthalic anhydride, polyvinyl chloride, cellulose acetates, polystyrene, and acrylic resins[4,6].

In 1901, Doctor Otto Rohm invented polymethyl methacrylate. It was not until 1937 that it was used by Dr. Walter Wright as a dental restorative material[7]. He cited its use as a casting resin for dental fixtures, as well as a filling material for dental caries. A major advantage of using the monomer as a filling material is that it eliminates the need for first placing a cement into the cary, and then applying the filling material. It was superior to Vulcanite in appearance, and left no taste or odor associated with rubber process chemicals (sulfur, amine accelerators, plasticizers). A major drawback was a lack of dimensional stability. When polymerized, the filling material exhibits shrinkage, eventually allowing decay-causing material to work in-between the filling and the tooth material.

Various approaches have been attempted since then to alleviate the problem of shrinkage. These include using inorganic fillers such as silica (SiO_2) and alumina (Al_2O_3), and using pastes made of methyl methacrylate monomer blended with powdered polymethyl methacrylate[8,9].

A new approach (circa 1960) was to devise co-monomers which were of a high molecular weight which would reduce shrinkage on polymerization, and which contained structures within the molecule which, when polymerized, would impart physical property enhancement such as compression strength, tensile strength, and flexural strength[10].

The following are considered to be the essential requirements for any material which is to be used as a dental filling material, or as a cement for bonding tooth attachments[4,8,9,11,12]:

1. It must have esthetic qualities of color, taste, odor, and cleanliness.

2. It must have high compatibility with oral tissues.

3. It must possess the strength to resist functional stress, i.e., transverse, impact, tensile, and flexure.

4. It must possess dimensional stability during, and subsequent to, processing, i.e., warpage and shrinkage.

5. It must possess low water sorbtion either by imbibation or surface adsorption.

6. It should possess good hardness.

7. It should possess resistance to flow.

8. It must possess adaptability to a simple technique of processing and successful repair.

9. It should possess resistance to the oral environment as well as aqueous and non-aqueous solvents.

10. It should possess the relative weight and density of the natural material.

11. It must have compatible coefficients of thermal expansion and thermal conductivity.

12. It should possess resistance to porosity during and after processing.

13. It should provide successful cementation to itself after processing.

14. It should resist breakage during adjacent restorative work.

Acrylic resins have been demonstrated to have the flexibility to be formulated into products which satisfy these requirements.

C. Theories of Adhesion

There are several ways in which an adhesive or sealant holds two substrates together. These are as follows:

1. Mechanical Interlocking is not truly a property of adhesion, but is rather a result of proper joint design on

the microscopic scale, or surface pits and fissures on the macroscopic scale. Dental amalgams stay in place within a tooth only when a properly designed inverted "V" shape is created by the dentist prior to filling the cavity.

2. Molecular Diffusion is said to occur by the intermingling of molecules from adhesive and adherend. This is primarily applicable when both the adhesive and adherend are polymers with long chains capable of movement. Solvent cementing, heat welding, and sonic welding of polymeric substrates are believed to affect adhesions via molecular diffusion.

3. Adsorption: adhesion results from molecular contact between two materials and the surface forces that develop. The process of establishing continuous contact between the adhesive and the adherend is called "wetting." For an adhesive to wet a solid surface, the adhesive should have a lower surface tension than the critical surface tension of the solid. Good wetting results when the adhesive flows into the valleys and crevices on the substrate surface. Poor wetting results when the adhesive bridges over the valleys and crevices, and results in a reduction of the actual contact area between the adhesive and adherend, giving rise to a lower over-all joint strength.

Wettability is most often determined by measuring the contact angle between the adherend surface and the candidate

adhesive. A small contact angle indicates that the liquid is wetting the adherend effectively, while a large contact angle shows that the wetting is poor. Every surface has a critical surface tension, y_c of wetting. Liquids with surface free energies below y_c will have zero contact angles, and will wet the surface completely, while liquids with surface-free energies greater than y_c will have finite contact angles.

Comprehensive discussions of surface wetting phenomena can be found in works by Zisman[15] and Patrick[16]. Newman, Snyder, and Wilson[17,18,19] have investigated the wetting phenomena of various adhesives on tooth surfaces which lays the groundwork for this thesis.

After initial contact is achieved between adhesive and adherend through wetting, it is believed that permanent adhesion results primarily through forces of molecular attraction. Two types of chemical bonds are thought to be involved in adhesion and cohesion: primary electrovalent and covalent, metallic, and secondary (Van der Waal's forces).

Electrovalent bonds involve an actual transfer of electrons from one atom to another. The two substances are held together by the electrostatic forces which occur due to each being oppositely charged-ions.

Covalent bonds involve a sharing of electrons between two atoms. Such bonds are usually unidirectional bonds and may be considered to be partly ionic and partly covalent. They

apply to metals and alloys, and will not be considered further as they do not apply to the body of this work.

Van der Waal's Forces consist of:

1. Debye forces which are due to the existence of induced dipoles.

2. Keesom forces which are due to the existence of permanent dipoles.

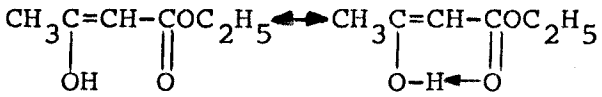
3. London dispersion forces which are the result of a non-polar dispersion effect which results from interaction between the random motions of internal electrons, molecules, atoms, and ions. These are by far the strongest of the Van der Waal's forces, with the exception of:

4. Hydrogen Bonding, which is a special case of dipole interaction. Hydrogen bonds are stronger than any of the first three types of electrostatic forces, although weaker than any of the chemical bonds to be discussed. Hydrogen bonding occurs when the electropositive hydrogen atom encounters a strongly electronegative species such as carboxyl or hydroxyl groups.

Hydrogen bonding is responsible for the high boiling point of water as compared to compounds of similar molecular weight (e.g., hydrogen sulfide or ammonia) which are gases at standard temperature and pressure. Only fluorine surpasses oxygen in the strength of its hydrogen bond. Hydrogen fluoride molecules remain in association even in the gaseous

state. A further example is that while water boils at 100 degrees Centigrade, and hydrogen fluoride boils at 19.54 degrees Centigrade, 35.5% (w/w) hydrogen fluoride in water boils at 120 degrees Centigrade.

Hydrogen bonding may not only link two or more molecules together, but may form rings (chelates) internal to a chemical substance, such as in the case of ethyl acetoacetate[9,20].



D. Biochemistry of the Tooth

In order to gain a more complete understanding of the intended manner in which the monomers may function as adhesives for dental restoratives, it is useful to discuss the structure and chemical constituents of the human tooth. Most important to orthodontics are the enamel and dentin (See Figure 1).

The enamel is the outermost portion of the tooth, and is 96 per cent inorganic in nature. The mineral content is primarily of the formula $Ca_{10}(PO_4)_6X_2$, where X is usually hydroxyl (hydroxyapatite) and, to a lesser degree, Fluoride (fluoroapatite). Approximately 3 per cent of enamel is water, and 0.6 per cent is organic matter. The remainder

varies from person to person, and consists of compounds containing sodium, magnesium, lead, zinc, tin, and other elements. Bonding to enamel, therefore, occurs primarily through mechanical interlocking and secondary (Van der Waal's) bonds with the hydroxyl function of the inorganic constituent as the major site for covalent bonding.

Dentin is more complex in nature than the enamel in that it is approximately 75 per cent inorganic and 20 per cent organic matrix, with 5 per cent of various other constituents, including 2-3 per cent water and the remainder being similar compounds as found in the enamel.

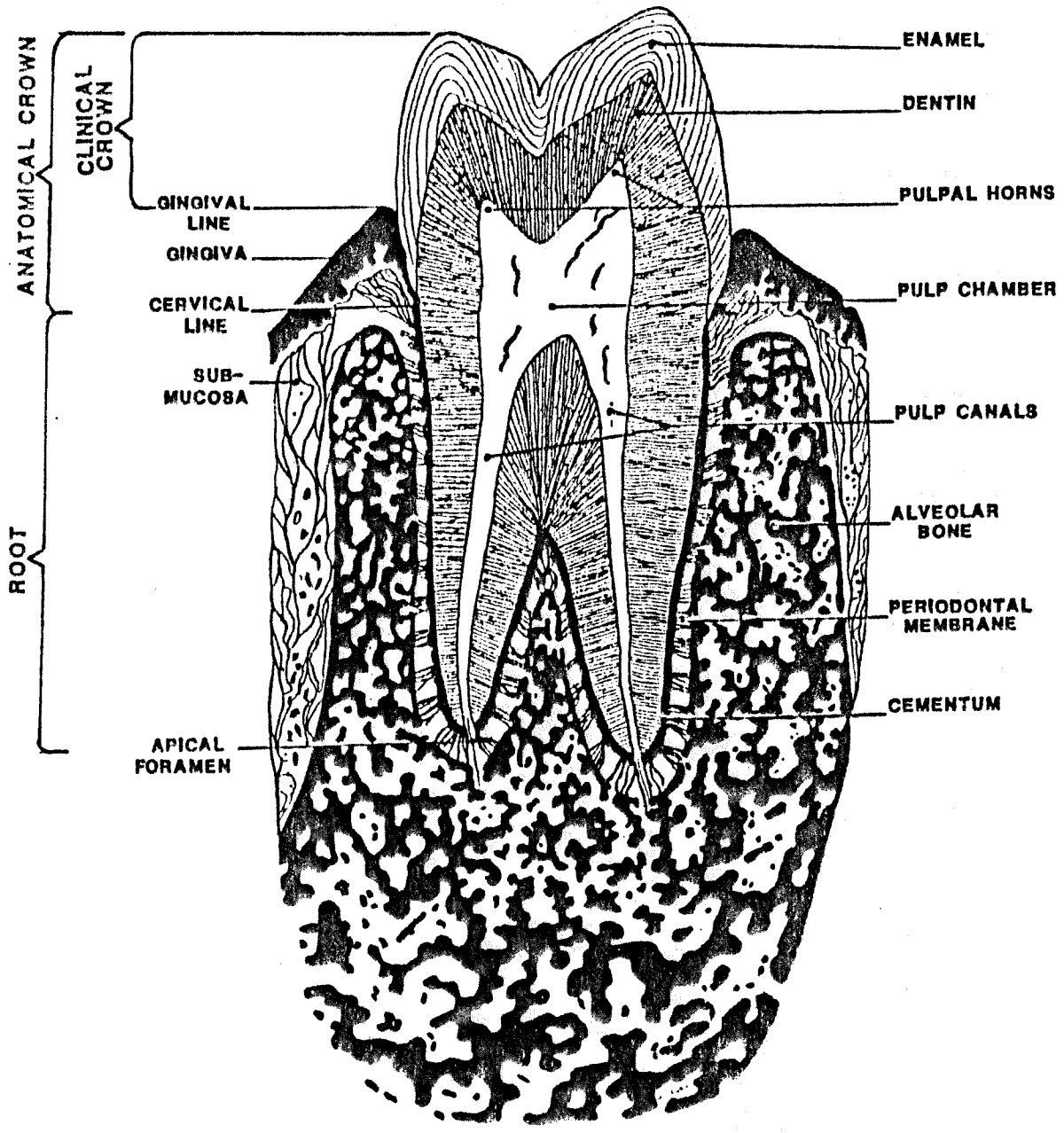


FIGURE 1
ANATOMICAL STRUCTURES OF AN ERUPTED TOOTH [55]

The Mineral Content of Dentin

The mineral content of dentin is primarily hydroxyapatite

$$Ca_{10}(PO_4)_6\ (OH)_2$$

often isomorphous substitution occurs in hydroxyapatites, particularly F^- or Cl^- for OH^- and Sr^{2+} for Ca^{2+}. The specific surface area of chemically-deproteinated bone and dentin is within the range of 100 to 200 m^2/g. For comparison, synthetically precipitated silica (SiO_2) has a specific surface area of 200 to 400 m^2/g.

Surface absorption studies have shown that water molecules were strongly absorbed for only two monolayers. A study of the uptake of stearic acid from cyclohexane solution showed that the long chain molecules lined up in parallel bundles perpendicular to the solid surface. Similar studies on the uptake of biological macromolecules in aqueous solutions indicate the same type of orientation. Strong interaction was found with the (Ca^{2+}) and (OH^-) of hydroxyapatite. This infers that collagen in bone and dentin is bonded in some way to the mineral, at least partially accounting for the biomechanical properties of these hard tissues. Additionally, it has been found that biological hydroxyapatite are about 10 per cent deficient in calcium (from stoichiometry). Also present is up to 4 weight per cent of CO_3^{2-}. Infrared studies of synthetically-precipitated hydroxyapatite

suggest that, in some way, CO_3^{2-} substitutes for PO_4^{3-}. One study has shown that approximately 50 per cent of the CO_3^{2-} can be washed out into solution inferring that it was present on the surface while the remainder was located at PO_4^{3-} positions of hydroxyapatite.

Organic Material in Dentin

Approximately 90 per cent of the organic matrix of dentin is collagen. The other 10 per cent consists of phosphoproteins, proteoglycans, glycosaminoglycans, gamma-carboxyglutamate-containing proteins, glycoproteins, and plasma proteins. These are all biological macromolecules. All of the non-collagenous proteins in dentin are anionic in nature. About 1 to 3 per cent of the non-collagenous proteins are non-separable from collagen and there is evidence that they are covalently bound. It has been suggested, but not conclusively proven, that these glycoproteins serve some function as an accelerator for the mineralization of the major matrix constituent, collagen.

The primary constituent of the organic matrix, collagen, consists of a highly insoluble, fibrillar material that is constructed of many elongated threadlike molecules which are cross-linked together. Microscopically, collagen fibers are layered and arranged in different ways within different

tissues, for example, in the cornea the fibers are arranged in orthogonally stacked sheets while in bone and dentin these fibers are swirled into a seemingly disordered array.

About 95% of an individual collagen molecule has an amino acid sequence with glycine in every third position. The structure could be represented as (Gly-x-y)n and in the case of interstitial collagen there are 338 to 342 of these repeat units. Also occuring are many proline and hydroxyproline units distributed throughout the alpha chain. The sum of proline and hydroxyproline is about one fourth of all the amino acids present. The alpha chain also contains short sequences at both the NH_2 and COOH-terminal ends that do not have this type of Gly-x-y sequence.

Collagen molecules consist of three alpha chains which are arranged in a coiled-coil fashion. Individual chains are twisted into a left handed minor helix with three amino acids per repeat. In turn, the three polypeptide chains are twisted about each other right-handedly composing the major helix. The triple helical array is stabilized by numerous hydrogen bonds formed between the peptide bond, amide and carbonyl groups of adjacent chains. Another significant stabilizing factor for the collagen triple helix is the presence of regularly spaced proline and hydroxyproline units. These imino acids contain five membered rings which prevent free rotation of the polypeptide chains within the major helix.

Table 1

Amino Acid Composition of Human Dentin[57]

Amino Acid	Residues/1000
Lysine	23
Hydroxylysine	8.4
Histidine	5.3
Arginine	47
Glutamic Acid	73
Aspartic Acid	55
Threonine	19
Serine	38
Hydroxyproline	101
Proline	115
Glycine	319
Alanine	112
Valine	25
Methionine	5.2
Leucine	26
Isoleucine	10
Tyrosine	2.3
Phenylalanine	14

E. The Use of Acrylics in Restorative Dentistry

There are currently many products commercially available as dental restorative resins which have been synthesized and subsequently formulated for ease of use by the dental professional. The use of methacrylates have gained wide acceptance due to their low toxicity and high color retentiveness. The color retentiveness is because the absence of an alpha hydrogen atom adjacent to the caybonyl group prevents oxidative free radical reactions which would form conjugated double bonds and consequent differential light absorption and discoloration.[24]

Early products were simple blends of methylmethacrylate monomers with pulverized polymethyl methacrylate, (and/or) glass beads, benzoyl peroxide initiator and a liquid diamine activator. This type of product, however, is not completely satisfactory due to its high coefficient of expansion in relation to tooth material and poor compressive strength.

Many efforts have been made to improve on the drawbacks of methyl methacrylate and Mao and Reegen [25] have studied the effects of various substituents on the side chain of methacrylates. They concluded that increases of polarity or introduction of aromatic ring structures greatly improved the peel strength and compressive strength of methacrylate polymers. In the former case decreased crystallinity was

postulated and in the latter case interaction of the pi electrons was postulated as a contributing factor to improved performance.

Recent advances in commercial products include Bisphenol-A glycidyl methacrylate (BIS-GMA)[9] and urethane dimethacrylate (Fotofil)[26] where high structure and the presence of difunctionality lead to higher strength in the polymerized resin. Polyacrylic acids have been shown to bond to dentin, however, moisture absorption by the monomer weakens the bond strength.[26] The use of methacrylate functional silanes have also been investigated as coupling agents for the fillers of various resin systems where the methacrylate functionality reacts with the monomer during the polymerization and the hydrolyzable group reacts with glass fillers and hydroxyl groups associated with the mineral content of the tooth. Bond strengths of BIS-GMA were increased almost threefold using this additive.[27]

In recent years there has been increasing interest in the use of thermosetting polyurethanes for dental applications.[14] Advantageous properties of polyurethanes are better prepolymerization wetting of the surface than acrylics and increased toughness versus acrylics due to the fact that they form strong intra- and inter-molecular bonds.[28,29]

Polyurethanes are characterized by the linkage -NH-C(O)O and are most commonly prepared by the reaction of di- or

polyfunctional isocyanates with hydroxyl or amine terminated polyesters or polyethers.[30] The most widely used commercial isocyanates are toluene diisocyanate (TDI) and 4,4-diphenyl methane diisocyanate (MDI). TDI is generally used commercially as an 80/20 blend of the 2, 4- and 2, 6- isomers respectively. The isocyanate (NCO) group in the 4 position of TDI is 8 to 10 times as reactive as that in the 2 position at 25°C. The 2 position increases in reactivity with increasing temperature until about 100°C where the reactivity of both positions is about the same. This allows synthesis of derivatives with predictable arrangement. Many excellent references discuss this chemistry.[30,31,32]

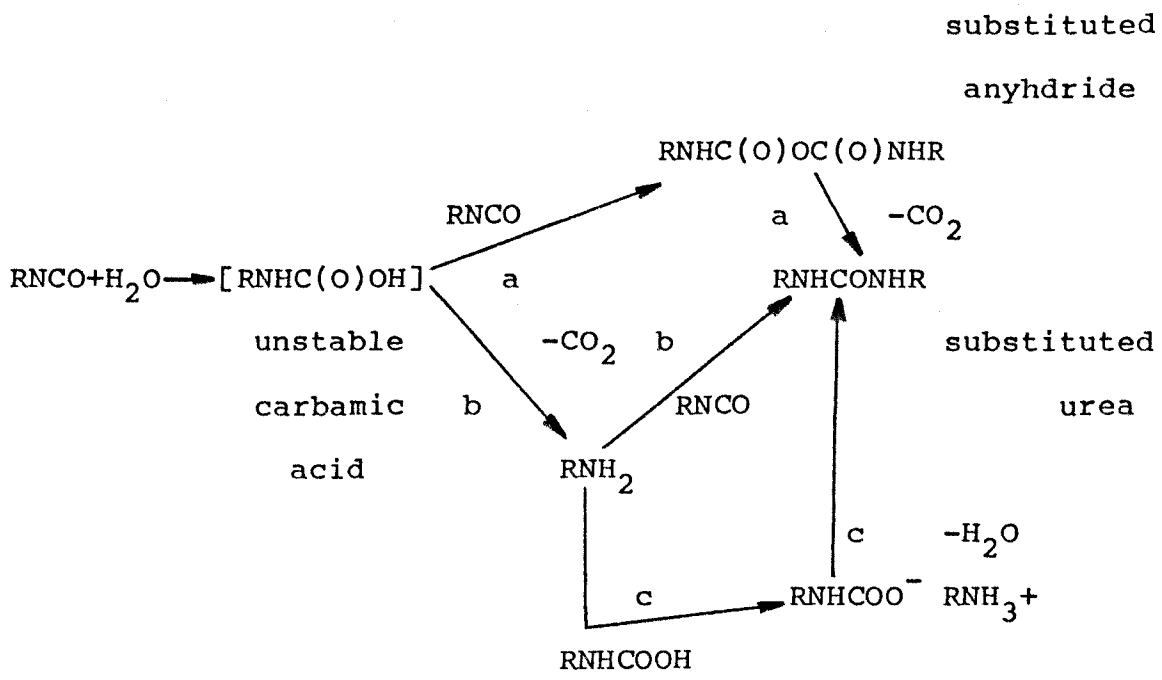
Several types of polymeric materials having urethane functionality have been reported as being useful for dental adhesives.[33,34,35] These include the moisture cure type consisting of a di- or polyisocyanate functional prepolymer; the two component type consisting of a di- or polyisocyanate functional adduct as a prepolymer and a di- or polyol functional prepolymer; and an adduct of a di- or polyfunctional isocyanate and a methacryloxy functional alcohol.

The first type has the drawback that it must be used in a thin film so that the carbon dioxide produced in the reaction with surface moisture is allowed to escape thereby preventing bubbles from forming in the film.

Many dental adhesives have been reported which are of the methacryloxy functional alcohol adduct type.[34,36] Buonocore and Casciani[34] reported the reaction products of various mono- and diisocyanates with 2-hydroxyethyl methacrylate as showing good adhesion to tooth surfaces and good physical properties. The isocyanates however were completely reacted and incapable of further reacting with tooth material. In effect these monomers are urethane containing acrylic monomers. Their advantages are that they exhibit lower shrinkage than unmodified acrylics and methacrylics and have some of the advantages of polyurethanes (toughness, wetting).

Antonucci, Brauer, and Termini[36] reported mono-adducts of 2-hydroxyethyl methacrylate with several diisocyanates. By using the mono-adduct they hoped to achieve reactivity between the free isocyanate function and the polar functional groups of collagen (OH, NH_2) and hydroxyapatite. They present physical evidence that indeed these monomers were able to bond to hard dental tissue, which is promising.

Isocyanate functional monomers and prepolymers have major drawbacks as can be seen from studying the isocyanate-water reaction.[35,37,38]



As can be seen the unstable carbamic acid can either immediately react with an additional NCO to form a substituted anhydride or lose CO_2 (which most often is the case) to form an amine. This amine group can further react with NCO to form a substituted urea (most often the case) or react with an unstable carbamic acid to form an ammonium salt which in turn may lose CO_2 to form a substituted urea. Additionally the anhydride may lose CO_2 to form a substituted urea. The end result for all possibilities in the reaction scheme is that one molecule of water consumes 2 molecules of NCO which are no longer available to react with the polar groups of dental tissue.

As an added concern, most aliphatic and aromatic isocyanates are irritating to the soft tissues and if the NCO groups are not fully consumed at the tooth surface the potential for patient discomfort may be significant. Any residual unreacted TDI or MDI will certainly be toxic.[39]

F. Blocked Isocyanate Adhesives

A possible solution to the difficulties encountered in attempting to design a molecule which will bond to dentin is the use of blocked isocyanates. This is especially beneficial toward solving the problem encountered by the isocyanate-water reaction. Blocked isocyanates are reported to be less reactive towards water and alcohols than the parent isocyanate compounds, and phenol blocked aromatic diisocyanates are reported to be unreactive toward hydroxyl containing materials but are very reactive to aliphatic primary and secondary amines at room temperature.[40] Various patents and books are available which discuss the chemistry of blocked isocyanates.[41-47]

The reaction which forms blocked isocyanates is reversible and can be represented as:

$$R\text{-}NH\text{-}COOR' \rightleftharpoons R\text{-}NCO + R'\text{-}OH$$

At elevated temperatures this equilibrium is disturbed and the reaction proceeds to the right hand side; this is commonly called "de-blocking." Thermal dissociation or de-blocking temperature have been reported for various blocked systems.[48]

Table II

De-blocking Temperatures of Isocyanates

	R	R'	
A)	Aryl-NHCOO-	Aryl	120°C
B)	Alkyl-NHCOO-	Aryl	180°C
C)	Aryl-NHCOO-	Alkyl	200°C
D)	Alkyl-NHCOO-	Alkyl	250°C

These temperatures are for illustrative purposes and substituent effects will cause some overlap. Generally, electron withdrawing groups on aromatic rings decrease stability while electron donating groups on the aromatic rings increase stability.[49] Therefore, it is essential that the proper choice of blocking agent is made in order to assure successful bonding to dentin. If the deblocking temperature is too low, the isocyanate may still react with water and, if the deblocking temperature is too high it may be unrealistic to be useful in an oral environment.

W.H. Snyder[50] believed that by using various substituted phenols as blocking agents for aromatic diisocyanates as well as co-reacting the diisocyanate with vinyl functional alcohols a suitable monomer could be synthesized which would bond to dentin as well as cross-link via free radical mechanisms which are typical of methacrylic and acrylic functional monomers.

