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Carl J. Sullivan
University of Massachusetts Amherst

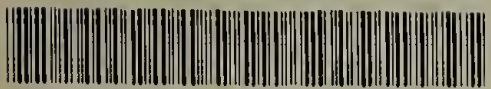
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MODIFICATIONS OF POLYASPARTIMIDE AND
POLY(ETHYLENE-CO-METHACRYLIC ACID): INVESTIGATION
OF POTENTIAL FUNGICIDAL SUPPORT POLYMERS
IN A NYLON 6 BLEND

A Dissertation Presented

By

Carl J. Sullivan

Submitted to the Graduate School of the
University of Massachusetts in partial
fulfillment of the requirements for the
degree of

DOCTOR OF PHILOSOPHY

February 1985

Polymer Science and Engineering

Carl J. Sullivan



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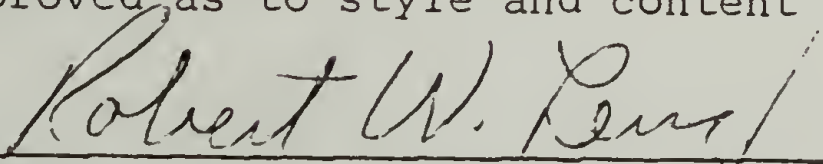
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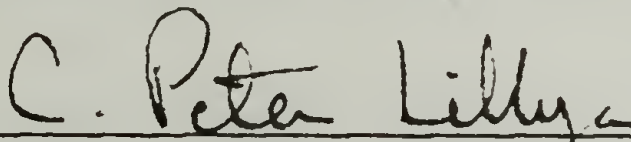
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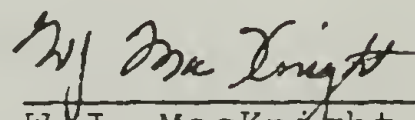
Carl J. Sullivan

Approved as to style and content by:


Robert W. Lenz, Chairman of Committee


William J. MacKnight, Member


C. Peter Lillya, Member


W.J. MacKnight, Head
Polymer Science and
Engineering

Dedicated to my wife, Joann.

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ABSTRACT

Modifications of Polyaspartimide and
Poly(ethylene-co-methacrylic acid);
Investigation of Potential Fungicidal
Host Polymers in a Nylon 6 Blend

(January 1985)

Carl J. Sullivan

B.S., Ursinus College

M.S., Ph.D., University of Massachusetts

Directed by: Dr. R.W. Lenz

The investigation of polyaspartimide derivatives and polyethylene-co-methacrylic acid derivatives as potential polymer supports for 2-(4-thiazolyl)benzimidazole in nylon 6 blends was conducted. Nucleophilic ring opening of the polyaspartimide repeat unit provided substituted polyamides with α and β repeat units which were found to be thermally unstable above 200 °C because of the presence of α -aminoacid amide structures. Hence, such a polyaspartimide derivative is unacceptable as a polymeric host for 2-(4-thiazolyl)benzimidazole in a nylon 6 blend. Blend properties of 90% nylon 6 and 10% polyethylene-co-methacrylic acid and derivatives were investigated. The specific derivatives investigated were the methyl ester, n-hexyl amide, ϵ -caprolactam imide, and the sodium salt of the methacrylic acid repeat unit in the copolymer.

Comparisons with previous results of the properties of blends of polyethylene-co-methacrylic acid with nylon 6 established that polyethylene-graft-nylon 6 copolymers formed as a result of amidation of the carboxylic acid derivatives, but only a fraction of these functional groups were amidated. Based upon the blend properties of these derivatives it is predicted that a polyethylene-co-methacrylic acid is an appropriate choice for a support polymer in nylon 6 blend. Chemical bonding of 2-(4-thiazolyl)benzimidazole to this copolymer was investigated. A direct amidation of polyethylene-co-methacrylic acid involving the acid chloride derivative was attempted but failed due to the steric bulk of the benzimidazole. Model acylations of 2-(4-thiazolyl)benzimidazole confirmed this conclusion. An N-carbamoyl adduct of 2-(4-thiazolyl)benzimidazole with toluene diisocyanate was found to be thermally and solvolytically unstable. 1-(2-hydroxyethyl)-2-(4-thiazolyl)benzimidazole was synthesized and subsequently reacted with polyethylene-co-methacryloyl chloride to obtain a polymerically bound derivative of this biocide. Biological activity of this derivative alone or in a nylon 6 blend have not been studied.

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C H A P T E R I

INTRODUCTION

Specialty Polymers - An Overview

The term "speciality polymers" has become a familiar phrase for any polymeric material synthesized or studied for a special or novel application. This is a very broad concept and from a historical perspective, it is by no means a new one. With the inception of polymer science and the wide application of polymers in the market place came continued growth from increasing research efforts and the development of polymer products with specialized applications. With time, these applications have become more and more specialized, and hence the terminology.

Work in this department exemplifies this continual trend. Johns¹ and Wojcik² studied the synthesis of malolactone esters and their polymerization for potential biomedical applications. Grosso⁴ synthesized vinyl substituted antioxidants, polymerized or copolymerized them, and studied the antioxidant capability of these products. Tirrell³ investigated the preparation of polymeric ultra-violet absorbers and biologically-active polymers. Waramkowski⁵ investigated the synthesis and doping of polyacetylene and its conductive properties.

In short, a great deal of the scientific research

being conducted in the field of polymer science stretches the boundaries of known applications to develop specialized materials. In researching novel materials and applications, basically three approaches are taken. One is the common method of incorporating low molecular weight additives in polymers. A second is the specific synthesis of a polymer or copolymer predetermined in its structure and use by the monomer, comonomer and polymerization technique. A third and rapidly growing approach is that of polymer blending.

In this thesis an approach combining the second and third above was examined. Specifically our intent is to study the potential of imparting a distinctive property in nylon 6 by functionalizing a second polymer material and subsequently blending this with nylon 6. The property in mind is an antibacterial and antifungal one, but our goal was not fully realized. Emphasis however has been given on the development of the approach and the complexity of the multitude of interacting parameters that are inherently present and could be utilized advantageously. A detailed description of this approach, its inherent complexity and the goals of this thesis can be more clearly described from the perspective of the three commonly used techniques mentioned above to develop specialized polymeric materials.

Polymer additives

This approach represents the simplest and oldest form of obtaining a specified performance in a polymeric material. The list of additives commonly used in compounding polymers is virtually endless. Typical examples of types of additives are plasticizers, lubricants, fillers, ultraviolet and oxidative stabilizers, flame retardants, and dyes. Of particular relevance here is the use of biocides in or on polymer materials.⁶ Most synthetic polymers and resins are inherently resistant to microbial attack, however bacteria and fungi may have a high affinity for additives in polymers, such as plasticizers and lubricants in PVC compositions.⁷ Also polymer materials can serve as a support for the microorganisms which can thrive on the dust, debris and any potential nutrient which may reside on the surface. This bacterial or fungal growth may or may not directly lead to the degradation of the material, however it poses a serious esthetic problem of unsightliness, cleanliness and odor formation. Bacterial or fungal growth is a common problem associated with coatings⁸ and many other materials such as carpet fibers,⁹ for which nylon 6 is used extensively. Biocides are, therefore, commonly added to the polymer.

Although polymer additives afford the simplest means of creating some desirable property such as biocidal

activity or oxidative stabilization, a common problem in their use is the gradual leaching of the additive with subsequent loss of the desirable properties. Any improvement in the decrease of their loss from leaching can, therefore, lengthen the lifetime of the use of the product and hence provide a value-added property to it. In the case of nylon 6, 2-(4-thiazolyl) benzimidazole has been added to impart antifungal properties, but during a steam or hot water extraction processing step, between 50 and 75% of the biocide is leached out.⁹ Again, any improvement would be of economic interest.

Specialized polymers and copolymers

In recent years a number of polymers and copolymers have been synthesized for the expressed purpose of studying the effect of bonding a specific functionality, which is normally used as an additive, to the polymer or copolymer backbone. Tirrell³ studied the chemical bonding of ultraviolet absorbers and antibacterial agents to a polymer backbone by synthesizing the vinyl substituted agents and copolymerizing them. Preliminary studies, however, showed no antibacterial activity. Grosso⁴ synthesized copolymers containing the antioxidant 2,6-bis-t-butylphenol bound to a vinyl polymer backbone at the 4-position, and he found reduced antioxidant properties compared to the use of this antioxidant as an additive.

Pittman and coworkers^{10,11} synthesized a series of vinyl substituted antibacterial and antifungal agents and copolymerized them with acrylate monomers and vinyl acetate. Films of these copolymers did show good antifungal properties, but the mechanism was not clearly understood. Whether the agent was biologically active while bound to the polymer backbone, or whether its bond was chemically or enzymatically cleaved, was neither understood nor thoroughly examined.

These are typical examples of the second approach of obtaining a specialized polymeric material by functionalizing the polymer backbone through copolymerization with a monomer functionalized with the desired agent. The expressed purpose of these research efforts was to ascertain whether a polymerically bound agent could have the same activity as the same agent used simply as an additive. By chemically binding the agent to a polymeric backbone, the problem of leaching can be eliminated, but as is evident from the work of Grosso⁴ and Tirrell³, chemically linking the agent to a polymer can compromise the chemical or biological activity. A well known approach to eliminating this uncertainty has been the synthesis of controlled release polymers.^{12,13} This technique is commonly associated with drug delivery systems, although there is no reason to restrict it to this area.

The above examples of polymerically bound agents are few, but illustrative. The list of specialized physical, mechanical, chemical or biological properties attainable by appropriate modification of the polymer itself is very long. However, in many cases, such as with high commodity polymeric materials, this general technique may not be desirable because of costly changes in plant facilities.

Polymer blending

Polymer blending is a rapidly expanding field of polymer science, and numerous articles and several books have been devoted to this subject.^{14,15,33} Such a blending of polymers has been utilized advantageously to obtain unique physical and mechanical properties unobtainable from the homopolymers alone. Polymer blending provides a simple, quick, and economic method of producing specialized materials, however, it is restricted to specialized physical and mechanical properties. To impart a specific chemical or biological activity an agent capable of providing such an activity must be added. An alternate method may be to chemically bond such an agent to a second polymer and subsequently blend this product with the polymer which requires the chemical or biological activity.

Functionalized Polymers in Blends

Technological advantages

Imparting specific chemical or biological activity to large volume commodity polymers commonly approached by compounding the polymer with specific additives; however, compounding the polymer with additives may suffer from the limitation of leaching of the additives. Chemically bonding the desired agent to the monomer or to a comonomer with subsequent polymerization may pose insurmountable economic obstacles. In addition, once bound, the specific chemical agent may no longer be effective. Furthermore, chemically binding the agent to the polymer after it is produced may not be possible because of the lack of a specific site in the polymer backbone for attachment. However, chemically binding the agent to a second polymer component, which can be subsequently blended with the commodity polymer product can, in principle, provide the desired value-added property.

Theoretical requirements

Binding a chemical or biological agent to a polymer backbone and subsequently blending this product with a commodity polymer is certainly more complicated than just stated. A variety of factors must be optimized, and these all necessarily interact. The chemical or biological agent bonded to the second component ideally should have the desired activity in the major component. Once bound to a polymer backbone, the polymeric agent should have an acti-

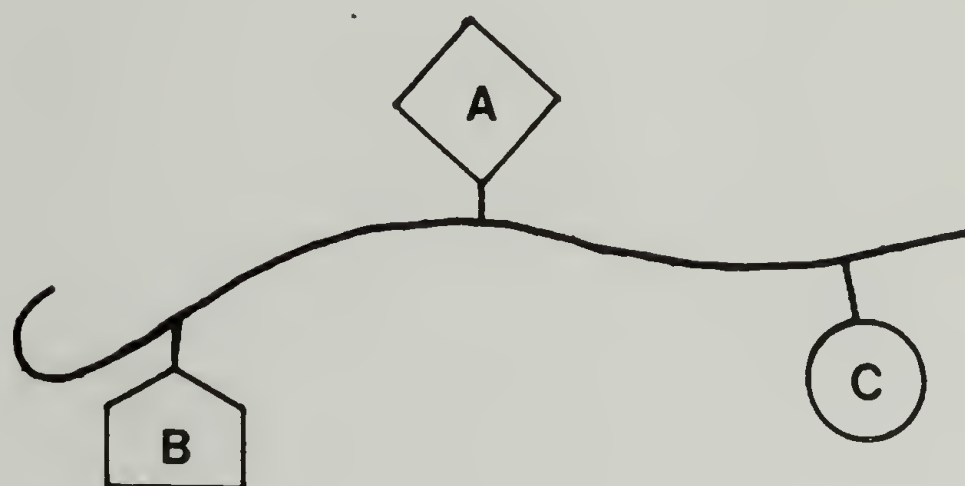
vity similar to that of the agent alone, or have some means of being chemically or enzymatically released. The thermal stabilities of both the agent and the second component should be suitable for blending with the major component. A relatively simple means of binding the agent to the second component is desirable. Finally, the overall physical and mechanical properties of the blend should not be adversely affected. That is, deleterious effects on the major component, such as loss of mechanical strength, should be minimized. On the other hand, any indication of a change in physical or mechanical properties which would be considered advantageous would be doubly rewarding.

A schematic means of simplifying these factors is provided by Ringsdorf's model for an ideal polymer-drug delivery system¹⁶, with some modifications. (Figure 1) As with the application of this model in drug delivery systems, a careful consideration of the exact structure of the polymer to which the agent will be attached can aid in the optimization of the final properties of the blended polymeric agent.

The first factor to be considered is the nature of the polymer backbone and the proportion to which the polymer will be added to the major component. The thermal properties must be such that the polymer is stable at the temperature at which it will be blended. Also, the polymer must have either a melting temperature or a glass transi-

FIGURE 1

Model For a Host Polymer in a Polyblend



A = Functional Agent

B = Compatibilizer

C = Anti-Compatibilizer or Other

tion temperature at or below the blending temperature to ensure a good mixing. Compatibility, by whatever measure used,¹⁵ can be variable with the only absolute requirement being that the polymeric agent, when blended with the major component, does not cause any serious loss of desirable properties. Some loss may be inevitable, but it should be minimized.

The second major factor is the means of binding the desired agent to a suitable polymer backbone. First there should be a chemical substituent on the backbone enabling such a binding to occur, and the stability of the resultant link should be known. Any thermal, hydrolytic or other chemical instability can be deleterious, but such sensitivity may also be utilized advantageously as a release mechanism. In addition, the agent itself must be stable at the temperature used for blending.

Finally, additional substituents may be utilized to vary the overall properties of the final blend. For example, a substituent which enhances compatibilization could be used to produce a more homogenous blend on the microscopic level. The concept of compatibilizers in polyblends has been discussed adequately in the past.^{15,17} Conversely, a substituent which decreases the interaction between the polymeric agent and the major component may be useful. In this case, the polymeric agent would likely be found in specific domains within the matrix of the major

component, which may have advantageous qualities in terms of the activity of the agent if a controlled release mechanism is utilized, and if these domains act as a reservoir for the slow diffusion of the agent into the matrix and out to the surface. Also, this morphology may give the blended product superior qualities, as is known for a number of systems, particularly rubber modified thermoplastics such as high impact polystyrene.

This description of the theoretical requirements and approach to a polymeric agent alloyed with another polymer is necessarily brief. The description is very general and hence it can have a wide range of applications. The blending of a polymeric agent to a commodity polymer is also extremely complex because of the interacting nature of substituents and polymers utilized, and, therefore, presents a considerable challenge to the polymer chemist. However, this outline embodies some of the basic requirements of such an approach to a specialized polymer.

Functionalized Polymers in Nylon 6 Blends

Introduction

Nylon 6 is extensively used in carpet fibers, and although it is resistant to fungal degradation and to most bacterial strains, such growth on its surface is common because of the presence of dust and debris. Presently, the

fungus and bacterial growth is adequately reduced by simply adding a biocide, 2-(4-thiazolyl) benzimidazole, to it; however, high proportions of the additive can be leached during processing.⁹ Therefore, using the additive approach to developing a specialty nylon 6 product, that is one with either an antifungal or antibacterial property, leaves room for improvement and creates a challenge for the polymer chemist.

The method of chemically bonding the biocide to a second polymer and subsequently blending the polymer biocide with nylon 6 appears to be the best approach. Given the myriad of interacting parameters just described, and thus, the multitude of avenues that such a research effort can pursue, a judicious stepwise approach is necessary. First an examination and selection of a polymer to which the biocide can be bound must be made. In addition, the method of bonding the biocide to the chosen polymer, in this case 2-(4-thiazolyl) benzimidazole, must be given careful consideration.

Choice of polymer

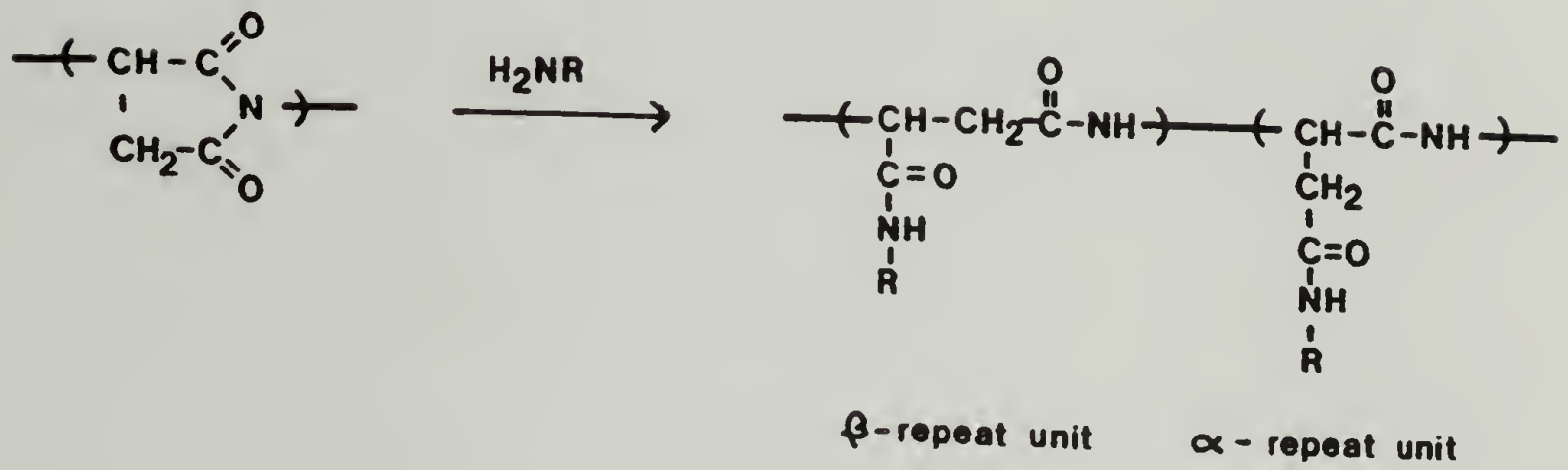
Two different polymers have been examined as possible hosts for the attachments of 2-(4-thiazolyl) benzimidazole. The first polymer studied was polyaspartimide, which can readily be substituted by a ring opening nucleophilic reaction on the cyclic repeat unit.¹⁸⁻²¹

(Figure 2) Such an addition reaction could yield a polyamide which may show a strong interaction with nylon 6, enabling a high compatibility and hence a more homogenous blending of the two polymers. In addition, a variable degree of addition is possible by using a less than molar equivalence of the nucleophile with the resulting product containing residual cyclic imide repeating units. This factor was utilized by Rypacek and coworkers²⁰ to study the pinocytosis of poly(2-hydroxyethyl aspartamide) by partially substituting the polymer backbone with a fluorescent marker prior to reacting the remaining cyclic imide units with 2-hydroxyethyl amine. Thus a variable degree of conversion to a polymeric biocide is available as an option, with an additional option of substituting the polymer backbone with alternate functionalities. Such an approach can, in principle, be utilized for optimizing the thermal properties of the resulting derivative and optimizing blending conditions with nylon 6.

Several key factors needed to be examined if polyaspartimide derivatives were to be used as the host polymer for the biocide, and subsequently, were to be blended with nylon 6. The synthesis of polyaspartimide from aspartic acid has been well documented,²²⁻²⁴ and polyaspartimide is known to be thermally stable.²⁴ In addition, the ring opening reaction of polyaspartimide with water as the nucleophile to form poly(aspartic acid)²⁵⁻²⁷ and with

FIGURE 2

Ring Opening Reaction of Polyaspartimide



amines to form polyaspartamides¹⁸⁻²¹ have been well documented. However, these reports were primarily concerned with the potential use of polyaspartimide derivatives in biomedical applications as a plasma expander or drug delivery system. As such, the solution properties of such derivatives have been carefully examined, but the thermal properties have not. These thermal properties need to be ascertained if the polyaspartimide derivatives are to be used as host polymers for the biocide in a nylon 6 blend.

In addition, as shown in Figure 2, although α and β polyaspartamide repeating units can be obtained by such a ring opening reaction of polyaspartimide, the proportions of these units have never been determined quantitatively. Only poly(aspartic acid) has been carefully examined by Picova and coworkers,^{28,29} and found to contain 50-80% of the β -repeating unit. The microstructure of the amine derivatives will effect the thermal properties of the polymer, and therefore, this variable needs to be examined.

A method of bonding 2-(4-thiazolyl) benzimidazole to the polyaspartamide backbone had to be developed for this study. Also, the effect of blending polyaspartimide with nylon 6 had to be examined.

The second polymer considered in this study as a potential host for the biocide was a copolymer of ethylene and methacrylic acid. Polyamide-polyolefin blends have been studied previously,¹⁷ and the blending properties of

nylon 6 and poly(ethylene-co-methacrylic acid) were examined in detail in this program.³⁰ In the preparation of polyethylene/nylon 6 blends,¹⁷ a two phase mixture was obtained because of the incompatibility of these two polymers. For low concentrations of polyethylene (5-12%), the domains formed by this component ranged from 0.5 to 5.0 microns in size. Because of this morphology and the apparent formation of grafted structures, which are believed to have formed during the mixing, and which can provide interfacial adhesion, impact strengths of the alloys were markedly higher than that of nylon 6 alone. MacKnight and coworkers³⁰ showed that when poly(-ethylene-co-methacrylic acid) copolymers were blended with nylon 6, a similar phase separation was observed, but the size of the polyolefin domain was highly dependent upon the methacrylic acid content of the copolymer used. At high acid contents in the copolymer (5.1-5.4 mole %), domains of the polyolefin were less than 0.5 microns and tensile properties of the blend were approximately the same as those of nylon 6 alone. This morphology and mechanical property analysis were explained in terms of polyolefin-graft-nylon 6 formation, by a condensation reaction of free amines and methacrylic acid groups, which can act as a compatibilizer.

Hence, poly(ethylene-co-methacrylic acid) has the prerequisite thermal stability necessary for blending with

nylon 6, and some basic properties of the blend, including morphology and tensile strength, have been established. Earnest³¹ reported the synthesis of poly(ethylene-co-methacrylyl chloride) from poly(ethylene-co-methacrylic acid) by a reaction with oxalyl chloride, and a subsequent reaction with methanol provided the methyl ester derivative. This synthetic procedure establishes a convenient method for converting the poly(ethylene-co-methacrylic acid) to a highly reactive acid chloride derivative. This reactive acid chloride derivative can be utilized in a synthetic procedure to chemically bond the biocide to the copolymer.

The effect of substituting the methacrylic acid repeat unit with the biocide on the blending properties of this polymer with nylon 6 was not known. Such a substitution may affect the compatibilizing effects that the methacrylic acid unit provides. This increased compatibilization is believed to result from the formation of grafted polyolefin structures by a condensation reaction in the melt. If the biocide or a derivative of it is bound to the methacryloyl repeat unit in the form of an ester or amide bond, then blending this polymer with nylon 6 could result in the same type of graft formation by reaction of the free amine with the ester or amide and release of the biocide. In addition, the molar ratio of methacrylic acid repeat units that are converted to grafted nylon 6 struc-

tures is not known, and therefore, the amount of amidation of a methacryloyl ester or the transamidation of a methacryloyl amide would have to be determined. Hence, the ratio of a biocide bound to a poly(ethylene-co-methacrylic acid) derivative after blending cannot be predicted.

This complicated scenario is best examined by first determining what effect esterification, amidation, or neutralization of the methacrylic acid repeat unit in poly(ethylene-co-methacrylic acid) has on the blend properties. Nylon 6 is known to be soluble in acidic solvents only³² because of the strong interaction of the acidic protons and amide functions. By converting the methacrylic acid unit to a non-acidic derivative, this strong interaction with the nylon 6 will be eliminated. An assessment of the properties of such blends would, therefore, be more appropriate for predicting the properties of a poly(ethylene-co-methacrylic acid) derivatized with the biocide.