These bifunctional monomers would be expected to deblock at the polymerization temperatures of the vinyl functional group and react with several of the amino acid units of the collagen present in dentin. The most likely amino acids to be reacted with the now free isocyanate are listed in Table III.

Table III

Amino Acids From Collagen Which May React With Free Isocyanate

Amino Acid	Functional Groups Present
Arginine	Primary amine, secondary amine
Cysteine	Thiol
Histidine	Imidazole NH
5-Hydroxylysine	Primary amine, secondary alcohol
3-Hydroxyproline	Secondary alcohol
Lysine	Primary amine
Serine	Primary alcohol
Threonine	Primary alcohol
Tyrosine	Phenolic OH

It is also expected that some limited amounts of isocyanate will react with the inorganic hydroxyapatite portion of the dentinal matrix.

Toward achieving this goal several masters theses have been directed.[51.52,53]

The object of this thesis, however represents a departure from previous attempts at the synthesis of blocked isocyanate monomers in that it is an attempt at creating the blocked isocyanate structure in the absence of an isocyanate as a part of the reaction scheme.

G. Preparation of Monomers

The objective of this thesis was to prepare four new monomers containing carbamate and vinyl functional groups. This research, however, represents a departure from previous work in this area in that it seeks to synthesize the carbamate functional group (or blocked isocyanate) by reacting a substituted aromatic amine (SAA) with diphenyl carbonate (DPC).

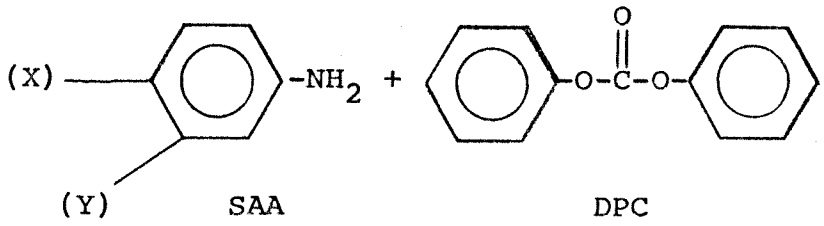
Specifically meta- and para- aminophenol were to be reacted with diphenyl carbonate to derive the carbamate functional group and with methacrylyl chloride in order to derive the methacryloxy or vinyl containing functional group and meta- and para- aminobenzoic acid were to be reacted with

diphenyl carbonate followed by reaction with 2-hydroxyethyl methacrylate (HEMA) in order to derive the desired functional groups.

All are two stage reactions and can be envisioned as having both a forward and reverse reaction scheme.

Thus, for the forward scheme:

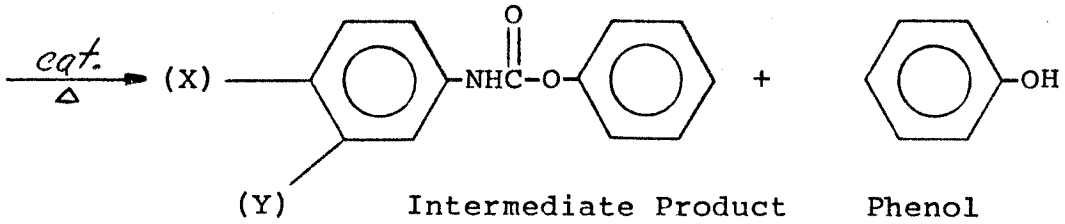
First stage:



SAA DPC

Where:

SAA	X	Y
#1	H	OH
#2	OH	H
#3	H	C(O)OH
#4	C(O)OH	H

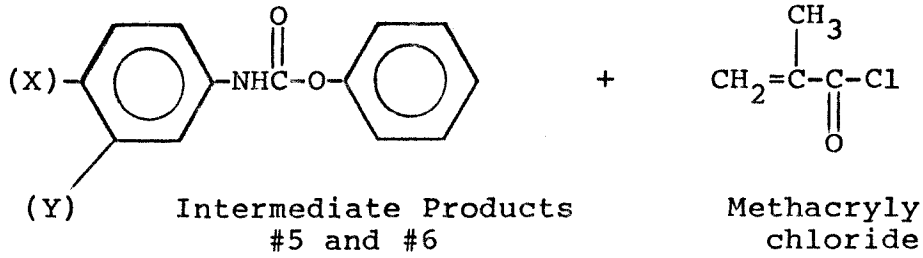


Intermediate Product Phenol

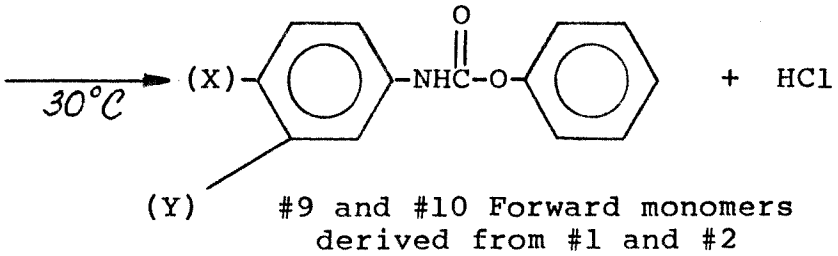
Where:

Intermediate Product	X	Y
#5	H	OH
#6	OH	H
#7	H	C(O)OH
#8	C(O)OH	H

Second stage:



Intermediate Products #5 and #6 Methacrylyl chloride

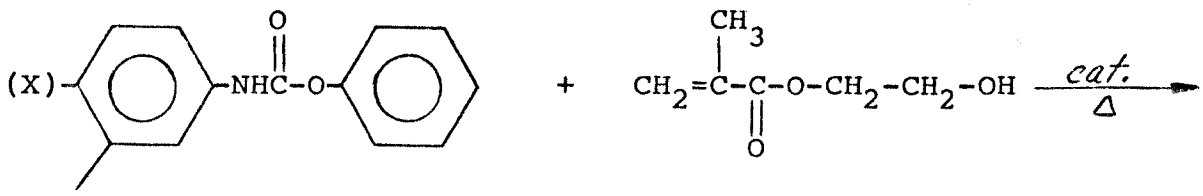


#9 and #10 Forward monomers derived from #1 and #2

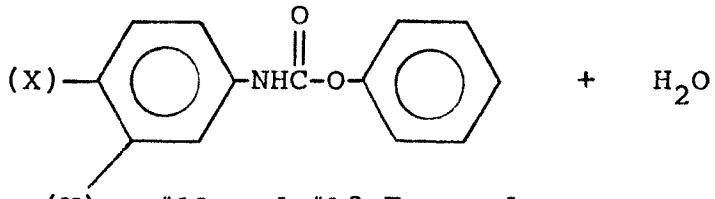
Where:

Forward Monomer	X	Y
# 9	H	$CH_2C(CH_3)C(O)O$
#10	$CH_2C(CH_3)C(O)O$	H

And



Intermediate Products #7 and #8 HEMA



#11 and #12 Forward monomers derived from #3 and #4

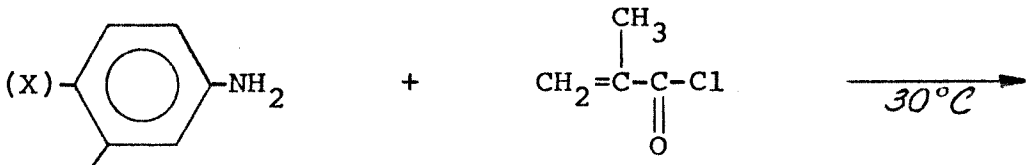
Where:

Forward Monomer	X	Y
#11	H	$CH_2C(CH_3)C(O)OC_2H_4OC(O)$
#12	$CH_2C(CH_3)C(O)OC_2H_4OC(O)$	H

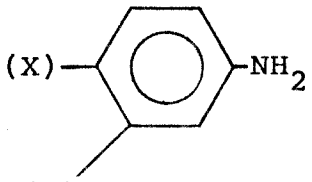
The reverse scheme first reacts the vinyl containing functional group with the SAA followed by the reaction with DPC.

Thus, for the reverse scheme:

First stage:



#1 and #2 methacrylyl chloride

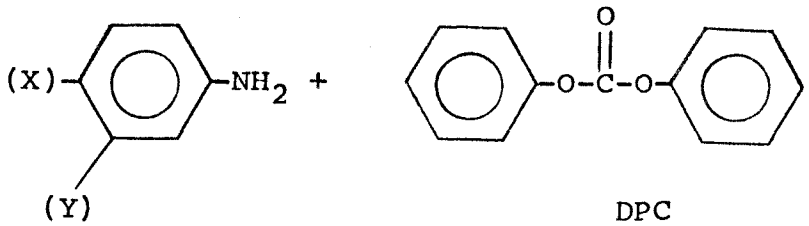


#13 and #14 Intermediate products derived from #1 and #2

Where:

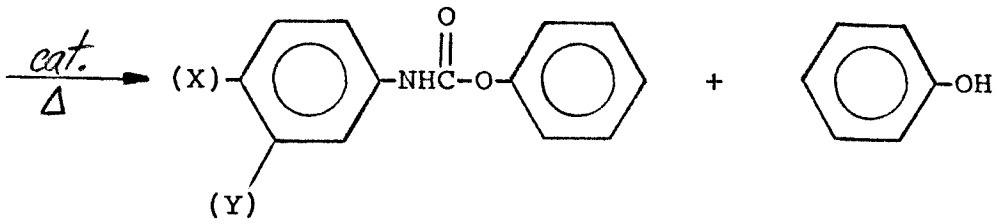
Intermediate Product	X	Y
#13	H	$CH_2C(CH_3)C(O)O$
#14	$CH_2C(CH_3)C(O)O$	H

Second stage:



DPC

#13 and #14 Intermediate products derived from #1 and #2



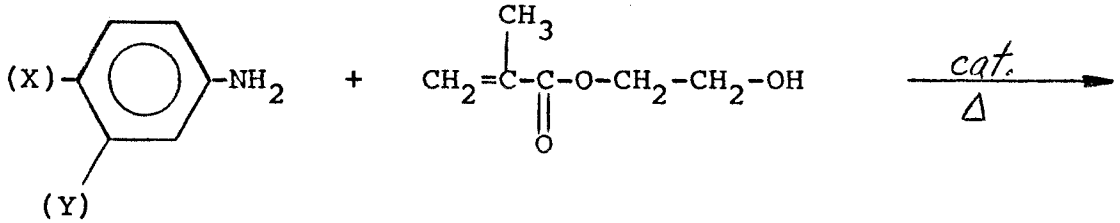
#15 and # 16 Reverse monomers derived from #1 and #2

phenol

Where: X and Y of #15 and #16 are the same as for #13 and #14

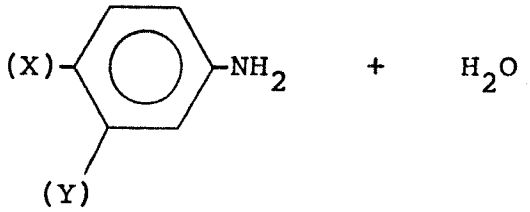
and

First stage:



#3 and #4

HEMA

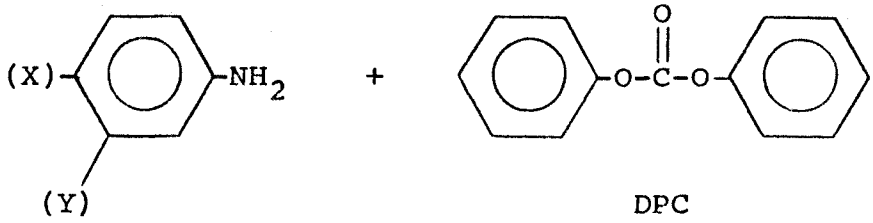


#17 and #18 Intermediate products derived from #3 and #4

Where:

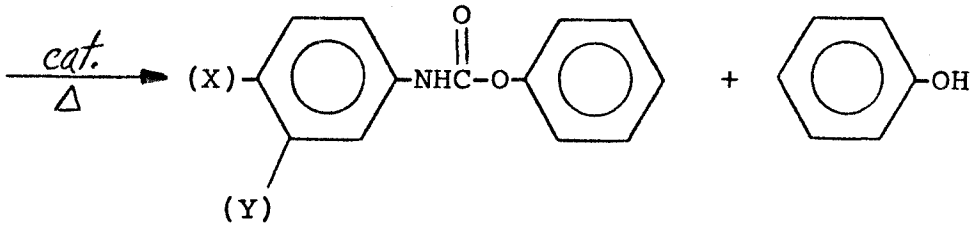
Intermediate Product	X	Y
#17	H	$CH_2C(CH_3)C(O)OC_2H_4OC(O)$
#18	$CH_2C(CH_3)C(O)OC_2H_4OC(O)$	H

Second stage:



DPC

#17 and #18 Intermediate products derived from #3 and #4



#19 and #20 Reverse monomers derived from #3 and #4

Phenol

Where: X and Y of #19 and #20 are the same as for #17 and #18

The forward scheme of preparation is preferred due to the fact that DPC and SAA reaction takes place at temperatures in excess of 120°C while it is desirable to prepare methacrylic esters at 70°C or below in order to prevent polymerization or the necessity of excessive amounts of inhibitors.

The DPC and SAA reaction was catalyzed by the use of zinc acetate (anhydrous) which is based upon a patent by Gurgiolo.[54] He states that no satisfactory mechanism has been found which fully accounts for the manner in which divalent zinc salts are able to catalyze this reaction. It is possible to envision a situation in which the acetate carbonyl oxygens form a chelate type structure with the amine hydrogens perhaps allowing the zinc central atom in turn to become sufficiently electropositive to weaken the carbonyl of the diphenyl carbonate allowing for the abstraction of a phenoxide ion from the diphenyl carbonate, followed by subsequent joining of the carbonyl with the amine nitrogen and elimination of phenol.

The reaction of m- and p- aminophenol with methacrylyl chloride was found to be extremely difficult and was modified by first reacting the aminophenols with sodium methoxide in an attempt to prevent formation of an amine hydrochloride without the necessity of using a protecting group on the amine. The reaction of meta- and para- aminobenzoic acid with HEMA was also found to be extremely difficult and several catalysts were utilized for this esterification reaction (for details see Experimental, Results, and Discussion Sections).

RESULTS AND DISCUSSION

During the course of this research several different approaches were attempted in an effort to synthesize the desired products. For the purpose of clarity they will be discussed in three discrete sections: Reactions of diphenyl carbonate with substituted aromatic amines, reactions of methacrylyl chloride with meta- and para-aminophenol, and reactions of 2-hydroxyethylmethacrylate with meta- and para-aminobenzoic acid.

A. Reactions of Diphenyl Carbonate with Substituted Aromatic Amines

The reaction of diphenyl carbonate (DPC) with the four substituted aromatic amines (SAA) was carried out utilizing a method described by Gurgiolo in his patent.[54] Method 1 was an attempt at utilizing the described process of the patent.

The reactants were all soluble in the reaction mixture at the reaction temperature as expected. The difficulty which arose in this research is that as the reaction proceeded and product was formed, a slurry resulted, the viscosity of which was high enough to prevent the mechanical stirrer from rotating. Gurgiolo states that the desired products were readily precipitated from the reaction mixture and upon examination of his examples it can be seen that he utilized

reactants which are liquids at room temperature. All of the reactants employed by this author are solids at room temperature and the products which were formed were not soluble at the reaction temperature.

Several attempts were made at recrystallization of the products formed by this reaction method, however, no suitable solvent was found. Many non-solvents were identified, however, which gave rise to the attempts using diethylene glycol dimethyl ether (diglyme) as a reaction medium.

Diphenyl carbonate is an excellent "solvent" for the aromatic amines used in this research and also acts as a co-solvent with diglyme to hold the aromatic amines in solution at room temperature. The boiling point of diglyme (162.2°C) is sufficiently high so that the desired reaction temperature (120°C) could be achieved. A sufficient quantity of diglyme was used so that as product precipitated out of the reaction mixture it would not prevent mechanical stirring. Additionally, at room temperature the products were readily collected via suction filtration and the reaction liquors were analyzed by gas chromatography for the presence of by-product phenol.

The reaction of DPC with meta-aminophenol (MAP) yielded a cream-colored platey precipitate, with para-aminophenol (PAP) a light brown platey precipitate, with meta-aminobenzoic acid (MABA) a faint purple powdery precipitate, and with

para-aminobenzoic acid (PABA) a cream-colored granular precipitate. The theoretical and actual yields are listed in Table IV.

TABLE IV

Yield Data From DPC + SAA Reactions

	SAA(g)	DPC(g)	Theoretical Yield (g)	Actual Yield (g)	% Yield
(MAP)	46.23	453.77	114.62	37.42	32.65
(PAP)	46.23	453.77	114.62	28.54	24.90
(MABA)	56.75	443.25	128.63	97.13	75.51
(PABA)	56.75	443.25	128.63	12.36	9.61

By-product phenol was found in all four reaction liquors. The percentage of the reaction liquor which is phenol is significantly higher than would be predicted by the theoretical yield in all cases except for the reaction with PABA. In all cases the percent phenol present is significantly higher than the actual yields would allow for. (See Appendix C, G.C. 1-4.) Table V lists the theoretical maximum percent phenol (adjusted for yield) which should be present in the reaction liquor, the percent found, and the percent found after adjusting for the relative ratios of a 10% (w/w) phenol in diglyme standard.

TABLE V

Phenol Yield Data

DPC + SAA Reactant	% Max. Theoretical Phenol	% Phenol Detected	Adjusted %
MAP	2.72	9.54	7.34
PAP	2.70	13.64	10.51
MABA	2.78	5.05	3.89
PABA	2.61	2.51	1.94

One would expect from this data that the desired product was not arrived at, however, infrared spectroscopy contradicts these results. (See Appendix A, I.R. 1-4.) The DPC + MAP product shows absorptions at 3270 cm^{-1} (N-H stretch), 1475 cm^{-1} (N-H bend), 1250 cm^{-1} (C-N stretch), and broad absorption between 3500 cm^{-1} and 3200 cm^{-1} (bonded OH). This would indicate that the aromatic nitrogen was still bonded to one hydrogen atom and therefore not trisubstituted. Also the presence of H-bonded OH would indicate that the phenolic OH had not been esterified.

The DPC + PAP product is perhaps suspect in that no distinct absorption is found in the vicinity of 3300 cm^{-1} which would indicate N-H stretch, however, there is evidence of N-H

bend at 1560 cm^{-1} and C-N stretch at 1400 cm^{-1}. There is also evidence of H-bonded OH between 3500 cm^{-1} and 3200 cm^{-1}.

The DPC + MABA product shows evidence of N-H stretch at 3240 cm^{-1}, and C-N stretch at 1265 cm^{-1} as well as H-bonded OH between 3500 and 3200 cm^{-1}. There is also an absorption at 1265 cm^{-1} which could indicate the presence of dimer acid in the KBr pellet.

The DPC + PABA product shows evidence of N-H stretch at 3300 cm^{-1}, and C-N stretch at 1285 cm^{-1}, as well as H-bonded OH between 3500 and 3200 cm^{-1}. There is an absorption at 1225 cm^{-1} which could indicate the presence of dimer acid in the KBr pellet. See Tables VI, VII, VIII, and IX for selected IR absorptions of these products. A possible explanation for the presence of unexpectedly high percentage of phenol as well as low yields is that substituted diphenyl ureas were formed which were soluble in the reaction liquor. This, however, was not investigated.

The elemental analyses of the DPC + SAA products are presented in Table X.

TABLE VI

Selected IR Absorptions of
DPC + MAP Reaction Product (IR #1)

Assignment	Wave Number, cm^{-1}
O - H bonded	3500-3100 (s)
N - H stretch	3280 (m)
C = O conjugated	1750 (m)
C = C aromatic skeletal stretch	1620 (s) 1590 (m) 1555 (m)
N - H bend ?	1475 (m) 1435 (m)
C - N stretch	1250 (m)
C - O stretch ?	1435 (m) 1130 (m)
C - H out of plane bending	935 (m) 850 (m)
N - H out of plane bending	755 (m)
meta disubstituted ring	775 (m) 675 (m)

TABLE VII

Selected IR Absorptions of
DPC + PAP Reaction Product (IR #2)

Assignment	Wave Number, cm^{-1}
O - H bonded	3500-3200 (m)
C = O conjugated	1760 (m)
C = C aromatic skeletal stretch	1620 (m) 1600 (m) 1500 (m)
N - H bend ?	1560 (m)
C - N stretch	1400 (m)
C - O stretch	1230 (m) 1175 (m) 1100 (m)
= C - H aromatic out of plane bending	830 (m) 745 (m) 680 (m)

TABLE VIII

Selected IR Absorptions of
DPC + MABA Reaction Product (IR #3)

Assignment	Wave Number, cm^{-1}
N - H stretch	3240 (s)
C = O conjugated, Aryl Acid	1690 (s)
C = C aromatic skeletal stretch	1590 (m) 1520 (m)
C - N stretch	1265 (s)
C - O stretch	1220 (m) 1190 (m) 1020 (m) 930 (m)
= C - H aromatic out of plane bending	780 (w) 745 (m) 705 (m)

TABLE IX

Selected IR Absorptions of
DPC + PABA Reaction Product (IR #4)

Assignment	Wave Number, cm^{-1}
N - H stretch	3300 (s)
C = O conjugated, Aryl Acid	1700 (s)
C = C aromatic skeletal stretch	1575 (m) 1520 (s)
C - N stretch	1285 (s)
C - O stretch	1225 (m) 1155 (m)
para substitution	850 (s)
= C - H aromatic out of plane bending	760 (s) 740 (m) 690 (w)

TABLE X

Elemental Analyses of DPC + SAA Products

Product of:	% C	% H	% N
DPC + MAP			
theoretical	68.12	4.84	6.11
actual	41.07	3.57	3.27
DPC + PAP			
theoretical	68.12	4.84	6.11
actual	70.05	4.91	5.18
DPC + MABA			
theoretical	65.37	4.31	5.45
actual	62.42	4.37	5.92
DPC + PABA			
theoretical	65.37	4.31	5.45
actual	57.11	4.29	6.13

The results for the DPC + MAP product are discouraging and can possibly be accounted for by the assumption that diglyme was not sufficiently removed from the sample. The high amount of oxygen in diglyme could account for the lower percentages of carbon and nitrogen detected. The results for the other three DPC + SAA products are much more encouraging although not exactly within experimental error.

B. Reactions of Meta- and Para-aminophenol with Methacrylyl Chloride

Three methods were attempted in an effort to derive the desired aminobenzoic ester. All three methods presumed that the desired product would be insoluble in water and soluble in an aromatic solvent. This was expected to be true because similar compounds such as 3-aminobenzoic acid, ethylester, and 4-aminobenzoic acid, ethyl, propyl, and butyl esters all exhibit this behavior.[57]

The first method was based upon discussions with W.H. Snyder. He believed that the phenolic OH would be sufficiently reactive toward the acid chloride so that further modification would not be required and that the presence of triethyl amine in the reaction mixture would be more likely to take up the resultant hydrochloric acid then the aminobenzoate. No aromatic soluble product was isolated, however, and it is believed that the water-soluble hydrochloride was formed.

The second method was based upon the belief that if the phenoxide ion could be made more reactive to the acid chloride the reaction would proceed more smoothly.[58] It was, therefore, attempted to react sodium methoxide with the aminophenol prior to reaction with the acid chloride. Significant quantities of methanol were produced, however, no aromatic soluble product could be isolated.

The third method was attempted based upon the belief that if a water-soluble solvent was used which was an extremely good solvent for all reactants, then addition of minor amounts of water would kick out the water incompatible product preferentially to the reactants. As it occurred, however, a brown precipitate formed in both reactions (meta and para) and it was decided to filter and wash the product as a recovery method.

The infrared spectrum of the MAP + methacrylyl chloride product shows a very weak absorption at 1640 cm^{-1} which could be a carbonyl shifted to lower frequency absorption due to both conjugation and hydrogen bonding. There appears to be evidence of N-H stretch at 3270 cm^{-1}, and C-N stretch at 1265 cm^{-1}. The broad absorption from 3500 cm^{-1} through 3200 cm^{-1} could be due to residual methacrylic acid which would have been formed during addition of deionized water which was used to dissolve by-product sodium chloride and destroy residual methacrylyl chloride. It could also be caused by residual amine hydrochloride mixed with the product. Both cases assume incomplete washing and drying of the product. There is some evidence for the latter possibility based on elemental analysis.

The PAP + methacrylyl chloride product has a similarly indistinct infrared spectra. Neither product, however, resembles the IR Spectrum of the parent aminophenol or

methacrylic acid (see Appendix A, IR#'s 5 and 6, Appendix B, IR#'s 10, 13, and 14). See Tables XI and XII for selected IR absorptions of these two products.

TABLE XI

Selected IR Absorptions of Methacrylyl Chloride + MAP Reaction Product (IR #5)

Assignment	Wave Number, cm^{-1}
N - H stretch	3270 (w)
C = O	1650 (w)
C = C aromatic skeletal stretch	1600 (m) 1535 (m) 1435 (m)
C - N stretch	1265 (s)
C - O stretch	1230 (m) 1200 (m) 1145 (m)
= C - H aromatic out of plane bending	850 (m) 770 (m) 675 (m)

TABLE XII

Selected IR Absorptions of
Methacrylyl Chloride + PAP
Reaction Product (IR #6)

Assignment	Wave Number, cm^{-1}
O - H bonded ?	3500-3200 Broad
C = O	1700 (w)
C = C aromatic skeletal stretch	1600 (m) 1585 (w) 1470 (w)
C - N stretch ?	1310 (w)
C - O stretch	1230 (w) 1190 (w)
= C - H aromatic out of plane bending	810 (w) 750 (w) 680 (w)

The elemental analyses of the two products look promising, however, neither are within experimental error. (See Table XIII.)

TABLE XIII

Elemental Analyses of MAP and PAP +

Methacrylyl Chloride Reaction Products

Product of:	%C	%H	%N	%Cl
Methacrylyl Chloride + MAP				
theoretical	67.78	6.26	7.90	0.00
actual	62.57	5.87	7.42	0.73
Methacrylyl Chloride + PAP				
theoretical	67.78	6.26	7.90	0.00
actual	62.55	5.64	7.22	$\angle$0.20

The elemental analysis of the MAP reaction supports the supposition that some amine hydrochloride was still present in the product. The low results for all C, H, and N percentages also could be accounted for by the presence of a small amount of residual triglyme.

The percent yields are presented in Table XIV.

TABLE XIV

Percent Yields of MAP and PAP

Reactions with Methacrylyl Chloride

Methacrylyl Chloride(g)	MAP(g)	PAP(g)	Theoretical Yield(g)	Actual Yield(g)	% Yield
57.50	54.57	--	88.61	50.34	56.81
57.50	--	54.57	88.61	28.62	32.30

The methanol yields for the two reactions were 8.71g (for MAP reaction) and 5.34g (for the PAP reaction) which correspond with intermediate yields of 54.37% and 33.33%, respectively. This is in very good agreement with the above results for total product collected.

C. Reactions of 2-Hydroxyethyl Methacrylate with Meta- and Para-aminobenzoic Acid.

Various attempts at esterifying the aminobenzoic acids with HEMA were unsuccessful. Method A was an attempt at azeotropic distillation with Lewis acid catalysts. Method B was based upon a patent assigned to Kurare Chemical Co.[59] which covers the synthesis of hydroxyalkyl methacrylates under mild conditions. Method D was hoped to be successful

as the method was purportedly very useful for esterifications of para-aminobenzoic acid which is typically very difficult due to its zwitter-ion properties.[60,61] This method made use of a boron-trifluoride etherate-alcohol catalyst and mild reaction conditions to synthesize the desired esters. No product was found in this research, however.

The approach taken in Method D also made use of the supposition that any product formed would be insoluble in water and highly soluble in an aromatic solvent. After 1 week at the reaction conditions no isolatable product was found.

Method C was the only one of the four which provided a product. It was highly viscous at room temperature and resinous in nature. It was very difficult to manipulate as it would adhere to many surfaces: glass, wooden tongue blades, paper, and stainless steel. This was true for the products derived from both MABA and PABA. This method made use of a general procedure described by DuPont for making use of its Tyzor organic titanates as esterification catalysts[62] but substituting Ken-React® KR-46B (tetra-n-octyl titanate, adducted with 2 moles of bis-tridecyl phosphite, Kenrich Petrochemicals, Inc.). The modification was made because Kenrich claimed that KR-46B has much improved thermal stability as compared to conventional tetra-alkoxy titanates, thereby promoting higher esterification yields.[63]

Yield data is very good as can be seen from Table XV.

TABLE XV

Percent Yields of MABA and

PABA Reactions with HEMA

		Theoretical		Actual	
HEMA(g)	MABA(g)	PABA(g)	Yield(g)	Yield(g)	% Yield
71.59	68.57	--	124.64	120.71	96.85
71.59	--	68.57	124.64	117.32	94.13

Elemental analyses of these products also appear to be reasonable. (See Table XVI.)

TABLE XVI

Elemental Analysis of MABA and

PABA Reactions with HEMA

Reactants	%C	%H	%N
MABA + HEMA			
theoretical	62.64	6.07	5.61
actual	60.68	6.25	5.58
PABA + HEMA			
theoretical	62.64	6.07	5.61
actual	64.40	6.23	6.06

Infrared spectroscopy also indicates that the desired esterification products were produced. The MABA + HEMA product shows aromatic NH_2-type N-H stretch at 3400 cm^{-1}, C-N stretch at 1300 cm^{-1}, conjugated carbonyl at 1710 cm^{-1} and several other characteristic absorptions. See Table XVII for selected IR absorptions of this product as well as Appendix A, IR#7.

TABLE XVII

Selected IR Absorptions of the MABA + HEMA Reaction Product (IR #7)

Assignment	Wave Number, cm^{-1}
N - H stretch	3400 (m)
C - H stretch, aromatic	3050 (m)
C - H stretch, aliphatic	2900 (w)
C = O	1710 (s)
C = C aromatic skeletal stretch	1610 (m) 1500 (m) 1470 (m)
C - N stretch	1300 (m)
C - O stretch	1220 (m) 1190 (m) 1120 (m) 980 (w)
= C - H aromatic out of plane bending	890 (w)

The PABA + HEMA product shows similar aromatic NH_2-type N-H stretch at 3400 cm^{-1}, C-N stretch at 1280 cm^{-1}, conjugated carbonyl at 1710 cm^{-1}, as well as several other characteristic absorptions. See Table XVIII for selected IR absorptions of this product as well as Appendix A, IR#8.

TABLE XVIII

Selected IR Absorptions of the PABA + HEMA Reaction Product (IR #8)

Assignment	Wave Number, cm^{-1}
N - H stretch	3400 (m)
C - H stretch, aromatic	3010 (m)
C - H stretch, aliphatic	2960 (m)
C = O	1710 (s)
C = C aromatic skeletal stretch	1610 (m) 1520 (m) 1475 (m)
C - N stretch	1280 (m)
C - O stretch	1180 (m) 1110 (m)
= C - H aromatic out of plane bending	850 (m)

CONCLUSIONS AND SUGGESTIONS

It is believed that the desired partial products were derived for the reactions of DPC + SAA and for the reactions of methacrylyl chloride and the aminophenols. Purification was not complete, however, which in some cases made it difficult to determine if the desired product was yielded. The products of the reaction of HEMA and the aminobenzoic acid appear to be esterified as desired but no longer monomeric. It is suggested that additional catalysts be explored for the DPC + SAA reactions as well as kinetic studies to determine the mechanism of this reaction.

A different method of arriving at the aminobenzoate ester might be to transesterify HEMA with the methylester of MABA and PABA.

An approach wherein the amino functionality of the aminophenols is protected prior to reaction with methacrylyl chloride may also be found useful.

Additional work in the area of deriving blocked isocyanate structures without the actual use of an isocyanate is worthwhile from the standpoint that moisture presents much less of an obstacle in the preparation of the desired blocked product as well as eliminating the hazards associated with residual isoycanate being present in the monomer.

EXPERIMENTAL

I. Reactions of Diphenyl Carbonate with Substituted Aromatic Amines:

A. Catalyst Selection: Six candidate compounds were screened for their efficacy as potential catalysts of the DPC + SAA reactions. These compounds were: zinc acetate (ZA), zinc acetylacetonate (ZAA), zinc octoate, 80% solution (ZO), dibutyltindilaurate (DBTDL), tin octoate (TO), and titanium acetylacetonate (TAA).

The mixture used for screening was 0.05 moles catalyst: 1.0 moles m-aminophenol (MAP): 5.0 moles DPC. A control with no catalyst was also used. The reaction mixture was placed in a 16 x 125 mm Pyrex® ignition tube which was immersed in mineral oil contained in a 2 liter Pyrex® beaker. The beaker had a cover which was fitted with a thermometer adapter and an inlet and outlet for nitrogen gas. The beaker was placed on a hot plate, a continuous flow of nitrogen gas was begun and the bath was heated for 2 hours at 120°C. After cooling to room temperature the individual reaction mixtures solidified. After removal from the tubes the reaction mixtures were ground with a mortar and pestle, added to 100g of dimethoxyethane, filtered over a Whatman number five filter paper, and the extract analyzed by gas chromatography

for the presence of the expected by-product phenol. (See Table XIX for quantities used.)

TABLE XIX

Reaction Mixtures For Catalyst Screening

DPC(g)	MAP(g)	ZA(g)	ZAA(g)	ZO(g)	DBTDL(g)	TO(g)	TAA(g)
9.08	0.92	-	-	-	-	-	-
9.00	0.92	0.08	-	-	-	-	-
8.98	0.91	-	0.11	-	-	-	-
8.91	0.91	-	-	0.18	-	-	-
8.83	0.90	-	-	-	0.27	-	-
8.92	0.91	-	-	-	-	0.17	-
8.95	0.91	-	-	-	-	-	0.14

B. Diphenyl Carbonate + Substituted Aromatic Amine Homogeneous Reactions.

Based upon the results of the catalyst screening it was desired to scale-up the system in order to obtain tractable quantities of products. The apparatus consisted of a 2 liter four-necked flask fitted with a thermometer, gas inlet, high

speed stirrer, condenser, gas bubbler, N_2, heating mantle, rheostat, and a scissor jack.

The reactants were placed into the apparatus, nitrogen flow was begun and heat was slowly applied until the reaction mixture reached 120°C. At this temperature the mixture was melted and stirring was begun. This method was abandoned in favor of the following method due to the fact that for all four DPC + SAA reaction mixtures after approximately 2 hours at 120°C the flask contents formed a thick slurry and eventually (approx. 2 1/2 hours) solidified. (See Table XX for quantities used for the above reactions.)

TABLE XX

Quantities Used In The Homogeneous Reaction Method

DPC(g)	MAP(g)	PAP(g)	MABA(g)	PABA(g)	ZA(g)
535.55	54.57	-	-	-	4.59
535.55	-	54.57	-	-	4.59
535.55	-	-	68.57	-	4.59
535.55	-	-	-	68.57	4.59

C. Solvent-Based Homogeneous Reaction System

Since it was known that at the reaction temperature the reactants were initially homogeneous, a solvent-based reaction system was attempted using a non-solvent for the desired products. The same apparatus was used as in the previously described method. Diethylene glycol dimethyl ether (Diglyme) was used as the reaction solvent.

The reactants and the solvent were placed into the apparatus. A continuous nitrogen flow was bubbled through the mixture and stirring was begun. After 15 minutes heat was slowly applied until the reaction mixture was at 120°C. Cold water was continuously flowing through the condenser. For all four DPC + SAA reactions at approximately 2 hours after reaching 120°C a gelatinous suspension formed. By-product phenol generation was monitored periodically by gas chromatography and the reactions were typically complete at 4-5 hours. The heating mantle was replaced by a room temperature water bath and the reaction mixture was reduced to 30°C. At this time the apparatus was dismantled and the reaction mixture was suction filtered over a Whatman number five filter paper.

The filtrate was then washed 3 times with dimethoxyethane and dried for 12 hours at 110°C with nitrogen flowing through the heating chamber. The following day the filtrate was ground with mortar and pestle and analyzed by infrared

spectroscopy. The reaction liquor was analyzed by gas chromatography for by-product phenol. (See Appendices A,B,C and D.) (See Table XXI for quantities used in these reactions.)

TABLE XXI

Quantities Used In The Solvent-Based Reaction Method

Diglyme(g)	DPC(g)	MAP(g)	PAP(g)	MABA(g)	PABA(g)	ZA(g)
1000.00	453.77	46.23	-	-	-	3.85
1000.00	453.77	-	46.23	-	-	3.85
1000.00	443.25	-	-	56.75	-	3.85
1000.00	443.25	-	-	-	56.75	3.85

II. Reactions of Meta- and Para-aminophenol with Methacrylyl Chloride

Three different methods were attempted for the preparation of the methacryloxy functional aromatic amines. The first method was to react methacrylyl chloride directly with the aminophenols, while the second and third methods involved a two stage reaction in which sodium methoxide was first reacted with the amino phenols in an attempt to increase the basicity of the phenoxy portion of the aminophenols prior to reaction with methacrylyl chloride.

Method A

The apparatus consisted of a 2 liter 4-necked round bottom flask fitted with a high speed stirrer, condenser, addition funnel vented to the flask, an ice bath, heating mantle, rheostat and a thermometer.

Procedure:

1 liter of xylene was placed into the flask to which was added 109.13g (1 mole) of m- or p-aminophenol, and 111.31g (1 mole) of triethyl amine. The flask was placed in an ice bath, the apparatus assembled and 114.99g (1.1 mole) of methacrylyl chloride added dropwise with stirring. The temperature of the batch gradually rose to 35°C at the end of methacrylyl chloride addition. The batch was mixed for one (1) hour at which time the ice bath was replaced with a heating mantle, the temperature increased to 100°C (methacrylyl chloride, B.P. = 96°C @ 760 mm Hg) and held for four (4) hours. At this time the heating mantle was replaced with an ice bath and the temperature brought down to 30°C. When the batch reached 30°C 250 ml of deionized water was added to the batch and stirred for 30 minutes. Next, the reaction mixture was placed into a 2-liter separatory funnel, the xylene phase retained and extracted again with 250 ml of deionized water. The xylene phase was collected and placed in a 2-liter, 3-necked round bottom flask and distilled to a dry flask @

160°C, 760 mm Hg. No product was found in the xylene phase. (See Results and Discussion Section.)

Method B

The apparatus for stage 1 consisted of a 2-liter, 4-necked round bottom flask equipped with a mechanical stirrer, thermometer, condenser, Dean-Stark trap, heating mantle, rheostat, and a stopper for the unused neck.

Procedure:

1 liter of xylene was placed into the flask to which was added 109.13g (1 mole) of m- or p-aminophenol. The apparatus was assembled and 59.43g (1.1 mole) of sodium methoxide was slowly added with stirring. The mixture was slowly raised to 120°C at which temperature methanol began distilling. Cold water was continuously flowing through the condenser. The batch temperature was raised to 160°C to bring the xylene to reflux. After two hours at 160°C no more methanol was being generated. The heating mantle was replaced with an ice bath and the temperature brought down to 30°C. The Dean-Stark trap was removed, the condenser refitted, and methacrylyl chloride added as in Method 1. The xylene phase recovery and distillation was carried out in the same manner as method A. Again no product was found in the xylene phase for either aminophenol.

Note: No triethyl amine was used in this reaction method.

Method C

The apparatus was identical to Method B. A homogeneous reaction method was employed by using triethylene glycol dimethyl ether (triglyme) as the reaction solvent.

Procedure:

To a 2 liter, 4-necked round bottom flask was added 1 liter of triglyme and 54.57g (0.5 mole) of m- or p-aminophenol. The apparatus was assembled and sodium methoxide was added. After sodium methoxide addition the temperature was slowly raised ultimately to 160°C. Although triglyme (B.P.=216.1°C @ 760 mm Hg) does not reflux at this temperature it was found sufficient to drive off the methanol generated by this reaction. After 3 hours at 160°C no more methanol was generated. The heating mantle was replaced by a cold water bath followed by an ice bath and the temperature of the batch brought down to 30°C. The Dean-Stark trap was removed and the condenser refitted. An additional funnel (vented to the flask) was added and 55.65 g (0.55 mole) of triethyl amine was added to the flask followed by the dropwise addition of 57.50g (0.55 mole) of methacrylyl chloride. The mixture was stirred for 30 minutes at 30°C after which the heating mantle was replaced and the mixture was heated at 100°C for four hours. A brown precipitate began to form within the first hour of heating. After heating the mixture

was brought down to 30°C by means of a cold water bath and 250 ml of deionized water was added to the flask and stirred for 30 minutes. At this time the reaction mixture was suction filtered over a Whatman number five filter paper and washed with three 100 ml portions of dimethoxyethane in order to remove the triglyme from the precipitate. The precipitate was dried for 12 hours under a continuous flow of nitrogen at 60°C. (See Results and Discussion Section for yield data and analysis.)

III. Reactions of Meta- and Para-aminobenzoic Acid with 2-Hydroxyethyl Methacrylate

Various attempts were made at esterifying the aminobenzoic acids with 2-hydroxyethyl methacrylate. Four distinct methods were used.

Method A

The apparatus consisted of a 2-liter four-necked flask equipped with a high speed stirrer, thermometer, condenser, Dean-Stark trap, gas inlet, N_2, gas bubbler, heating mantle, and a rheostat.

Procedure:

To the flask was added 1 liter of xylene, m- or p-aminobenzoic acid, HEMA and catalyst. The apparatus was assembled

and nitrogen was bubbled through the mixture for 30 minutes with stirring. At this time heating was begun and the temperature of the batch was slowly raised to 120°C. Nitrogen was continuously bubbled through the mixture and cold water was continuously flowing through the condenser. After approximately two hours at 120°C the HEMA gelled in the flask. No by-product water was produced by azeotropic distillation. Quantities used were: xylene-1 liter, meta- or para-aminobenzoic acid-137.14g (1 mole), HEMA-143.18g (1.1 moles) and 1.4g of catalyst (0.5% based upon the weight of the reactants). Catalysts used were: concentrated sulfuric acid, dibutyltin dilaurate, para-toluene sulfonic acid, and tetra-n-octyl titanate.

Method B

The apparatus was identical to that used in Method A with the exception that it was fitted for vacuum distillation. Toluene sulfonic acid was the catalyst, and oxygen gas was substituted for nitrogen gas. The reaction was carried out at 70°C and 100mm Hg for 8 hours, 24 hours and 1 week with no by-product water generated. The amounts of reagents used were xylene-1 liter, aminobenzoic acid-137.14g (1 mole), HEMA-143.18g (1.1 mole) and para-toluene sulfonic acid-1.4g (0.5% on total reactants).

Method C

The apparatus and general method was the same as Method A; however, the procedure was modified.

Ken React KR-46B (tetra-n-octyl titanate, adducted with 2 moles of bis-tridecylphosphite, Kenrich Petrochemicals, Inc.) was used as the catalyst. Phenothiazine and nitrobenzene were used as polymerization inhibitors.

Procedure:

To the flask were added 1 liter of xylene, 68.57g (0.5 mole) of the respective aminobenzoic acid, 71.59g (0.55 mole) of HEMA, 2.0g phenothiazine, 0.5g nitrobenzene, and 0.7g KR-46B (0.5% based on the weight of the reactants). The apparatus was assembled and nitrogen was bubbled through the mixture for 30 minutes. At this time heating was begun and the temperature was raised to 120°C. After 2 hours at 120°C 2 ml of water had been collected but after 3 hours only an additional 0.5 ml of water was generated. The temperature was gradually raised to 160°C and xylene was removed as well as small amounts of water. After 4 hours at 160°C the reaction produced 4.8 ml of water for the meta reaction and 4.5 ml of water for the para reaction. The temperature was gradually raised to 225°C and held for an additional 2 hours. A total of 7.8 ml of water for the meta reaction and 7.2 ml of water for the para reaction were collected. The batch was

cooled to 100°C and poured out into glass jars and sealed. The product was transferred at this temperature due to a noticeable increase in viscosity within the flask.

The resultant products were, at room temperature, very high viscosity fluids which were dark brown in color.

Method D

This is a homogeneous method using boron trifluoride etherate as the catalyst. The reactants were used in the ratio of aminobenzoic acid-1 mole, HEMA-15 mole, and boron trifluoride etherate-2 mole.

The apparatus consisted of a 2-liter, four-necked, round bottom flask equipped with a high speed stirrer, gas inlet, an adapter with a septum, a y-shaped adapter with a thermometer and a condenser, a gas bubbler, dry oxygen, a heating mantle and a rheostat.

Procedure:

To the flask was added 411.31g (3.16 mole) HEMA and 28.89g (0.21 mole) of the respective aminobenzoic acid. The aminobenzoic acid soon dissolved in the HEMA. Chemically pure dry oxygen was bubbled through the batch for 30 minutes. At this time 59.8g (0.42 mole) of boron trifluoride etherate was added to the flask via a syringe. Extreme care must be taken so as to prevent the introduction of moisture

to the system or the catalyst will be rendered inactive. The temperature was slowly raised to 70°C and held for 1 week with the oxygen bubbling through the mixture and cold water continuously flowing through the condenser.

After 1 week, the flask was cooled to 25°C and 100 ml of deionized water was added to the mixture to inactivate the catalyst. The reaction mixture was then added to 2 liters of deionized water, split into smaller quantities and extracted with xylene. The xylene extracts were combined and distilled to a dry pot with no product found.

IV. Gas Chromatography of Dipheny Carbonate Reaction Liquors

A Hewlett Packard model HP-5830A Gas Chromatograph equipped with Hewlett Packard G.C. terminal 18850A was used. The detector was of the thermal conductivity type. The column was 12 foot by 1/8 inch, stainless steel. The carrier gas was helium and the flow rate was 30 cc/min for the DPC/MABA and DPC/PABA liquors. The sample size was 1-1 1/2 microliters.

V. Infrared Spectroscopy

Where feasible samples were prepared as 2% sample in KBr. Approximately 5 mg of sample was added to 200 mg of KBr and ground with an agate mortar and pestle. The target was prepared in a Beckmann Mini-Die. The instrument used was the Perkin Elmer 710B.