Choice of 2-(4-thiazolyl)benzimidazole

The concept of bonding specific chemically or biologically active compounds to polymeric structures has attracted considerable interest as a means of controlling the agents activity in the sense of the application lifetime and leaching problem. However, the concept of using such a polymerically bound agent in a blend is new. The interest in investigating such a polymerically bound 2-(4-thiazolyl)

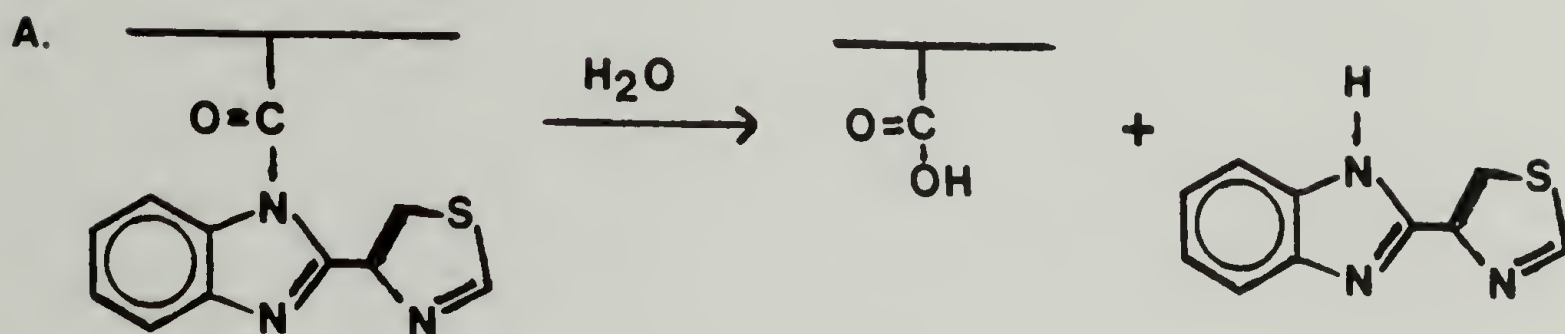
benzimidazole blended with nylon 6 resulted from the problem of the leaching of this agent from nylon 6 as described above.

The manner to which 2-(4-thiazolyl)benzimidazole is bound to a polymer backbone can conceivably alter this biocide's activity. For example, Tirrell³ reported a lack of antibacterial activity for polymeric salicyclic acid derivatives. Therefore, careful consideration must be given to the mode of bonding of 2-(4-thiazolyl)benzimidazole to the polymer.

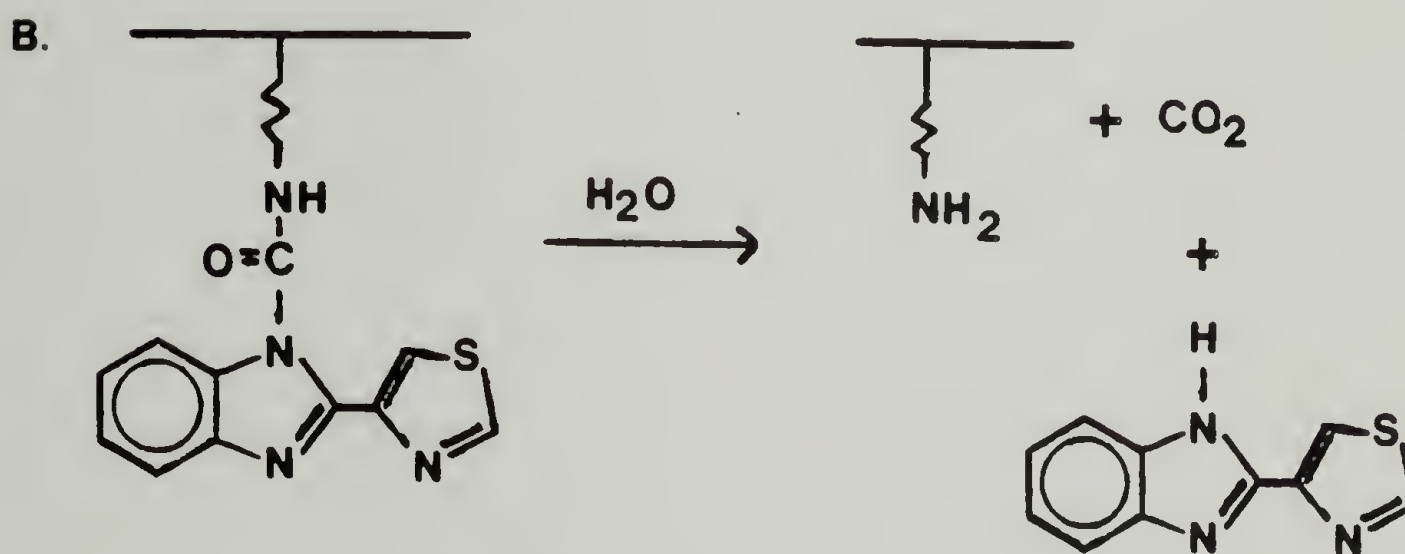
Necessarily, any mechanism for the release of the biocide from the polymeric backbone would be desirable. Such a release of the biocide can be realized by bonding 2-(4-thiazolyl)benzimidazole to the polymer in the form of 1-acyl-benzimidazole derivative or a 1-carbamoyl-benzimidazole derivative, both of which can undergo hydrolysis with release of 2-(4-thiazolyl)benzimidazole as shown in Figure 3. Acyl imidazoles, such as carbodiimidazole, are known to hydrolyze rapidly in water, and acyl benzimidazoles undergo a similar hydrolysis at a slower rate. For example, the half life of N-acetyl imidazole in water at 25°C is 41 minutes, while the half life of 1-acetyl benzimidazole is 760 minutes.³⁴ Similarly, Hegerty and coworkers reported an extremely rapid hydrolysis of 1-carbamoylimidazole which had a half life of about 10^{-4} seconds, and 1-carbamoyl

FIGURE 3

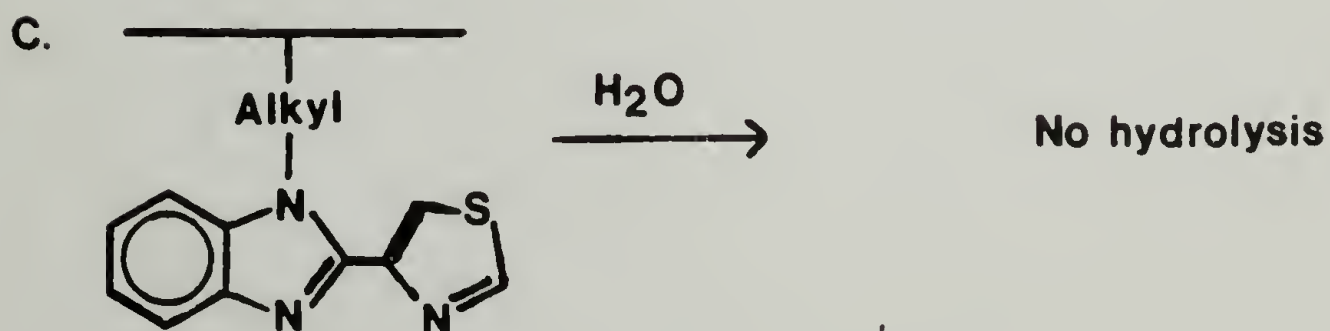
Models of Polymer Derivatives of 2(4Th)B
and Expected Hydrolysis Behavior



Moderate rate



Rapid rate



benzimidazoles.³⁵ Similar hydrolysis behavior would, thus, be expected to occur for 1-acyl-2(4-thiazolyl)benzimidazole derivatives and 1-carbamoyl-2(4-thiazolyl)benzimidazole.

A release mechanism may not be necessary and could be detrimental. That is the blending process itself could lead to a total release because of the high temperature used. Thus a hydrolytically and thermally stable bonding of 2-(4-thiazolyl)benzimidazole was considered. Alkylation at the 1-position could provide such stability, as shown in Figure 3c.

It is interesting to note in this regard that in a literature review of 2-(4-thiazolyl)benzimidazole applications and reactions, several patents have been reported for 1-acyl derivatives of this biocide, which showed antifungal or anthelmintic activity similar to that of 2-(4-thiazolyl)benzimidazole.³⁶⁻³⁸ Similarly, a number of 1-carbamoyl derivatives of the antifungal agent 2-(methylcarbamate)benzimidazole showed similar biological activity as the 2-carbamate benzimidazole.³⁹⁻⁴¹ Considering the hydrolytic instability of such derivatives, it is likely that these derivatives of the biocides hydrolyzed back to the original biocide, and hence were biologically active.

Very few reports of the preparation of 1-alkyl-2(4-thiazolyl)benzimidazole derivatives have appeared in the literature,^{42,43} and the fungicidal activity of these derivatives have not been thoroughly studied. Hence the

activity of a polymeric 1-alkyl derivative of this type, as shown in Figure 3c, cannot be predicted.

Thus, the three approaches depicted in Figure 3 were examined as potential methods of bonding 2-(4-thiazolyl) benzimidazole to a polymeric backbone. What would happen to such polymeric derivatives when blended with nylon 6 was difficult to predict. Possible routes to obtain derivatives of this type were examined.

Present Investigation Objectives in Summary

To evaluate the concept of bonding 2-(4-thiazolyl) benzimidazole to a polymer and subsequently blending this functionalized polymer with nylon 6 to impart antifungal properties in the latter, a number of factors must be considered, so a stepwise approach was taken.

First, the potential use of polyaspartimide derivatives as depicted in Figure 2 was examined. The relative reactivity of the cyclic imide unit with a number of amines needed to be determined along with the possibility of a similar ring opening reaction with 2-(4-thiazolyl)benzimidazole. The physical properties of these polyamide derivatives needed to be examined, in particular their thermal properties, to ascertain the success of blending with nylon 6. (Chapter II)

Poly(ethylene-co-methacrylic acid) blends with nylon 6 have previously been studied, but substituent

effects on the former have not. Thus, the effect of derivatizing the methacrylic acid unit needed to be examined. (Chapter III)

Potential methods of chemically bonding 2-(4-thiazolyl)benzimidazole to each of these polymer backbones were also examined utilizing the approaches depicted in Figure 3. (Chapter IV)

C H A P T E R I I

POLYASPARTIMIDE AND DERIVATIVES

Synthesis and Properties of Polyaspartimide

PAIm was synthesized from D,L-aspartic acid by the thermal polycondensation technique of Neri and coworkers¹⁸ with typical yields of 80-90%. (Figure 4) The cyclic succinimide repeat unit structure was clearly identified by infrared spectroscopy with carbonyl absorptions at 1800 and 1720 cm^{-1} . ^1H -NMR showed broad absorption peaks at 5.25 ppm (CH) and 3.17 ppm (CH_2). The ^{13}C -NMR spectra showed peaks for the carbonyl carbons at 173.25 and 172.00 with additional absorptions at 47.17 ppm (CH) and 32.73 ppm (CH_2). This structure was additionally verified by elemental analysis.

Vlasak and coworkers²⁴ developed the following Mark-Houwink equation for this polymer dissolved in 0.1M LiCl in dimethyl formamide:

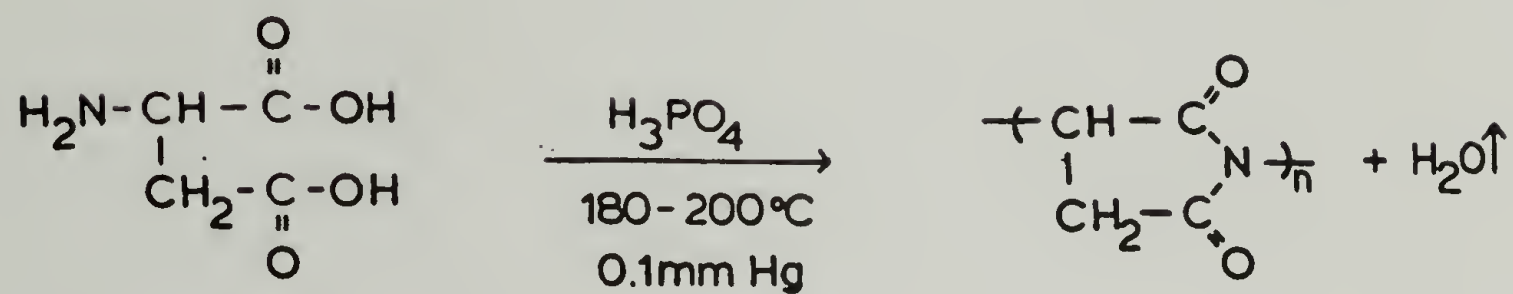
$$[\eta] = 1.32 \times 10^{-4} M^{0.76}$$

An intrinsic viscosity of 0.49 g/dl was obtained for polyaspartimide synthesized in the present work, which correlates to a viscosity average molecular weight of 51,000 a m u.

DSC analysis of PAIm showed no transition below 300°C except a broad endotherm at about 110°C which was

FIGURE 4

Polymerization of Aspartic Acid to Polyaspartimide



attributed to absorbed water volatilization. Re-scanning several times resulted in a gradual decrease in this endotherm until the fourth scan in which case it completely disappeared. The lack of a transition is surely due to the rigidity of the chain. The lack of an apparent melting transition suggested a completely amorphous structure and this was verified by X-ray diffraction analysis. This lack of crystallinity can be attributed to the repeat units being of a racemic modification.

Thermogravimetric analysis (TGA) also indicated the presence of absorbed water because 2-3% weight loss was observed when a 1 gram to 15 gram sample was held at 125°C for at least 20 minutes. TGA also showed that PAIm is thermally stable above 300°C, with an onset of degradation at 407°C (first 5% weight loss excluding water loss). A rapid volatilization ensued with the maximum rate occurring at 448°C. (Appendix D, thermograph #1, heat rate = 20°C/minute.)

Blend of Polyaspartimide with Nylon 6

A 10% PAIm/90% nylon 6 (N6) mixture was added to a Brabender mixing apparatus and melt-mixed for 20 minutes at 250°C with rolling pins spinning at 30 rpm. The resultant blend was clearly inhomogenous with the PAIm particles visible to the eye. This was to be expected given the

thermal properties of PAIm. Because of the lack of a glass transition temperature below 300°C it would remain an amorphous solid unless it could be solubilized in the N6 melt. Solubilization obviously did not occur.

One additional factor that was totally unexpected was an apparent degradation in the blend. The N6 matrix was considerably blackened, however the PAIm particles on or near the surface were white to yellow. Solution viscosity analysis of the blend was conducted and it was found that the average DP of the N6 was reduced. A portion of the blend was dissolved in formic acid and the PAIm was filtered off to obtain a final concentration of 0.45 g/dl. The inherent viscosity at 25.0°C was found to be 1.40 dl/g, while for a 0.45 g/dl solution of N6 which was similarly treated, an inherent viscosity of 1.79 dl/g was obtained. This observed degradation was not understood until a thorough study of the thermal properties of PAIm derivatives was conducted and the observed degradation would be better explained after these results are described.

Synthesis and Properties of Ethanolamine

Derivatives of PAIm

Copolymer syntheses

Because of the cyclic imide repeat unit and the resultant rigidity in the PAIm chain, no glass transition temperature was observed below its degradation temperature.

Ring opening by nucleophilic attack would therefore be expected to decrease this inherent rigidity and lower the energy barrier to rotations and chain mobility. Thus the glass transition temperature would be expected to decrease. In light of the interest in bonding a biocide to a poly-aspartimide derivative by such a nucleophilic addition and subsequently blending this product with N6, this anticipated lowering of the glass transition temperature needs to be examined. With a transition temperature below the melting point of N6, a more homogenous blend with it can be obtained. Therefore, a correlation between the degree of conversion of cyclic imide to amide repeat units and glass transition temperature needs to be ascertained. Such a structure-property correlation requires the synthesis of a series of copolymers with varying cyclic imide to amide repeat units.

The ring opening addition reactions of the PAIm repeat unit by amines^{18-21,44,45} and by hydroxide ion^{26,28,29,46} have been described previously. Because the primary interest in most of these research efforts was to examine its use in the biomedical application field as a plasma expander or drug delivery system, thermal properties were not examined. The most widely studied derivative is that of PAIm with ethanolamine. Neri and coworkers¹⁸ examined what effects time, temperature, and molar ratio of

ethanolamine to PAIm had on the conversion and molecular weight of the PAIm derivative. From their work it is clear that varying degrees of conversion can be obtained by simply adjusting the concentration of amine and/or the time of reaction.

Hence, PAIm was reacted with ethanolamine according to the procedure of Neri and coworkers and is depicted in Figure 5. The stoichiometry for these reactions are compiled in Table I. The exact structure of the resultant polymer is expected to be a combination of unreacted cyclic imide and the α and β amide repeat units. In addition all imide and amide asymmetric centers will have equal proportions of the D and L stereoisomer. The ratios of amine to polymer repeat unit utilized in the syntheses are indicated in the table below the synthetic equation. The composition of the resultant copolymer products are determined by infrared spectroscopy, elemental analysis and nuclear magnetic resonance. These analyses and results are described in the following section. The effect this polymer modification has on the physical properties in relation to its copolymer structure are described in the second section to follow.

Copolymer composition

Infrared Characterization. As depicted in Figure 5, the synthesis of PAIm-co-(2-hydroxyethyl aspartamide) by

FIGURE 5

Reaction of Polyaspartimide with Ethanolamine

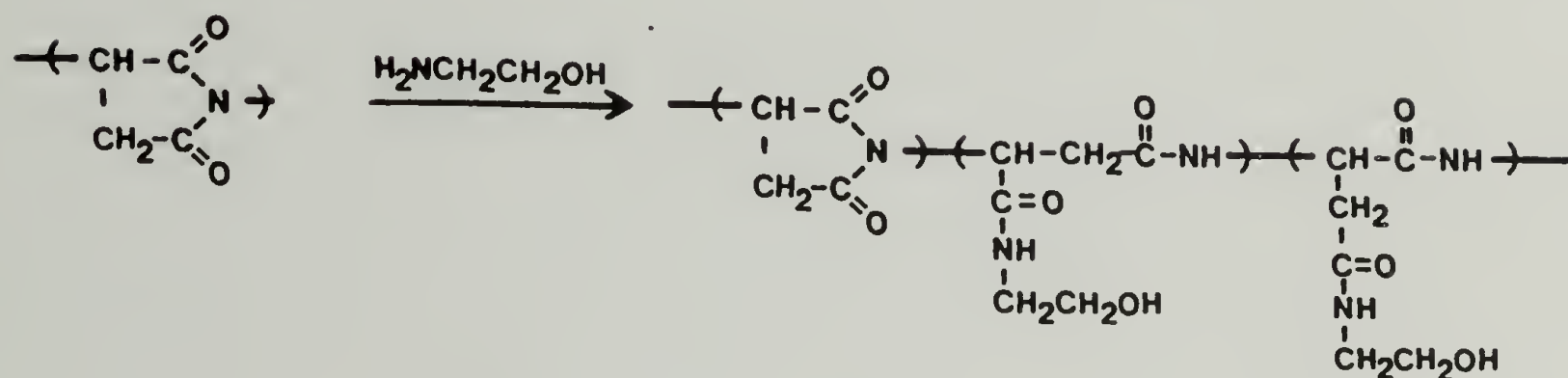


TABLE 1

Stoichiometry of Reaction of Polyaspartimide
with Ethanolamine^{a)}

Sample	[PAIm] (moles/l) ^{b)}	[EA] (moles/l)
1-10A	1.3	2.8
1-10B	1.6	1.8
1-10C	1.6	1.4
1-10D	1.6	0.90
1-10E	1.6	0.52

a) room temperature, two hours in DMF

b) concentration of repeating unit

nucleophilic addition to the cyclic imide repeat unit leads to the formation of amide bonds which will have specific infrared absorptions different from those of the cyclic imide. The infrared spectra for the five copolymers synthesized (KBr pellet), 10A through 10E, are presented in Appendix A, numbers 2 through 6 respectively. A qualitative assessment of these spectra indicates a continuum of copolymer composition by the relative decreases in imide absorptions at 1800 cm^{-1} and 1720 cm^{-1} ; simultaneously, an increase in amide absorptions at $3300\text{--}3400\text{ cm}^{-1}$ (amide I), 1650 cm^{-1} (C=O) and 1530 cm^{-1} (amide II) is observed as the conversion to amide repeat units is increased in the order of 10E to 10A.

A quantitative evaluation of the copolymer composition could thus be performed by accurately measuring the concentration of cyclic imide or amide repeat units in a solution of the copolymer by first calculating the molar absorptivity of either the imide absorption or amide absorptions. Because PAIm has imide repeat units only, the molar absorptivity of the carbonyl absorption at 1800 cm^{-1} or 1720 cm^{-1} are more conveniently calculated. Because the absorption at 1720 cm^{-1} overlaps that of the amide carbonyl at 1640 cm^{-1} , quantitative evaluation of imide concentration in a solution of the copolymer would be subject to potentially large errors if this frequency is used. Hence, the

absorption at 1800cm^{-1} was utilized. Although it overlaps slightly with the peak at 1720cm^{-1} , its absorption is distant enough from the amide carbonyl absorption for the absorbance to be independent of the amide repeat unit concentration.

To determine the molar absorptivity of the infrared absorption of the cyclic imide carbonyls at 1800cm^{-1} , PAIm solutions in dimethyl formamide were made with concentrations of 0.916×10^{-4} moles/l, 2.08×10^{-4} moles/l and 4.05×10^{-4} moles/l. The absorbances at 1800cm^{-1} for these solutions were 6.0, 13 and 27 respectively. The molar absorptivity was calculated from Beer's Law:

$$A = \epsilon cl = \epsilon' c$$

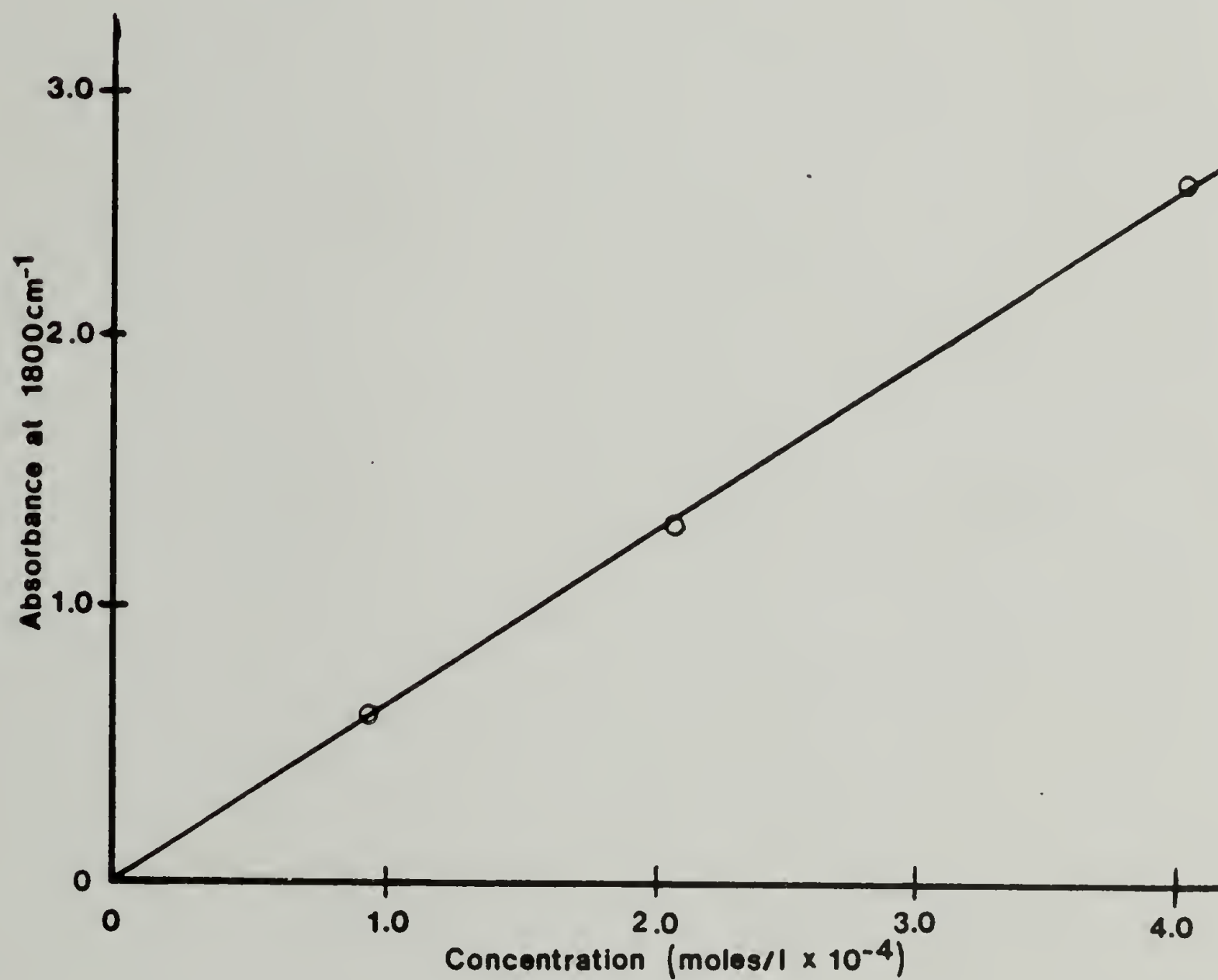
Because the path length (l) of the infrared solution cell does not change, this unknown value was included in the calculated molar absorptivity (ϵ') for convenience. The ϵ' for the three PA solutions were found to be 6.6×10^4 l/mole, 6.3×10^4 l/mole and 6.7×10^4 l/mole respectively.

A plot of the absorbances versus concentration was made to verify that Beer's Law is valid for this system. This plot is reproduced in Figure 6 and Beer's Law appears to be valid over this range.