VI. Elemental Analysis of Isolated Products

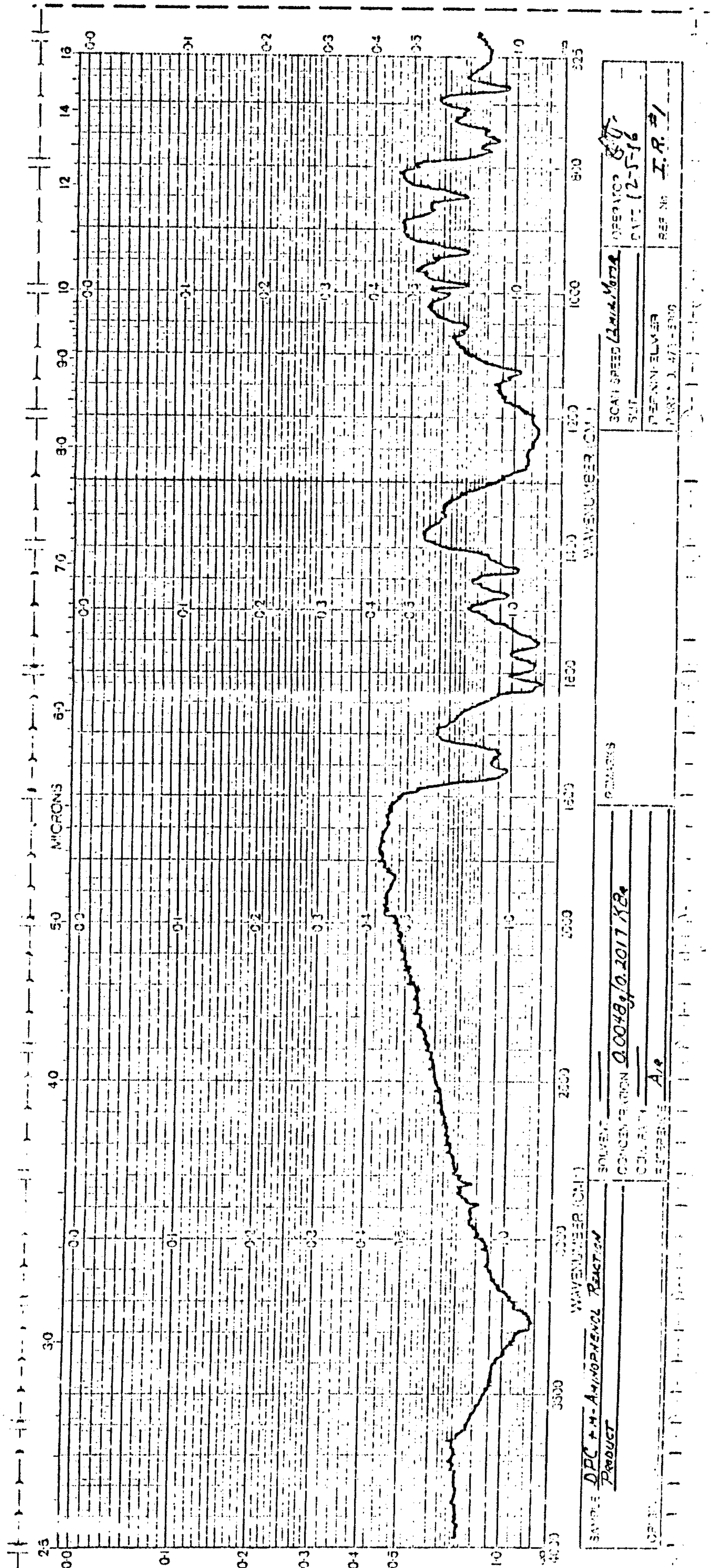
The analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

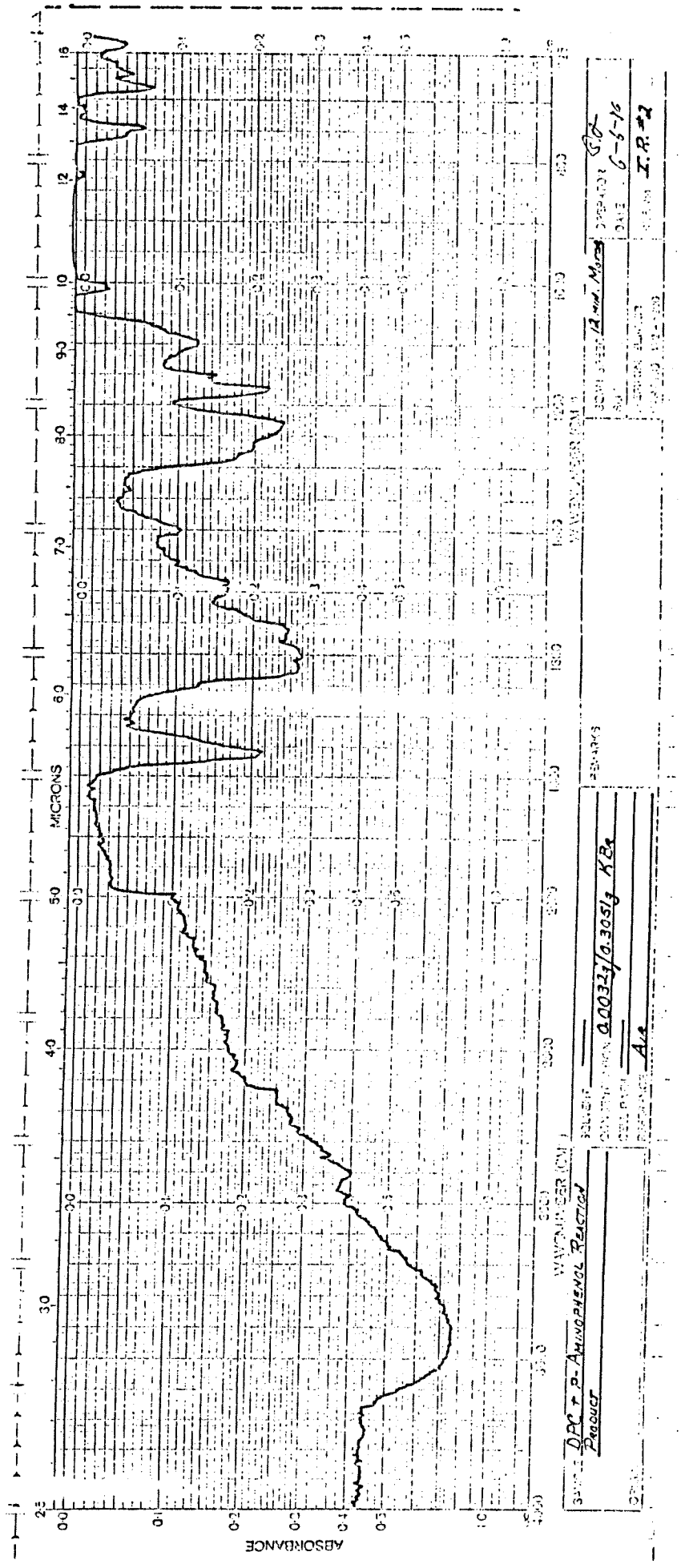
All products were analyzed for percent carbon, hydrogen and nitrogen. The products from the methacrylyl chloride reactions were also analyzed for percent chlorine.

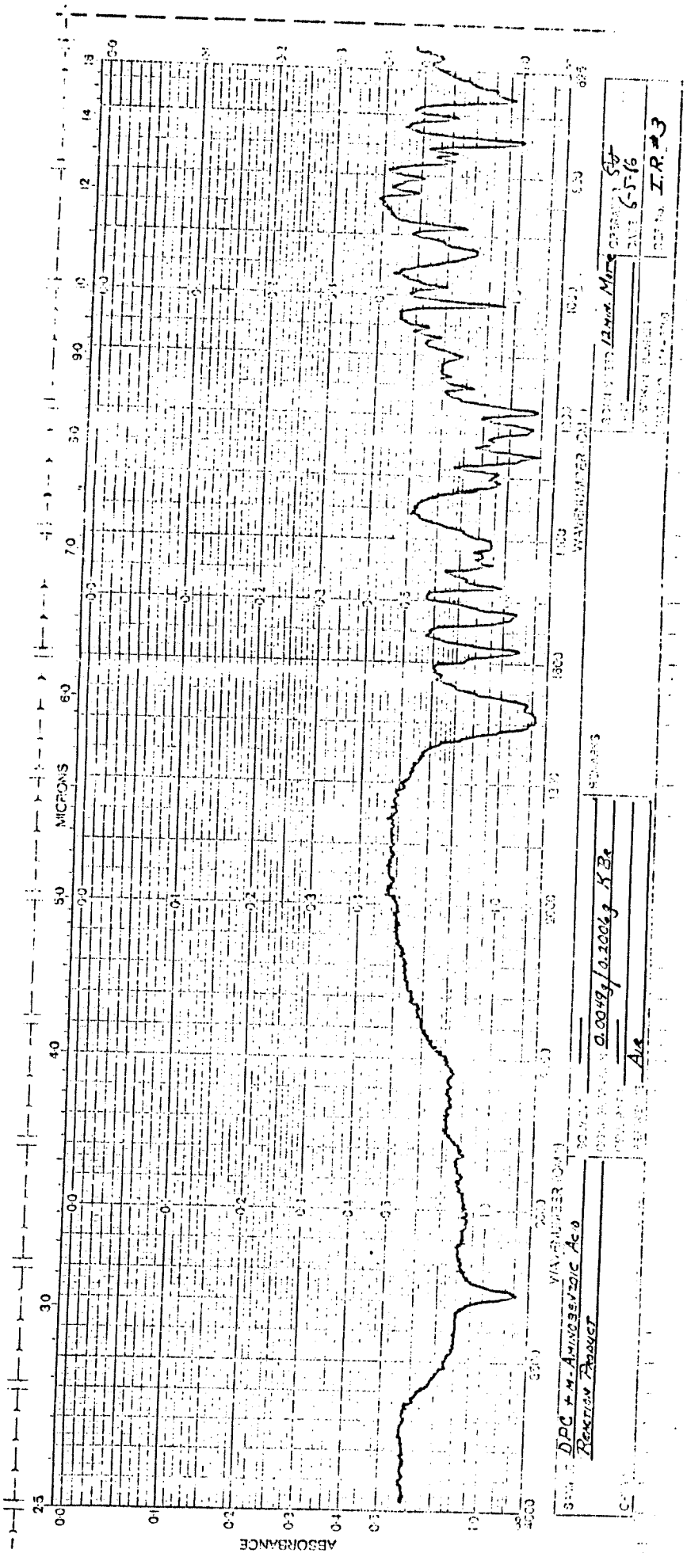
APPENDIX A

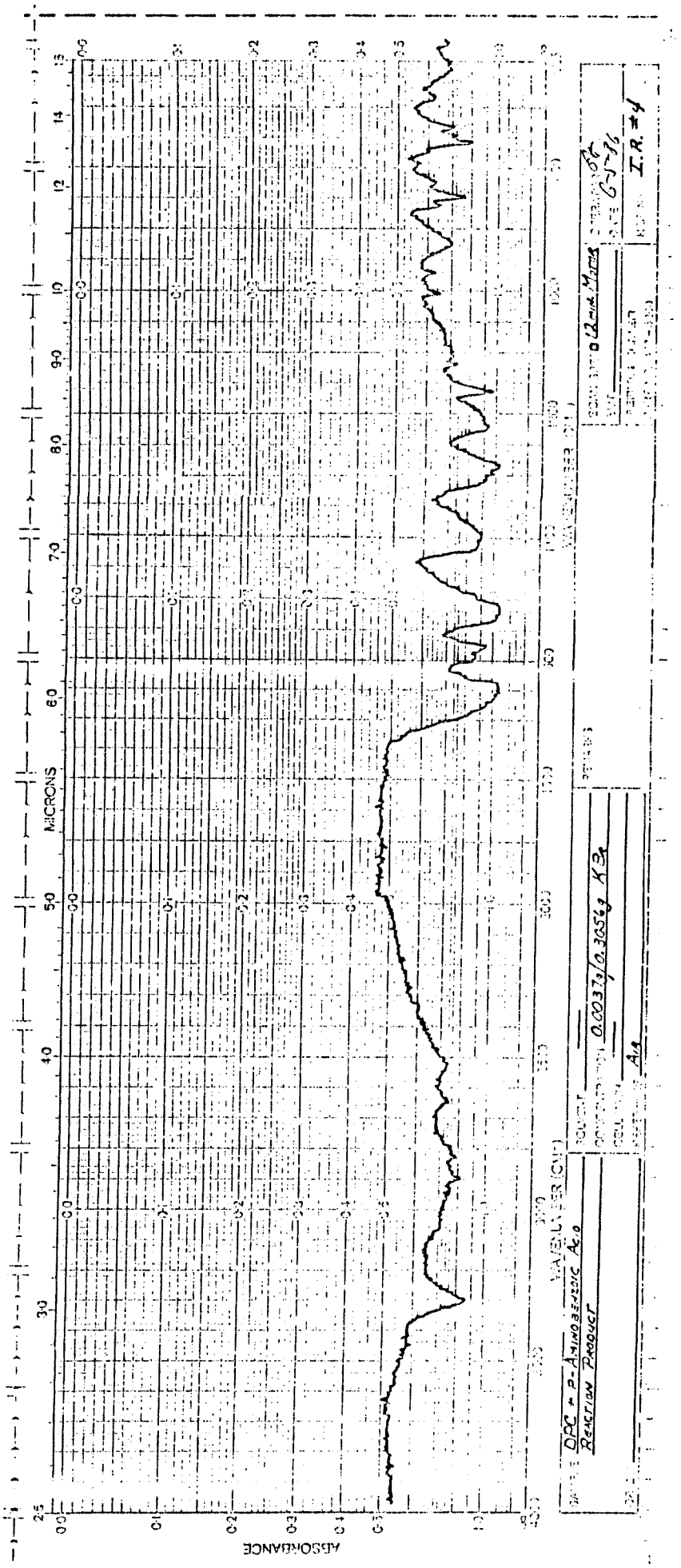
INFRARED SPECTRA OF PRODUCTS

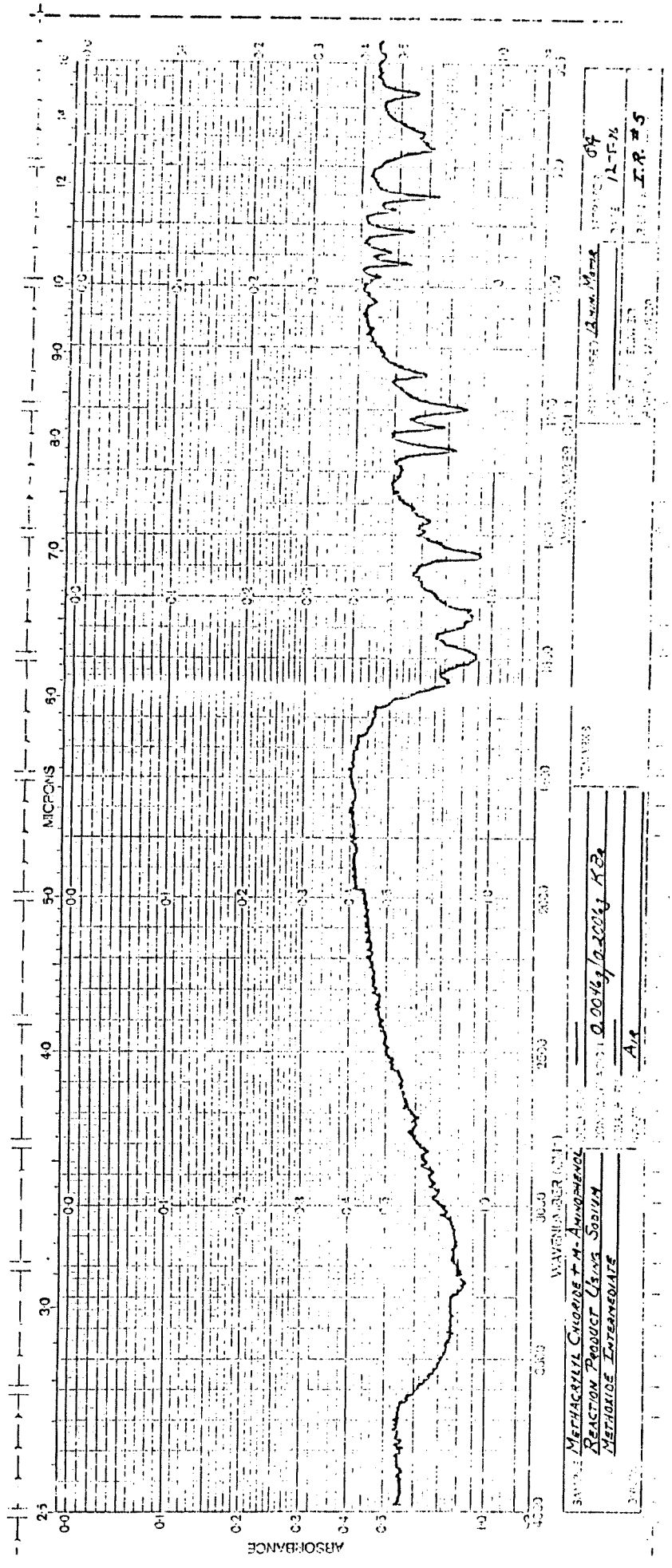
(I.R. #'s 1 through 8)

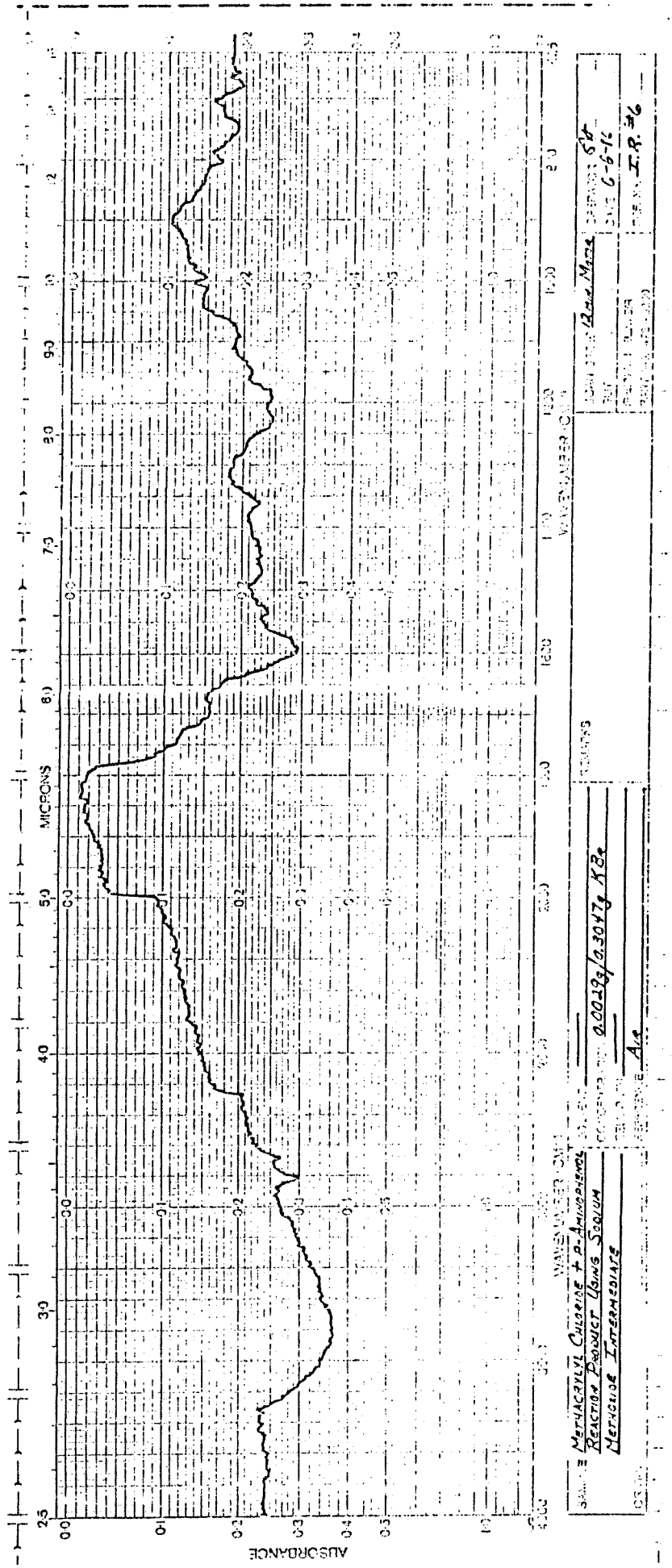

MICRONS
WAVENUMBER (CM-1)
ABSORBANCE
SAMPLE DPC + M-AMINOPHENOL REACTION PRODUCT
SOLVENT
CONCENTRATION 0.0048g/0.2017 KBr
REFERENCE Air
REMARKS
SCAN SPEED
PERKIN-ELMER
I.R. #1


ABSORBANCE
MICRONS
WAVENUMBER (CM⁻¹)
DPC + p-AMINOPHENOL REACTION
Reagent
0.00324/0.305g KBr
6-5-76


ABSORBANCE
MICRONS
WAVENUMBER (CM-1)
DPC + M-Aminobenzoic Acid
Reaction Product
0.0049g/0.200g KBr
Air
6-5-16
I.R. #3


ABSORBANCE
MICRONS
WAVENUMBER (CM⁻¹)
DPC + p-Aminobenzoic Acid
Reaction Product
0.0037g/0.305g KBr
Nujol
I.R. #4


ABSORBANCE
MICRONS
WAVENUMBER (CM-1)
Methacryl Chloride + M-Aminophenol
Reaction Product Using Sodium
Methoxide Intermediate
0.0046 g/2.2006 g KBr
Air
Dow Mark
12-5-76
I.R. #5


ABSORBANCE
MICRONS
WAVENUMBER (CM-1)
Methacryl Chloride + p-Aminophenol
Reaction Product Using Sodium
Herbicide Intermediate
0.00429/0.3047g KBr
Air

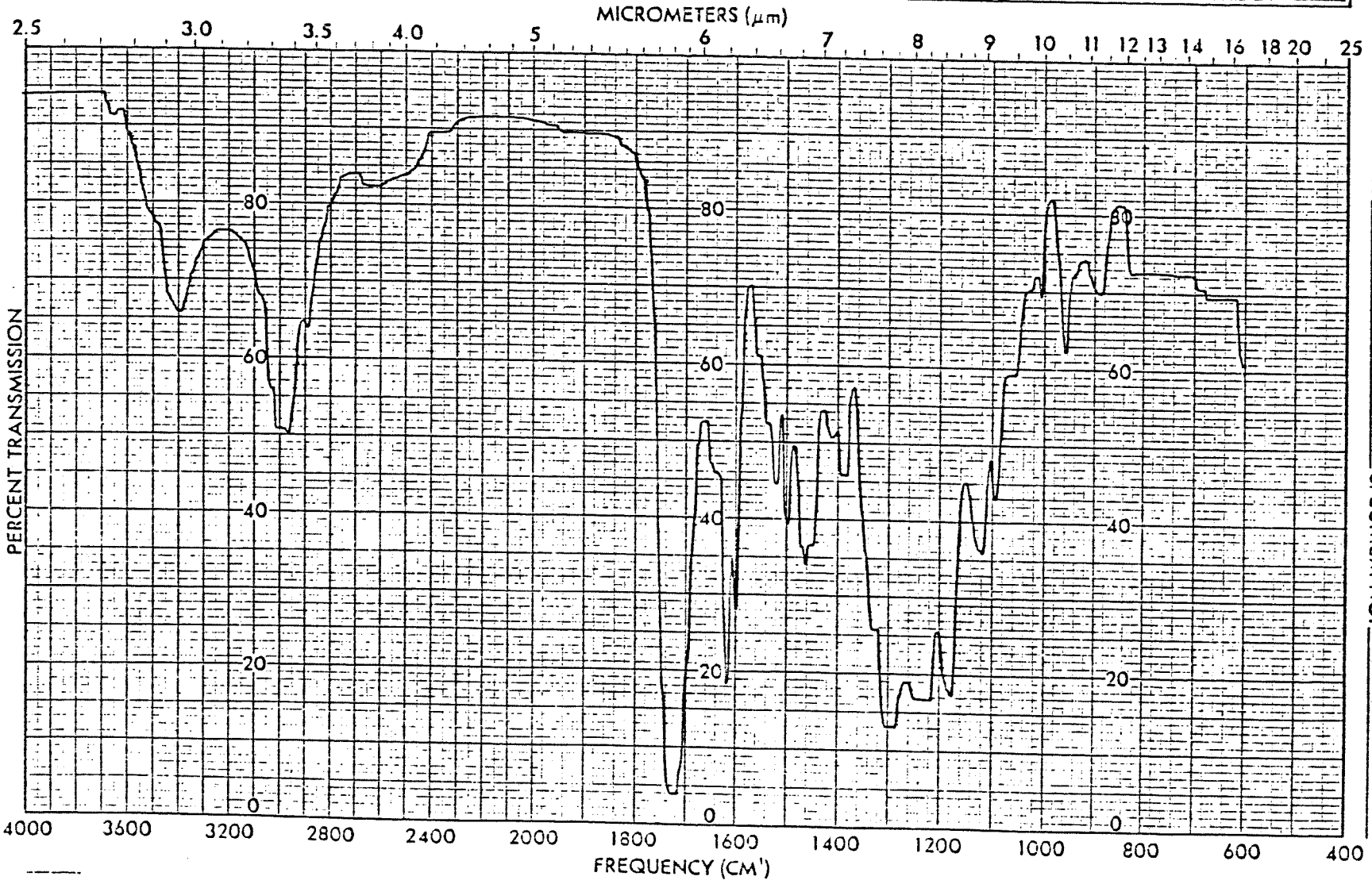
NO. 007-1493

PERKIN-ELMER

CONCENTRATION 5% w/w in Chloroform
THICKNESS 0.1 mm Cell
PHASE Double Beam
REMARKS Resinous Product

SCAN MODE ACCY. ☐ SURVEY ☐
HI ENERGY ☐ CAL. ☐
RESOLUTION ☐
OPERATOR G.A. DATE 5-18-86

SPECTRUM NO. I.R. #7
SAMPLE HEMA + m-Aminobenzoic Acid Reaction Product, KR-46 B Catalyzed