The value for the molar absorptivity utilized in determining the copolymer composition was an average of the three values obtained - $6.5 \times 10^4 \pm 0.2 \times 10^4$ l/mole. A

FIGURE 6

Beer's Law Plot of Absorbance of Polyaspartimide
Repeating Unit Carbonyl at 1800 cm^{-1} Versus Concentration



more precise value could be obtained from the Beer's Law plot, but this precision would not be realistic for this technique due to the inherent low sensitivity and potential error in measuring the absorbance, particularly at low concentration.⁴⁷ However, from the validation of Beer's Law the average of the three molar absorptivities with an absolute error of 0.2×10^4 l/mole sufficiently incorporates instrumental and experimental errors while maintaining an adequate level of precision for determining the copolymer composition.

The partial infrared spectra for polyaspartimide and copolymers 10A through 10E in dimethyl formamide solutions are reproduced in Figure 7. The molar concentration of cyclic imide repeat units (C_I) in the copolymers solutions can be obtained directly from Beer's Law:

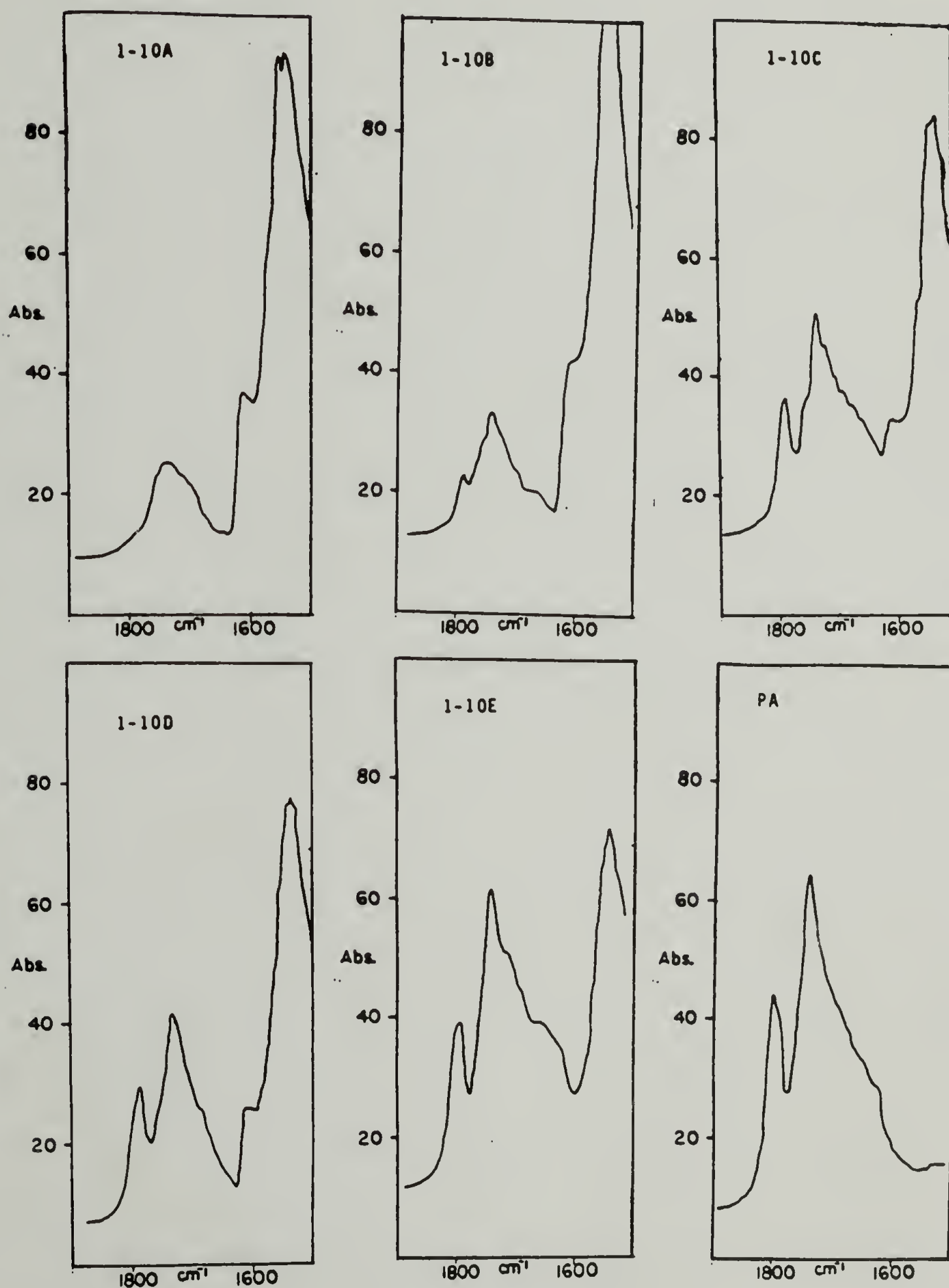
$$C_I = A/\epsilon'$$

Converting this to a mass concentration by multiplying by the molecular weight of the imide repeat unit, 97g/mole, and subtracting this from the mass concentration of the copolymer solution provides the mass concentration of the amide repeat units. Multiplying by the reciprocal of the molecular weight of the 2-hydroxyethyl aspartamide repeat unit, 158g/mole, provides the molar concentration of these amide repeat units in solution. (C_A) Thus:

$$C_A = [\text{Copolymer Conc. (g/l)} - (C_I \times 97\text{g/mole})] \times \text{mole}/158\text{g}$$

FIGURE 7

Partial IR Spectra of Products of Polyaspartimide
with Ethanolamine



The molar ratios of cyclic imide and amide repeat units is then:

$$R_I = C_I / (C_A + C_I) \quad R_A = C_A / (C_A + C_I)$$

The values of copolymer concentration, C_I , C_A , and R_A are listed in Table 2. It is clear that a range of copolymer composition was obtained as desired.

NMR characterization. Whereas the infrared analyses and elemental analyses provide quantitative information regarding gross structural composition of the copolymers, nuclear magnetic resonance can provide information about the microstructure of the copolymers. NMR analyses have been proven to be effective in elucidating polymer microstructures⁴⁸ and reviews on its usage in peptide and poly (amino acid) characterization have appeared.^{49,50} In particular, NMR spectroscopy has been used extensively to analyze helical conformations of poly(α -amino acid)s.⁵¹ No attempt will be made here to duplicate these reviews, however several cogent facts require description.

First, polymer conformation is known to effect the exact chemical shifts of poly(α -amino acid) protons but it is secondary to the electronegativity and magnetic anisotropy consideration. Thus, chemical shifts for the individual protons will fall within an expected theoretical range for similar protons: i.e. aspartyl methine protons will be in the 4.0-5.0 ppm range based on comparison with

TABLE 2

Copolymer Composition of PAIm Derivatives
from Reaction with Ethanolamine by Infrared Analysis

<u>Sample</u>	<u>Copolymer Conc. (g/ml)</u>	<u>C_I (moles/ml)</u>	<u>C_A (moles/ml)</u>	<u>R_A (% conv.)</u>
10A	4.20×10^{-2}	7.73×10^{-6}	2.61×10^{-4}	97
10B	4.97×10^{-2}	7.73×10^{-5}	2.67×10^{-4}	78
10C	2.00×10^{-2}	7.73×10^{-5}	7.89×10^{-5}	51
10D	5.09×10^{-2}	2.47×10^{-4}	1.70×10^{-4}	41
10E	5.14×10^{-2}	3.24×10^{-4}	1.26×10^{-4}	28

poly(L-aspartic acid) and ester derivatives.

Secondly, most of the work in this area has been conducted using configurationally pure polymers and as a result of the structural regularity, helical conformations can be attained in the appropriate solvent. Poly(L-aspartates) in chloroform have been shown to form either left hand α helical conformations or right hand α helical conformations depending upon the ester group, while addition of trifluoroacetic acid induced a helix to random coil transformation. All three conformations showed slightly different CH and NH proton chemical shifts and were clearly identified by Bradbury and coworkers.⁵² The converse of this generally observed phenomena would be that a racemic modification of polymer repeat units would not attain a helical or otherwise ordered macrostructural conformation and this is often assumed. In the case of poly (β - benzyl-D,L-aspartates), Paolillo and coworkers⁵³ verified that this assumption is valid. Therefore, it is believed that PAIm and copolymers of PAIm and poly(2-hydroxyethyl aspartamide) (PHEA) will not attain such macrostructural conformations.

Although it is believed that PHEA and PAIm/PHEA copolymers will have α and β peptide bonds, and that this in itself would inhibit ordered conformation, using this argument to determine- α and β ratios would be circuitous-

ly faulted. Additionally, it might be assumed that a PAIm/PHEA copolymer also would be lacking an ordered conformation in solution due to different repeat units in the polymer chain, but again this assumption is faulted by intuitively assuming a random copolymer and the lack of extended blocks of either PAIm or PHEA. Based upon Paolillo's work these two assumptions need not be made. In addition, because helical conformations of poly(α amino acid) derivatives is highly dependent upon solvent, with polar hydrogen bonding solvents (donor or acceptor) normally inducing a helix-coil transformation, the use of DMSO-d₆ as the solvent for these copolymers is expected to further inhibit such ordering. Specifically, Bradbury showed that poly(β -benzyl-L-aspartate) was a random coil in DMSO-d₆.⁵⁴

With the concept that there is a total lack of ordered structures in PAIm/PHEA copolymers and homopolymers established, long range field effects of distant repeat units on each other can be ignored. From Bradbury's⁵² analysis of poly(α -aspartates) CH and NH protons absorptions are clearly dependent upon polymer conformations. Such a dependency is expected to hold for PAIm/PHEA copolymers, however it will be the immediate conformations of the aspartyl repeat unit or adjacent repeat unit which will effect the magnetic field seen by these protons. It is these protons that have been utilized in determining the

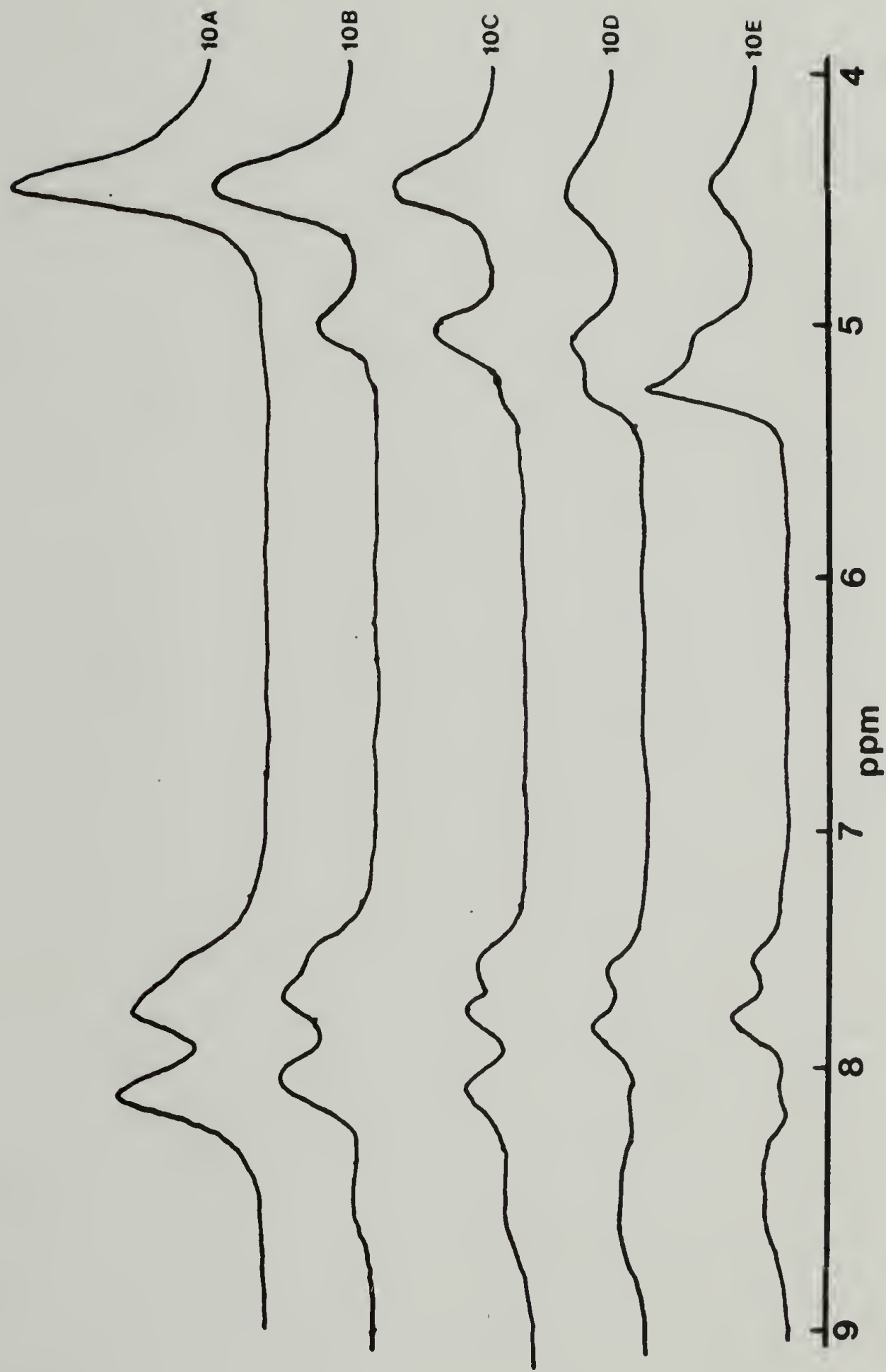
percent conversion, as a comparison to the IR technique, and the α and β ratios.

Of the derivatives of PAIm reported in the literature only poly(α, β -D,L-aspartic acid) has been studied by NMR and the ratios of α and β repeat units were estimated.²⁷⁻²⁹ Depending upon the exact hydrolysis procedure, ratios of β peptide links were in the range of 0.55 to 0.8. These workers utilized changes in pD of the D₂O solution of the poly(aspartic acid) to enhance a chemical shift differences in the α and β peptide CH₂ absorptions in ¹H-NMR and ¹³C-NMR. However, this technique is not applicable for the poly(aspartamides) studied here.

NMR characterization - percent conversion. The percent conversion of cyclic imide to amide repeat units is straightforward. The partial ¹H-NMR spectra for PAIm and the 5 products of the reaction of PA with ethanolamine (10A through 10E) are reproduced in Figure 8. The absorption from 4.9 ppm to 5.5 ppm is clearly due to the methine proton of cyclic imide repeat unit. The absorption at 4.48 ppm is by comparison with poly(α aspartic acid)²⁸ and poly(β -benzyl aspartate)⁵² assigned to the methine proton of the aspartamide and to the hydroxyl proton of the ethanol amide residue. Additionally, the two amide protons absorb downfield in the 7.4 ppm to 8.8 ppm range. Thus, the percent cyclic imide repeat units is calculated from the

FIGURE 8

Partial ^1H -NMR Spectra of Products of Polyaspartimide and Ethanolamine



relative peak heights of these absorptions. The areas, percent imide and thus percent conversion to amide are presented in Table 3. Comparison with Table 2 shows a very good agreement between the infrared and NMR techniques of determining percent conversion.

Additional peaks not shown in Figure 8 are the aspartimide CH_2 (3.17 ppm), aspartamide CH_2 (2.4 - 2.7 ppm) and ethanol amine residue of $\text{NHCH}_2\text{CH}_2\text{OH}$ (3.45 ppm, 3.10 ppm respectively). The areas of these absorbances are consistent with the percent conversion given in Table 3.

NMR characterization - copolymer microstructure.

An examination of the imide CH absorption in PA and the copolymers indicates that there are two overlapping absorptions in the copolymers of intermediate conversion. These occur at 5.25 ppm and 5.05 ppm and it can be seen from Figure 8 that as conversion increases, the former diminishes while the latter increases. The peak at 5.25 ppm corresponds exactly with the chemical shift of the PAIm methine proton. Because long range effects are ignored due to an absence of macrostructural conformations, the only conceivable means for a cyclic imide in the copolymer to maintain the exact same methine chemical shift as PAIm is for the adjacent units to be identical to those in PAIm: cyclic imide repeat units. That is, the absorption at 5.25 corresponds to a triad of cyclic imide units.

TABLE 3

Copolymer Composition of PAIm Derivatives
from Reaction with Ethanolamine by ^1H -NMR Analysis

Sample	Rel.Area ^{a)} of <u>NH</u>	Rel.Area of ^{b)} <u>Imide CH</u>	Rel.Area of ^{c)} <u>Amide CH & OH</u>	% Conv.
10A	22 \pm 1	0	23 \pm 1	100
10B	20 \pm 1	3 \pm 1	21 \pm 1	78 \pm 7
10C	13 \pm 1	6 \pm 1	13 \pm 1	56 \pm 8
10D	8 \pm 1	7 \pm 1	8 \pm 1	37 \pm 9
10E	7 \pm 1	12 \pm 1	8 \pm 1	25 \pm 8

a) Absorption from 7.4-8.8ppm

b) Absorption from 4.9-5.5ppm

c) Absorption from 4.3-4.6ppm

The peak at 5.05 is therefore a result of the conversion of one or both of these adjacent cyclic imide structures to an amide by ring opening. All that is needed is for one or the other to be ring opened and considerable rotational freedom is provided thus reducing the rigidity of the chain. By doing so the imide methine protons will on the average see a slightly different magnetic field as a result of the different rotational conformations.

Quantitative evaluation of the ratio of cyclic imide triads to all triads containing an imide repeat unit is therefore attainable from the relative areas. For copolymers 10A through 10E the relative areas beneath the 5.25 ppm and 5.05 ppm are listed in Table 4. Percent triad is obtained by dividing the area below the triad peak at 5.25 ppm by the total area of the methine proton absorptions. These values also are listed in Table 4.

Also listed in Table 4 are theoretical values for the percent trimer in the copolymers based upon the percent imide content calculated from ^1H -NMR data and the assumption that they are randomly placed in the copolymer. The agreement is very good indicating that the assumption of random placement is accurate. For this to be true, nucleophilic addition by ethanolamine upon the polyaspartimide must be random and free of any enhancement or inhibition by nearby repeat units, whether they are amides or imides.

TABLE 4

Determination of Percent Cyclic Imide Triad

Sequence of Product of the Reaction of

Ethanolamine with PAIm: ^1H -NMR Analysis of Triads

<u>Sample</u>	<u>Relative Area</u>		<u>Exp.% Cyclic Imide Triad</u>	<u>Theor. %^{b)} Cyclic Imide Triad</u>
	<u>5.25ppm</u>	<u>5.05ppm</u>		
10A	-	23 \pm 1	0	0
10B ^{a)}	2 \pm 1	40 \pm 2	5 \pm 3	5
10C ^{a)}	4 \pm 1	20 \pm 2	17 \pm 4	19
10D ^{a)}	9 \pm 1	16 \pm 1	43 \pm 6	40
10E	11 \pm 1	11 \pm 1	50 \pm 6	56

a) taken from vertically expanded scale

b) calculated from % conversion of Table 3

NMR characterization - α , β ratios. As stated earlier, PAIm and its ethanolamine derivatives are believed to be totally lacking any preferred conformations; that is, it is a random coil in solution due to its racemic modification of aspartyl residues. Because DMSO is known to disrupt helical conformation of poly(β -benzyl-L-aspartate), using DMSO-d₆ as the NMR solvent strengthens this assumption. Additionally, due to conversion to 2-hydroxy aspartamide repeat units and their random placement relative to imide repeat units, further irregularity is placed in the polymer chain inhibiting any ordered conformation of the copolymers in solution. Thus, the polymer or copolymer is assured of remaining in a random coil state in solution and long range interactions between distant repeat units (> 2) and between polymer chains can safely be assumed to average out. With this established, a determination of α and β aspartyl repeat units can be determined from the amide NH absorptions.

By comparison with poly(β -benzyl-L-aspartate) and other poly(L-aspartates) the absorptions at 7.95 ppm to 8.80 ppm shown in Figure 8 can be assigned to the main chain aspartyl NH protons. At low conversion to 2-hydroxyethyl aspartamide, these absorptions are broadened to higher chemical shifts due to adjacent cyclic imide repeat units. As conversion increases, the peak narrows and moves

upfield due to increasing mobility, with the absorption of the PHEA (100% conversion) at 8.10 ppm. This coincides exactly with the NH absorption of poly(β -benzyl-L-aspartate) in the random coil state. Because of this dependency of the main chain aspartyl NH absorption on the nature of adjacent repeat units, α/β ratios cannot be reliably determined from it. The side chain 2-hydroxyethyl aspartamide NH absorption, however, can be utilized. The peaks at 7.52 ppm and 7.76 ppm for the low conversion copolymers have been assigned to this NH absorption. As conversion increases, each increases until they overlap but it does not appear that their individual chemical shifts change. This consistency and the lack of band broadening are direct result of its increased rotational mobility independent of the type of repeat unit - imide or amide - adjacent to that particular aspartamide unit. That is, regardless of the exact nature of the adjacent repeat units, this 2-hydroxyethyl aspartamide NH proton sees a specific environment which dictates its chemical shifts. In the absence of ordered structures and the presence of direct dependency upon adjacent repeat units, the unequal splitting of this NH absorption must be related to the α/β ratios.

By a first approximation, it may be assumed that a β -2-hydroxyethyl aspartamide (α -repeat unit) will show a lower chemical shift and therefore the absorption at 7.52

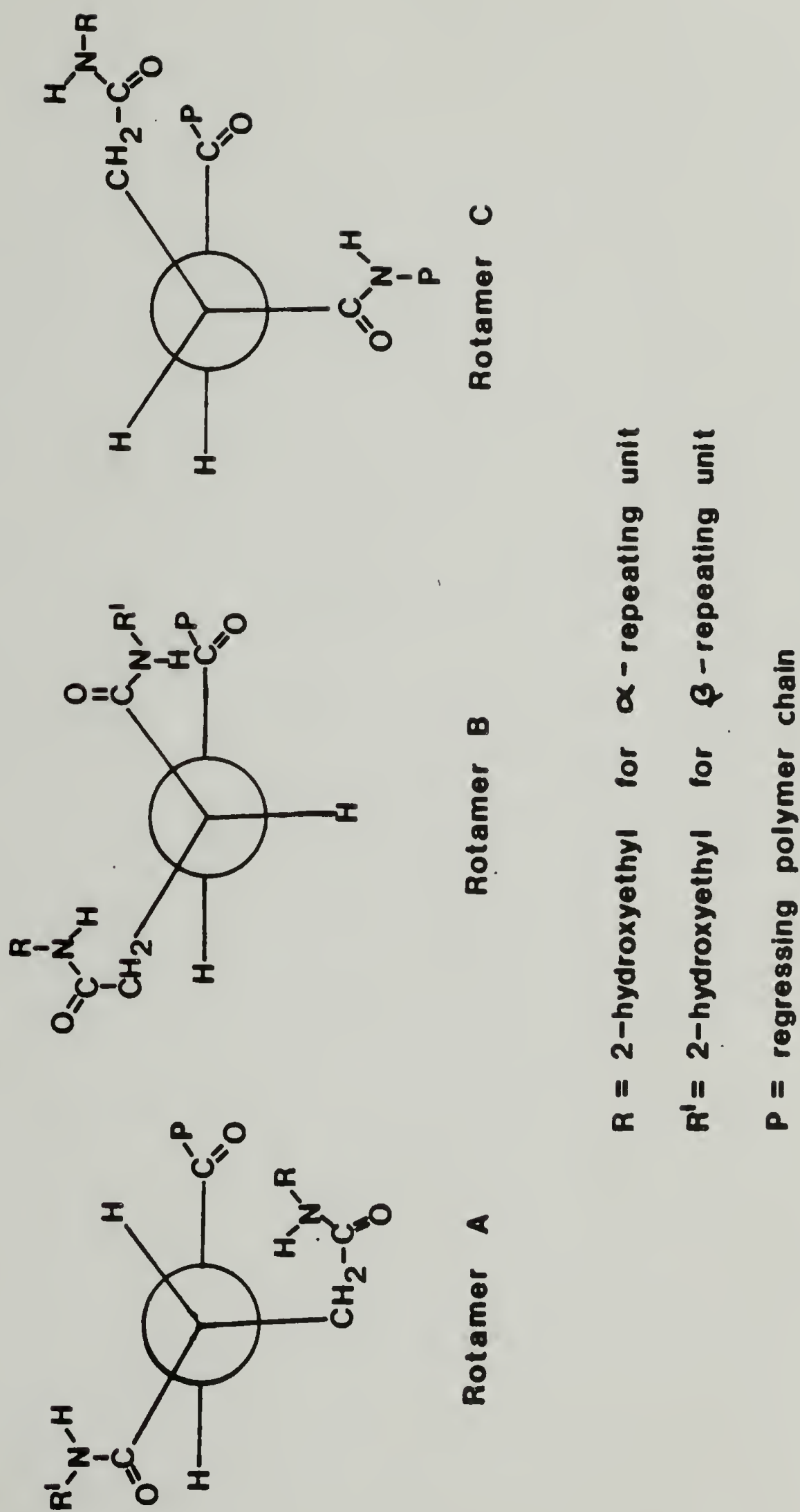
would be assigned to it. However, this assumption completely disregards rotational conformations of the aspartamide repeat unit which place the NH proton in close proximity to main chain amide bonds which can influence the magnetic field seen by this proton. Such long range conformational effects in poly(β benzyl aspartate) were responsible for a change in the NH chemical shift in the helical form (8.36ppm) as compared to the random coil form (8.10 ppm).⁵³