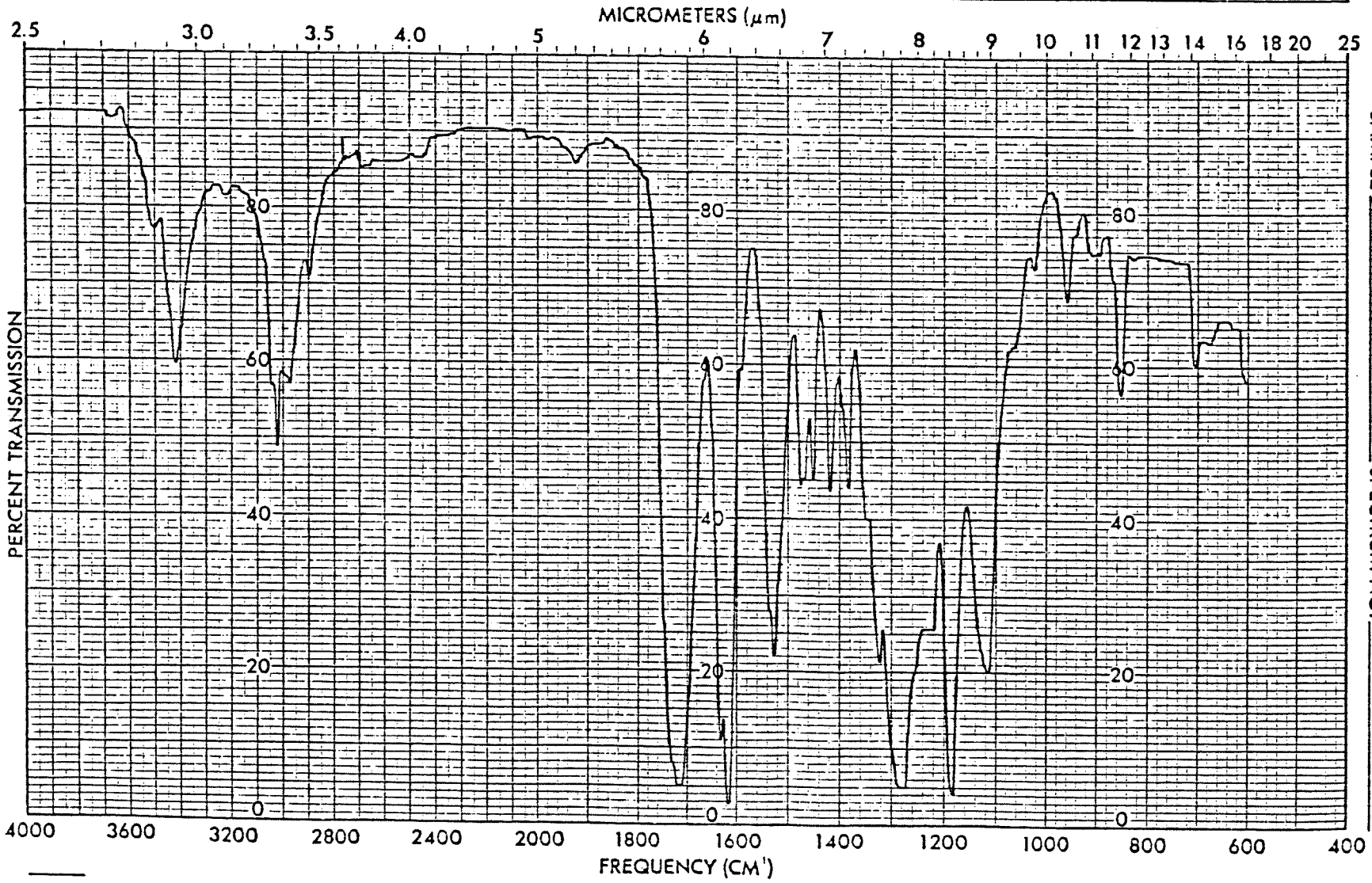
NO. 007-1493

PERKIN-ELMER

CONCENTRATION 5% w/w in Chloroform
THICKNESS 0.1 mm Cell
PHASE Double Beam
REMARKS Resinous Product

SCAN MODE ACCY. ☐ SURVEY ☐
HI ENERGY ☐ CAL. ☐
RESOLUTION ☐
OPERATOR GM- DATE 5-9-86

SPECTRUM NO. I.R. #8
SAMPLE HEMA + p-Aminobenzoic Acid Reaction Product, KR-46 B Catalyzed



APPENDIX B

INFRARED SPECTRA OF RAW MATERIALS

(I.R. #'s 9 through 19)

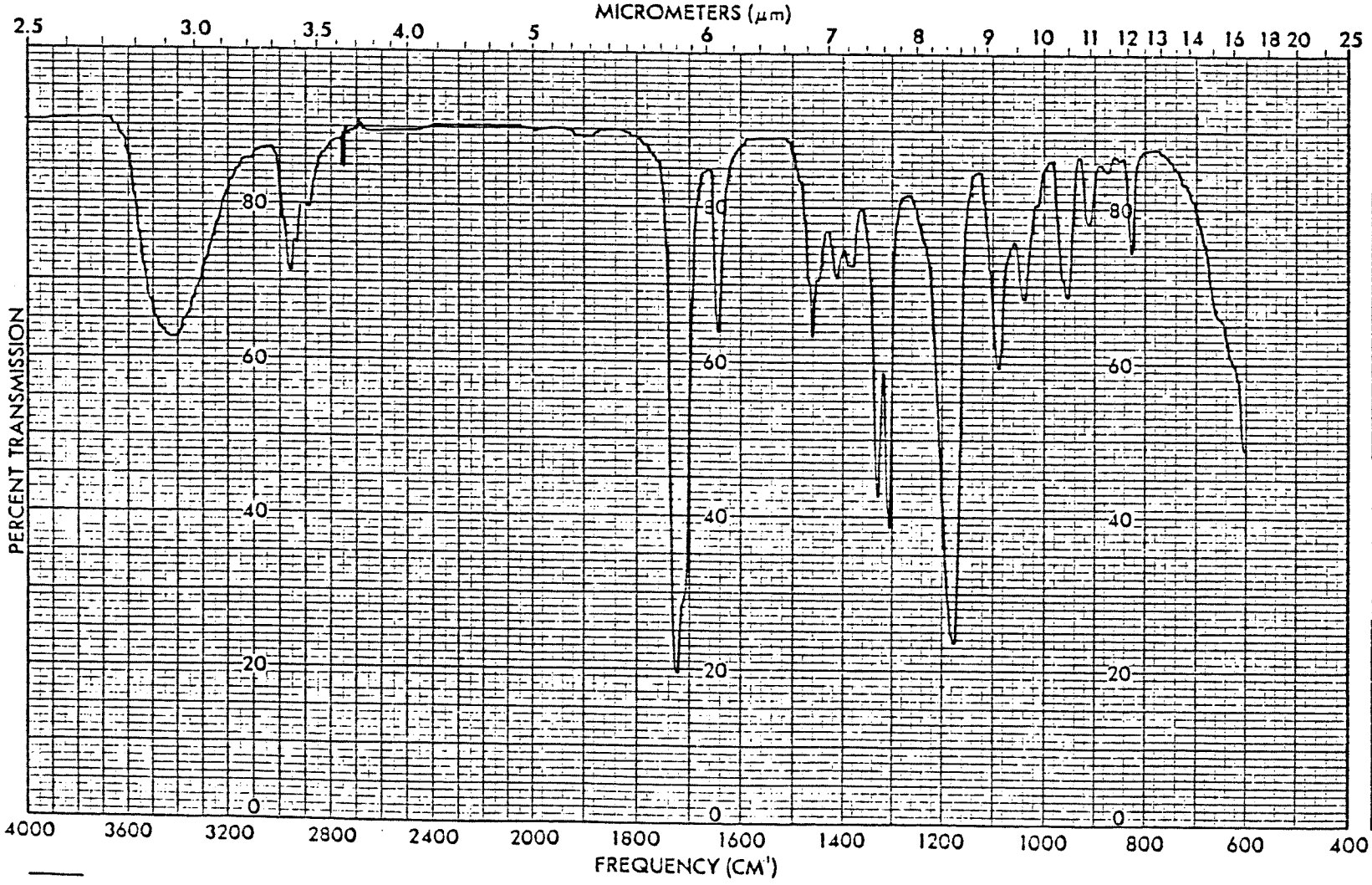
NO. 007-1493

PERKIN-ELMER

CONCENTRATION Neat, Salt Discs
THICKNESS
PHASE Double Beam
REMARKS Reference to Air

SCAN MODE ACCY. ☐ SURVEY ☐
HI ENERGY ☐ CAL. ☐
RESOLUTION ☐
OPERATOR GK DATE 5-17-16

SPECTRUM NO. I.R. #9
SAMPLE 2-Hydroxyethyl Methacrylate
ORIGIN Rohm & Haas



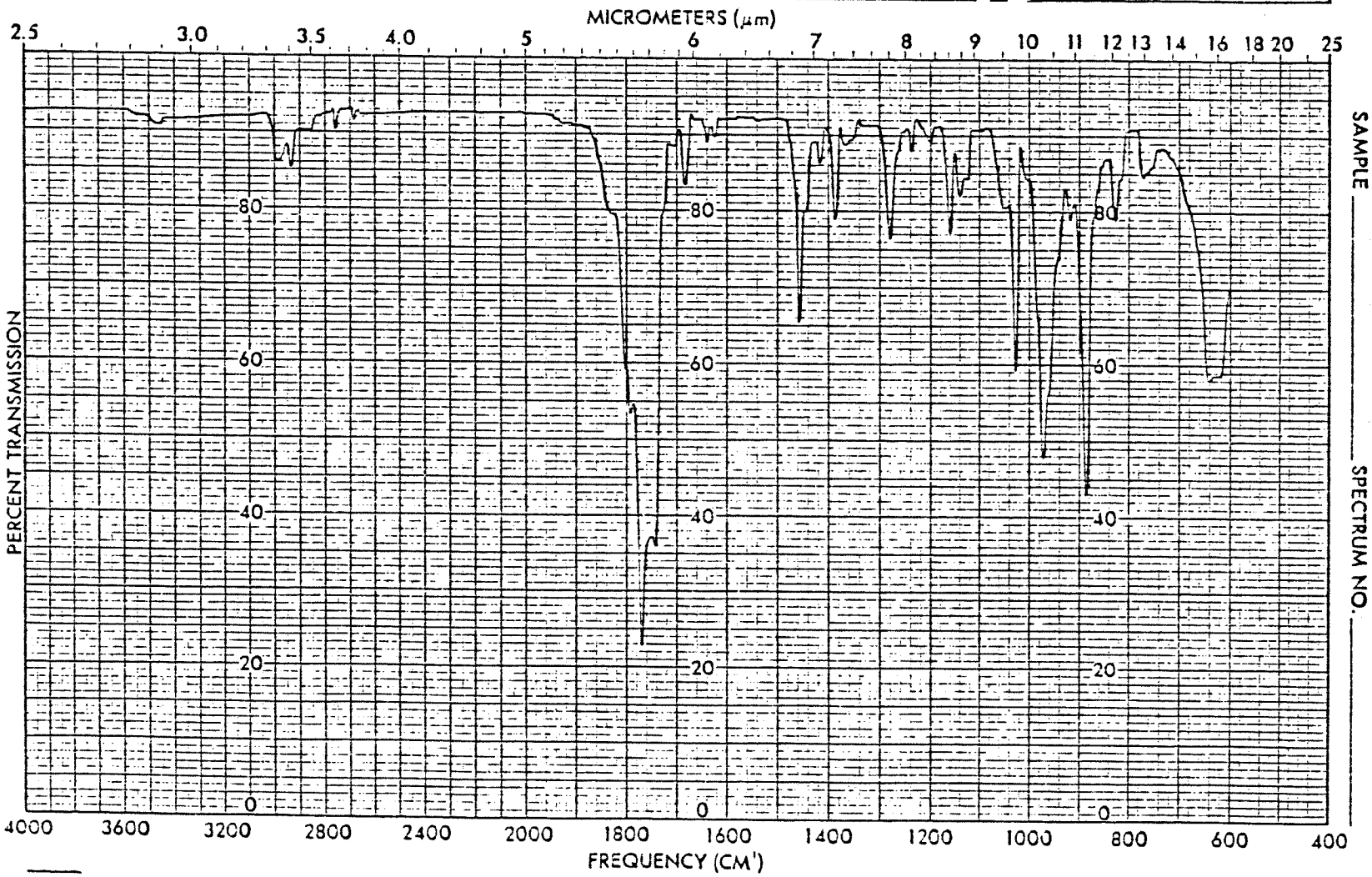
NO. 007-1493

PERKIN-ELMER

CONCENTRATION: NEAT, NaCl DISCS
THICKNESS: —
PHASE: DOUBLE BEAM
REMARKS: REFERENCE TO AIR

SCAN MODE: ACCY. ☐ HI ENERGY ☐ RESOLUTION ☐ SURVEY ☑ CAL. ☐
OPERATOR: GA DATE: 5-19-86

SPECTRUM NO: I. R. #10
SAMPLE: METHACRYLYL CHLORIDE
ORIGIN: POLYSCIENCES INC., CAT. NO. 1518



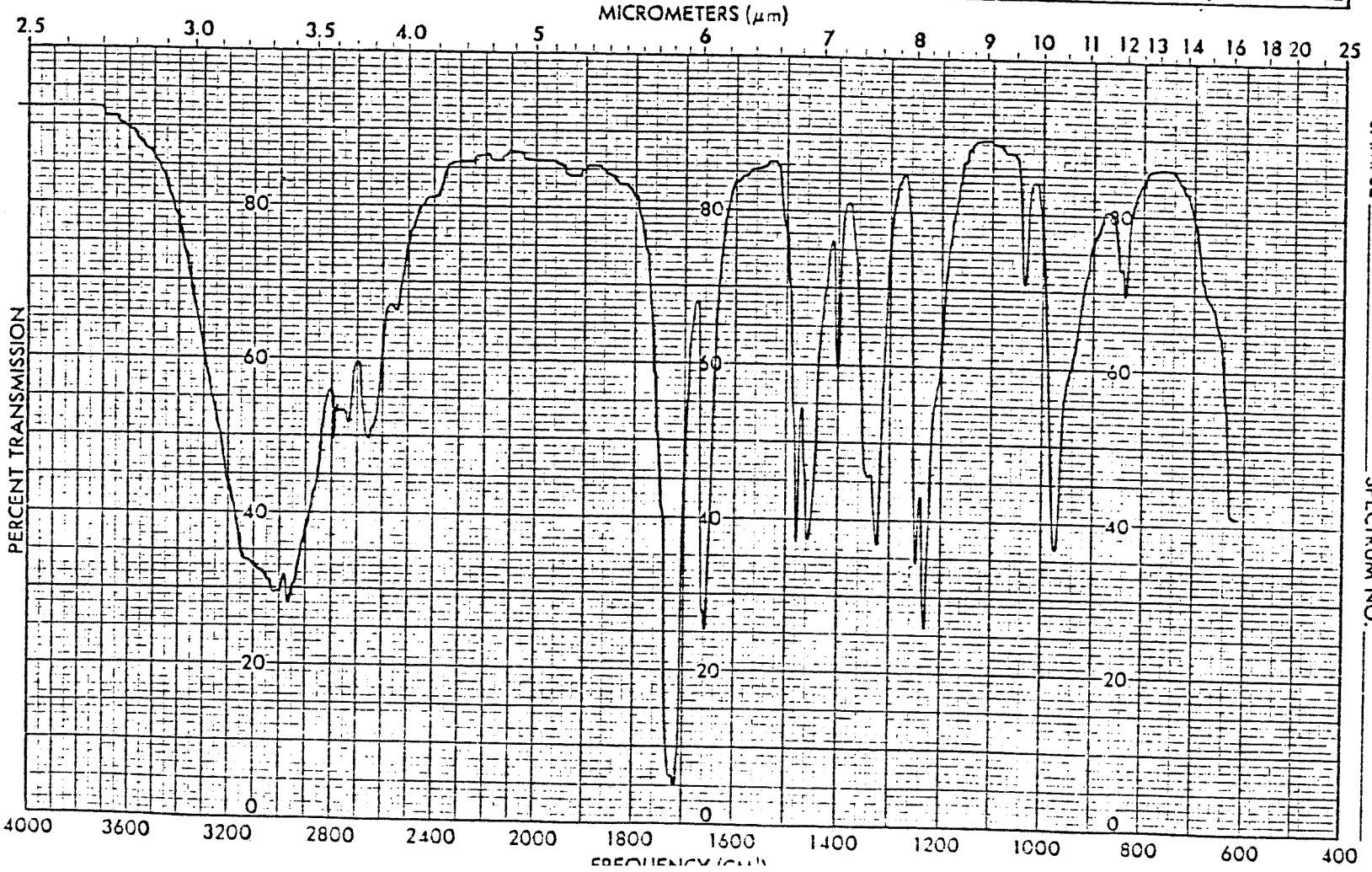
NO. 007-1493

PERKIN-ELMER

CONCENTRATION NEAT, SALT DISCS
THICKNESS —
PHASE DOUBLE BEAM
REMARKS REFERENCE TO AIR

SCAN MODE ACCY. ☐ SURVEY ☐
HI ENERGY ☐ CAL. ☐
RESOLUTION ☐
OPERATOR GA DATE 5-18-86

SPECTRUM NO. I.R. #11
SAMPLE METHACRYLIC ACID, GLACIAL
ORIGIN ROHM & HAAS, LOT NO. 308443



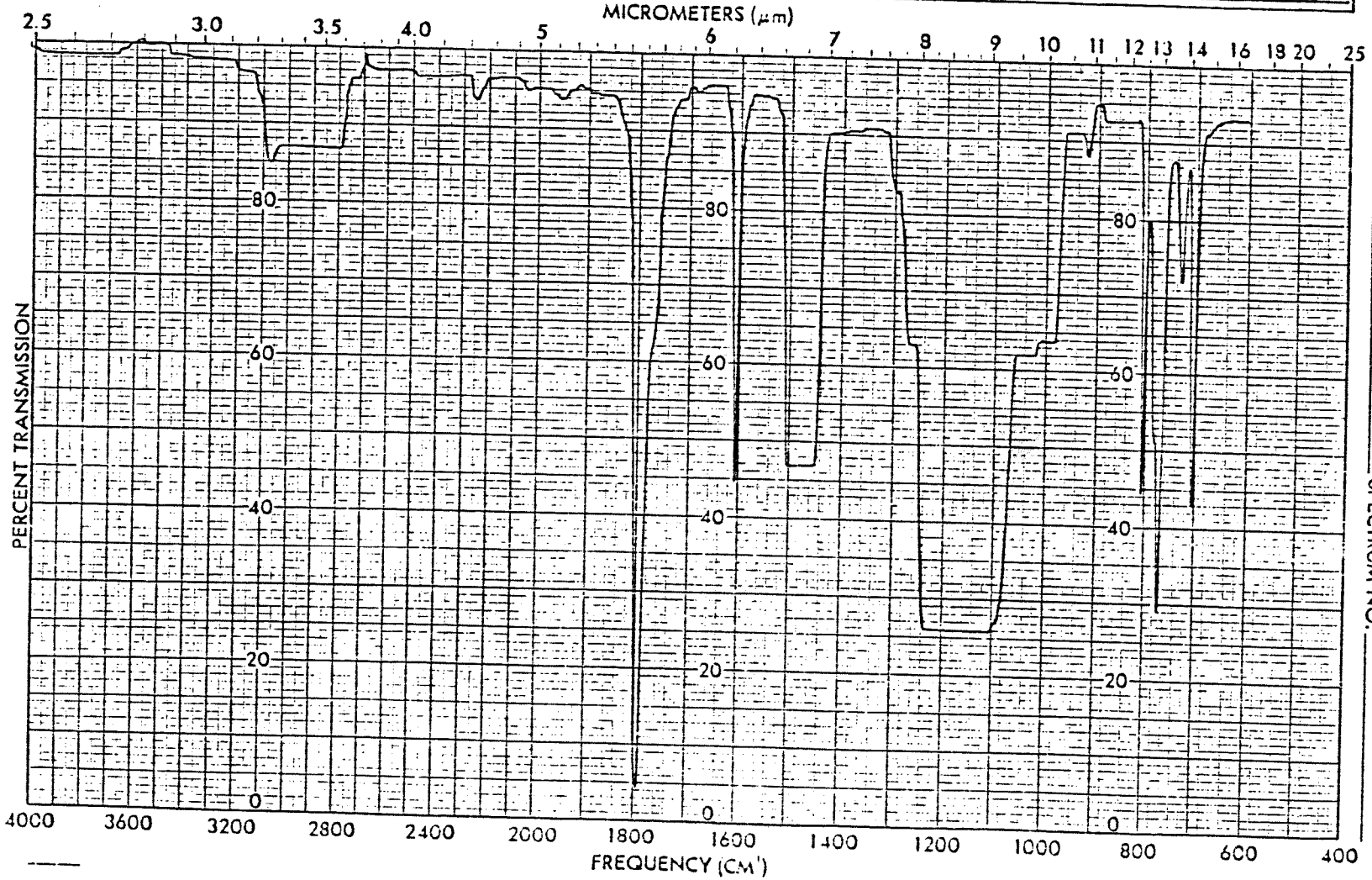
NO. 007-1493

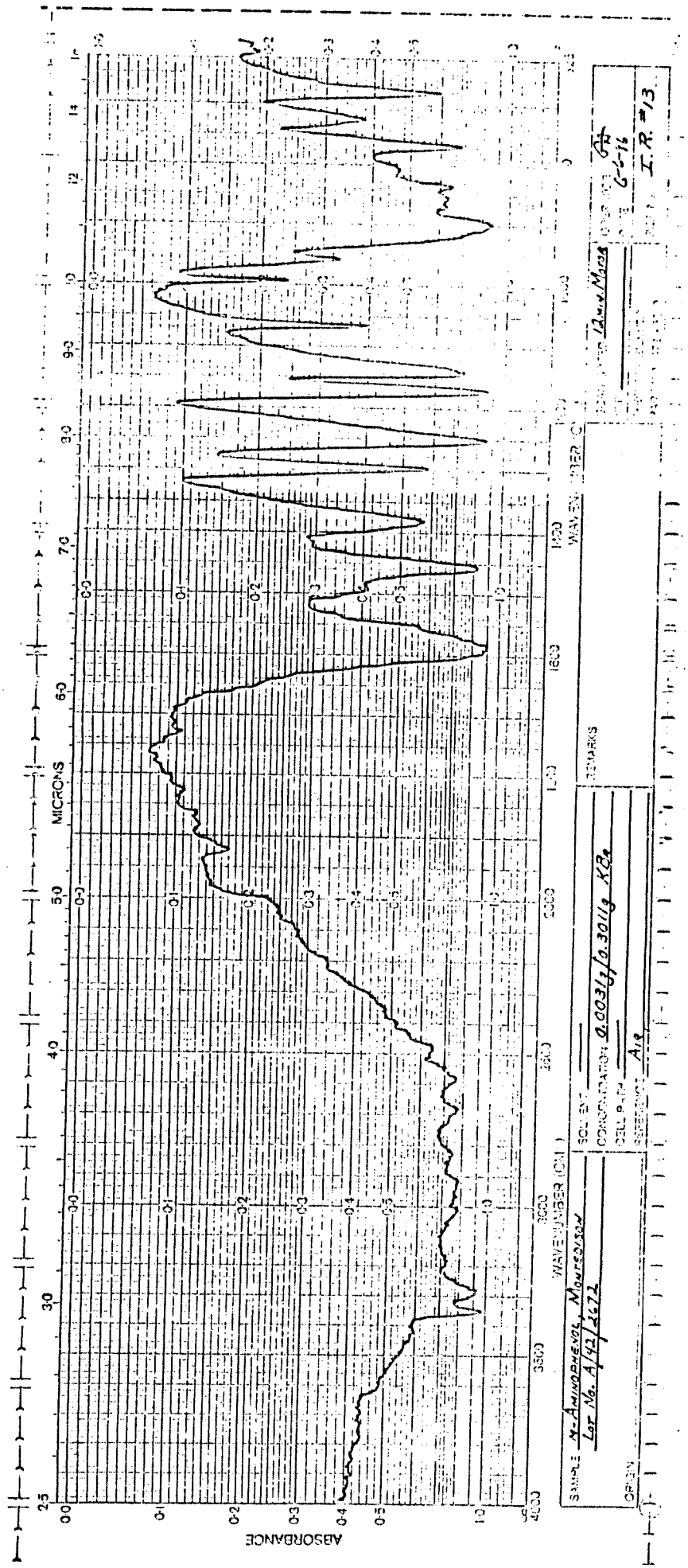
PERKIN-ELMER

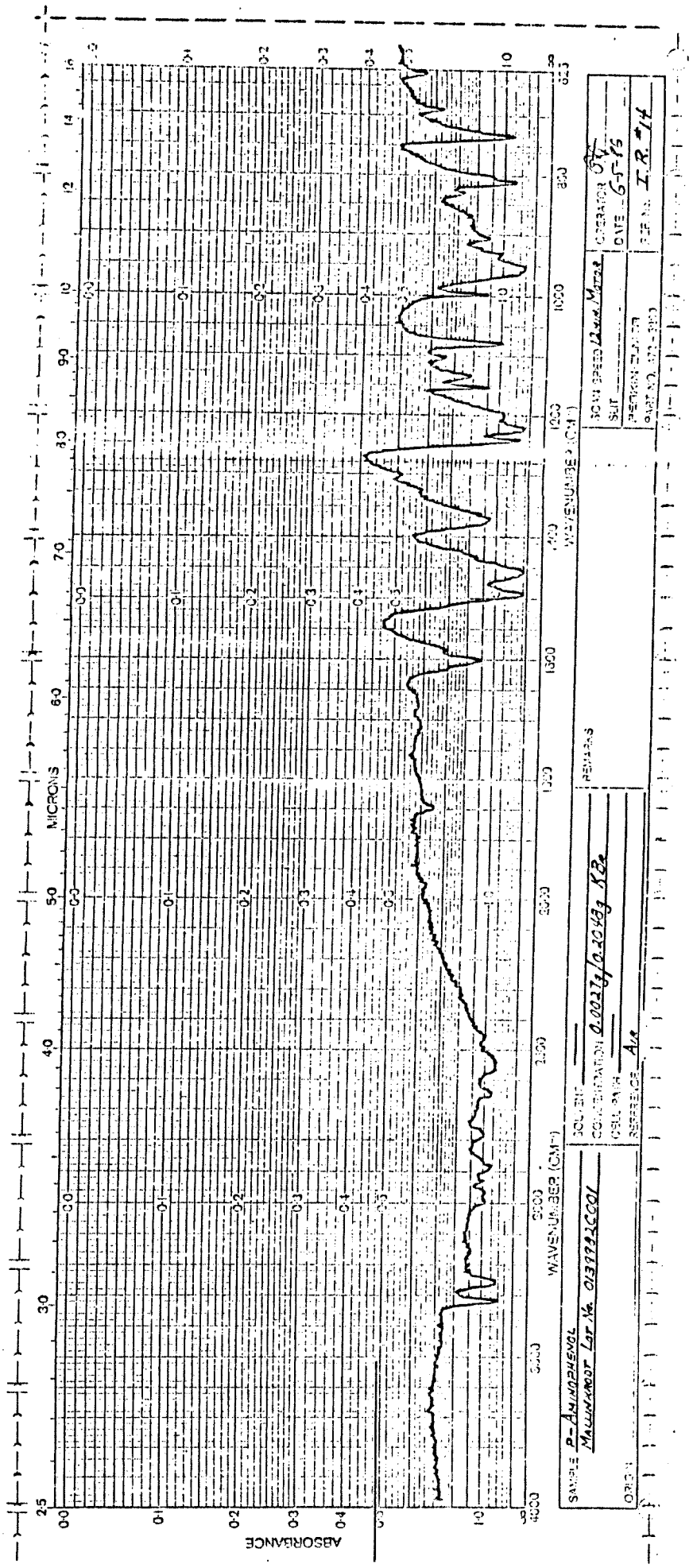
CONCENTRATION 5% w/w IN DME
THICKNESS 0.1 MM CELL
PHASE DOUBLE BEAM
REMARKS REFERENCE TO DME