In Figure 9, Neuman projections of the rotational conformations of the 2-hydroxyethyl aspartamide repeat unit are presented with the view from α methine carbon back to the nitrogen of the pentultimate repeat unit. Both α and β repeat units are indicated by selecting R and R' as the 2-hydroxyethyl substituent respectively. "P" represents the pentultimate unit and regressing polymer chain. If the pentultimate unit is assumed to be an aspartamide repeat unit, rotamer C can be assumed to have a negligible contribution. Rotamer A, which closely fits a planer zig-zag conformation places the β amide in close proximity to the pentultimate amide and the NH proton will thus feel a slight deshielding effect through space when compared to the α amide bond. Rotamer B, which is close to the rotational conformation assumed by poly(α amino acids) in a helical conformation,⁵¹ shows the α amide closer to the

FIGURE 9

Rotational Conformations of Poly(2-hydroxyethyl aspartamide)

Repeating Unit. View From α Methine Back to Pentultimate Amide Nitrogen



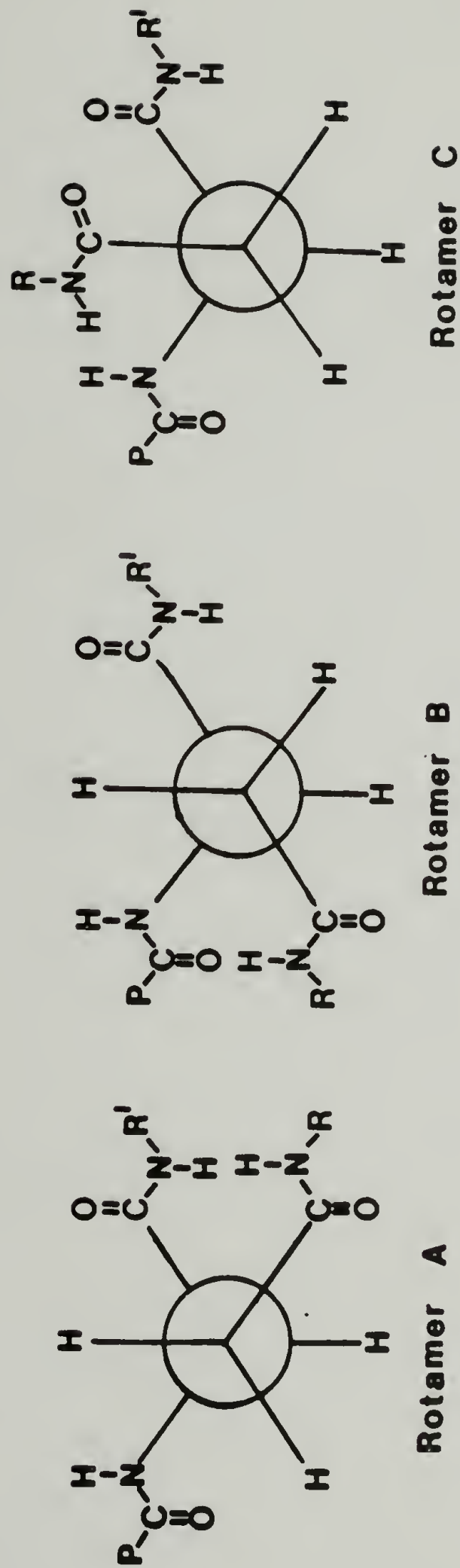
pentultimate amide. However, to avoid steric overlap, the amide bond would preferentially situate itself with the NH proton and R' group directed away from pentultimate unit. This is substantiated by diagrams of poly(α amino acids) in an α helix in which case the methine - pentultimate amide does assume a rotational conformation identical to that of rotamer B.⁵¹ Therefore, although it will feel the effect of the pentultimate amide it will be less than what the β amide sees in rotamer A. This argument has been made assuming that the pentultimate unit was an aspartimide, however, the same conclusions can be made if the pentultimate unit is shown as a cyclic aspartimide. Also, only one stereoisomer is shown, but the same arguments can be made for the other.

This argument has been made based on rotomers diagrammed in Figure 9. In Figure 10, Neuman projections of the possible rotational conformations about the α methine/ β methylene bond are depicted with the view from the methylene carbon back to the methine carbon. R, R' and P have the same meanings. Again, rotamer C can be considered negligible. Rotamer A shows the α amide and β amide in close proximity, and therefore, a slight deshielding of both NH protons is expected. Rotamer B, however, shows that only the β amide will experience a deshielding effect of the NH proton due to its proximity to the pentultimate

FIGURE 10

Rotational Conformations of Poly(2-hydroxyethyl apartamide)

Repeating Unit. View From β Methylene Back to α Methine



R = 2-hydroxyethyl for α -repeating unit

R' = 2-hydroxyethyl for β -repeating unit

P = regressing polymer chain

amide. If the pentultimate unit is the cyclic aspartimide it will still experience this spacially induced deshielding.

Thus, with the rapid rotational changes occurring about these two bonds depicted in Figure 9 and Figure 10, and about the substituents of these two bonds, the absolute chemical shift observed for the α amide and β amide NH protons will be an average of all conformations. Thus, the β amide NH will see on the average a slightly greater deshielding effect than the α amide NH.

That this deshielding effect will actually occur and be observed is substantiated by numerous reports of chemical shift differences observed for poly(α amino acid)s and ester derivatives which occur in helical or random coil conformations. These shift differences are normally a result of long range interactions, and therefore, the short range deshielding effects described here would be expected.

Hence, with the β NH experiencing a slightly greater deshielding, the chemical shift at 7.76 ppm has been assigned to this proton. Therefore, this absorption corresponds to the α repeat unit (β -2-hydroxyethyl amide), and the absorption at 7.52 ppm is assigned to the β repeat unit (α -2-hydroxyethyl amide). The ratios of each can be obtained from the area of each and these values

are tabulated in Table 5. Only copolymers 10E, 10D and 10C were tabulated because the overlap of the peaks is not sufficient to cause large potential error in the area measurement. However, the same trend appears to hold for 10B and 10A; that is, the peak at 7.76 is considerably larger than that at 7.52.

TABLE 5

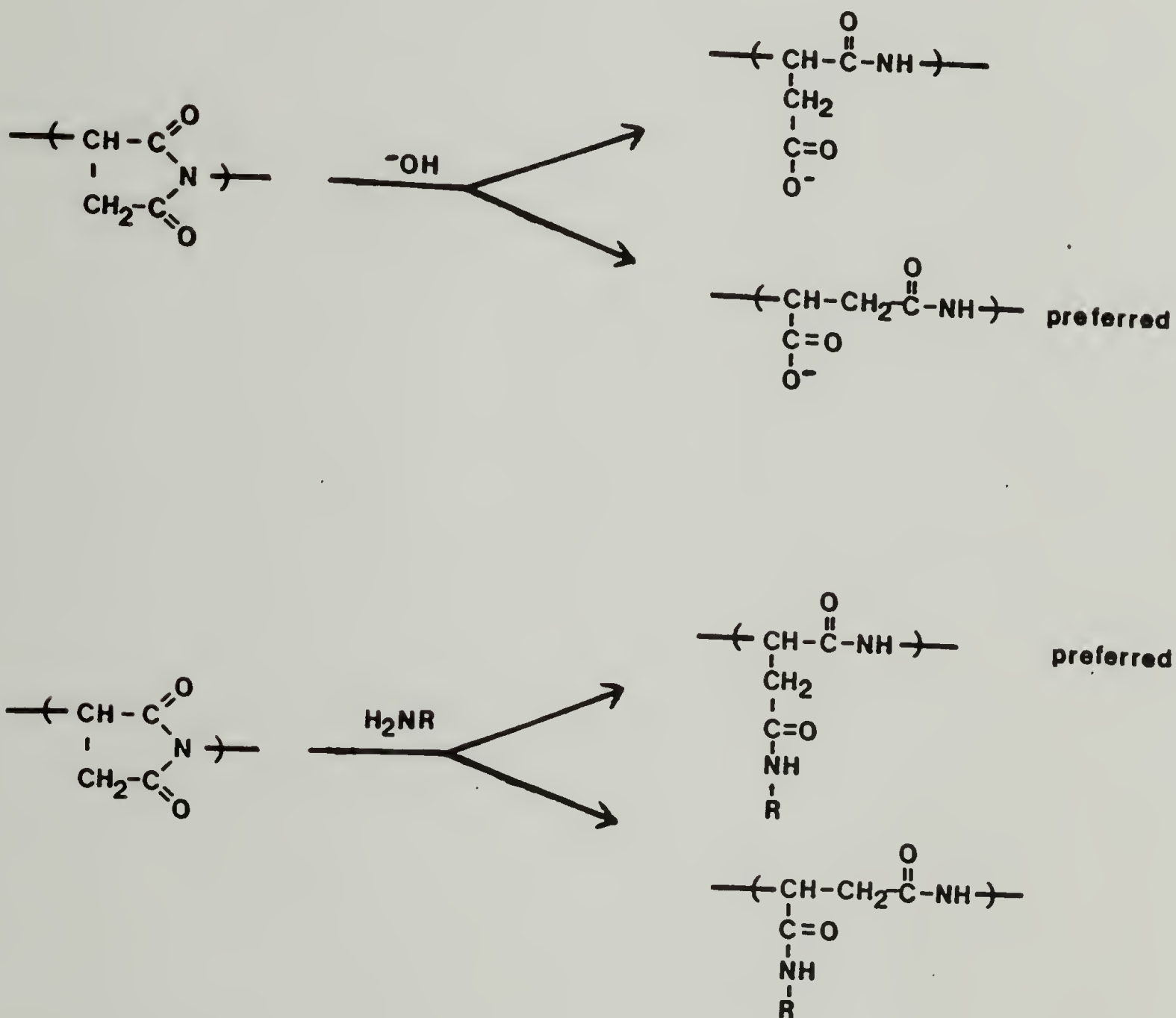
Percentage of α Repeat Unit from Peak Areas of NH Absorption: 7.52 = β repeat unit, 7.76 = α repeat unit.

<u>Sample</u>	<u>Area at 7.52 ppm</u>	<u>Area at 7.76 ppm</u>	<u>%α repeat unit</u>
10E	15 \pm 3	30 \pm 3	67 \pm 9
10D	15 \pm 3	25 \pm 3	63 \pm 10
10C	20 \pm 3	40 \pm 4	67 \pm 9

As a result, the ratio of α -repeat units (β 2-hydroxyethyl aspartamide) is 66 \pm 6%. Picova and coworkers^{28,29} established the ratio of α repeat units to be 0.2-0.4 in poly(aspartic acid) synthesized by basic hydrolysis of PAIm. This apparent conflict is a result of preferential attack by different nucleophiles at either carbonyl of the cyclic imide. The PAIm α carbonyl is more sterically hindered, yet more electrophilic due to the proximity of the amide. Nucleophilic attack by hydroxide ion will not be substantially affected by the steric hindrance, and therefore, higher ratios of β repeat units were obtained by basic hydrolysis of PAIm. (Figure 11) Nucleophilic

FIGURE 11

Nucleophilic Ring Opening of Polyaspartimide
Repeating Unit by Hydroxide or by Amines



attack by an amine will however be sterically hindered at the α carbonyl and therefore preferential attack at the β carbonyl leads to a higher ratio of the α repeat unit as determined here.

Summary of characterization

From infrared, elemental and NMR analyses, the percent conversion for the PAIm/PHEA copolymers has been determined and these values are listed in Table 2 and alternately in Table 3. All compounds have a small percent moisture even after drying to constant weight. The NMR data indicates that the placement of 2-hydroxyethyl aspartamide repeat units is random and that there is a definite preference for the α repeat unit - $66 \pm 6\%$.

Effect of composition on properties

As desired, a series of copolymers with varied conversion to the PHEA repeat unit has been achieved. Basic physical properties are listed in Table 6.

The inherent viscosities for these copolymers decreased as the percent conversion to PHEA repeat units increased, probably due to a less rigid polymer structure and not to a significant decrease in the average chain length because of the potential for chain breakage by a transamidation reaction. The viscosity average molecular weight for sample 10A can be obtained from the Mark-Houwink equation for PHEA derived by Neri¹⁸ :

TABLE 6

Physical Properties of PAIm/PHEA Copolymers

<u>Sample</u>	<u>η_{inh} (dl/g) a)</u>	<u>Other^{b)} Solvents</u>	<u>DSC^{c)} Analysis</u>	<u>Deg. d) Onset</u>	<u>TGA^{c)} Maxima</u>	<u>Wght Loss at 500°C</u>
PAIm	0.46	A	310°C(deg)	340°C	440°C	69
10E	0.37	A	275°C(deg)	295°C	315°C, 385°C	35
10D	0.33	A	225°C(deg)	265°C	300°C, 370°C	30
10C	0.32	A	225°C(deg)	250°C	300°C, 375°C	36
10B	0.30	A, B, C	210°C(deg)	245°C	295°C, 370°C	48
10A	0.26	A, B, C, D	210°C(deg) Tg=188 °C	235°C	280°C, 400°C	50

a) 0.1M LiCl in DMF, Polymer Conc.=0.50 g/dl

b) A=DMSO, B=Formic Acid, C=H₂O, D=E-caprolactam at 75°C

c) heating rate=20°C/minute

d) First 1% weight loss

$$[\eta] = 2.32 \times 10^{-5} M^{0.87}$$

A plot of the inherent viscosity and specific viscosity at varied concentration provided straight lines and extrapolation to zero concentration yielded $[\eta] = .32$. This yields a viscosity average molecular weight of 57,000. Hence, by comparison of inherent viscosities and the molecular weight of PAIm (50,000) and 10A (57,000), the remaining copolymers are likely to have average molecular weights within this range.

Comparison of the potential solvents for these materials showed that at high conversions, the PAIm derivatives were soluble in alternate solvents. In particular, 10A was soluble in formic acid, which is a good solvent for N6, and in ϵ -caprolactam at 75°C. Hence a solubilization of it in a N6 melt may be expected. 10B, due to its solubility in formic acid, may also show favorable interaction with N6 and might be expected to be solubilized in a N6 melt. 10E, 10D, and 10C would be expected to show the same incompatibility with N6 as displayed by PAIm.

These qualitative predictions based on solvents does not take into account the thermal properties. DSC analysis showed that only 10A exhibited a glass transition temperature ($T_g = 188^\circ\text{C}$). However, this transition was closely followed by an endotherm at about 210°C which appeared to be the onset of degradation. The remaining copolymers exhibited similar endotherms in the range of

210-230°C and for this reason thermogravimetric analysis (TGA) was conducted. The data in Table 6 indicates that these polymers are thermally unstable in comparison with PAIm.

Polyblend of Nylon 6 and poly(2-hydroxyethyl aspartamide)

To verify the previous predictions that poly(2-hydroxyethyl aspartamide) (sample 10A) would be too thermally unstable to undergo a melt blending procedure with N6, two such blends were performed. One contained 10% 10A/90% N6 and the second contained 1% 10A/99% N6. A third control blend was also performed (100% N6).

Table 7 list the physical appearance of the blended products and the inherent viscosities in formic acid solution at 0.5g/dl. From the gross discoloration of the blends it is evident that the sample 10A degraded in the melt and from a comparison of the inherent viscosities this degradation clearly caused some degradation of the N6. Inherent viscosities for the melt mixed N6 were recorded at the three different concentrations to compensate for the fact that the amount of N6 in the blended products are 99% and 90% of the melt mixed N6. Therefore, the drop in inherent viscosities for the blends cannot be attributed to a dilution effect and must be due to a degradation of the N6 with a resultant lower average molecular weight.

A degradation of N6 was also observed and des-

TABLE 7
Properties of Nylon 6 and PHEA blend

<u>Blend</u>	<u>%PHEA</u>	<u>Color</u>	<u>Conc. (g/dl)^(a)</u>	<u>Inh.Vis. (dl/g) ^(a)</u>
23A	10	Black	0.490	.92
23B	1	Brown	0.494	1.46
23C	0	Pale Yellow	0.501	1.65
23C	0	Pale Yellow	0.495	1.61
23C	0	Pale Yellow	0.447	1.78

(a) in 98% formic acid

cribed previously when PAIm was added to the melt in a concentration of 10% and identically mixed. In that case, the drop in inherent viscosity was not as great as the 10% 10A mixture, but PAIm was visibly inhomogenous. Therefore, it would not be expected to cause as much of a degradation of the N6 when compared with 10A. However, a reaction of free amines with surface cyclic imide repeat units will produce aspartamide repeat units which could be as thermally unstable as the PAIm/PHEA copolymers were. Therefore the thermal stabilities of similar amine derivatives of PAIm would be of interest.

Polyaspartimide Derivatives

With this obvious thermal instability of the PHEA and the PAIm/PHEA copolymers the potential applicability for similar derivatives to be used as a host polymer in a N6 blend appears slim. However, to eliminate such derivatives completely as potential hosts requires confirmation that similar derivatives are also thermally unstable. Such amine derivatives have been synthesized and subsequently analyzed. Also, poly(aspartic acid) was synthesized by hydrolysis of PAIm for similar thermal analysis. In addition, an attempt was made to synthesize a poly(methyl aspartate) by nucleophilic addition to the PAIm repeat unit be methanol. The syntheses, characterizations

and thermal analyses are described in the sections to follow.

Poly(aspartic acid) (PAAc)

PAAc was synthesized from PAIm by the procedure of Picova et.al.²⁸ The infrared analysis showed a complete hydrolysis by a lack of imide carbonyl absorption at 1800 cm^{-1} and a broad carbonyl centered at $1700\text{--}1650\text{ cm}^{-1}$. The proton NMR showed the characteristic methine and methylene absorptions. In the ^{13}C -NMR (D_2O as solvent) splitting was observed for the methylene carbon (39.47 ppm and 38.25 ppm), for the amide carbon (174.59 ppm and 174.29 ppm) and also for the carboxylic acid carbon (176.98 ppm and 176.71 ppm). These absorptions are in excellent agreement with Picova's²⁸ analysis of polyaspartic acid and from relative peak heights it is estimated that β peptide links are predominant.

Several groups have reported that PAAc will recyclyze to the amide if vigorous drying conditions are utilized and therefore this was avoided. However, moisture still remains as evidenced by IR, ^1H -NMR and elemental analysis and this was considered in the thermal analyses.

DSC initially showed a broad endotherm centered at about 110°C , however rescanning several times caused it to decrease and thus this was attributed to moisture volatilization. Repeated attempts to establish a stable baseline

up to 200°C to determine a Tg or Tm continually failed apparently due to decomposition or a cyclization reaction mentioned previously. Therefore, neither a Tg nor a Tm have been determined.

TGA analysis (Thermograph No. 2, Appendix D) was conducted by bringing the sample to 125°C under nitrogen atmosphere and holding for 10 minutes to volatilize absorbed moisture. A six percent weight loss was thus observed. Analysis was then continued by heating at a 20°C per minute rate up to 500°C. A slow volatilization was observed to begin at 150°C, and this increased, with the next 5% weight loss occurring by 195°C and a broad maximum in rate of weight loss centered at 210°C. Continued heating caused a continuous weight loss with a second, sharper maximum at 330°C, and a final weight loss at 500°C of 50% (excluding the 6% H₂O absorbed). Given the instability below 200°C, it is obvious why neither a Tg nor a Tm could be obtained for PAAc. The mechanism for the initial degradation may be the thermal cyclization with H₂O evolution but this is not definite. However, the degradation at higher temperatures must surely be due to chain breakage.

Attempted synthesis of poly(methyl aspartate) (PMA_t)

Two attempts were made to ring open the aspartimide repeat unit by nucleophilic attack with methanol using triethylamine catalyst or sodium methoxide catalyst. In both

cases, PAIm was reisolated with no conversion. This is not surprising in light of the very specific and simple method of synthesizing succimide derivatives from the succinamide acids.⁵⁵

Amine derivatives of PAIm: synthesis and characterization

A series of amine derivatives of PAIm were synthesized by the same procedure utilized for the ethanolamine derivatives. However, longer times were generally employed to ensure high conversion to the amide derivative so that thermal instabilities can more accurately be assessed in terms of the polyamide chain structure. The specific conditions for each are given in Chapter VI.

Of the amines used, aniline, dicyclohexyl amine and 2-(4-thiazolyl) benzimidazole failed to react with PAIm. The failure of aniline to undergo the nucleophilic addition is due to its lower basicity, while dicyclohexyl amine is too sterically hindered. 2-(4-thiazolyl) benzimidazole fails on account of both of these factors. Only alkyl amines and 4-ethoxy aniline - which is more basic than aniline - successfully induced ring opening of the PAIm repeat unit. The remaining amines utilized are listed in Table 8 with the percent conversion and the abbreviations used in the text to follow. Percent conversion was determined by the infrared analysis and ¹H-NMR analysis techniques des-

TABLE 8

Amine Derivatives of PAIm

Reagent	% Conv. to Amide ^{b)}	% α repeat unit ^{a)}	Copolymer Code
Phenethylamine	77+3	65	PPhEAm77
Benzylamine	72+2	-	PBAm72
Benzylamine	88+2	-	PBAm88
Cyclohexylamine	92+2	75	PChAm92
Methylamine	60+7	65	PMAm60
Methylamine	96+4	67	PMAm96
4-Ethoxyaniline	40+7	-	PEtPhAm40
2-Hydroxypropylamine	79+9	60	PHPrAm79
n-Hexylamine	98+2	55	PnHAm98
3-Phenylpropylamine	92+3	60	PPhPrAm92

a) $\pm 10\%$ b) mean of values obtained by IR and $^1\text{H-NMR}$ analysis

cribed previously and the conversions listed in Table 8 are the average of the two methods with the deviation given. Elemental Analysis for these samples were also consistent with structures except for small percent of moisture present that was not completely removed by drying to constant weight. This moisture content was observed in the thermal analysis of these copolymers and accounted for.

^1H -NMR analysis of most of these products also indicated NH absorptions which were structurally similar to those of the 2-hydroxyethyl amine derivatives. The side chain amide NH absorption appears as a broad peak which resembles two overlapping peaks. In all cases, the lower field absorption is clearly dominant, with the higher field absorption occurring as a distinct shoulder on the former. Because the arguments made for the PAIm/PHEA derivatives were independent of the exact nature of adjacent repeat units and side chain amide substituents, then the conclusions must hold here also. Therefore, these products have a predominance of α repeat units. Estimates of the exact ratios were made based on the proportional areas of the overlapping absorbances and these are tabulated in Table 8.

Three of the products could not be directly interpreted in this fashion. PBAm72 and PBAm88 exhibited all NH absorptions in one broad peak centered at 8.1 ppm and therefore α/β ratios were not obtainable. This higher

chemical shift for the side chain could be expected from a benzyl amide due to the proximity of the aromatic ring. PEtPhAm40 exhibited all NH protons centered at 8.2 ppm and therefore α/β ratios could not be ascertained. However, based upon the preponderance of evidence for all amine derivatives, it would be expected that these three products would likewise contain a greater proportion of α repeat units.

Two products exhibited slightly different NH absorption patterns. PnHAM98 shows a triplet of overlapping peaks with centers at 7.77 ppm, 8.06 ppm and 8.11 ppm. From the integration it appears that the area beneath the peaks at 7.77 ppm and 8.11 ppm are approximately equal. Based on the conformational interpretation of NH absorption splitting previously given, the peak at 7.77 ppm should be the α -n-hexyl amide substituent and therefore the peak at 8.11 ppm could be assigned to the main chain aspartimide NH proton in a β -linkage based upon the area alone. The conformational argument, however would also predict this because the β -aspartamide repeat unit in the main chain NH should have a higher chemical shift than the α -aspartamide repeat unit and this absorption at 8.11 ppm is the furthest downfield from TMS. The larger absorption at 8.06 ppm must therefore be due to the β -n-hexyl amide side chain NH and the α -aspartamide main chain amide NH . Estimation of the

relative areas yields an α -repeat unit of 0.55 ± 0.06 .

PChAm92 shows a more complex cyclohexyl amide NH absorption with peaks at 7.28 ppm (α -cyclohexyl amide NH) and 7.52 ppm and 7.67 ppm (β -cyclohexyl amide NH). This splitting is likely a result of hindered rotational mobility due to the bulk of the cyclohexyl substituent. From the relative areas, an α -repeat unit ratio of 0.75 ± 0.07 was obtained. This somewhat higher ratio of α -repeat units as compared to the rest is a result of the steric bulk of the cyclohexyl amine and the hinderance to nucleophilic addition at the α -carbonyl of the imide repeat unit in PAIm.

^{13}C -NMR analysis did not provide any additional information. As with the ethanolamine derivatives, chemical shifts could be assigned to the methine and methylene carbons but band broadening prevented analysis of microstructure. Side chain amide residues showed absorptions typical of their structures. Amide carbon absorptions occur at 168 to 172 ppm with some fine structure evident, but absolute assignments could not be made.

X-ray diffraction analysis indicated a lack of crystallinity for all samples.