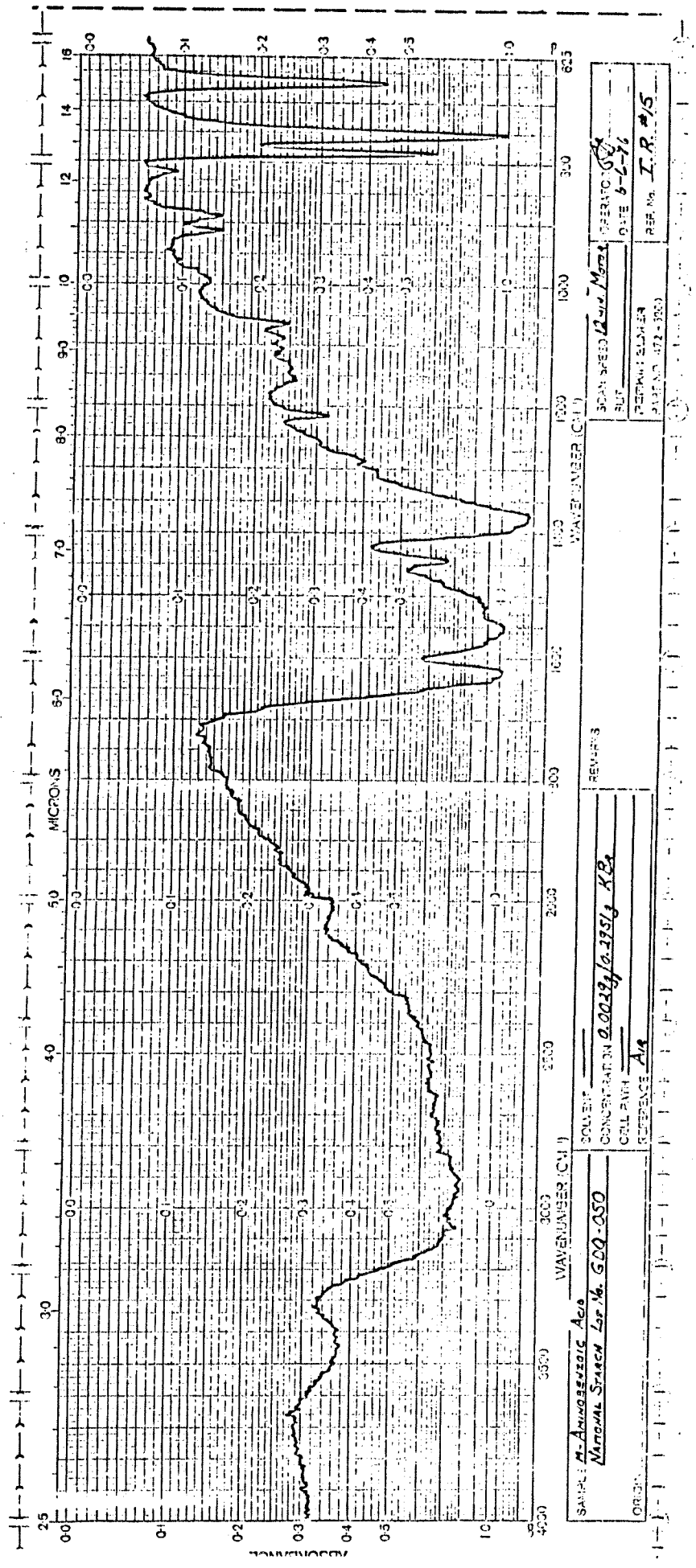
SCAN MODE ACCY. ☐ SURVEY ☐
HI ENERGY ☐ CAL. ☐
RESOLUTION ☐
OPERATOR GA DATE 5-17-86

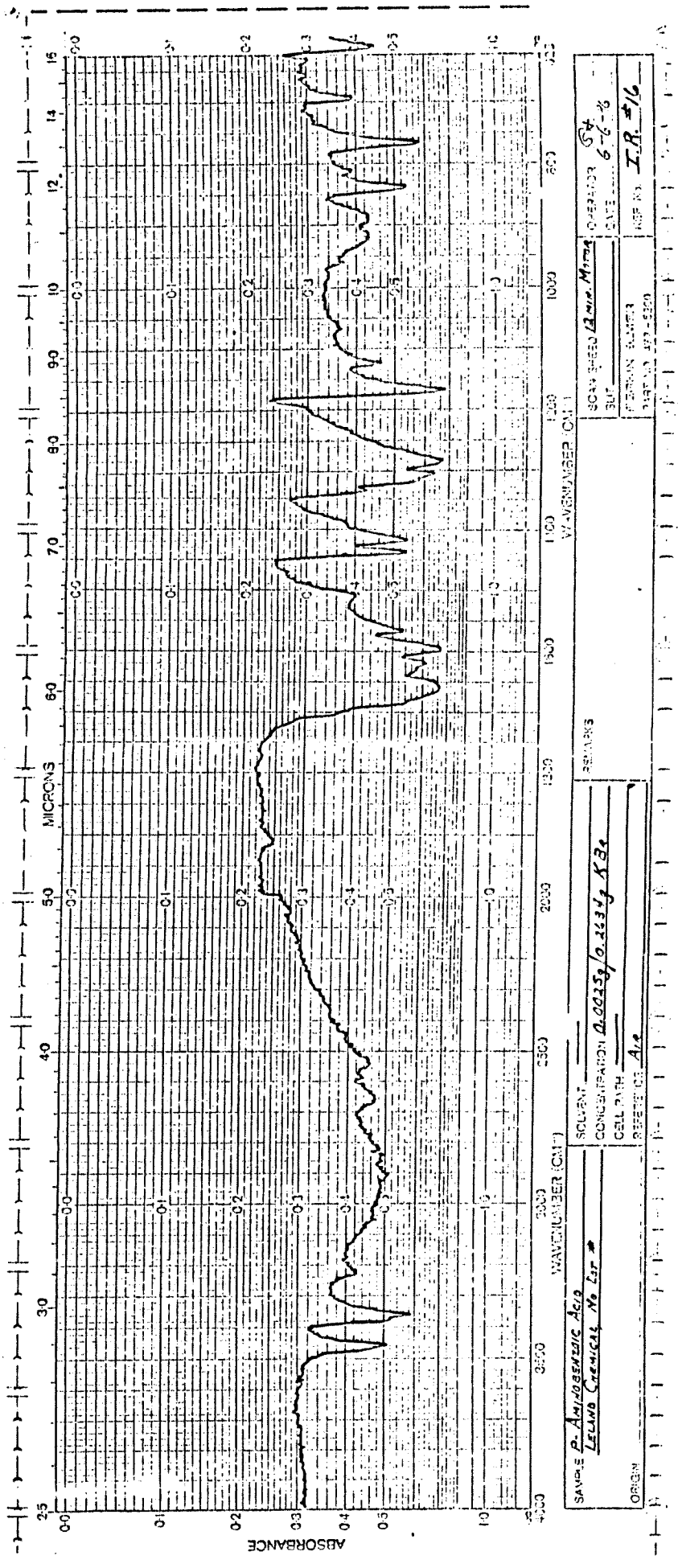
SPECTRUM NO. I.R. #12
SAMPLE DIPHENYL CARBONATE (DPC)
ORIGIN PPG




ABSORBANCE
MICRONS
WAVENUMBER (CM-1)
SAMPLE N-Aminobenzyl Morpholine
Lot No. A/42/4472
SOLVENT
CONCENTRATION 0.0031g/0.301lg KBr
CELL PATH
REFERENCE Air
REMARKS
OPEN
I.R. #13


ABSORBANCE
MICRONS
WAVENUMBER (CM-1)
SAMPLE P-AMINOPHENOL
MALLINCKROT Lot No. 0337242 COL
SOLVENT
CONCENTRATION 0.0021g/0.2ml KBr
CELL PATH
REFERENCE Air
REMARKS
SCAN SPEED Usual Manual
SLIT
DETECTOR TGS
BEAM SPLITTER KBr
OPERATOR
DATE 6-5-75
FILE NO. I.R. #14


MICRONS
WAVENUMBER (CM⁻¹)
ABSORBANCE
SAMPLE: M-Aminobenzoic Acid
ORIGIN: National Starch Lot No. GOQ-050
SOLVENT:
CONCENTRATION: 0.0024g/1.435g KBr
CELL PATH:
REFERENCE: Air
REMARKS
SCAN SPEED: 12 min Mode
SLIT:
RESPONSE:
RANGE: 4000 - 400
DATE: 6-6-91
REF. No. I.R. #15


ABSORBANCE
MICRONS
WAVENUMBER (CM⁻¹)
SAMPLE P-Aminobenzoic Acid
Lecuna Chemicals No Lot #
ORIGIN
SOLVENT
CONCENTRATION 0.0025g/0.443g KBr
CELL PATH
REMARKS
SCAN SPEED 12 min. Mins
BUF
OPERATOR
DATE 6-6-78
I.R. #16

NO. 007-1493

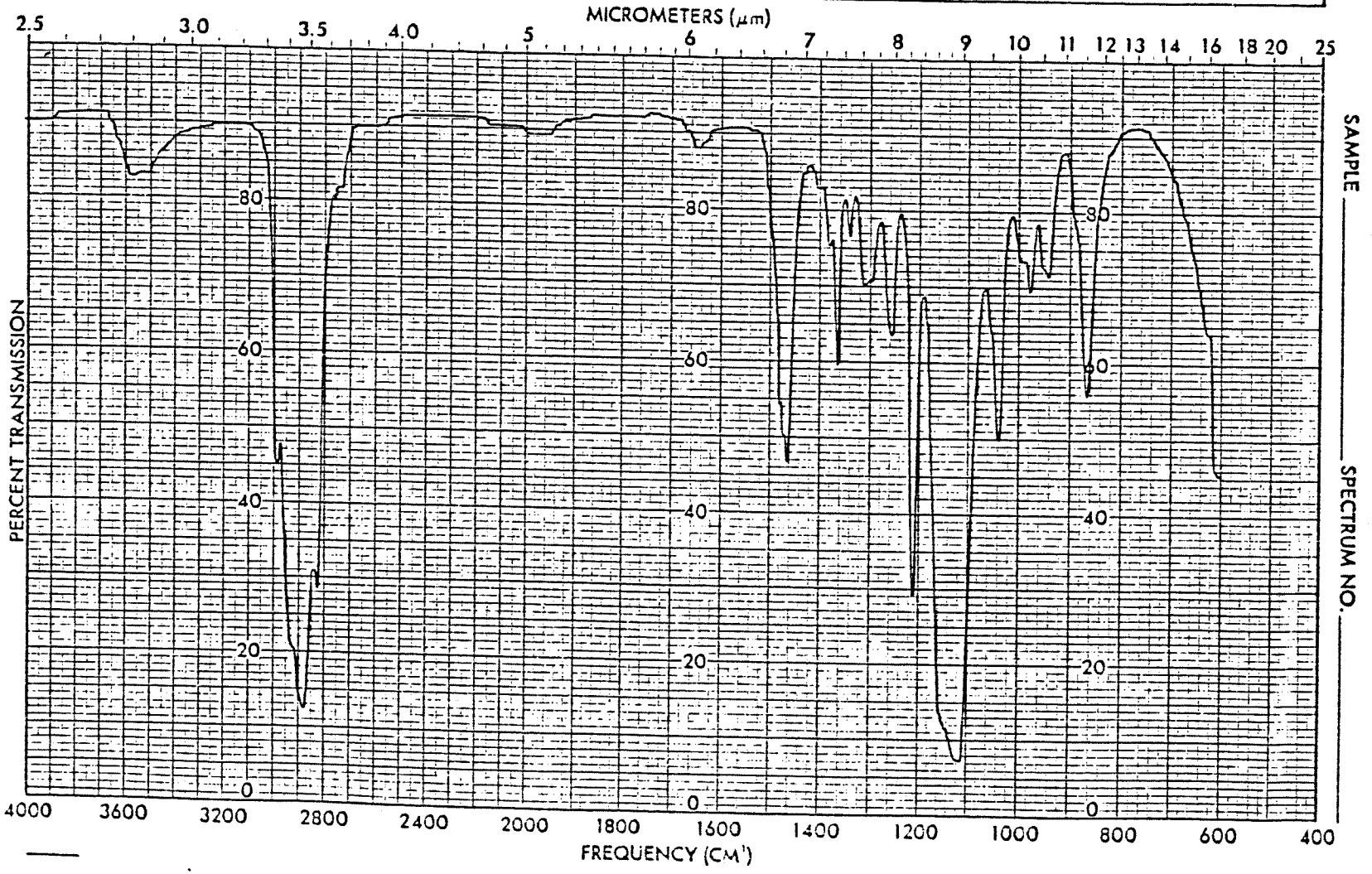
PERKIN-ELMER

CONCENTRATION Neat, NaCl Discs
THICKNESS
PHASE Double Beam
REMARKS Reference to Air

SCAN MODE ACCY. ☐ SURVEY ☒
HI ENERGY ☐ CAL. ☐
RESOLUTION ☐
OPERATOR BH DATE 5-14-86

SPECTRUM NO. I.R. #17
SAMPLE Diglyme

ORIGIN Grant Chemical, No Lot #



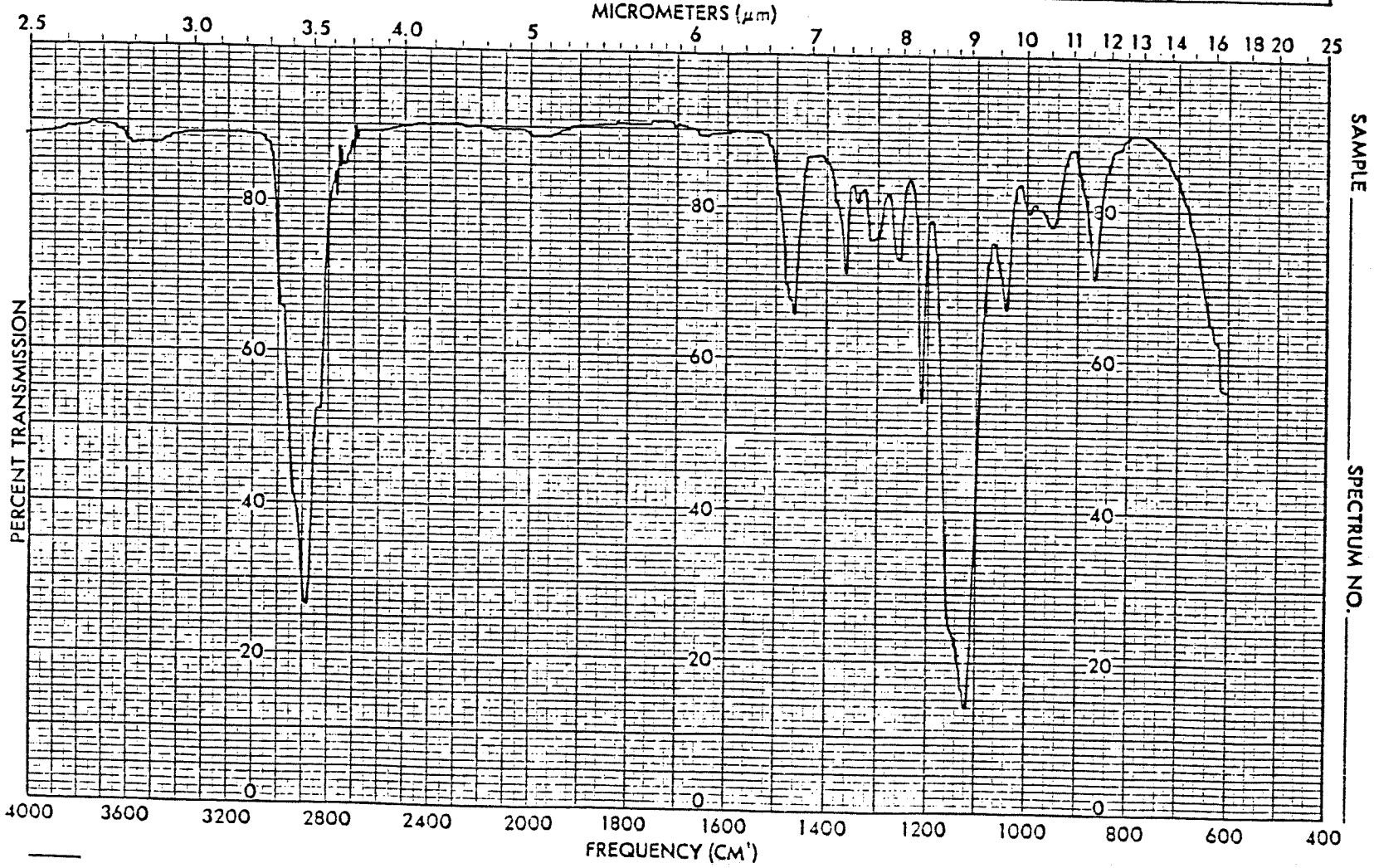
NO. 007-1493

PERKIN-ELMER

CONCENTRATION NEAT, NaCl DISCS
THICKNESS —
PHASE DOUBLE BEAM
REMARKS REFERENCE TO AIR

SCAN MODE ACCY. ☐ HI ENERGY ☐ RESOLUTION ☐ SURVEY ☒ CAL. ☐
OPERATOR GT DATE 5-19-16

SPECTRUM NO. I. R. #18
SAMPLE TRIGLYME
ORIGIN GRANT CHEMICAL, No LOT #



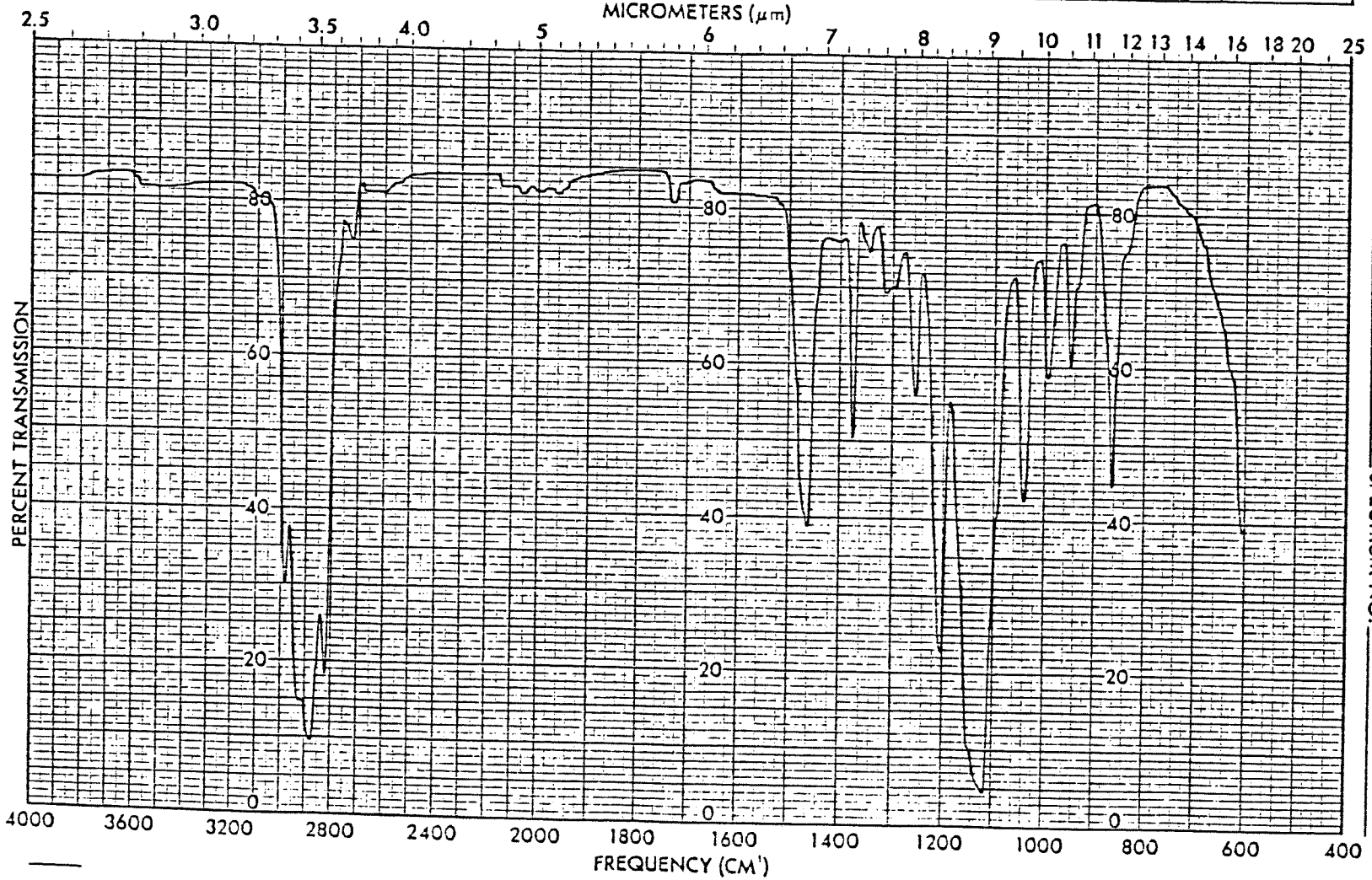
NO. 007-1493

PERKIN-ELMER

CONCENTRATION NEAT, NaCl DISCS
THICKNESS ——
PHASE DOUBLE BEAM
REMARKS REFERENCE TO AIR

SCAN MODE ACCY. ☐ SURVEY ☒
HI ENERGY ☐ CAL. ☐
RESOLUTION ☐
OPERATOR [illegible] DATE 5-19-86

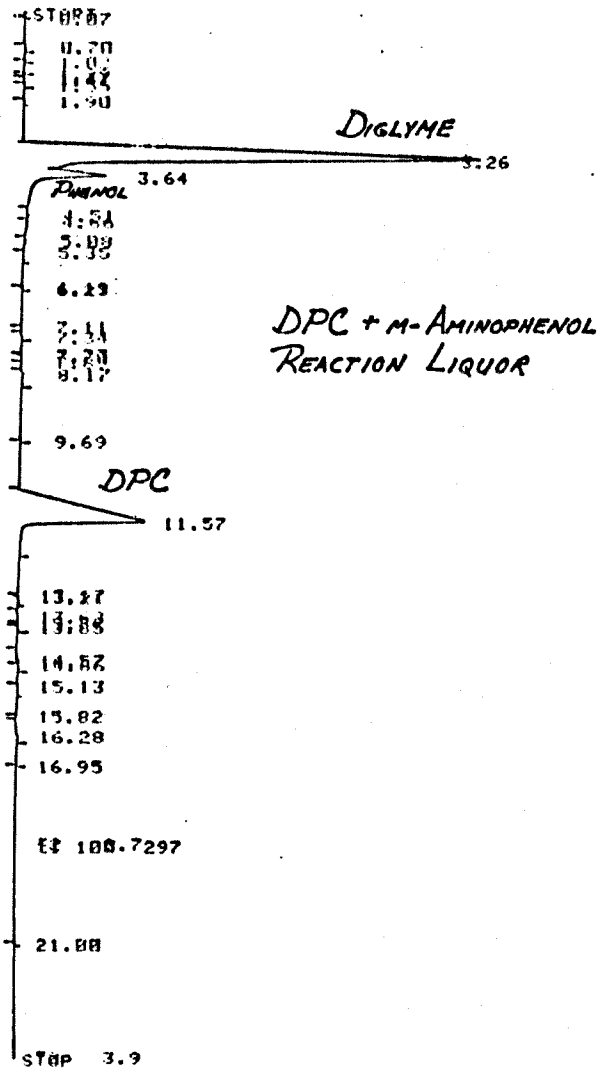
SPECTRUM NO. I.R. #19
SAMPLE GLYME
(DIMETHOXYETHANE, DME)
ORIGIN ANSUL CHEMICAL, NO LOT #