Thermal Analyses

DSC analysis of all the products listed in Table 9 showed a broad endotherm centered at 100°C for all

TABLE 9

Thermal Properties of PAIm Amine Derivatives

<u>Copolymer</u>	<u>T_g (a, c)</u>	<u>Deq. Onset (a, b, d)</u>	<u>Degradation (a, d) Rate Maxima</u>	<u>% wght loss at 500°C</u>
PPhEAm77	143°C	-	-	-
PHEA	188°C	253°C	280°C, 400°C	50
PBA _m 72	155°C	255°C	320°C, 380°C	71
PBA _m 88	152°C	220°C	310°C, 370°C	69
PChAm92	195°C	225°C	300°C, 345°C	69
PMAm60	211°C	260°C	295°C, 365°C	52
PMAm96	174°C	240°C	300°C, 370°C	60
PEtPhAm40	188°C	260°C	295°C, 365°C	61
PHPr _m 79	140°C	205°C	300°C, 360°C	56
PnHAm98	189°C	250°C	315°C, 385°C	81
PPhPrAm92	121°C	250°C	305°C, 430°C	78
PAIm	-	340°C	440°C	69

a) heating rate = 20°C/minute

b) First 1% volatilized

c) by DSC for samples quenched to 48°C from 200°C

d) by TGA

products and this was attributed to moisture volatilization. The samples were, therefore, heated to 200°C at 20°C per minute and quenched back to 48°C and the DSC trace was rescanned. Normally heating to 200°C once was sufficient to remove the majority of the moisture and enable a true reading of the T_g without baseline irregularities or significant plasticization effects. The T_g's obtained and listed in Table 9 are, therefore, from samples quenched to 48°C from 200°C. As can be seen, high percent conversions to aspartamide derivatives leads to the creation of a glass transition temperature which would be desirable if such a product was used as a host polymer in a N6 blend. Comparison of these T_g's with those of other polyamides indicate that these are consistent. The T_g for nylon 3 is 111°C, and the T_g for N6 is in the range of 40-50°C.⁵⁶

The results of the TGA analysis are also listed in Table 9. The individual graphs are compiled in Appendix D. The data for PAIm is also listed for comparison. The degradation onsets as measured by the first 1% weight loss are in the range of 235-260°C. The thermal instability of these materials in comparison to PAIm clearly indicates that poly(aspartamide) derivatives would decompose under blending conditions with N6 regardless of the side chain substituent.

All products demonstrated two or more peaks in the

rate of weight loss plot with the two strongest given in Table 9. The first maximum fell within the range of 275-320°C and a second in the range of 360-385°C. The complex rate profiles for these products and the similarities between them lead the author to believe that it is a result of a thermally induced main chain fragmentation. The percent weight loss at 500°C are presented for comparison, however, no information of the residue or the products volatilized can be deduced from this data.

Numerous kinetic analyses of TGA data for polymer degradation have been reported and reviews have been published.⁵⁷⁻⁵⁹ An attempt was made to use the Freeman-Carroll⁶⁰ approach to obtain an energy of activation for the thermal degradation of the products listed in Table 8. By the Freeman-Carroll approach, a plot of specific variables taken from the constant heating rate TGA curve should yield a straight line for which the slope is related to the activation energy. Such a plot for these materials was made, however the data points were extensively scattered and a straight line could not be drawn. Again, this failure to fit the theoretical plot is a direct result of the complexity of the polyaspartamide degradation and the oversimplification of this kinetic approach. However, other approaches, as argued by Still,⁵⁷ are equally faulted on a theoretical basis; that is measurement of weight loss alone does not indicate the mechanism, changes in mechanism or

multiple mechanisms of thermal degradation. Hence, only exceedingly simple thermal degradations will provide energy of activations by this kinetic approach or others. In light of this result, the polyaspartamide degradations must necessarily be complicated.

The mechanism of thermal degradation must be a result of the polymer structures, for which all polyaspartamides contain both α and β repeat units. Poly(α amino acid)s are known to be thermally unstable and Obata and Ogawa have published the TGA curves for six different poly (α amino acid)s.⁶¹ These curves illustrate the thermal instabilities of the α amino acid repeat unit with the onset of degradation occurring between 150°C and 230°C for the polymers studied. Hayase and coworkers⁶² reported that poly(α amino acid)s pyrolyzed at 150°C to 250°C resulted in the formation of amino acid and peptide sequences as a result of peptide cleavage but the peptide or amino acid isolated was not necessarily the same as the repeat unit, indicating secondary cleavage of the polymer substituent. Johnson and coworkers⁶³ have reported that poly(α amino acid)s thermally degrade by a free radical mechanism at elevated temperatures (>500°C). In addition, the non-volatile thermal degradation products of aspartic acid and PAIm have been analyzed by Smith and coworkers⁶⁴ and these authors have proposed that an initial deamination of the

α carbon led to a the formation of succinic, fumaric and maleic acid derivatives.

As such, the thermal instabilities of the α amino acid repeat unit are clearly substantiated, and hence, the thermal instabilities of the PAIm derivatives which contain these peptide links will suffer from this limitation. All derivatives of PAIm contain both α and β repeat units but all contain α peptide links in the form of the repeat unit or the side chain amide substituent.

Conclusions

The thermal instability of polyaspartimide derivatives makes such a system unacceptable as a polymer support for a chemical agent in a N6 blend. This thermal instability is readily understood in terms of the instability of poly(α amino-acid)s and as such cannot be avoided because the ring opening reaction of PAIm leads to the formation of these peptide links. The properties of the blend of PHEA with N6 demonstrated the degradative effect this poly(amino acid) has on the N6. PAIm blends showed a similar discoloration, probably as a result of a slight degree of ring opening of the imide by free amine present with formation of thermally unstable α aminoacid repeating units.

C H A P T E R I I I

P(E/MAA) AS A POTENTIAL POLYMER SUPPORT

Introduction

Unlike the PAIm derivatives, copolymers of ethylene and methacrylic acid, P(E/MAA), have sufficient thermal stability to undergo blending with N6 at 250°C, and such blends have been studied.⁶⁶ These results are to be published by MacKnight and coworkers and, therefore, only a qualitative summary will be given here. All blends studied were 90% N6 and 10% LDPE or P(E/MAA), the latter having varying mole percents of MAA. Scanning electron microscopy of the blend fractured at liquid nitrogen temperature clearly showed decreased domain sizes of the polyolefin component with higher mole percent MAA in the copolymer utilized. DSC studies of the blends indicated a constant T_g for the N6 matrix and no appreciable change in the degree of crystallinity of the N6 phase, confirming that the binary mixture remained essentially incompatible. When dissolved in formic acid, all blends formed a stable emulsion (the Molau test⁶⁷) as a result of grafted structures, and these were most likely formed by amidation of the MAA by free amine in the N6. Additionally, grafted copolymers were indicated by attempts to extract the polyolefin component from the blend by refluxing xylene. The percent extracted clearly decreased as the MAA content

increased with only trace amounts obtained with MAA mole percent content of 4.3 and 5.4. In addition, tensile properties were also examined and showed that with increasing MAA content the tensile properties approached those of 100% N6.

Thus, some basic characteristics of the P(E/MAA) N6 binary allow have been clearly defined. In particular, it should be noted that at higher MAA content, the tensile properties approached those of N6 and, therefore, P(E/MAA) appears to be a practical choice as the polymer backbone to which the biocide could be bound to. P(E/MAA) has also been shown to be readily esterified by converting it to its acid chloride, poly ethylene-co-methacryloyl chloride (P(E/MACl)) derivative with oxalyl chloride and subsequently reacting it with methanol.⁶⁸ Hence, a convenient method is available for derivatizing it with a biocide by the very reactive P(E/MACl). Specific methods of bonding the biocide to P(E/MAA) will be addressed in Chapter IV.

However, it is not known what effect converting the methacrylic acid repeat unit to an amide or ester derivative will have on the blending properties with N6. Clearly the MAA component interacted with the N6 with the formation of grafted structures, and if an amide or ester derivative is utilized, such grafted structures would be expected, more so with the latter. However, it may be

argued that because of the solubility of N6 in acidic solvents only, when it is blended with P(E/MAA), there is an inherent interaction with the MAA repeat unit. This interaction may enable a more intimate mixing and thus induce graft formation. Ester or amide derivatives, although they can form hydrogen bonds with the polyamide repeat unit, might not interact as strongly with N6 as P(E/MAA) obviously did. This lower interaction may significantly effect grafting and as a result, may effect the blend properties. Hence, the analysis of such derivatives would be of interest.

In the tensile analysis study of the N6/P(E/MAA) blends by MacKnight and coworkers,⁶⁶ moisture content was held constant by pretreating in a 50% relative humidity environment. Because of the strong dependence of the tensile modulus of N6 upon absorbed moisture content, it was of interest to know what effect P(E/MAA) has on the moisture absorption and subsequently what is the effect different levels of absorbed water have on the tensile properties of the blend. The effect of moisture absorption will be discussed first. The modifications of P(E/MAA) and the blends of these products with N6 will be treated in the subsequent sections.

Varied moisture content effects on N6/P(E/MAA) blends

A series of 90% N6, 10% P(E/MAA) blends were made

with varied MAA content in the P(E/MAA) as indicated in Table 10. Films of each product were obtained by compression molding at 250°C for 7-10 minutes between Teflon sheets at 10,000 psi and allowed to cool. Dumbell shape strips were cut according to ASTM specification #D.638 type V and placed in gently refluxing distilled water for one hour. One series of tensile runs were obtained for strips that remained in water until analyzed, and a second from strips that were stored in an 80% relative humidity chamber for at least 24 hours. Weight percent water content was gravimetrically determined for these two series by drying in an oven at 100°C and 0.1 mm Hg pressure after the above treatment. A third set of tensile analyses was conducted on strips that received no treatment at all and a fourth from samples that were dried at 105°C at 0.1 mm Hg pressure for 12 hours and stored in a dessicator until utilized. This data is compiled in Table 10.

As expected, increased levels of moisture significantly lowered the tensile modulus for N6 and all of the blends examined. As much as a 60% drop was observed when the dry and the saturated materials were examined. With regard to the relative amounts of moisture absorbed within a series of treated specimens, there was no significant difference in the water content of the blends when the percent MAA content of the copolymer was changed. Also, within a series of specimens with the same treatment, there

TABLE 10

Tensile Properties of N6/P(E/MAA) Blends (90:10)

at Varied Moisture Content

Minor (a) Component	Young's Modulus (b)		
	<u>Saturated</u>	<u>80% R.H.</u>	<u>No Treatment</u>
None	4.3x10 ³ (6.7%H ₂ O)	5.7x10 ³ (3.1%H ₂ O)	7.5x10 ³ 10x10 ³ (0%H ₂ O)
P(E/1.3MAA)	3.6x10 ³ (7.5%H ₂ O)	4.6x10 ³ (3.2%H ₂ O)	6.1x10 ³ 9.5x10 ³ (0%H ₂ O)
P(E/3.5MAA)	3.7x10 ³ (6.8%H ₂ O)	4.4x10 ³ (2.6%H ₂ O)	5.8x10 ³ 8.7x10 ³ (0%H ₂ O)
P(E/4.2MAA)	3.6x10 ³ (5.9%H ₂ O)	4.5x10 ³ (3.0%H ₂ O)	6.6x10 ³ 8.7x10 ³ (0%H ₂ O)
P(E/5.4MAA)	3.3x10 ³ (6.2%H ₂ O)	4.1x10 ³ (3.0%H ₂ O)	6.2x10 ³ 8.9x10 ³ (0%H ₂ O)

- a) All blends contain 10% minor component with mole percent MAA as indicated.
- b) Units of kg/cm² with moisture content in parentheses.

was no significant difference in the tensile modulus, with the exception that the values for the blends were slightly lower than that of N6. Hence, the polyolefinic component exerted no effect upon the moisture absorption. With 90% N6, these blends still absorbed large amounts of water. The moduli were strongly dependent upon this major component, and thus, these values reflected the moisture content regardless of the exact nature of the polyolefinic component.

Modified P(E/MAA) and Blends with N6

Complete conversion to amide or ester.

P(E/5.1MAA) was converted to its acid chloride derivative, poly (ethylene-co-methacrylyl chloride), (P(E/5.1MACl), by reacting it with oxalyl chloride in carbon tetrachloride. Mechanistically, the action of oxalyl chloride upon acids in general leads to the initial formation of a complex anhydride of the acid, oxalyl residue, and another molecule of acid.⁶⁹ Further reaction of this anhydride with oxalyl chloride leads to the formation of the desired acid chloride and carbon monoxide, carbon dioxide, and hydrogen chloride by-products. This was visually observed in the P(E/5.1MAA) system. The hazy polymer solution initially formed a highly swollen gel due to the complex anhydride formation with methacryloyl units

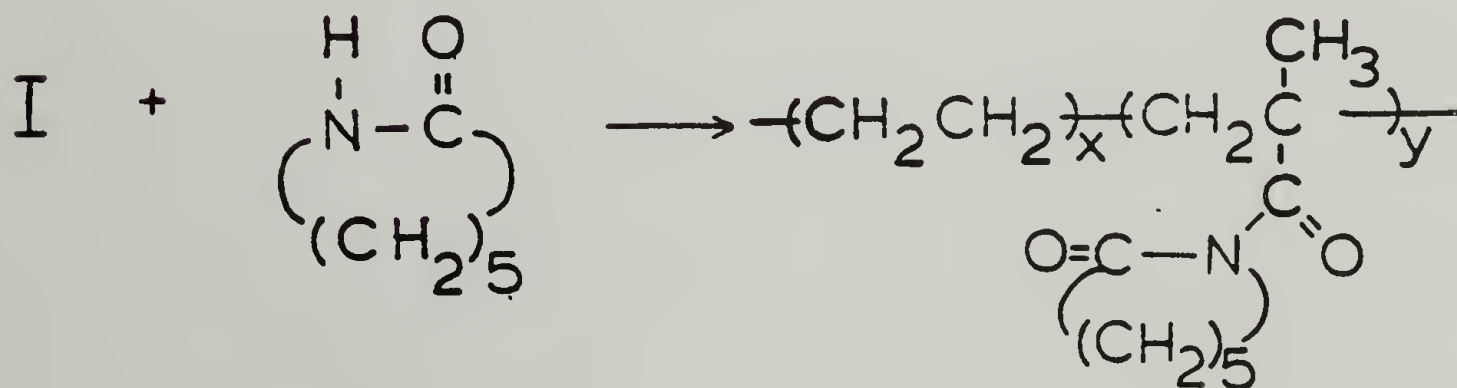
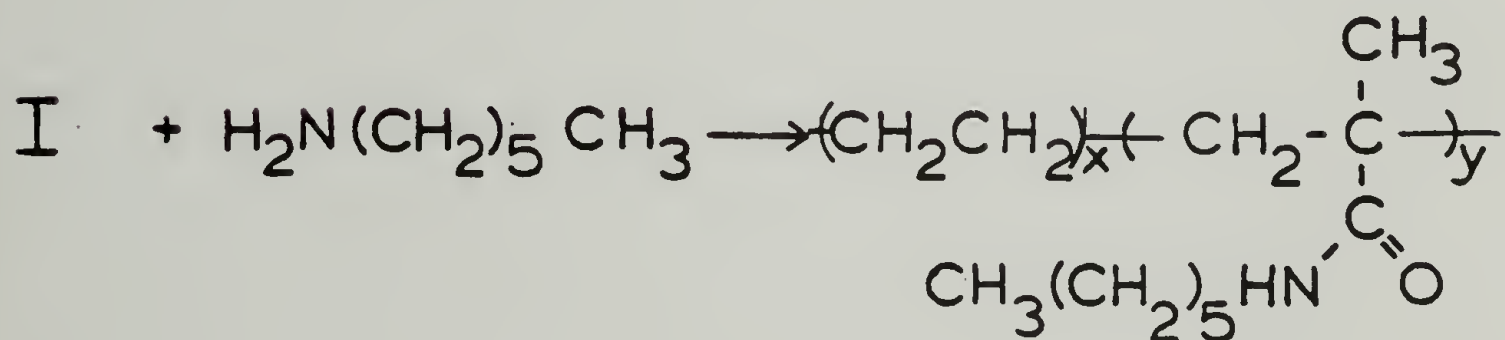
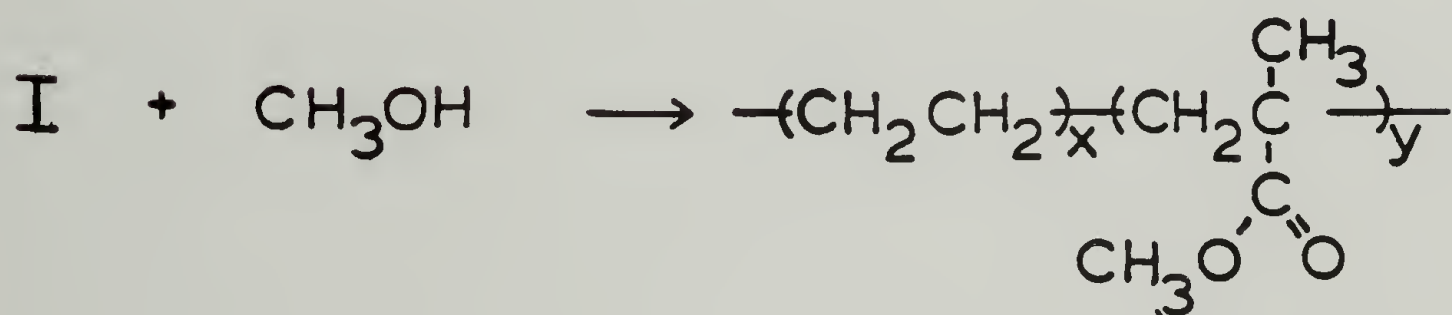
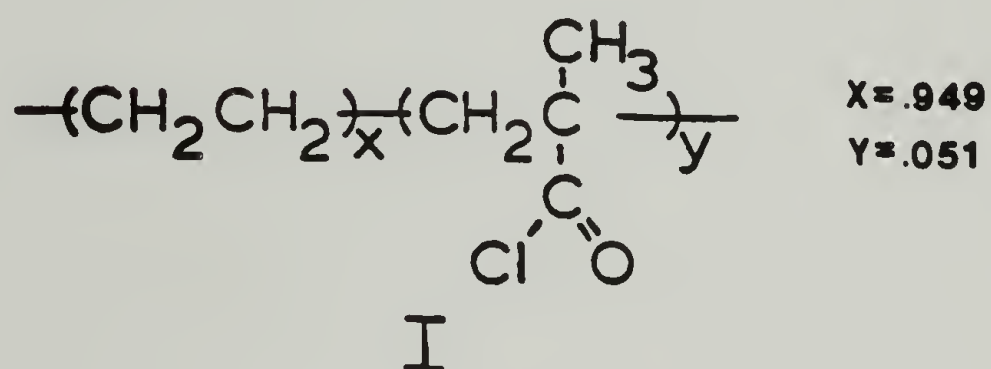
of different chains, and this gel gradually forms a clear homogenous solution of the P(E/5.1MACl). Gaseous by-products were readily observed by the formation of bubbles in the swollen gel which eventually escaped as the reaction went to completion and the polymer completely dissolves. Percent conversion was determined by removing a small aliquot, casting a film on a NaCl plate and observing the infrared spectra. A strong carbonyl absorption appeared at 1800 cm^{-1} while the acid peak at 1700 cm^{-1} completely disappeared, indicating 100% conversion. Gaseous by-products and excess oxalyl chloride were then readily removed by refluxing and allowing the condensate to pass through a sodium hydroxide trap.

Three separate P(E/5.1MACl) solutions were subsequently reacted with methanol, n-hexyl amine or ϵ -caprolactum. (Figure 12) Infrared and elemental analysis confirmed 100% conversion for each. DSC analysis was conducted on each of the products and the crystallization exotherms were observed after maintaining the samples at 400°K for 15 minutes. The peaks for each of these products are as follows: P(E/5.1MMA) - 344°K ; P(E/5.1nHMA) - 340°K ; P(E/5.1N-MACap) - 341°K .

Blends of each with N6 were made with the weight concentration of N6 at 90%. All blends displayed a positive Molau test; that is, dissolving the blend in formic

FIGURE 12

Modification of Poly(ethylene-co-methacrylic acid)
by Conversion to the Acid Chloride Derivative and
Subsequently Reacting with Alcohol, Amine, or Lactam



acid formed an emulsion that was stable for longer than 28 days with no phase separation of the P(E/MAA) derivatives, which are by themselves insoluble in formic acid. Thus, N6 grafted polyethylene derivatives must be present and as with the 90% N6/10% P(E/MAA) blends, these grafted structures are attributed to amidation of the MAA derivative. MacKnight and coworkers⁶⁶ and Iling⁷⁰ showed that in a blend of N6 and LDPE of the same proportions, an emulsion was formed in formic acid but this was not as stable with the LDPE particles gradually precipitating out. Only with methacrylic acid or an ester or amide derivative is a stable emulsion formed. The formation of a stable emulsion can only be attributed to significantly more grafted products as a result of amidation of this functionality.

Scanning electron microscopy of cryogenically fractured specimens of blends of the above derivatives of P(E/MAA) was performed. All polymers showed very small, almost undetectable domains of the polyolefin component dispersed within the N6 phase. The size of these domains were 0.1 micron or less and this identical morphology was obtained from the N6/P(E/5.4MAA) blend.⁶⁶

All blended products were additionally examined by differential scanning calorimetry. Samples were heated at 10°K per minute from 325°K to 520°K, held there for 15 minutes to remove thermal hysteresis effects, and subse-

quently cooled at 10°K per minute to 325°K . The relevant experimental data is compiled in Table 11 with the data for melt mixed N6 and the N6/P(E/MAA)⁶⁶ included for comparison. All blends displayed melting and crystallization peaks typical for the individual components with heats of fusion and degree of crystallinity all about the same.

With these similarities of thermal properties, morphology and positive Molau tests among the P(E/5.1MAA) derivatives and P(E/5.4MAA) blended with N6, it can be concluded that the methacryloyl functionality strongly effected the ultimate blend properties, but it did not have to be in the acid form. That is, whether the acid or an ester, amide or imide derivative was studied a more intimate mixing of the polyolefin and N6 was achieved with LDPE and N6. With the N6/P(E/5.4MAA) system, it was believed that grafted PE formed by amidation of the methacrylic acid unit by end group amines in the N6 caused this improved mixing of the incompatible polymers by acting as a compatibilizer. However, with acidic repeat units present the same compatibilization could conceivably occur due strictly to the strong polar attraction between the acid and the N6 amide functions. Additionally, this strong polar interaction itself could lead to an increase contact between the phases and an improved likelihood of graft formation by amidation of the acid or by free radical coupling between polyamide and

TABLE 11

Thermal Analysis of Blends of N6 and

P(E/5.1MAA) Derivatives (90:10) by DSC

Minor Component	Thermal Analysis (d)				Hf ^(a)	Cryst. ^(b) %
	Melting Peaks (°K)		Recrystal Peaks (°K)			
	T1	T2	T1	T2		
P(E/5.1MMA)	363	491	346	455	12.2	29.7
P(E/5.1nHMA)	360	491	342	454	11.8	28.8
P(E/5.1N-MCap)	366	492	340	457	12.0	29.2
P(E/5.4MAA) ^{c)}	369	489	-	458	11.0	26.8
None	-	490	-	457	11.5	25.2

- a) Hf of blend
 b) % Crystallinity corrected for weight contribution of minor component
 c) data in this row taken from reference 66
 d) 10°K/minute heating rate, maintained at 520°K for 15 minutes, and cooled at 10°K/minute. T₁-due to polyolefin, T₂-due to polyamide.

polyolefin radicals formed by shearing^{70,71} polymer chains, and therefore a strongly positive Molau test was obtained. The derivatives of P(E/5.1MAA) lack this acidic character, and although they can have a polar attraction for the N6 amides it is certainly not as strong as the acid. As carboxylic acid derivatives, they can undergo the same amidation as the P(E/5.4MAA) and hence grafted structures can form and act as interfacial compatibilizers. Hence, the acidic proton was not necessary for the more intimate mixing in comparison to LDPE, but the carboxylic functionality was.

Partial esterifications of P(E/5.4MAA)

A series of copolymers with varied conversion of the methacrylic acid repeat unit to methyl ester were synthesized. Five different P(E/5.4MAA) samples were reacted with different molar ratios of oxalyl chloride with only one yielding the soluble P(E/5.4MACl) and the remaining yielding swollen gels of the complex anhydride. Excess methanol was then added to give the copolymer with methacrylic acid and methyl methacrylate repeat units in varying ratios.

Percent conversion was determined from infrared analysis of films cast on a sodium chloride plate. The absorption at 2850 cm^{-1} can be attributed to the methylene symmetrical stretch of the copolymer by comparison with

normal alkanes.⁷² Conversion of the MAA unit to the methyl ester (MMA) should have an almost negligible effect on this peak absorbance. Methyl esters typically show peak C-H symmetrical stretching absorbances at 2897-2867 cm^{-1} , and thus, the formation of it in this copolymer would not significantly overlap with the methylene stretch at 2850 cm^{-1} , especially when one considers that at most, only 5.4 mole percent will form. Based upon methylene and methyl ester content, at most there can only be a 2.7 relative mole percent of the methyl ester. Hence, the ratio of the carboxylic acid peak absorbance at 1700 cm^{-1} to the peak absorbance at 2850 cm^{-1} in P(E/5.4MAA) can be used to calculate the molar ratio of acid groups that remain after the partial esterification, and thus the percent conversion. That is:

$$\% \text{ Conversion} = 1 - \frac{A(1700\text{cm}^{-1})/A(2850\text{cm}^{-1})}{A_0(1700\text{cm}^{-1})/A_0(2850\text{cm}^{-1})}$$

A_0 refers to the peak absorbance for P(E/5.4MAA) and the A values for the modified P(E/5.4MAA).