APPENDIX C

GAS CHROMATOGRAPHS OF DPC + SUBSTITUTED AROMATIC AMINE REACTION LIQUORS

(GC-1 through GC-4)



DPC + m-AMINOPHENOL REACTION LIQUOR

RT	AREA	AREA %
0.07	21	0.001
0.70	1009	0.043
1.02	65	0.003
1.29	94	0.004
1.37	15	0.001
1.41	69	0.003
1.55	57	0.002
1.90	102	0.004
3.26	1470000	62.266
3.64	225100	9.535
4.51	17430	0.738
4.66	14860	0.630
5.08	7624	0.323
5.35	1351	0.057
6.19	22	0.001
6.23	111	0.005
7.11	125	0.005
7.34	572	0.024
7.73	72	0.003
7.78	44	0.002
7.89	36	0.002
8.17	4103	0.174
9.69	25	0.001
11.57	611400	25.898
13.17	104	0.004
13.21	305	0.013
13.62	578	0.024
13.77	396	0.017
14.57	1337	0.057
14.66	1089	0.046
15.32	77	0.003
16.28	2567	0.109
16.95	9	0.000
21.00	61	0.003

XF: 1.0000 E+ 0

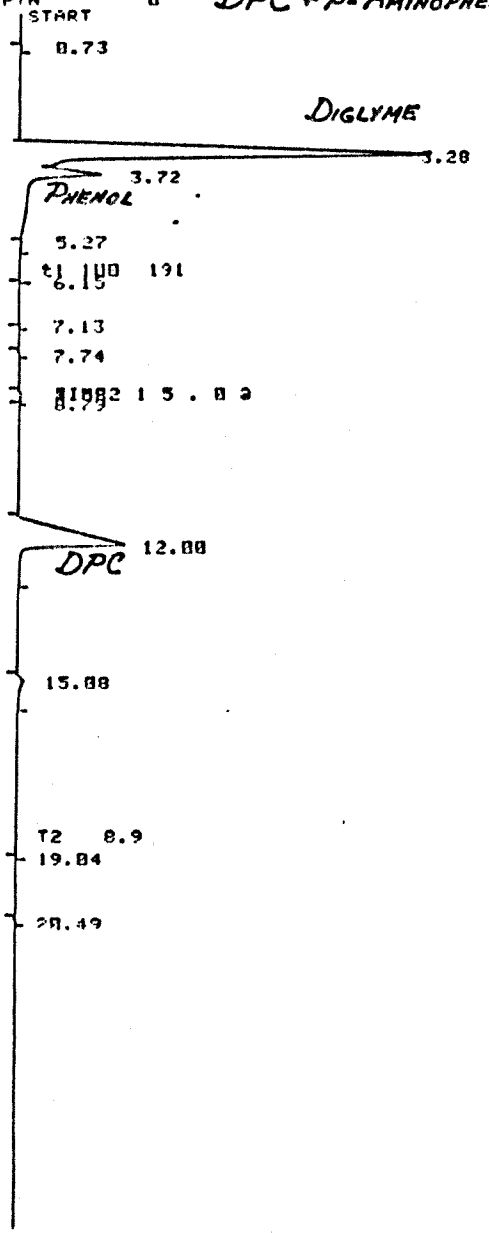
152

GC-1

```
TEMP1      100  100
TIME1        0.0
RATE        20.00
TEMP2      350
TIME2       20.0
INJ TEMP   350  350
TCD TEMP   375  375
OVEN MAX   400

CHT SPD      1.00
ATTN 2^     10
TCD SGNL    A
SLP SENS     0.20
AREA REJ     1
FLOW  A      0
FLOW  B      0
OPTN         0
```

DPC + p-Aminophenol Reaction Liquors



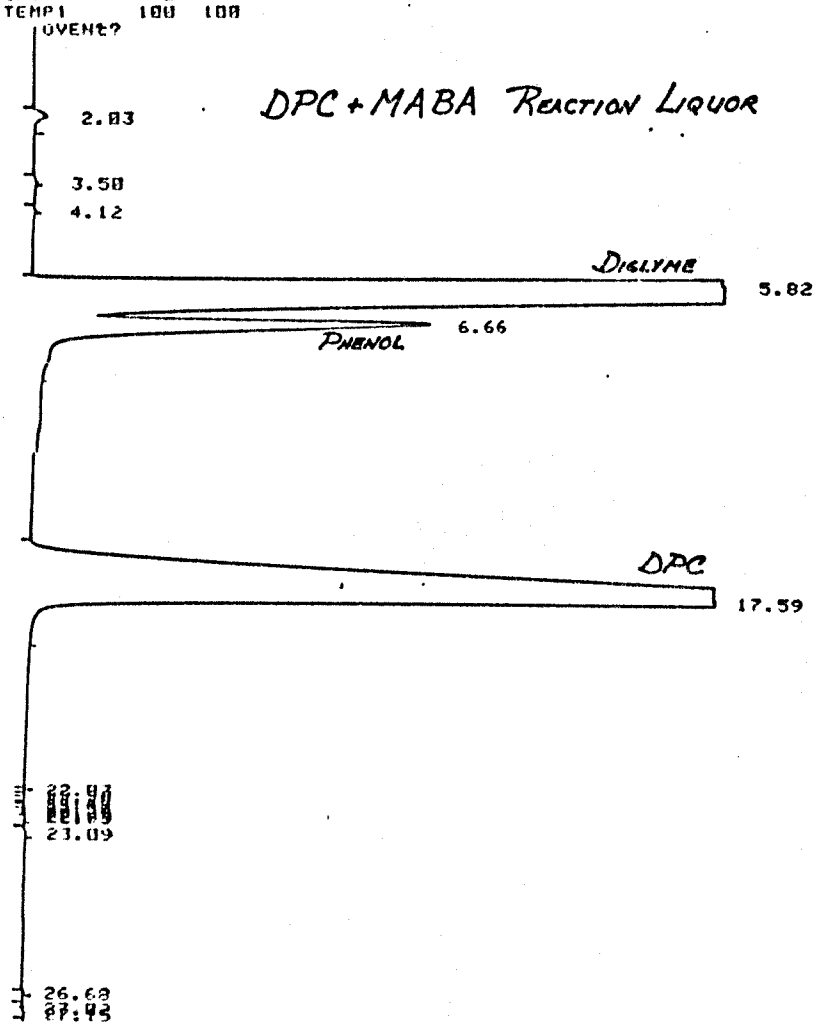
BOTTLE 0
HP 5830A
AREA %

RT	AREA	AREA %
0.73	1945	0.095
3.28	1264000	61.824
3.72	279000	13.641
5.27	2797	0.137
6.15	16	0.001
7.13	14	0.001
7.74	77	0.004
8.58	1902	0.097
8.79	121	0.006
12.00	473400	23.155
15.08	20700	1.012
19.84	330	0.016
20.49	244	0.012

GC-2

```
TEMP1      100  101
TIME1        0.0
RATE        20.00
TEMP2      350
TIME2       15.0
INJ TEMP   350  350
TCD TEMP   375  375
OVEN MAX   400

CHT SPD      1.00
ATTN 2^      0
TCD SGNL     A
SLP SENS     0.20
AREA REJ     1
FLOW  A      0
FLOW  B      0
OPTN         0
TEMP1      100  100
```



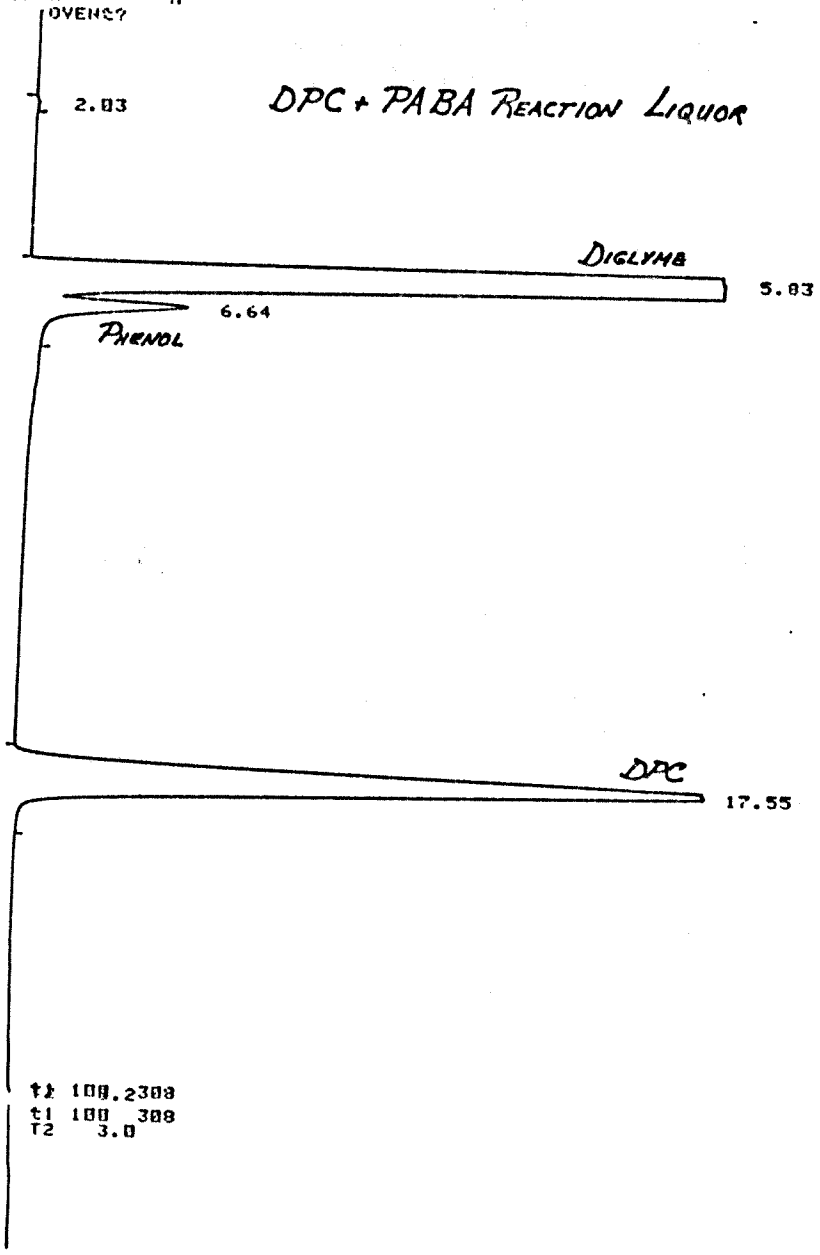
BOTTLE 0
hp 5830A
AREA %

RT	AREA	AREA %
2.03	7318	0.111
3.50	635	0.010
4.12	253	0.004
5.82	4394000	66.429
6.66	333900	5.049
17.59	1877000	28.377
22.07	0	0.000
22.28	141	0.002
22.29	146	0.002
22.39	82	0.001
22.50	132	0.002
22.56	95	0.001
22.62	147	0.002
22.69	196	0.003
22.73	276	0.004
23.09	135	0.002
26.68	48	0.001
27.02	71	0.001
27.15	29	0.000

XF: 1.0000 E+ 0

GC-3

TEMP1	100	102
TIME1	0.0	
RATE	20.00	
TEMP2	350	
TIME2	15.0	
INJ TEMP	350	350
TCD TEMP	375	375
OVEN MAX	400	
CHT SPD	1.00	
ATTN 2↑	8	
TCD SGNL	A	
SLP SENS	0.20	
AREA REJ	1	
FLOW A	0	
FLOW B	0	
OPTN	.1	



980

087

BOTTLE 0
* 5830A
AREA %

PT	AREA	AREA %
2.03	1337	0.026
5.83	3899000	75.636
6.64	129600	2.514
17.55	1125000	21.824

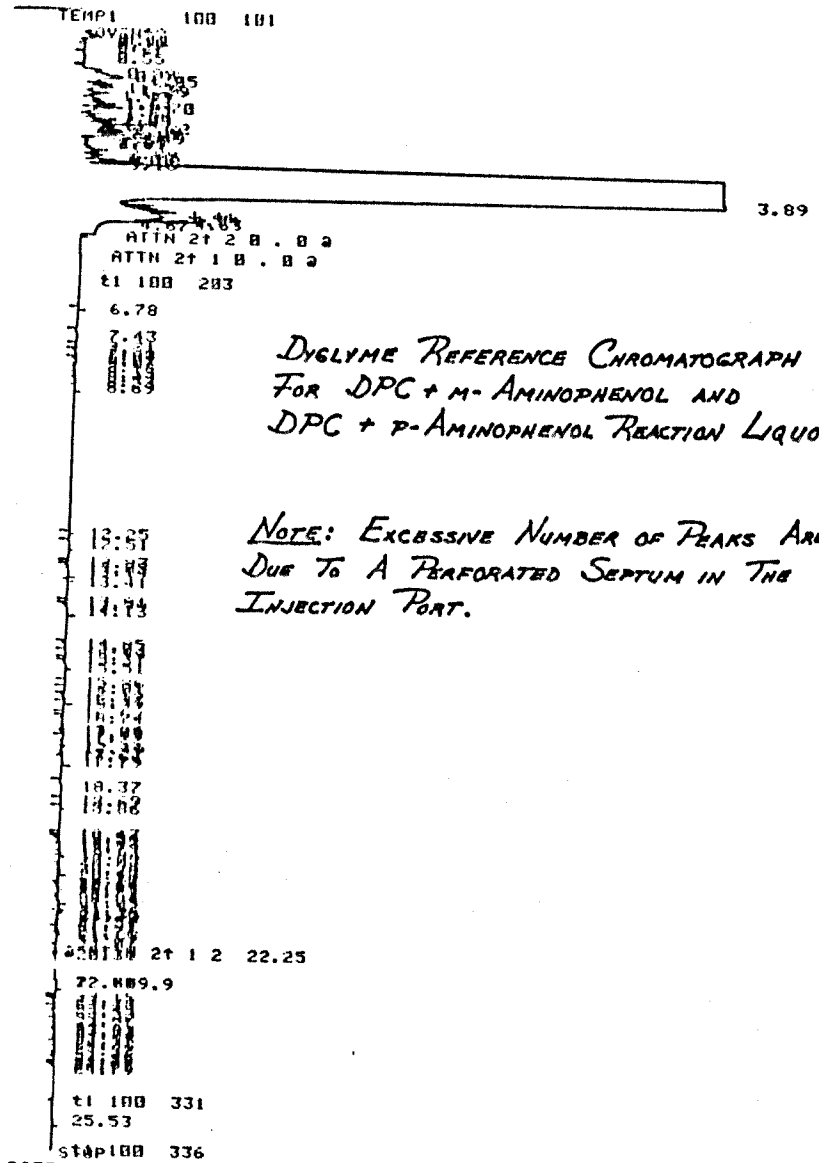
XF: 1.0000 E+ 0

GC-4

APPENDIX D

GAS CHROMATOGRAPHS OF RAW MATERIALS, SOLVENTS, AND POSSIBLE BY-PRODUCTS OF DPC + SUBSTITUTED AROMATIC AMINE REACTIONS

(GC-5 through GC-13)



DYGLYME REFERENCE CHROMATOGRAPH FOR DPC + m-AMINOPHENOL AND DPC + p-AMINOPHENOL REACTION LIQUORS

NOTE: EXCESSIVE NUMBER OF PEAKS ARE DUE TO A PERFORATED SEPTUM IN THE INJECTION PORT.

138

BOTTLE 8
** 5838A
AREA %

RT	AREA	AREA %
0.11	2604	0.046
0.16	119	0.002
0.22	71	0.001
0.27	198	0.003
0.55	643	0.011
0.89	3437	0.061
0.96	4407	0.078
1.05	12970	0.230
1.23	4380	0.078
1.26	4368	0.077
1.29	2353	0.042
1.43	6572	0.117
1.57	3586	0.064
1.62	2478	0.044
1.64	876	0.016
1.70	5655	0.100
1.81	8152	0.145
1.95	2425	0.043
2.00	1518	0.027
2.05	3325	0.059
2.11	4971	0.088
2.22	11670	0.207
2.29	4365	0.077
2.35	3896	0.069
2.40	4503	0.080
2.49	9238	0.164
2.55	1316	0.023
2.61	1224	0.022
2.65	1595	0.028
2.89	7820	0.139
3.03	6478	0.115
3.08	802	0.014
3.16	7722	0.137
3.89	5219000	94.363
4.44	44080	0.782
4.54	34410	0.610
4.63	10480	0.186
4.57	6318	0.112
6.78	8	0.000
7.43	236	0.004

GC-5
(P.1 of 2)

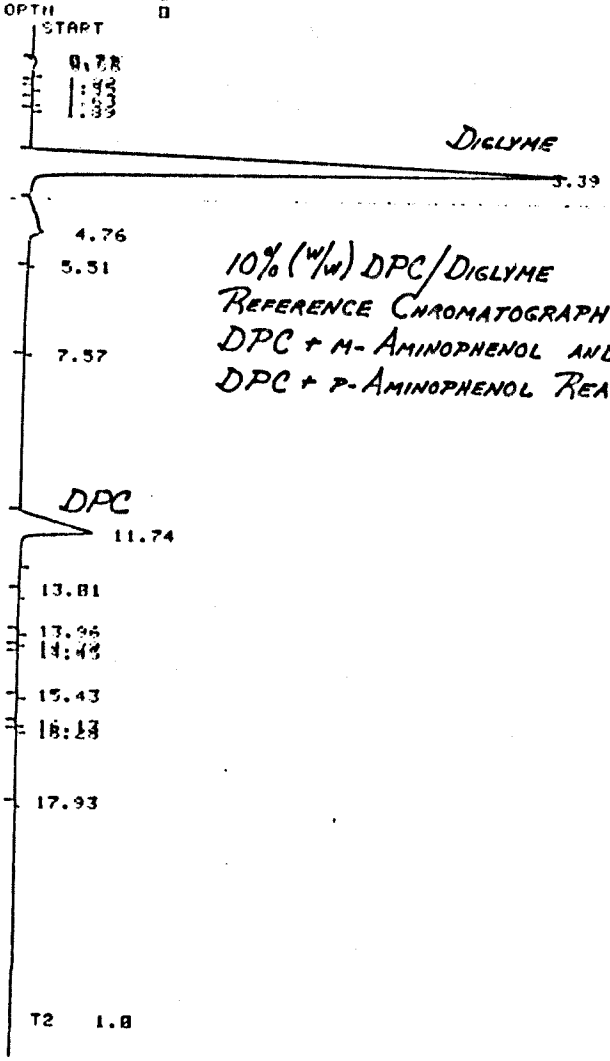
7.81	23	0.000
7.90	145	0.003
8.01	107	0.002
8.07	244	0.004
8.18	7	0.000
8.33	131	0.002
8.43	218	0.004
8.53	274	0.005
8.69	203	0.004
12.25	48	0.001
12.51	68	0.001
12.93	55	0.001
13.05	48	0.001
13.14	115	0.002
13.41	34	0.001
13.91	133	0.002
13.99	168	0.003
14.13	798	0.014
14.95	70	0.001
15.03	160	0.003
15.19	53	0.001
15.31	54	0.001
15.51	279	0.005
15.36	168	0.003
16.01	276	0.005
16.19	94	0.002
16.31	241	0.004
16.39	87	0.002
16.74	201	0.004
17.05	1255	0.022
17.09	238	0.004
17.15	419	0.007
17.22	742	0.013
17.44	594	0.011
17.49	1288	0.023
17.62	154	0.003
17.66	134	0.002
17.79	1177	0.021
18.37	1397	0.025
18.69	475	0.008
18.86	43	0.001
19.47	138	0.002
19.54	107	0.002
19.59	119	0.002
19.68	453	0.008
19.74	457	0.008
19.79	1245	0.022
19.94	1317	0.023
20.08	3114	0.055
20.24	787	0.014
20.29	1123	0.020
20.40	1362	0.024
20.51	2612	0.046
20.60	554	0.010
20.64	347	0.006
20.67	182	0.003
20.75	778	0.014
20.83	1463	0.026
20.94	925	0.016
21.05	1160	0.021
21.17	4147	0.074
21.26	2026	0.036
21.31	1928	0.034
21.35	2036	0.036
21.40	2205	0.039
21.51	1612	0.029
21.54	322	0.006
21.61	442	0.008
21.71	585	0.010
21.76	624	0.011
21.83	2530	0.045
22.03	3212	0.057
22.11	81	0.001
22.25	388	0.007
22.31	88	0.002
22.50	587	0.010
22.61	692	0.012
22.75	860	0.015
23.15	118	0.002
23.24	119	0.002
23.33	73	0.001
23.45	140	0.002
23.53	505	0.009
23.67	1574	0.028
23.75	698	0.012
23.91	2781	0.049
23.93	434	0.008
23.98	2416	0.043
24.04	3059	0.054
24.15	2608	0.046
24.21	1733	0.031
24.26	4034	0.072
24.37	3233	0.057
24.48	1578	0.028
24.55	1174	0.021
24.58	3092	0.055
24.67	117	0.002
24.71	84	0.001
24.79	1155	0.020
25.53	689	0.012

XF: 1.0000 E+ 0

Diglyme Reference
Chromatograph
P-2

GC-5
(P.2 of 2)

TEMP1	100	100
TIME1	0.0	
RATE	20.00	
TEMP2	350	
TIME2	15.0	
INJ TEMP	350	350
TCD TEMP	375	375
OVEN MAX	400	
CHT SPD	1.00	
ATTN 21	10	
TCD SGNL	A	
SLP SENS	0.20	
AREA REJ	1	
FLOW A	0	
FLOW B	0	
OPTN	0	



10% (w/w) DPC/DIGLYME
REFERENCE CHROMATOGRAPH FOR
DPC + M-AMINOPHENOL AND
DPC + P-AMINOPHENOL REACTION LIQUORS

153

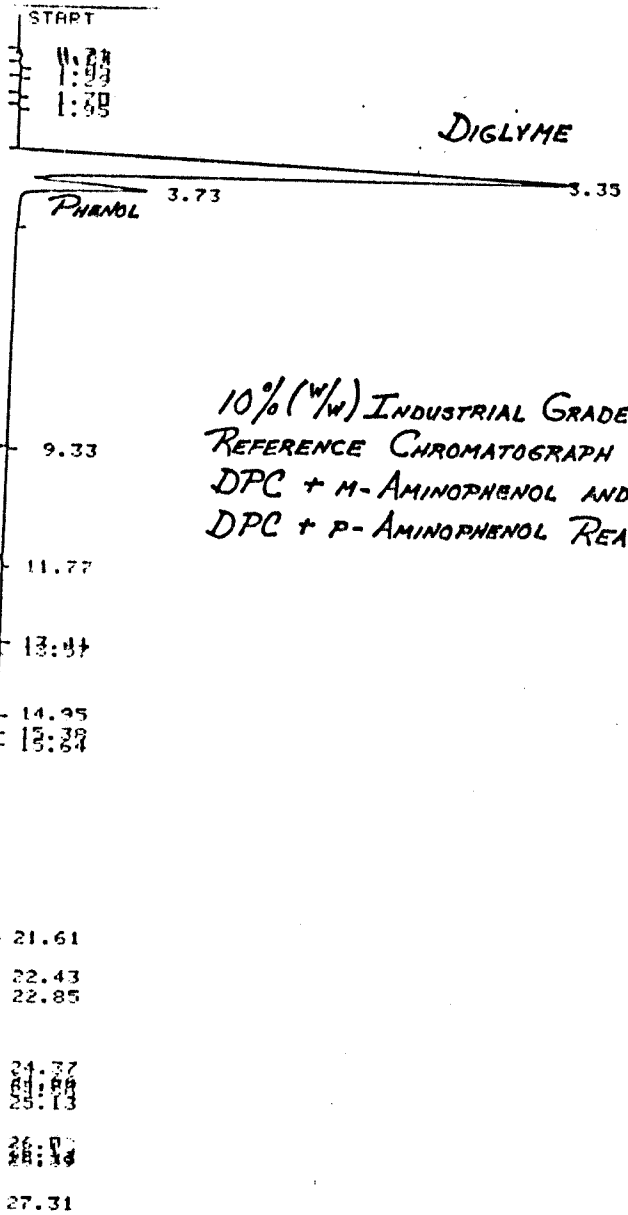
BOTTLE 0
hr 5830A
AREA %

RT	AREA	AREA %
0.71	1849	0.073
0.77	1836	0.072
0.83	6042	0.237
1.22	563	0.022
1.35	297	0.011
1.63	922	0.036
1.89	217	0.009
3.39	2162000	84.980
4.76	85448	3.358
5.51	73	0.003
7.57	9	0.000
11.74	284400	11.179
13.81	99	0.004
13.96	66	0.003
14.29	47	0.002
15.43	25	0.001
16.13	133	0.005
16.28	57	0.002
17.93	66	0.003