Table 12 lists these percent conversions and data from DSC analysis, for which all samples were heated to 400°K and held at that temperature for 15 minutes and then cooled at 10°K per minute to 325°K. The table lists the crystallization exotherm peak and the heat of crystallization for all of the copolymers modified, and that of P(E/5.4MAA) for comparison. No significant change is observed in the crystallization peak but a slight decrease in the heat of fusion

TABLE 12

Analysis of Partially Esterified P(E/5.4MAA)

<u>Sample</u>	<u>% Conv.</u>	<u>Cryst. Peak(k)</u>	<u>Heat of Cryst.</u>	<u>Copolymer Abbreviation</u>
50	100	338	6.4	ME 100
51	80	341	6.8	ME 80
51A	54	341	6.8	ME 54
51B	32	339	8.3	ME 32
51C	15	340	7.9	ME 15

is observed as the methyl ester content increases.

Table 13 summarizes the analyses for these blends. The Molau test for all blends were positive indicating the presence of grafted structures. Scanning electron microscopy indicated polyolefin domains of 0.1 micron or less as a result of these grafted structures acting as compatibilizers. DSC cooling curves for all samples preheated at 520 °K for 15 minutes demonstrated the peak crystallization temperatures and heats of crystallization indicated. In addition, dried compression molded strips of these blends were utilized to determine the Young's modulus and these are reported in Table 13.

This data is consistent with the previously described results of modified P(E/5.1MAA) with 100% conversion to ester, amide or imide derivative. Grafted structures were formed as a result of amidation of carboxylic functionalities in the P(E/5.4MAA) and its derivatives. The two components were inherently incompatible as evidenced by the presence of extremely small domains of the polyolefin within the N6 matrix. However, in comparison, the domains of LDPE in an identically prepared blend were significantly larger - 0.5 to 2.0 microns - and the morphology of the blends analyzed here was a result of the compatibilizing nature of these grafted structures. The initial tensile strength of these blends was governed by the N6 and was not signifi-

TABLE 13

Analysis of Nylon 6 Blends with Partially Esterified P(E/5.4MAA)

Minor Component	Molau Test	Polyolefin ^{a)} Domain	Thermal Analysis ^{b)}			Young's ^{c)} Modulus (kg/cm ²)
			T _I (°K)	T ₂ (°K)	H _c (T ₂) (Cal./g)	
P(E/5.4MMA)	+	<0.1	342	458	12.8	8.0x10 ³
ME 15	+	<0.1	346	452	13.8	10.6x10 ³
ME 32	+	<0.1	351	453	13.0	9.4x10 ³
ME 54	+	<0.1	350	455	13.3	9.2x10 ³
ME 80	+	<0.1	345	453	13.3	11.9x10 ³
ME 100	+	<0.1	347	455	13.5	9.6x10 ³
Nylon 6	-	-	-	454	13.7	11x10 ³

- a) by SEM, cryogenically fractured specimens, microns
- b) Cooling thermograph data at 10°K/minute after maintaining at 520°K/minute, T₁=polyolefin, T₂=polyamide. T₁ and T₂ represent peak exotherm temperature.
- c) For dry specimens

cantly weakened or strengthened by the 10% polyolefin dispersed within it. Finally, the overall properties of the blends were not changed by varying the ratio of conversion to the methyl ester, and thus, these properties are insensitive to the absolute concentration of the carboxylic acid. The presence of the carboxylic functionality in either the acid or ester form was sufficient to cause graft formation which control the morphology.

Partial Neutralizations of P(E/5.4MAA)

A series of P(E/5.4MAA) samples were partially neutralized by addition of an aqueous sodium hydroxide solution to a refluxing tetrahydrofuran solution of the copolymer. The percent neutralization was determined by using the relative peak absorbances of the carboxylic acid carbonyl at 1700 cm^{-1} and the methylene symmetric C-H stretch at 2850 cm^{-1} as described in the previous section. These values are recorded in Table 14.

Also listed in this table are the maxima in the crystallization exotherms for all samples and P(E/5.4MAA) for comparison. All samples were heated to 400°K and maintained at this temperature for 15 minutes prior to recording the crystallization exotherms at 10°K per minute cooling rate. The decrease in crystallization with increased percent neutralization was a direct result of the ionic nature of these copolymers. It has been reported that ethylene/

TABLE 14

Neutralized P(E/5.4 MAA)-Percent Conversion
and Crystallization Peaks

<u>Sample</u>	<u>% Neutralization</u>	<u>Cryst. Peak(°K)</u>	<u>Copolymer Code</u>
52A	68	332	Na 68
52B	72	327	Na 72
52C	59	329	Na 59
52D	40	332	Na 40
52E	22	339	NA 22

methacrylic acid copolymers and ethylene/acrylic acid copolymers showed slowed crystallization kinetics when the acid was partially neutralized⁷³ and that for fast crystallizations the polyethylene component formed disordered spherulites when the copolymer is in the acid form, but rodlike lamellar aggregates when partially neutralized.⁷⁴ These results have been interpreted to be a result of ionic clustering which is a well known phenomena of "ionomers".⁷⁵ Hence, the rapid cooling ($10^{\circ}\text{K}/\text{minute}$) and the decreased rate of crystallization and slight change in crystalline form can account for the lower crystallization temperatures for these samples.

Each of these products were blended with N6 and the analyses are summarized in Table 15. The properties of these blends were almost identical to those of the blends with partially esterified P(E/5.4MAA) listed in Table 13. The Molau test was positive for all, indicating the presence of PE-graft-N6. These acted as compatibilizers and encouraged a more intimate mixing with the polyolefin component located in very small domains of 0.1 micron or less in size. The DSC cooling curves indicated an unchanged crystallization exotherm at about 455°K with only a slight variation in the heat of fusion for this N6 crystallization. Also, the polyolefinic component displayed an almost imperceptible broad crystallization exotherm below 350°K . The

TABLE 15

Blends of Nylon 6 and Partially Neutralized P(E/5.4MAA)

Minor Component	Molau Test	Polyolefinic Domain	T ₁ (K)	Thermal Analysis T ₂ (K)	H _c ^{a)} (cal/g)	Young's Modulus kg/cm ²
Na 68	+	<0.1	347	453	13.3	1.15x10 ³
Na 72	+	<0.1	340	452	12.8	1.13x10 ³
Na 59	+	<0.1	342	452	13.5	1.31x10 ³
Na 40	+	<0.1	340	451	13.1	1.28x10 ³
Na 22	+	<0.1	345	454	13.8	1.24x10 ³
P(E/5.4MMA)	+	<0.1	340	454	13.8	0.86x10 ³

a) Heat of crystallization for T₂ - Nylon phase

tensile tests indicated again that the initial modulus was controlled by the N6 major component with no significant effect incurred by ionizing the P(E/5.4MAA).

Unlike P(E/MAA) and the ester, amide and imide derivatives, these neutralized copolymers are not as likely to undergo amidation because of the inherently higher stability of the carboxylate salt in comparison to the amide. However, there is in all cases some unionized, free carboxylic acid that can act as the site for graft formation. It can, therefore, be concluded that only a small amount of grafted structures are responsible for the increased mixing and smaller polyolefin domains when compared to N6/LDPE blends. In the series of N6/P(E/MAA) blends studied by MacKnight and coworkers⁶⁶ it was clear that with increasing MAA content in the copolymer utilized, the morphology demonstrated a decrease in the size of the domains of the polyolefinic component. This decreased domain size was believed to be due to increased grafting, a parameter which is very difficult to analyze independently. Therefore, the results of the partially ionized P(E/5.4MAA) blends with N6 are in contradiction with this conclusion. With fewer free carboxylic acid groups available less grafting should have occurred, and therefore, larger domains of the polyolefin would have been present. This contradiction needs to be addressed.

In all of the blends with high methacryloyl content in the copolymer utilized, very small domains of the polyolefin occur as a result of the compatibilizing action of the graft structures that form. Because of the inherent incompatibility of the two components, such grafting must occur at the interface. It is known that shearing forces in such blending procedures can produce free radicals⁷¹ and in the case of N6/LDPE it has been reported that graft structures can be formed between the two different macroradicals,⁷⁰ but because of the great incompatibility and repulsive nature of such macroradicals, such grafting is low and can be assumed to be constant for all of the P(E/MAA) blends. With the carboxylic acid, ester or amide, graft structures can additionally form by amidation and this leads to the smaller domains. These must necessarily form at the interface also.

Hence, the extent of grafting must be dependent upon the microenvironment at the interface. With LDPE this interaction is essentially repulsive. With P(E/MAA) of varying MAA content this interaction would still be repulsive but the presence of MAA provides a slight polar attraction and the potential for amidation. With higher MAA content, this inherently repulsive interface is less so, and thus, more graft structures occur with a concurrent decrease in domain sizes. With P(E/5.1MAA) ester and amide deriva-

tives and the P(E/5.4MAA) methyl ester derivatives the slight increment of positive interaction would still be present. Thus, a less repulsive interface is in effect and grafting occurs by amidation.

The extent of grafting as evidenced by the morphology and strong Molau test could then be concluded to be dependent upon just the concentration of MAA or a slight decrease in the interfacial repulsion with an increase in MAA content. The former explanation was utilized in the previous report⁶⁶ but the latter more adequately describes the effect seen for the partially neutralized P(E/5.4MAA) blended with N6. In these blends, because of the ionic nature, the polyolefin will demonstrate a lower interfacial repulsion with N6 than LDPE, enabling significant grafting to occur even though the absolute concentration of carboxylic acid units capable of being amidated is lower. The blending process is a dynamic one and within the polyolefin domain, which is well above its melting point, interdomain flow and mixing is sure to occur with a continual flux of acid groups to and from the surface. It is reasonable to assume that the amidation itself is relatively slow in comparison to this flux and therefore the extent of grafting is more dependent upon the relative repulsive nature of the interface. With higher MAA content (or MAA derivative) this interface would be less repulsive.

This theory adequately fits the experimental results of MacKnight and coworkers⁶⁶ and the results obtained here for the derivatives of P(E/5.1MAA) and P(E/5.4MAA). In particular, it is consistent with the data obtained for the partially neutralized P(E/5.4MAA). An important implication of this theory is that only relatively few methacryloyl units be grafted to obtain the strong Molau test and small polyolefin domains. This in itself may be intuitive in that a 100% grafting would be considerably unlikely and experimentally would yield a crosslinked system. However, due to this factor, P(E/MAA) seems to be an ideal polymeric support for a biocide in a N6 blend. If the biocide is bound to P(E/MAA) at the MAA unit, only a fraction would be released by amidation during the blending process. The remainder would remain bonded and be available for a slow release if such a mechanism could be devised. This topic is treated in Chapter 4 with respect to bonding 2-(4-thiazolyl) benzimidazole to P(E/MAA).

Attempted Synthesis of Polyethylene-graft-N6

The general action of graft copolymers or block copolymers as compatibilizers is well established⁷⁶ and the presence of graft structures formed during the blending of N6 and P(E/MAA) or its derivatives has been described. Similar graft structures have been proposed to be formed in other polyolefin-polyamide blends.⁷⁰ Specific polyethylene-

graft-oligomeric N6 have been synthesized by reacting P(E/MAA) with low molecular weight end capped N6 (DP=6.8) and these grafts did show effective compatibilizer activity in a N6/LDPE blend.⁷⁶

Because of the effect of P(E/MAA)-graft-N6 structures on the blend properties, such structures are of interest. The synthesis of the ϵ -caprolactam derivative of P(E/5.1MAA) previously described yields a polymeric N-acyl lactam. N-acyl lactams are known to be very active promoters for the strong base catalyzed polymerization.^{77,78} Hence, it is expected that the polymeric N-acyl lactam would also activate the anionic polymerization of ϵ -caprolactam with the formation of graft copolymers as indicated in Figure 13.

Such polymerizations were performed with two different P(E/N-MACap) synthesized via the P(E/MACl) and ϵ -caprolactam. One had a molar ratio of N-MACap of 5.4% and the second had a ratio of 1.4%. All polymerizations were performed in refluxing xylene as the solvent (135 °C) to effect complete solution of the P(E/5.4NMACap) or P(E/1.4NMACap) and the pertinent experimental data are recorded in Table 16 and Table 17. Because N6 is insoluble in ϵ -caprolactam and xylene, the polymerized product phase separated as expected. Also as expected, this phase separation occurred within minutes of addition of the strong base

FIGURE 13

Attempted Synthesis of PE-graft-N6

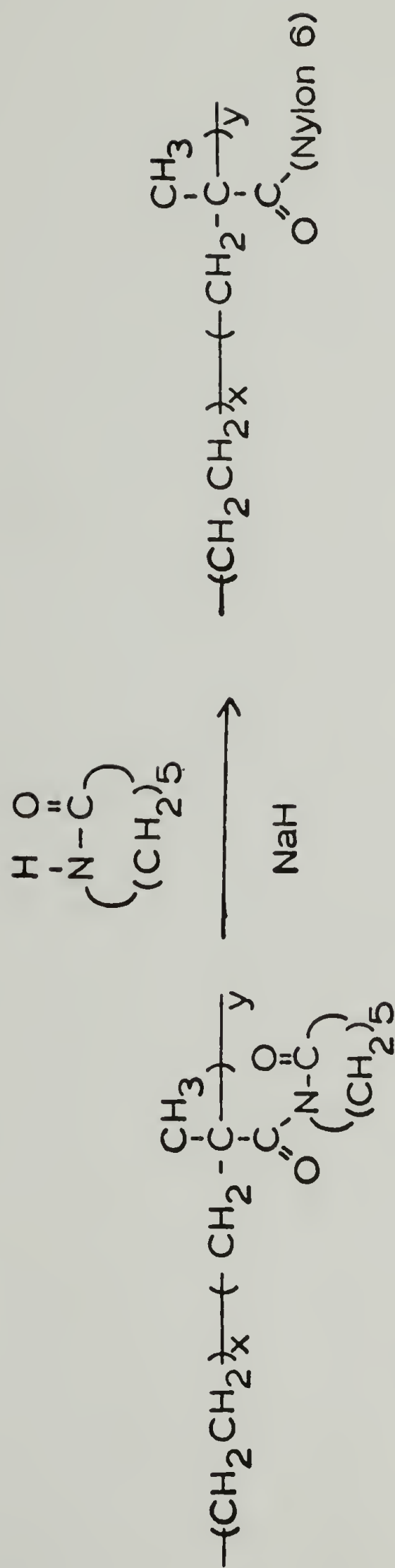


TABLE 16

Stoichiometry of Attempted Graft-N6
Syntheses from P(E/5.4 % N-MACap) (a)

<u>Code</u>	<u>Mass(g) of P(E/N-MACap)</u>	<u>Moles N-MACap</u>	<u>Vol.(ml) Xylene</u>	<u>Yield (g)</u>
G-1	3.75	0.0055	50	13.76
G-2	1.70	0.0024	50	11.65
G-3	0.785	0.0011	50	1.33
G-4	0.388	0.00057	50	0.44
G-5	0.375	0.00055	25	2.39
G-6	0.365	0.00054	10	0.83

a) 12.4g (0.113 moles) 6-caprolactam
0.26g (0.011 moles) NaH
1 hour reaction time

TABLE 17

Stoichiometry for Attempted Graft-N6
 Syntheses from P(E/1.3 % N-MACap) (a)

<u>Code</u>	<u>Mass(g) of P(E/N-MACap)</u>	<u>Moles of N-MACap</u>	<u>Yield(g)</u>
G-7	0.51	2.2×10^{-4}	0.54
G-8	1.26	5.5×10^{-4}	1.35
G-9	2.50	11×10^{-4}	3.30
G-10	5.00	22×10^{-4}	12.44

a) 12.5g (0.113 moles) 6-Caprolactam
 0.26g (0.011 moles) NaH
 30 ml xylene, 1 hour reaction time

(sodium caprolactam) to the solution of ϵ -caprolactam and P(E/NMACap). Because an inhibitory period of several hours is commonly associated with the strong base initiated polymerization without N-acyl lactams or other suitable coinitiator present, it is safe to assume that N6 homopolymer did not form.

The products isolated were found to have the nitrogen content as indicated in Table 18 and from this the weight percent N6 in the product was determined. A summary of the DSC studies is given in Table 18. All products were completely insoluble in formic acid or xylene and no other solvent could be found for the products. In addition, all products were insoluble in an N6 melt and were, therefore, completely useless as compatibilizers. The apparent lack of flow of each of these products in the N6 melt was also determined by examining the flow behavior at 250°C between glass plates. All products were distinctively rubbery at 250 °C indicating a crosslinked network prohibiting flow when the temperature is above the melting point.

The reason for the crosslinking can be adequately explained in terms of the mechanism of base initiated ϵ -caprolactam polymerization. Branching is known to occur, especially at high conversion, by the mechanism depicted in Figure 14. With this system, such branching resulted in a crosslink. Referring back to Tables 16-18, it can be seen

TABLE 18
Analyses of PE-graft-N6

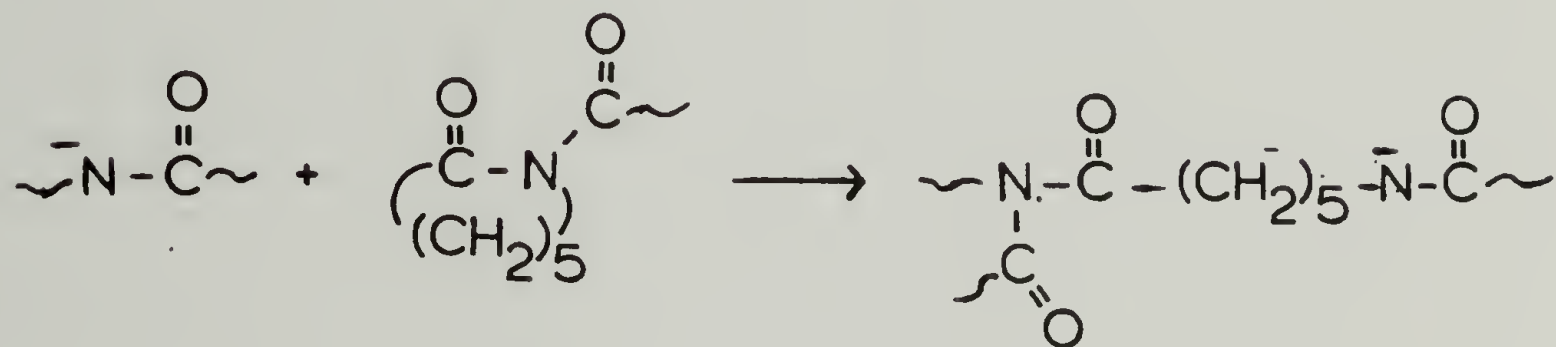
Graft Product	%N ^{a)}	%Nylon 6	Thermal Analysis ^{b)}	
			T ₁	T ₂
G-1	8.90	72	-	469
G-2	10.00	81	-	482
G-3	6.19	50	370	467
G-4	4.84	39	374	-
G-5	10.56	85	-	485
G-6	10.38	84	-	484
G-7	0.58	4.7	375	-
G-8	1.06	8.6	374	-
G-9	3.01	24	373	470
G-10	8.16	66	372	480

a) Elemental Analysis

b) DSC, heating rate = 10°C/minute T₁-polyethylene
portion T₂ nylon 6 Fraction

FIGURE 14

Mechanism of Graft Formation in Base Initiated
Polymerization of ϵ -Caprolactam



that at higher polymeric N-acyl lactam concentration a much higher N6 content was observed. At higher concentration, more chains polymerized rapidly, and as the entire N6 portion began to crystallize, crosslinks had an improved chance of forming because of the high local concentration of end groups, chain amides and base. At lower concentration of the polymeric N-acyl lactam, fewer chains polymerized rapidly and again these N6 chains could aggregate increasing the likelihood of crosslink formation. However, these crosslinks formed at a much lower conversion and forced the polymer to phase separate with a complete stop in polymerization. Thus, lower conversions, or lower N6 contents, were observed as the concentration of polymeric N-acyl lactam decreased.

An attempt was made to solubilize the cross-linked materials by hydrolyzing the N6 portion in acetic acid with 1% water at 100°C. No significant hydrolysis occurred over a 24 hour period, and the products remained rubbery at 250°C. Additionally, there was no change in the fusion endotherms for these samples. Hence, PE-graft-N6 compatibilizer cannot be obtained by this unique procedure.

C H A P T E R I V

INVESTIGATION OF CHEMICALLY BONDING

2(4Th)B TO P(E/MAA)

Introduction

A study of the reactions of 2-(4-thiazolyl) benzimidazole (2(4Th)B) has been conducted in an effort to develop a viable means of chemically bonding it to poly-(ethylene)-co-(methacrylic acid) (P(E/MAA)). The results of this study are reported in this chapter.

An attempt to synthesize a polyaspartimide derivative with a 2(4Th)B substituent by a ring opening reaction was described in Chapter II; however, this failed due to the low nucleophilic character of the substituted benzimidazole. The thermal instabilities of the polyaspartamides make them poor candidates as polymer supports to be blended with N6 and therefore further attempts to bond the 2(4Th)B to it were not made.

P(E/MAA) has the proven thermal stability to undergo blending with N6 and such blends have been studied.⁶⁶ Chemically bonding 2(4Th)B to this polymer, as with other reactions on polymers, must be free of deleterious side reactions which may cause degradation or cross-linking. With P(E/MAA), it has been shown in Chapter III and elsewhere,⁶⁸ that the conversion of P(E/MAA) to poly

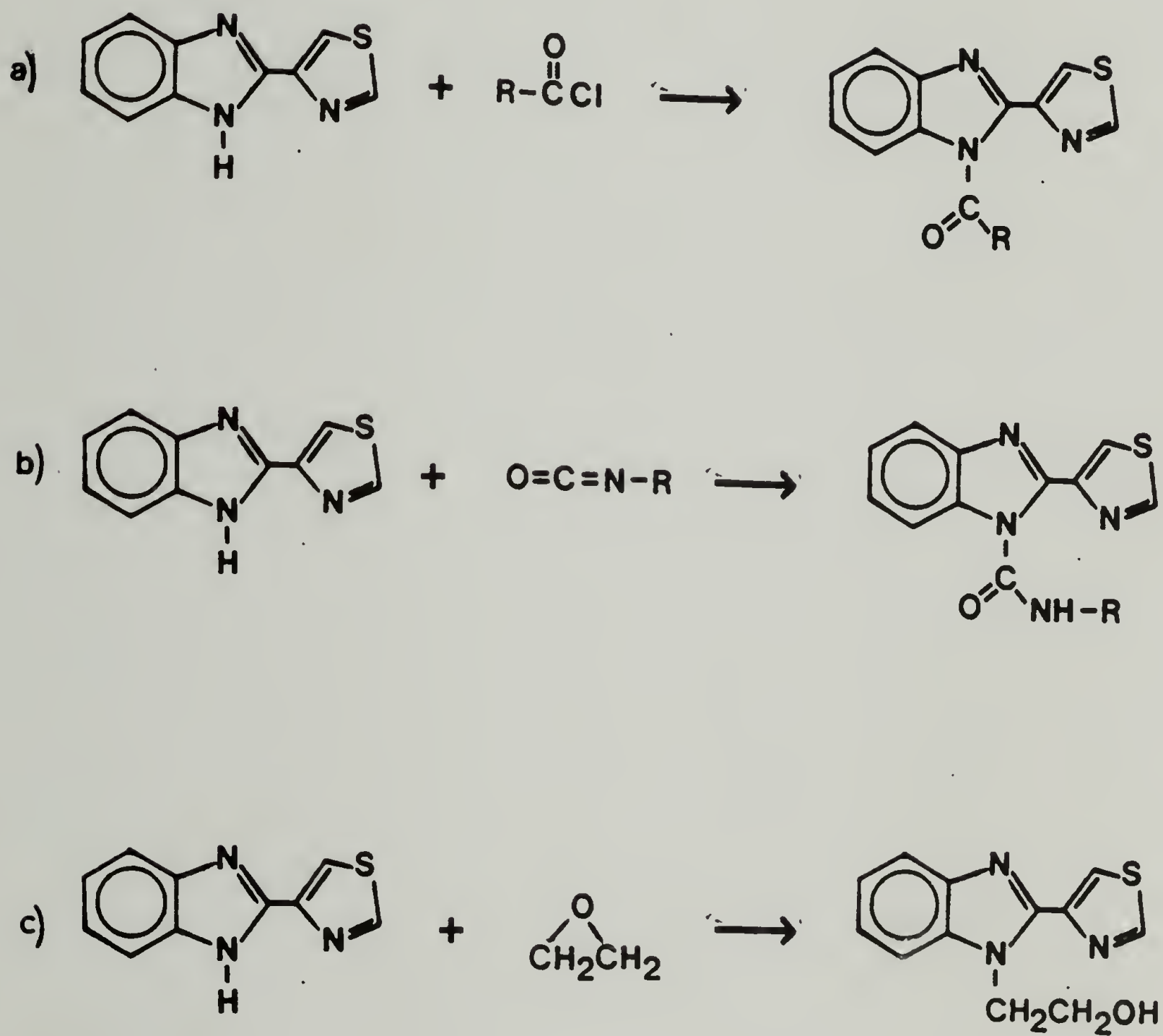
(ethylene)-co-(methacryloyl chloride) (P(E/MACl) is high yielding and clean. Subsequent reaction of P(E/MACl) with methanol or n-hexyl amine yielded ester and amide derivatives free of any apparent side reactions. In addition, these products, when blended with N6, showed properties similar to those of the N6/P(E/MAA) blends. Hence, chemically bonding 2(4Th)B, or a derivative of it, to P(E/MAA) by the P(E/MACl), with formation of an ester or amide link to the polymer, would be the preferred mode.