XF: 1.0000 E+ 0

154

GC-6



10% (W/W) INDUSTRIAL GRADE PHENOL/DIGLYME
REFERENCE CHROMATOGRAPH FOR
DPC + M-AMINOPHENOL AND
DPC + P-AMINOPHENOL REACTION LIQUORS

150

BOTTLE 0
HP 5830A
AREA %

RT	AREA	AREA %
0.71	887	0.040
0.77	999	0.045
0.84	3199	0.146
1.05	1227	0.056
1.29	50	0.002
1.70	177	0.008
1.95	94	0.004
3.35	1904000	86.656
3.73	285300	12.985
9.33	43	0.002
11.77	144	0.007
13.41	41	0.002
13.57	105	0.005
14.95	134	0.006
15.38	49	0.002
15.64	79	0.004
21.61	11	0.001
22.43	46	0.002
22.85	43	0.002
24.37	51	0.002
24.66	28	0.001
24.74	68	0.003
24.86	3	0.000
25.13	137	0.006
26.02	69	0.003
26.19	48	0.002
26.33	33	0.002
26.39	79	0.004
27.31	52	0.002

XF: 1.0000 E+ 0

GC-7

151

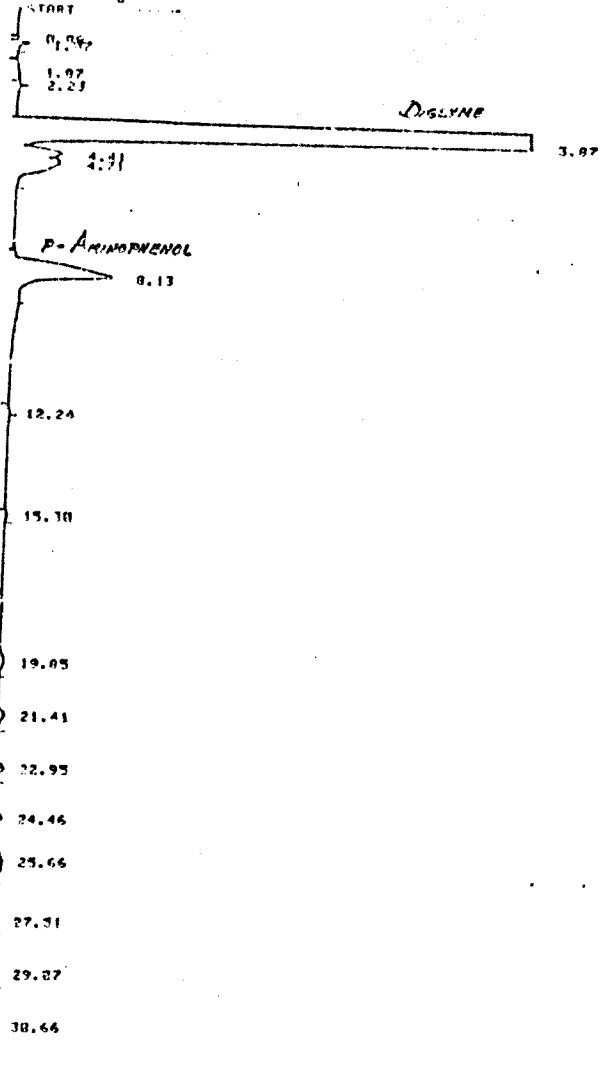
10% (w/w) p-Aminophenol/Diglyme
Reference Chromatograph

```
TEMP1      150  150
TIME1        0.0
RATE        20.00
TEMP2       350
TIME2        20.0
INJ TEMP    350  350
TCD TEMP    325  339
OVEN MAX    400

CHT SPD      1.00
ATTN 2^      8
TCD SGNL     A
SLP SENS     0.20
AREA REJ     1
FLOW  A      0
FLOW  B      0
OPTN         6
TEMP1 100.0 °C
TEMP1 100.0 mA
TEMP1       100  140

TEMP1       100  101
TIME1        0.0
RATE        20.00
TEMP2       350
TIME2        30.0
INJ TEMP    350  350
TCD TEMP    325  375
OVEN MAX    400

CHT SPD      1.00
ATTN 2^      8
TCD SGNL     A
SLP SENS     0.20
AREA REJ     1
FLOW  A      0
FLOW  B      0
OPTN         0
  START
```




```
BOTTLE    0
** 5030A
0
   RT          AREA       AREA %

  0.89          717        0.021
  1.07         4411        0.130
  1.07         1402        0.041
  2.23          420        0.005
  3.97      3016000       89.622
  4.41        50300        1.495
  4.71        80040        2.367
  8.13       151500        4.501
 12.24          904        0.027
 15.30         1403        0.034
 19.05         6664        0.197
 21.41         7466        0.220
 22.95         7320        0.218
 24.46         6014        0.178
 25.66        20950        0.618
 27.31         4511        0.133
 29.27         4132        0.122
 30.66         1506        0.044

          XF=  1.0000 E+ 0
```

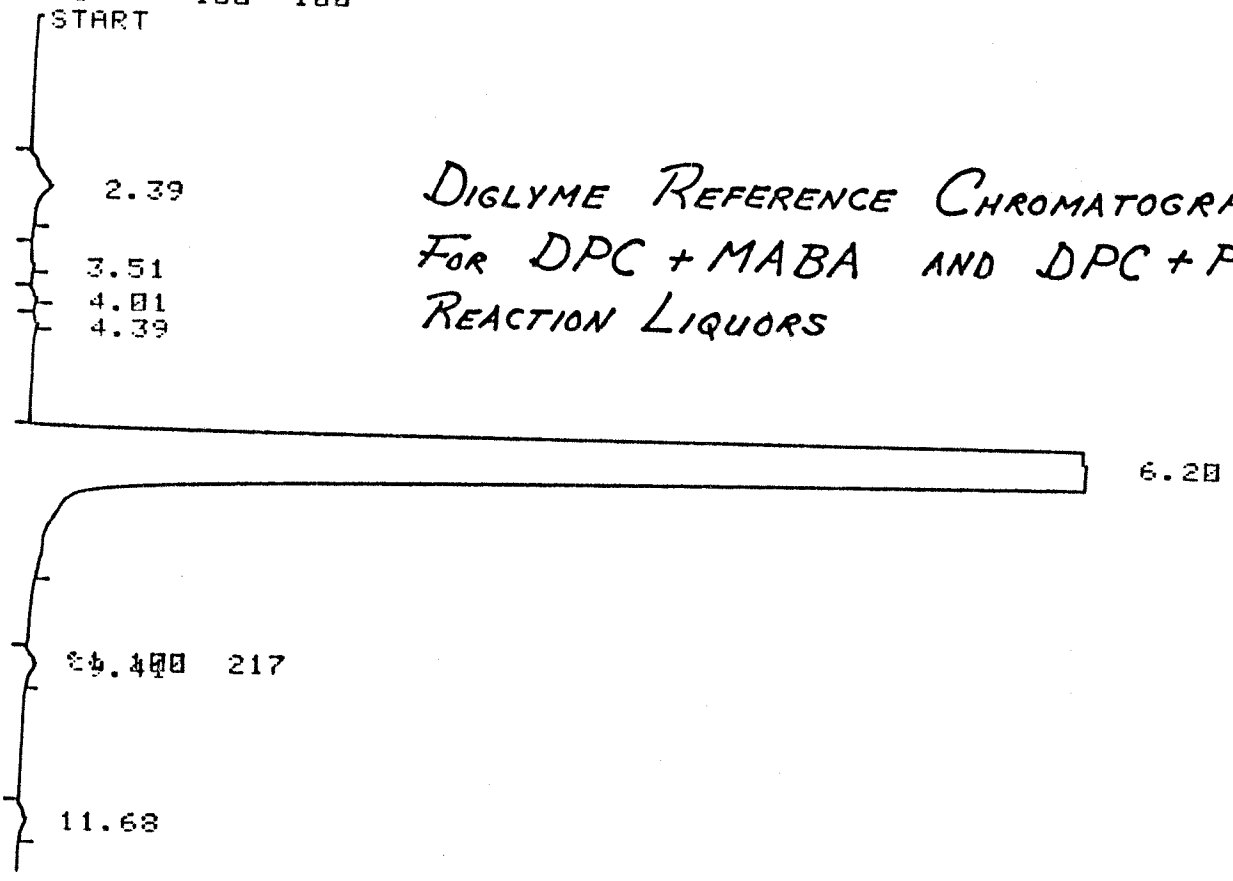
GC-8

133

134

078

TEMP1	100	71
TIME1	0.0	
RATE	20.00	
TEMP2	350	
TIME2	0.0	
INJ TEMP	350	350
TCD TEMP	375	375
OVEN MAX	400	
CHT SPD	1.00	
ATTN 2↑	8	
TCD SGNL	A	
SLP SENS	0.20	
AREA REJ	1	
FLOW A	0	
FLOW B	0	
OPTN	0	
TEMP1	100	100



Diglyme Reference Chromatograph For DPC + MABA and DPC + PABA Reaction Liquors

BOTTLE 0
hp 5830A
AREA %

RT	AREA	AREA %
2.39	15480	0.340
3.51	734	0.016
4.01	766	0.017
4.39	534	0.012
6.20	4531000	99.430
9.41	4767	0.105
11.68	3695	0.081

XF: 1.0000 E+ 0

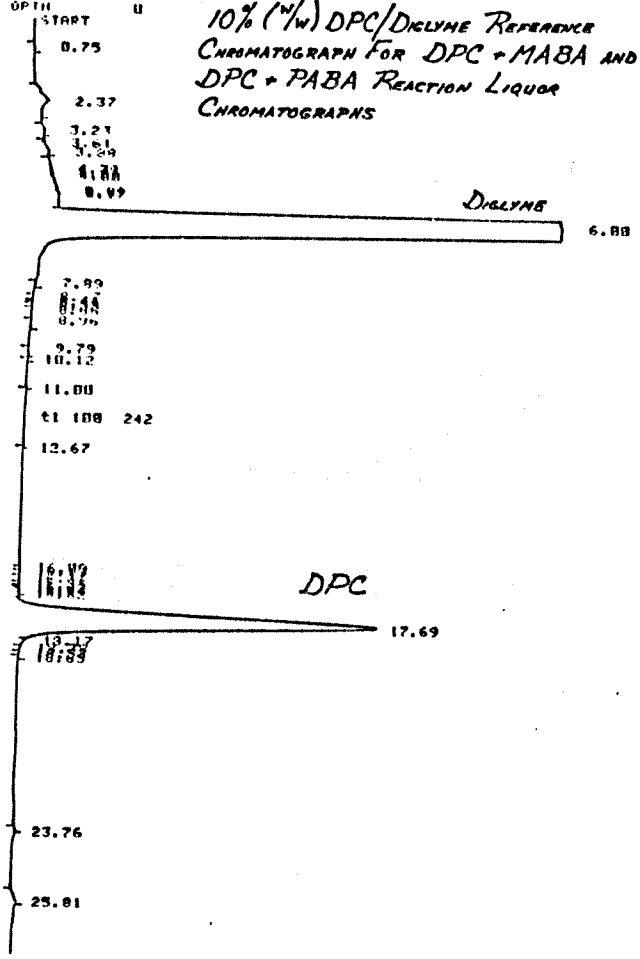
GC-9

TIME2 [5 . 0]

TEMP1	100	100
TIME1	0.0	
RATE	20.00	
TEMP2	350	
TIME2	15.0	
INJ TEMP	350	350
TCD TEMP	375	375
OVEN MAX	400	

CHT SPD	1.00
ATTN 2#	0
TCD SGNL	A
SLP SENS	0.20
AREA REJ	1
FLOW A	0
FLOW B	0
OPTN	0

10% (%w) DPC/Diglyme Reference Chromatograph For DPC + MABA and DPC + PABA Reaction Liquor Chromatographs



081

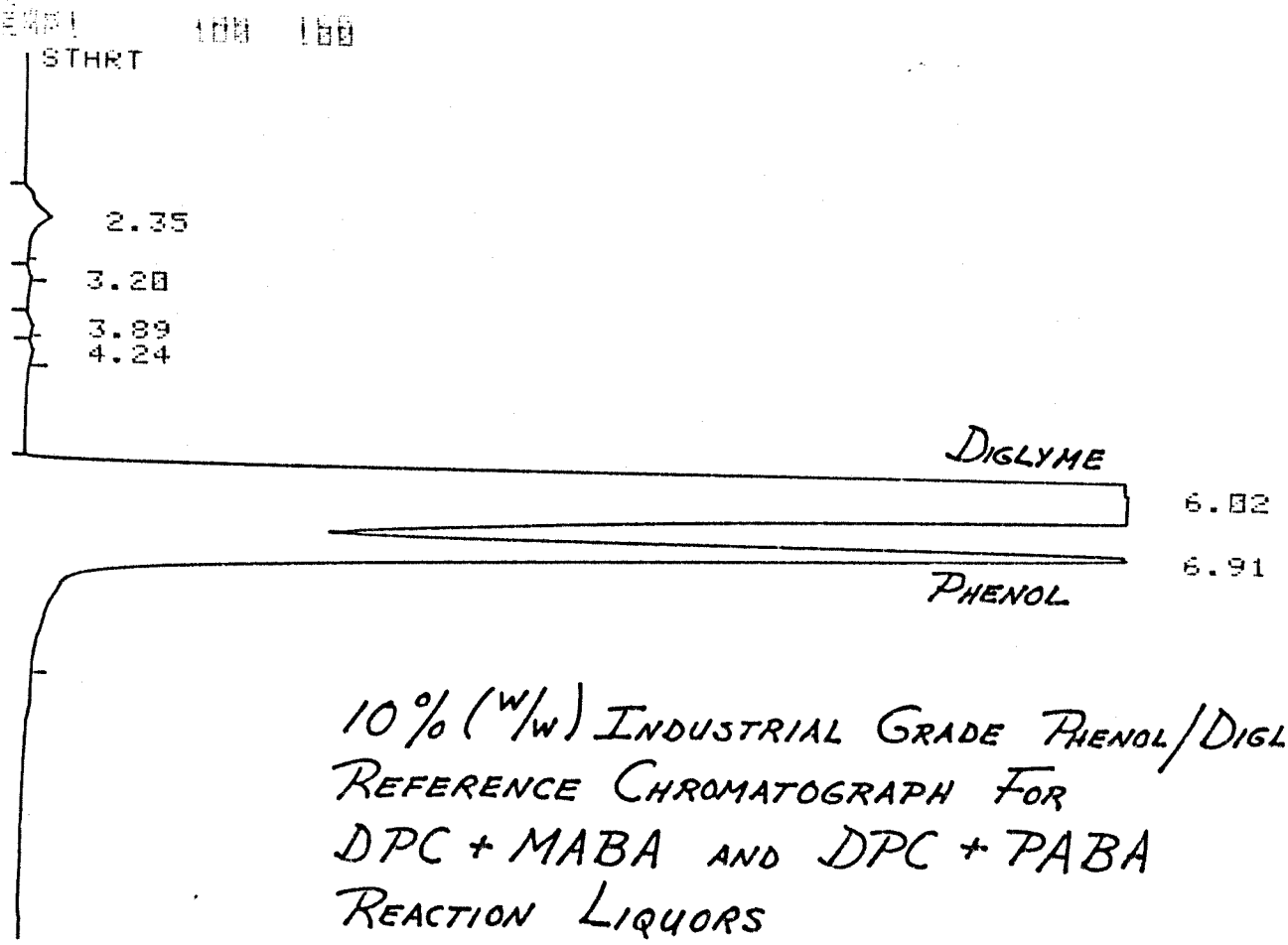
BOTTLE 0
▶ 5030A
AREA %

RT	AREA	AREA %
0.75	154	0.003
2.37	13220	0.242
3.21	53	0.001
3.61	1	0.000
3.88	1393	0.026
4.39	902	0.017
4.51	168	0.003
4.60	62	0.001
5.09	962	0.018
5.17	46	0.001
6.88	4823000	88.714
8.27	51	0.001
8.41	50	0.001
8.48	60	0.001
8.53	94	0.002
8.66	240	0.004
8.96	566	0.010
9.79	141	0.003
10.12	43	0.001
11.00	32	0.001
12.67	20	0.000
15.09	9	0.000
16.19	121	0.002
16.37	44	0.001
16.53	58	0.001
16.62	53	0.001
16.67	24	0.000
16.74	152	0.003
16.82	36	0.001
17.69	611500	11.197
18.17	3627	0.066
18.38	1125	0.021
18.53	859	0.016
18.65	270	0.005
23.76	374	0.007
25.81	1639	0.030

XF1 1.0000 E+ 0

082

GC-10



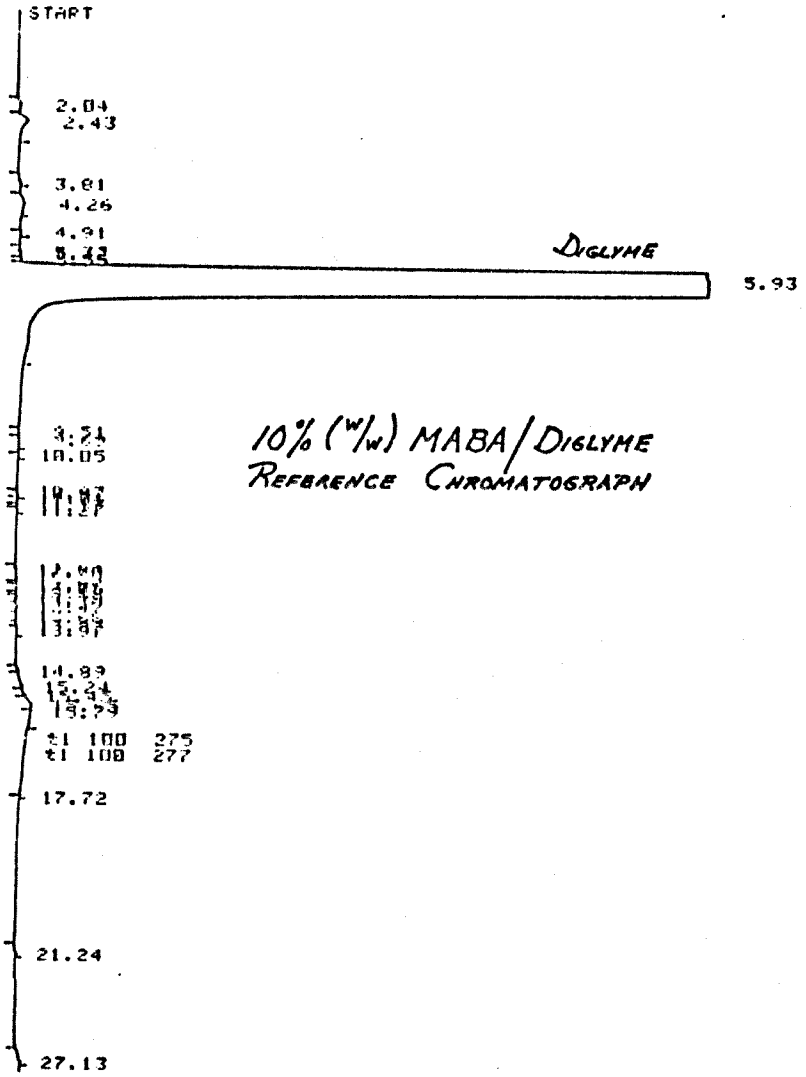
10% (W/W) INDUSTRIAL GRADE PHENOL/DIGLYME
REFERENCE CHROMATOGRAPH FOR
DPC + MABA AND DPC + PABA
REACTION LIQUORS

BOTTLE 0
hp 5830A
AREA %

RT	AREA	AREA %
2.35	16960	0.322
3.20	408	0.008
3.89	1331	0.025
4.24	1276	0.024
6.02	4581000	86.933
6.91	668600	12.688

AF: 1.0000 E+ 0

GC-11



10% (w/w) MABA/DIGLYME
REFERENCE CHROMATOGRAPH

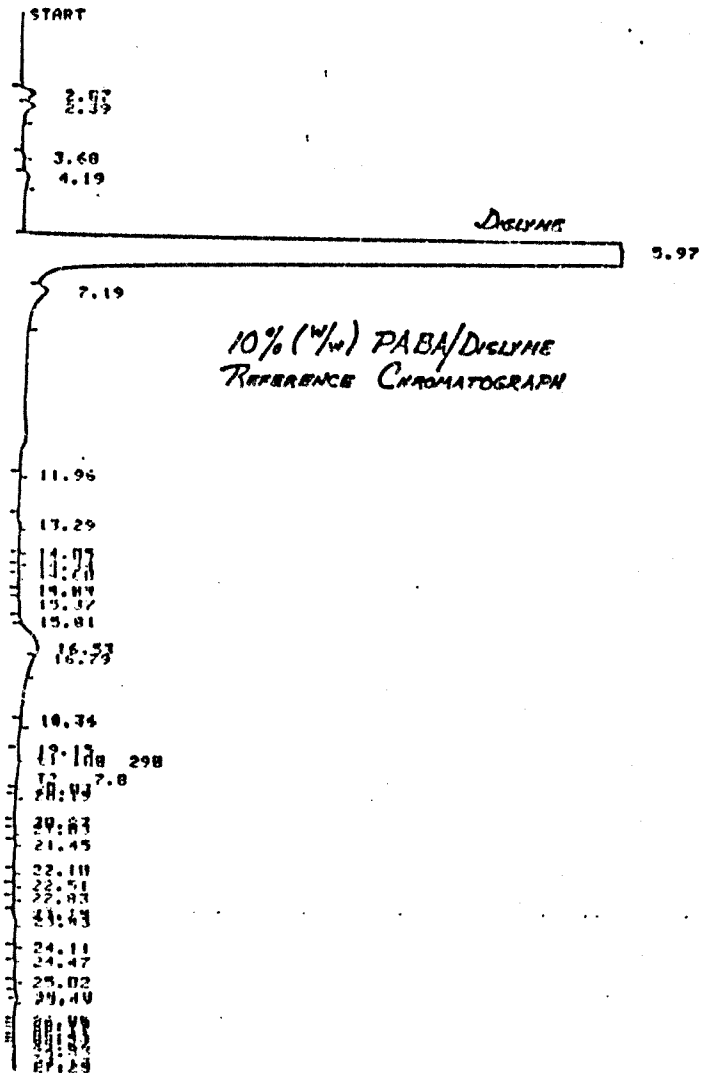
083

BOTTLE 8
** 5830A
AREA %

RT	AREA	AREA %
2.04	1190	0.026
2.43	6692	0.144
3.81	249	0.005
4.26	3407	0.074
4.91	117	0.003
5.37	130	0.003
5.42	28	0.001
5.55	212	0.005
5.93	4604000	99.355
9.51	102	0.002
9.69	84	0.002
10.05	86	0.002
10.67	69	0.001
10.92	53	0.001
11.01	176	0.004
11.17	48	0.001
11.27	87	0.002
12.64	145	0.003
12.70	359	0.009
12.97	120	0.003
13.05	284	0.006
13.18	418	0.009
13.29	587	0.013
13.36	308	0.007
13.47	577	0.012
13.68	338	0.007
14.87	158	0.003
14.97	418	0.009
14.89	142	0.003
15.24	984	0.021
15.45	1250	0.027
15.65	4931	0.106
15.79	4902	0.106
17.72	105	0.002
21.24	359	0.008
27.13	1006	0.022

084

GC-12



085

BOTTLE 0
** 5030A
AREA %

RT	AREA	AREA %
2.07	9466	0.196
2.39	10130	0.210
3.68	211	0.004
4.19	3282	0.066
5.97	4719000	97.872
7.19	35720	0.741
11.96	164	0.003
13.29	371	0.008
14.07	18	0.0008
14.34	29	0.001
14.88	39	0.001
15.37	37	0.001
15.81	165	0.003
16.53	129	0.003
16.79	28910	0.600
18.34	9730	0.202
19.13	17	0.0008
20.03	48	0.001
21.45	46	0.001
22.48	28	0.0008
22.51	29	0.001
23.03	153	0.003
23.43	52	0.001
24.11	347	0.007
24.47	7	0.0008
25.02	87	0.002
25.40	87	0.002
25.49	48	0.001
26.05	78	0.001
26.15	776	0.016
26.31	33	0.001
26.43	39	0.001
26.53	55	0.001
26.67	662	0.014
26.93	381	0.008
27.13	223	0.005
27.25	14	0.001
	97	0.002
	222	0.005
	27	0.001
	128	0.003
	498	0.010
	16	0.000
	93	0.002

XFI 1.0000 E+ 0

GC-13

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