For reasons discussed in Chapter I, three types of reactions with 2(4Th)B have been studied and are depicted in Figure 15. The first, (Figure 15a) involves acylation at the one position and in this case the R group could be the methacryloyl repeat unit of P(E/MACl). Alternately, a spacer group could be placed between the polymer backbone and the 1-acyl-2(4Th)B. This possibility was also examined.

In the second, a reaction of 2(4Th)B with an isocyanate should yield a 1-carbamoyl derivative (Figure 15b). If a diisocyanate is used, a 1-carbamoyl derivative with an R group possessing a terminal isocyanate functionality could possibly be obtained. Subsequent reaction of this terminal isocyanate with an excess diamine or diol would then form a urea or urethane link and a terminal amine or diol, which could in turn be reacted with

FIGURE 15

Methods of Bonding 2(4Th)B to a Polymer Backbone
to be Examined



P(E/MACl) .

In the third, nucleophilic ring opening of ethylene oxide (Figure 15c) would yield a 1-alkylated benzimidazole which possesses a terminal hydroxy functionality, which should readily react with P(E/MACl) .

Therefore, these three types of reactions have been studied with the emphasis placed on developing a viable means of bonding 2(4Th)B to P(E/MAA) .

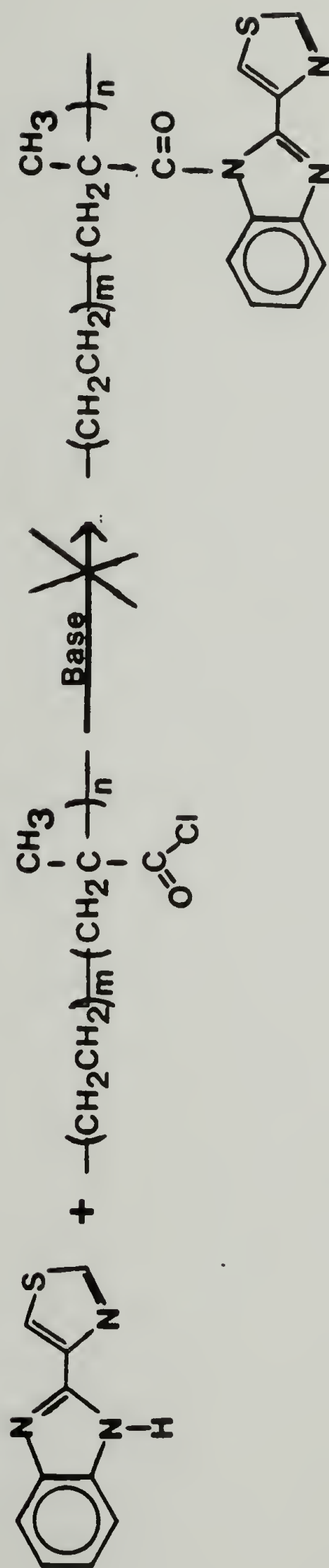
1-Acylation Reactions of 2(4Th)B

Reaction of 2(4Th)B with P(E/MACl)

Figure 16 schematically depicts the attempts made to bond 2(4Th)B directly to P(E/MAA) in the form of an amide bond via P(E/MACl); however, under a variety of conditions no amide bond formation was observed. The conditions involved adding 2(4Th)B to the freshly prepared solution of P(E/MACl) in carbon tetrachloride or xylene, and either triethylamine or excess 2(4Th)B was added as a base catalyst and hydrogen chloride scavenger. Infrared analysis of the reaction in progress showed the carbonyl absorption of the P(E/MACl) at 1800 cm^{-1} unchanged, with no additional carbonyl absorptions typical of a 1-acyl benzimidazole present. In addition, reactions which included triethylamine showed no absorptions in the $2800\text{-}2400\text{ cm}^{-1}$ range typical of triethylamine hydrochloride. Initially, it was believed

FIGURE 16

Attempted Synthesis of Polymer Bound 2(4Th)B as a 1-Acyl Substituent



that the low solubility of 2(4Th)B was the cause for lack of conversion, but repeat runs at higher dilution in which the 2(4Th)B completely dissolved, afforded the same results. Precipitation of the polymer in methanol, followed by extraction of impurities with methanol, resulted in the formation of poly(ethylene)-co-(methyl methacrylate) (P(E/MMA)) as evidenced by elemental analysis and infrared spectroscopy.

From the ready conversion of P(E/MACl) to P(E/MMA) and the lack of amide bond formation with 2(4Th)B it was believed that steric factors may be in play. The effect of steric bulk in addition-elimination reactions of carboxylic acids has been well documented and reviewed.⁷⁹ In the case of the reaction between P(E/MACl) and 2(4Th)B, both reagents are sterically hindered towards a nucleophilic attack at the carbonyl carbon. However, the ready conversion of P(E/MACl) to P(E/MMA) is clear proof that, with the appropriate nucleophile, the methacryloyl carbonyl is not so sterically hindered that it cannot be forced into the four centered intermediate of an addition-elimination pathway.

Steric effects in acylations of benzimidazoles and 2-substituted benzimidazoles have also been documented. Benzimidazoles have routinely been acylated at the one position by a reaction with the appropriate carboxylic

acid chloride in the presence of triethylamine or stronger base catalyst.⁸⁰ Such a benzoylation of benzimidazole in benzene at 25 °C showed a rate constant of $k=1.02 \pm .04 \text{ l m}^{-1} \text{ s}^{-1}$ ⁸¹, but for 2-ethyl benzimidazole a rate constant of $k=0.022 \pm .001 \text{ l m}^{-1} \text{ s}^{-1}$ ⁸² was obtained. Pittman and coworkers⁸³ attempted synthesizing 1-acryloyl-2(4-thiazolyl)benzimidazole by reacting 2(4Th)B and acryloyl chloride in a non-polar solvent with triethylamine catalyst, but this failed. They also attempted to form the amide by using dicyclohexyl carbodiimide and acrylic acid, but 2(4Th)B failed to react with the DCC-acrylic acid adduct. In both cases, a lack of conversion was assumed to be due to the steric bulk of 2(4Th)B, and hence, its low nucleophilic character.

2(4Th)B, in spite of the bulk at the 2 and 9 positions, has been successfully acylated with acetyl chloride and benzoyl chloride at the one position⁸⁴ by first converting it to its sodium salt. Similarly, a 2-aryl benzimidazole was acylated with acetyl chloride by first converting the benzimidazole to its anion.⁸⁵ Pittman therefore reacted 2(4Th)B with sodium hydride and subsequently added acryloyl chloride to obtain 1-acryloyl-2(4Th)B in 16% yield.⁸³ Thus, it appears that prior conversion of 2(4Th)B to its anionic form increases the nucleophilic character of the benzimidazole nitrogen and

thus compensates for the lower activity caused by the steric bulk.

Therefore, this approach was taken in an effort to bond 2(4Th)B to P(E/MAA). Conversion of 2(4Th)B to its sodium salt was effected in polar solvents such as dimethyl formamide or dimethyl acetamide/toluene. Using non-polar solvents only was not effective due to the low solubility of 2(4Th)B and its salt. The use of polar solvents, created a problem with the attempted reaction of sodium-2(4Th)B and P(E/MACl) in that P(E/MACl) is completely insoluble in such solvents. Whether the sodium 2(4Th)B solution was added to the P(E/MACl) solution or vice versa, the polymer precipitated. In all cases, the polymer product isolated showed no nitrogen content by elemental analysis and therefore even a small, partial conversion to the amide did not occur.

Theoretically, conditions could be adjusted so that the sodium 2(4Th)B could be sufficiently solubilized in a non-polar solvent by the use of an appropriate phase transfer catalyst, such as a crown ether.⁸⁶ Once solubilized, the anion could potentially undergo an addition-elimination reaction with a carboxylic acid chloride, such as P(E/MACl), if the steric hindrance was not too great. The important factor is that the anion and acid chloride be co-dissolved so heterogeneity cannot be cited as the

cause for lack of conversion.

Hence, a study of model acylations of 2(4Th)B with low molecular weight analogs was conducted to determine the likelihood of a successful reaction of the salt of 2(4Th)B with P(E/MACl), and under what conditions conversion would occur. Acetyl chloride and pivalyl chloride were the low molecular weight analogs. Acetyl chloride was chosen for its lack of steric bulk, whereas pivalyl chloride was chosen because of its structural similarity to the sterically hindered methacryloyl chloride repeat unit.

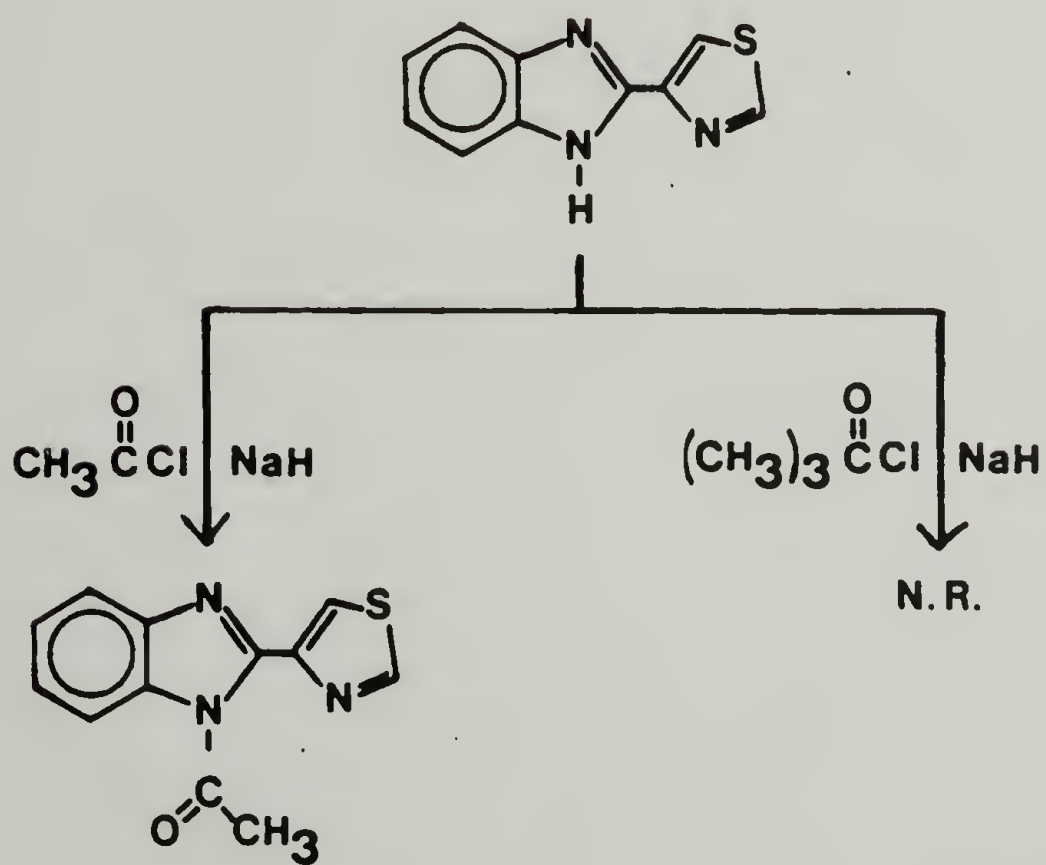
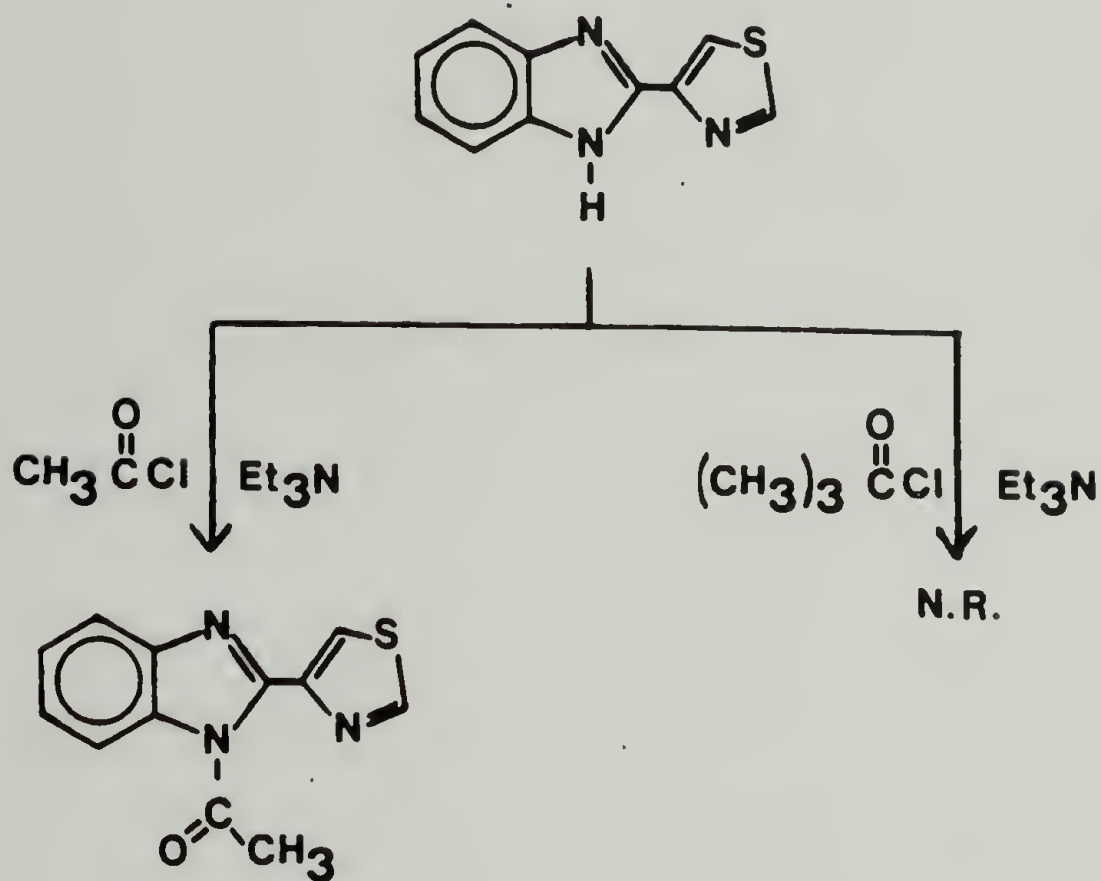
Model acylations of 2(4Th)B

The model acylation reactions discussed in this section are schematically depicted in Figure 17 with the success or failure indicated. Prior to a study of acylation attempts with the anionic form of 2(4Th)B, a study was conducted using conditions similar to those utilized initially for the reaction of 2(4Th)B and P(E/MACl).

1-Acetyl-2-(4-thiazolyl)benzimidazole (1-Ac-2(4Th)B) was successfully synthesized by adding acetyl chloride to a heterogeneous mixture of 2(4Th)B and triethylamine in benzene and stirring for 48 hours at room temperature. 2(4Th)B is very sparingly soluble in benzene (0.23%),⁸⁷ however it appears that enough dissolved and reacted with acetyl chloride, forming the more soluble 1-Ac-2(4Th)B. The hydrogen chloride by-product was con-

FIGURE 17

Model Acylations of 2(4Th)B



sumed by the triethylamine present in solution, forming an insoluble salt which was isolated by precipitation. The crude 1-Ac-2(4Th)B, 57%, was recrystallized from a 50/50 cyclohexane/benzene solution to give a final yield of 28%.

An identically run reaction of 2(4Th)B and pivalyl chloride in benzene with triethylamine catalyst was made. However, in this case, near quantitative recovery of 2(4Th)B was obtained. Also, there was no indication of triethylamine hydrochloride formation. A repeat at higher temperature (80°C), in which case the 2(4Th)B was completely dissolved, gave the same results. Considering that the same procedure afforded 1-Ac-2(4Th)B, it can therefore be concluded that the lack of formation of the 1-Pivalyl derivative is a result of the greater steric bulk bonded to the carbonyl of pivalyl chloride.

The conditions used for the synthesis of 1-acetyl-2(4Th)B are very similar to those used initially for the attempted reaction of 2(4Th)B with P(E/MACl). The successful synthesis of 1-Ac-2(4Th)B under these mild conditions verifies that 2(4Th)B has the nucleophilic character to undergo an addition-elimination reaction, provided the steric constraints at the acid carbonyl are minimal. Thus, the failure to isolate 1-pivalyl-2(4Th)B, supports the belief that the failure of the 2(4Th)B/

P(E/MACl) reaction under such mild conditions is a result of steric hindrance.

A failure to isolate the 1-pivalyl-2(4Th)B is, of course, not conclusive proof that the amide bond is not formed considering the hydrolytic instability of 1-acyl benzimidazoles.⁸⁸ The reaction of 2(4Th)B with pivalyl chloride in benzene at room temperature with triethyl amine catalyst was repeated with periodic monitoring of the heterogenous solution by infrared spectroscopy. Over a 48 hour period no change in the carbonyl absorption of pivalyl chloride at 1810 cm^{-1} was observed.

An additional study of the acylation of 2(4Th)B with acetyl chloride and pivalyl chloride and triethylamine catalyst in DMSO was conducted. The reagent concentrations were 0.17M for 2(4Th)B, 0.2M in triethylamine and 0.2M in acetyl chloride or pivalyl chloride. Infrared analysis of the acetyl chloride/2(4Th)B solution after two hours indicated a conversion to the amide by the near complete disappearance of the carbonyl absorption at 1810 cm^{-1} and the appearance of a strong absorption at 1735 cm^{-1} , typical of a carbonyl C=O stretch of a 1-acyl benzimidazole. Infrared analysis of the pivalyl chloride/2(4Th)B reaction solution over the next 20 hours showed no such conversion to the amide bond. Only a weak absorption at 1700 cm^{-1} appeared and this was attributed to a slight

hydrolysis of pivalyl chloride because of residual moisture in the DMSO.

Thus, in benzene and DMSO, 2(4Th)B failed to react with pivalyl chloride, while with acetyl chloride, amide bond formation readily occurred. The bulky t-butyl group of pivalyl chloride as opposed to the methyl group of acetyl chloride provided too great a steric hindrance to nucleophilic substitution of the chlorine atom by 2(4Th)B. This argument can be made for the attempted reactions of 2(4Th)B with P(E/MACl). As discussed previously, there is ample evidence that conversion of 2(4Th)B to its anionic form increases its nucleophilic character. Thus, acylation attempts using the lithium salt of 2(4Th)B were conducted. Also, as stated before, if amide bond formation occurs when acylated with pivalyl chloride, then it is just a matter of choosing proper solvent and catalyst for a successful amidation of P(E/MACl).

A series of attempted acylations with acetyl chloride of the lithium salt of 2(4Th)B in solvents of intermediate polarity (tetrahydrofuran or glyme) unexpectedly gave high recovery (75-90%) of unreacted 2(4Th)B or its lithium salt. Addition of acetyl chloride to the solubilized lithium salt of 2(4Th)B would be expected to yield the 1-acetyl-2(4Th)B, but none was isolated. One possible explanation for the apparent lack of formation of

2(4Th)B could be due to a tight ion pair formation of the lithium-2(4Th)B in a weakly polar solvent. Such a tight ion pair formation is known to lead to a slower rate of nucleophilic substitution.

Hence, an attempt to synthesize the 1-acetyl-2(4Th)B by addition of acetyl chloride to a DMSO solution of the lithium-2(4Th)B was made. 2(4Th)B was dissolved in DMSO (0.17M) and converted to its lithium salt by the slow addition of n-butyl lithium. Acetyl chloride was added slowly to a final concentration of 0.20M. After 2 hours, infrared analysis showed only a weak absorption at 1810 cm^{-1} , but a strong carbonyl absorption indicative of a 1-acyl benzimidazole at 1735 cm^{-1} . Thus, 1-acetyl-2(4Th)B is readily synthesized from the lithium-2(4Th)B in DMSO, as opposed to using tetrahydrofuran or glyme as a solvent, because of the greater capability of DMSO to separate the ion pairs. This procedure was therefore utilized in studying the possibility of synthesizing 1-pivalyl-2(4Th)B by addition of pivalyl chloride to a DMSO solution of lithium-2(4Th)B. The concentrations of the reagents in DMSO were identical to those above. In this case, periodic infrared analysis of the reaction solution over the next 24 hours, showed the strong carbonyl absorption of pivalyl chloride unchanged. No carbonyl absorption typical of a 1-acyl benzimidazole was observed.

The inability to synthesize 1-pivalyl-2(4Th)B under the most advantageous conditions - from the lithium salt in a polar, strongly ion solvating solvent such as DMSO - can only be explained in terms of a strong steric hindrance to the formation of the tetrahedral intermediate in the addition-elimination pathway. Because of the structural similarity of pivalyl chloride to P(E/MACl), this same steric hindrance will be in effect. Hence, it is believed that there is no possibility of obtaining any conversion to a realistic time frame by attempting to react 2(4Th)B with P(E/MACl) under any conditions.

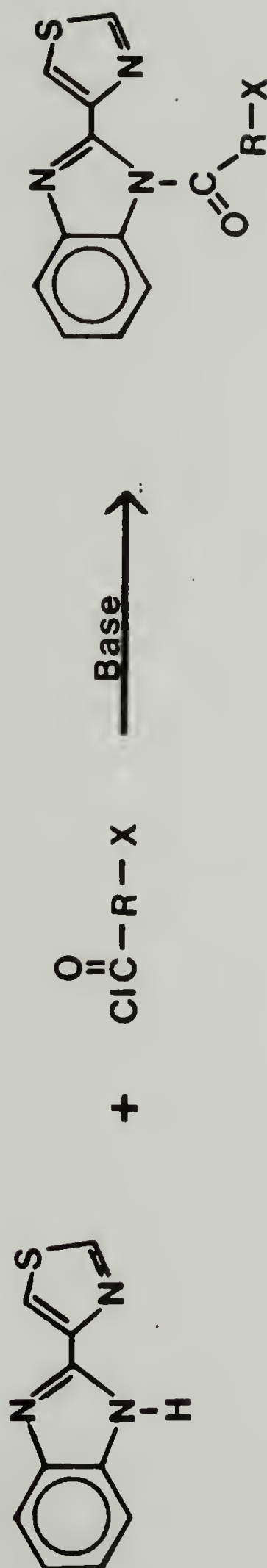
For this reason a polymer functionalized with 2(4Th)B in the form of a 1-acyl-2(4Th)B substituent (Figure 15a) is not possible by a direct amidation of the methacrylic acid repeat unit of P(E/MAA). To do so, therefore, requires a spacer group between the methacrylyl repeat unit and the 1-acyl-2(4Th)B functionality. This approach has been attempted.

Reactions of 2(4Th)B with adipyl chloride or terephthalyl chloride

On considering the low nucleophilic character of 2(4Th)B, it was decided to attempt forming a 1-acyl spacer by a reaction with an acid chloride, which if appropriately functionalized could then be chemically bound to P(E/MAA) (Figure 18). Obviously, the appropriate functionality

FIGURE 18

Model of an Acyl Spacer Bonded to 2(4Th)B at the 1-Position



R = Alkyl or Aryl

(X in Figure 18) must not react with the acid chloride group and for this reason, reactions of 2(4Th)B with adipyl chloride or terephthalyl chloride were studied. In this case, X of Figure 18 would be an acid chloride also. If the desired 1-acyl derivative of 2(4Th)B is isolable, it could then be synthetically manipulated to obtain a terminal hydroxy or amine group capable of reacting with P(E/MACl).

Thus, 2(4Th)B was reacted with a large excess of adipyl chloride in the presence of triethylamine. A 15 molar excess of the diacid chloride was utilized to minimize bis-amide formation. In experiments using glyme, toluene or benzene, the reaction solutions were heterogeneous due to the low solubility of 2(4Th)B and triethylamine hydrochloride by-product. After 48 hours a filtration afforded triethylamine hydrochloride in both experiments, however infrared analysis indicated that there were no apparent absorptions typical of 2(4Th)B in this precipitate. The complete solubilization of 2(4Th)B can only be explained by its conversion to a more soluble amide derivative.

Attempts to isolate this possible adipyl chloride derivative of 2(4Th)B failed. The solution containing the suspected derivative was placed under reduced pressure and most of the solvents were removed. This did not induce

crystalization so cyclohexane was added. After several days, still no precipitate formed.

It was believed that the excess of adipyl chloride used was solubilizing the derivative and therefore its removal would be necessary. The first attempt to do so utilized the benzene solution containing the suspected derivative. The benzene was removed under a vacuum and the solution remaining was heated gently to distill adipyl chloride from the mixture. Several drops of adipyl chloride were thus collected, but the residue soon discolored and charred.

An attempt was also made to extract excess adipyl chloride from a toluene solution of the suspected derivative. The toluene solution was washed several times with aqueous potassium carbonate. A precipitate formed between layers and was identified as 2(4Th)B. Acidification and partial evaporation of the aqueous layer afforded adipic acid crystals only. Drying and evaporation of the toluene extract yielded 2(4Th)B again with no carbonyl containing impurities. It is suspected, given the hydrolytic instability of 1-acyl-benzimidazoles,⁸⁸ that the 1-adipyl-2(4Th)B derivative was hydrolyzed during the extraction and thus only 2(4Th)B and adipic acid were isolated. This, however, is not conclusive because the formation of the 1-adipyl-2(4Th)B has not been confirmed.

Because of the inability to isolate the 1-adipyl-2(4Th)B derivative, an attempt at reacting 2(4Th)B with terephthalyl chloride was made. Because of its aromatic structure it was expected that the amide adduct would be more prone to crystallize than the adipyl product. By using toluene as the solvent, triethylamine hydrochloride was isolated as before and in addition a 10% recovery of 2(4Th)B was noted. Attempts to crystallize the 2(4Th)B adduct (or 2(4Th)B if no conversion occurred) by cooling failed.

By using glyme as the solvent, triethylamine hydrochloride was again isolated with no recovery of 2(4Th)B by filtration. The glyme was then removed under vacuum, leaving a white residue. Addition of cyclohexane to the residue and refluxing was expected to dissolve the excess terephthalyl chloride only and leave unreacted 2(4Th)B and/or its adduct undissolved. This treatment did yield a small white residue, but proton NMR indicated no thiazolyl protons and only a complex pattern of aromatic proton absorptions. Infrared analysis showed carbonyl absorptions at 1790 cm^{-1} and 1735 cm^{-1} which are typical for aromatic acid chlorides ($1780\text{-}1800\text{ cm}^{-1}$) and aromatic anhydrides ($1720\text{-}1740\text{ cm}^{-1}$ and $1780\text{-}1800\text{ cm}^{-1}$). This product was, therefore, considered to be oligomeric terephthalyl anhydride as a result of a small amount of hydrolysis during handling.

Again neither 2(4Th)B nor its terephthalyl derivative were isolated. Because of the extremely low solubility of 2(4Th)B in cyclohexane, this treatment should have yielded some unless it was converted in a high percentage to the amide derivative. Coupled with the triethylamine hydrochloride formation, this would indirectly indicate that amidation has occurred. However, it was not possible to selectively crystallize the terephthalyl derivative and therefore conclusive proof of its formation was not obtained.

Reaction of 2(4Th)B with succinic anhydride

An alternate approach to obtaining such a dicarboxylic acid derivative of 2(4Th)B is by reacting it with an acid anhydride. By doing so, the difficulty of isolating the desired product from the excess diacid chloride can be eliminated. Thus, a reaction between 2(4Th)B and succinic anhydride was attempted by refluxing the two in toluene, however, no conversion was obtained and both the anhydride and 2(4Th)B were reisolated.

Concluding remarks

At this time, a polymeric derivative of 2(4Th)B with the biocide attached in the form of a 1-acyl derivative has not been attained. Attempting to bond 2(4Th)B directly to the methacryloyl repeat unit of P(E/MAA) was

unsuccessful and model acylation reactions indicated that it could not be successful because of steric hindrance. Hence, an approach utilizing a spacer unit between the polymer backbone and 2(4Th)B was imagined and attempts described above to construct such a unit were not successful. These attempts, however, do not support a conclusion that it cannot be done, but that an alternate approach would be advisable.

Considering the low nucleophilic character of 2(4Th)B, it is believed that the best method of synthesizing a polymerically bound l-acyl derivative is via an amidation with an acid chloride. Given the difficulty of synthesizing and isolating a suitably functionalized l-acyl spacer of 2(4Th)B, a preferred method may be to use a polymeric acid chloride with the acid chloride suitably removed from the backbone. That is, construct the spacer functionality from the polymer backbone such that 2(4Th)B can be reacted with a less sterically hindered polymeric acid chloride. This approach has not been attempted but is presented for consideration in future research efforts.

Reactions of 2(4Th)B with Isocyanates

Introduction

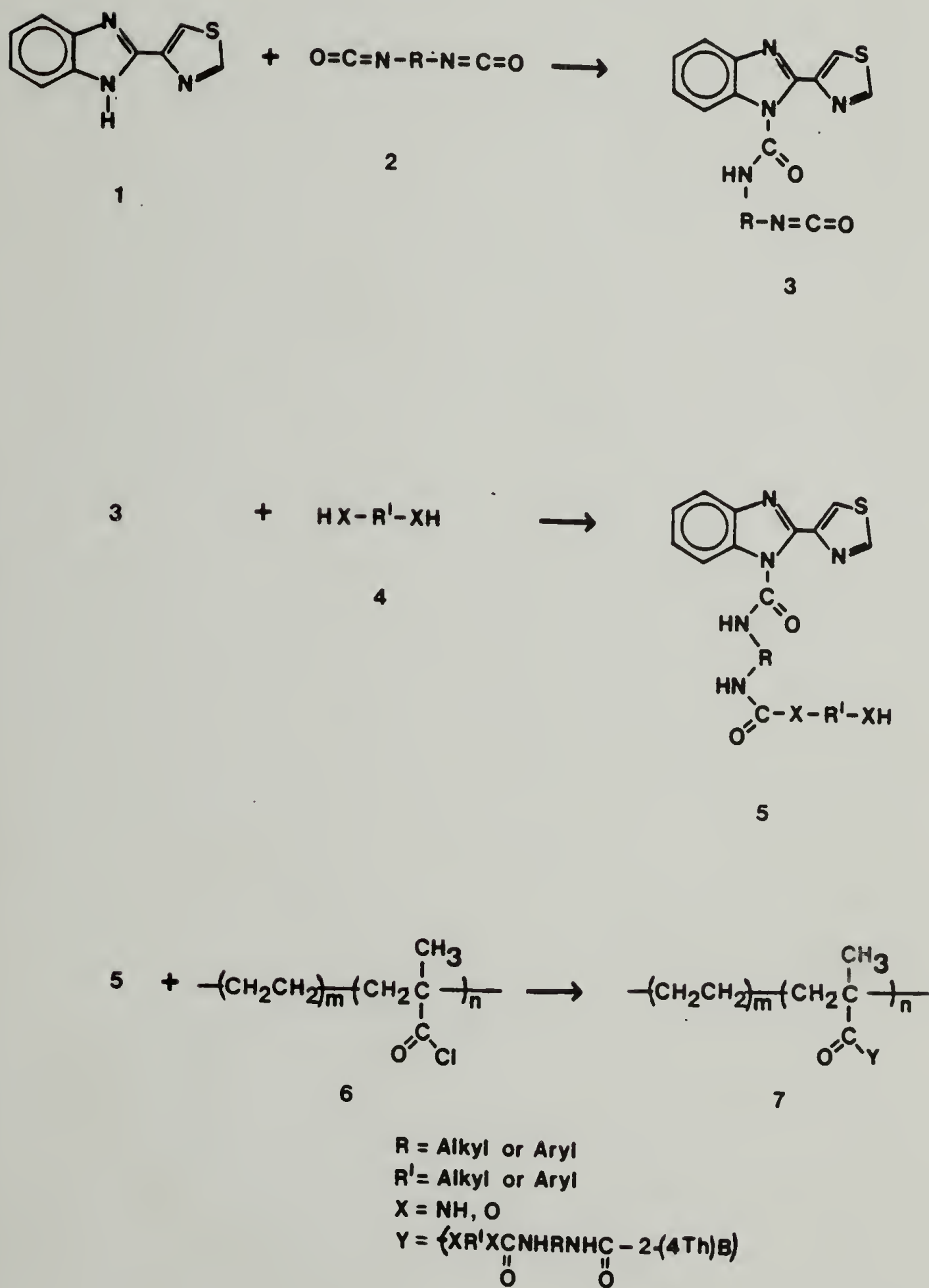
As stated earlier, it is one of the objectives of this thesis to study the potential of bonding 2(4Th)B to

P(E/MAA) such that it is chemically bound in the form of a 1-carbamoyl substituent of 2(4Th)B. 1-phenylcarbamoyl benzimidazole has been reported by Hegarty and coworkers⁸⁹ to undergo a rapid hydrolysis by zwitterion mechanism. A polymer bound 1-carbamoyl-2(4Th)B would, therefore, be expected to be a rather labile binding of 2(4Th)B, and thus, a mechanism for its release is provided by such a functionality.

The approach to achieve such a functionalized P(E/MAA) is depicted in Figure 19. In the first step, reaction of 2(4Th)B with a diisocyanate (toluene diisocyanate was used) should yield the desired 1-carbamoyl substituted 2(4Th)B with a terminal isocyanate function. (Structure 3) Atakuziev and coworkers⁹⁰ reported a similar synthetic reaction of 2-methylcarbamate-benzimidazole with diisocyanatohexane, toluene diisocyanate, or methylene bis-4-phenyl isocyanate with high yields of the isocyanate substituted alkyl or aryl 1-carbamoyl 2-methylcarbamate benzimidazole. Atakuziev and coworkers⁹⁰ also reported that methanol added to the isocyanate function of 1-(6-isocyanatohexyl carbamoyl)-2-methylcarbamate benzimidazole (product of reaction with diisocyanatohexane) to give a terminal urethane product. Thus, a similar addition of a bis-nucleophile to structure 3 can conceivably yield structure 5. In this case 2-hydroxy-1-propylamine is

FIGURE 19

Route to a Polymer Bound 2(4Th)B as a
1-Carbamoyl Substituent



chosen as the bis-nucleophile. Because a primary amine is much more reactive towards addition to an isocyanate than a secondary alcohol,⁹¹ the urea adduct is expected to predominate. This in turn leads to a terminal hydroxy functionalized spacer which could be reacted with P(E/MACl) to obtain an ester link to P(E/MAA).

This synthetic scheme was taken, however, it has not been achieved because of the extreme reactivity of compound 3. The synthesis of structure 3 and the cause for the inability to accomplish the second step, and thus the third, depicted in Figure 19 are detailed below.

Reaction of 2(4Th)B with phenyl isocyanate

Prior to an attempt to synthesize compound 3 in Figure 19, an attempt was made to synthesize 1-(phenyl-carbamoyl)-2(4Th)B by reacting phenyl isocyanate with 2(4Th)B, for the purpose of gaining experience in the synthetic approach and handling of the product. Unexpectedly, this compound could not be isolated. Addition of phenyl isocyanate to a heterogenous mixture of 2(4Th)B in benzene at room temperature, (2(4Th)B incompletely dissolved) or to a refluxing solution of 2(4Th)B in glyme, (2(4Th)B completely dissolved) yielded 2(4Th)B only in high percent recovery.

Phenyl isocyanate was added to a solution of 2(4Th)B in DMSO (0.10M) and the mixture monitored periodi-

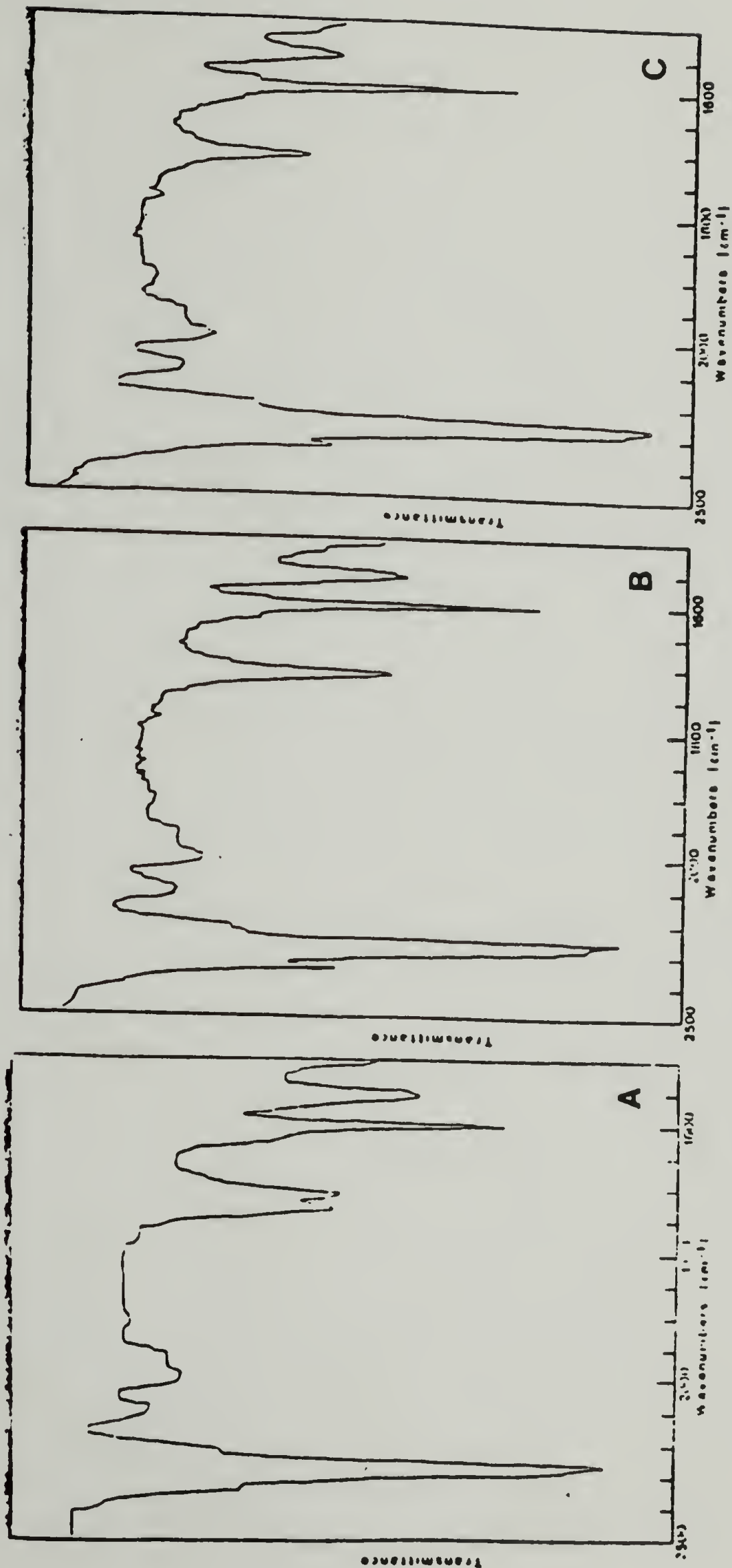
cally over the next 40 hours by infrared spectroscopy. A weak absorption at 1730 cm^{-1} which could be attributed to the carbamoyl carbonyl, was observed after 2 hours but it did not change with time. (Figure 20a) In addition, a weak absorption at 1710 cm^{-1} appears and this is believed to be due to a slight degree of trimerization by comparison with the infrared spectrum of the phenyl isocyanate trimer.⁹²

A second analysis using a DMSO solution containing 2(4Th)B (0.10M) and triethylamine (0.10M) as a catalyst⁹³ showed the same weak absorption at 1730 cm^{-1} and a stronger absorption at 1710 cm^{-1} attributed to the trimer for which its formation is known to be catalyzed by triethylamine.⁹³ The IR spectrum of this mixture and that of phenyl isocyanate alone in DMSO (0.1M) for comparison, are depicted in Figure 20. In all cases the isocyanate absorption remained strong even after 40 hours.

The lack of urea formation in benzene solution was thought to be due to steric hindrance, since similar procedures routinely yield 1-carbamoyl benzimidazoles^{89,94} for less sterically hindered benzimidazoles. Ortho-substituted aromatic reactants are known to be sterically hindered to addition as evidence by decreased rates of addition.⁹⁵ The infrared analysis studies of the reaction in DMSO appear to indicate that some conversion is occurring, as evidenced by

FIGURE 20

Analysis of Phenyl Isocyanate Reactions of DMSO by IR Spectroscopy



A 0.1 M Phenyl Isocyanate + 0.1 M 2(4Th)B

B 0.1 M Phenyl Isocyanate + 0.1 M Et₃N

C 0.1 M Phenyl Isocyanate

the initial absorption at 1730 cm^{-1} . However, this peak does not increase with time; nor does the isocyanate peak decrease, as would be expected for a sterically hindered slow addition. It more readily fits the pattern of an equilibrium mixture in which the 1-phenylcarbamoyl-2(4Th)B initially forms but can subsequently dissociate back to phenyl isocyanate and 2(4Th)B. Using triethylamine apparently had no effect except to catalyze trimer formation which is known to form an equilibrium mixture of the isocyanate and its trimer in solution.⁹¹

Whether 2(4Th)B and phenyl isocyanate form a true equilibrium mixture of the reagents and the adduct was not thoroughly examined, but the evidence indicates that a stable, isolable 1-carbamoyl-2(4Th)B derivative may be difficult if not impossible to obtain.

Reaction of 2(4Th)B with toluene diisocyanate

Toluene diisocyanate is known to be more reactive than phenyl isocyanate because of the electron withdrawing nature of the second isocyanate function⁹⁶ and this higher reactivity may be enough to overcome the steric hindrance of addition by 2(4Th)B encountered with phenyl isocyanate. The sample of toluene diisocyanate used in the reactions to follow was technical grade TDI, which contains 80% of the 2,4-isomer and 20% of the 2,6-isomer. Because of the known decreases in rate as a result of steric effects of

aromatic isocyanates with ortho substituents compared to isocyanates with meta and para substituents⁹⁵ and the obvious steric hindrance of 2(4Th)B, any addition to isocyanate is expected to occur at the 4-position. Sole addition to the 4-position will be assumed, although it will not be strictly proven. Any addition to an isocyanate function ortho to the methyl group would none the less have no effect on the second step depicted in Figure 19.

The reaction of 2(4Th)B with toluene diisocyanate was attempted several times by adding a large excess of TDI to a slurried mixture of 2(4Th)B in non-polar solvents and in one case 2(4Th)B was slurried in TDI only. In all cases products were isolated by filtration and washed with benzene or cyclohexane. One synthetic approach utilized gently refluxing glyme as the solvent to completely solubilize the 2(4Th)B and after several hours of reaction the solution was allowed to cool. 2(4Th)B subsequently crystallized out. (46% recovery) After filtration, a 1/3 volume of cyclohexane was added to the glyme filtrate causing precipitation of the TDI/2(4Th)B adduct.

Infrared analysis of all products showed an isocyanate absorption at 2290cm^{-1} and a carbonyl absorption at 1720cm^{-1} . In addition, the fine structure in the $900\text{-}700\text{cm}^{-1}$ region clearly indicates a change from that of 2(4Th)B, but with most of the reactions run under

heterogenous conditions the spectral features appear to have peaks superimposed on the absorptions of 2(4Th)B. The product isolated from the glyme filtrate showed the greatest difference from 2(4Th)B. Comparison of these spectra, therefore, appeared to indicate partial conversion to the TDI/2(4Th)B adduct, but all, with the possible exception of the glyme product, showed signs of 2(4Th)B impurity.

Elemental analysis of these products supported this hypothesis. These are collected in Table 19. As can be seen, product 2-20 is within acceptable limits of the calculated value of the TDI/2(4Th)B adduct. All others show carbon content intermediate in value and therefore are probably mixtures.

To determine the percent composition of the above products and to verify the purity of the adduct obtained from the glyme solution, all products were analyzed by ^1H -NMR. By measuring the area of the thiazole protons in the $\delta=8.0-9.5$ ppm region and comparing this with the areas of the absorption of the tolyl methyl protons - expected to be near $\delta = 2.0$ ppm - absolute composition can be determined.

Doing so with the adduct from the glyme solution, (2-20) the relative area for thiazolyl protons at $\delta = 9.30$ ppm, 9.18 ppm, 8.49 ppm, and 8.41 ppm was equal

TABLE 19
 Elemental Analysis of 2(4Th)B and TDI
 Reaction Products

<u>Sample</u>	<u>%C</u>	<u>%H</u>	<u>%N</u>
1-93 ^{a)}	60.29	3.48	18.27
2-12 ^{b)}	60.20	3.55	19.38
2-21 ^{c)}	60.03	3.44	18.33
2.20 ^{d)}	60.73	3.52	18.50
2(4Th)B ^{e)}	59.63	3.50	20.95
Adduct ^{e)}	60.79	3.49	18.66

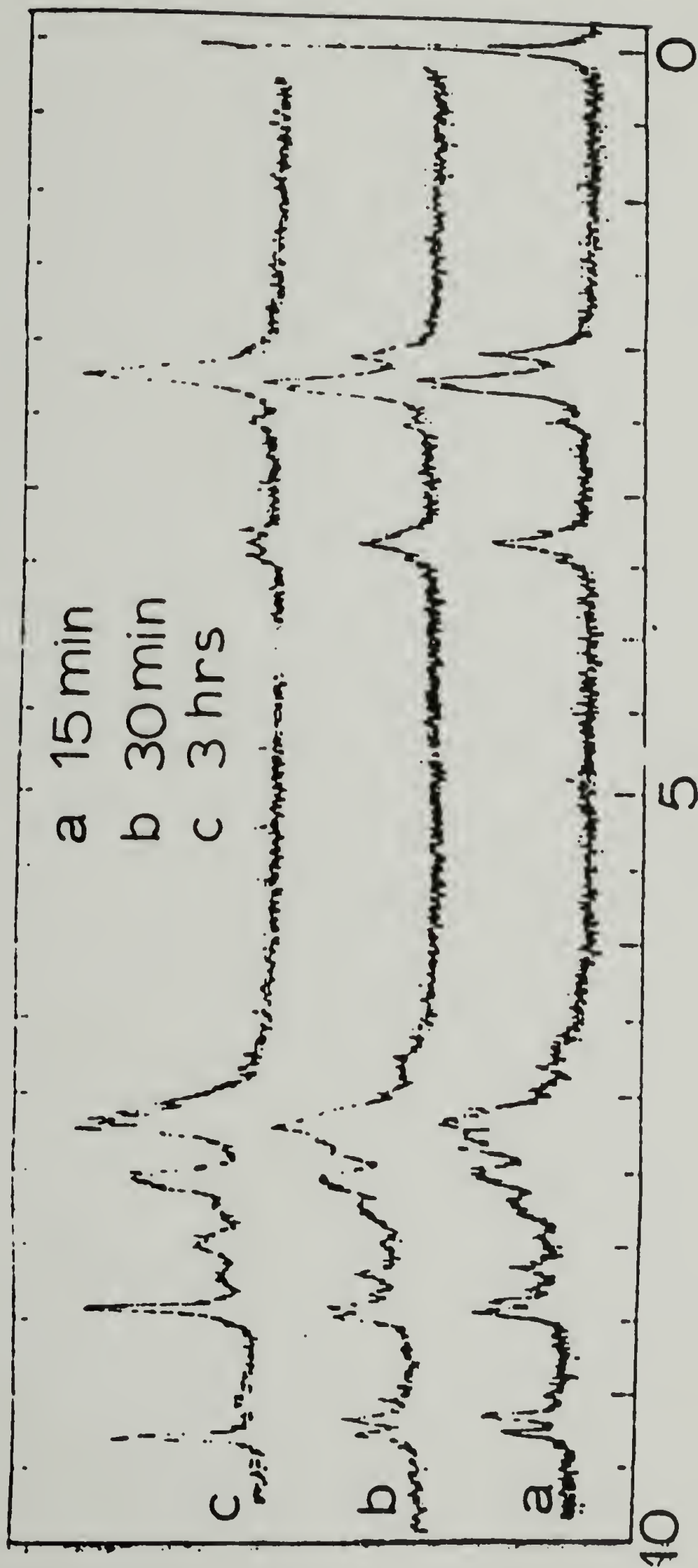
- a) 0.50g 2(4Th)B, 10 ml TDI, 200 ml benzene, 48 hours
 b) 0.50g 2(4Th)B, 15 ml TDI, 200 ml toluene, 50 hours
 c) 2.00g 2(4Th)B, 50 ml TDI, no solvent, 48 hours
 d) 5.00g 2(4Th)B, 75 ml TDI, 200 ml glyme, 5 hours, 80°C
 e) Theoretical Values

to 2. The area of the methyl protons from $\delta = 2.40$ ppm to 2.00 ppm was equal to 3. The thiazole protons were clearly identified by their doublet formation due to long range coupling ($J = 0.9$ Hz) with each other.⁹⁷ The two outer absorptions at $\delta = 9.30$ ppm and 8.41 ppm were assigned to 2(4Th)B, which shows these identical chemical shifts. The inner absorptions at $\delta = 9.18$ ppm and 8.49 ppm were attributed to the TDI/2(4Th)B adduct. Such an assignment would indicate that a mixture of 2(4Th)B and its TDI adduct were present, however, the tolyl methyl protons had a total area greater than 3/2 times the area of the inner thiazolyl proton absorptions, as would be expected for the TDI/2(4Th)B adduct. (See Figure 19, Structure 3) However, its area was 3/2 times the area of all the thiazolyl protons.

Running the spectrum again, curiously showed a change in the thiazolyl proton absorptions. The chemical shifts had not changed, but the peak heights and thus the area of the inner thiazolyl proton shifts decreased. (Figure 21) It can be seen in Figure 21 that at three hours after the TDI/2(4Th)B adduct obtained from the glyme solution was added to the deuterated DMSO solvent for NMR analysis, the inner thiazolyl protons had drastically decreased in size. The tolyl methyl protons had shifted to a final chemical shift of 2.37 ppm. After 3

FIGURE 21

^1H -NMR of TDI/2(4Th)B Adduct



Chem. shift ppm

hours no further change was observed. Apparently the TDI/2(4Th)B adduct dissociated back to TDI and 2(4Th)B.

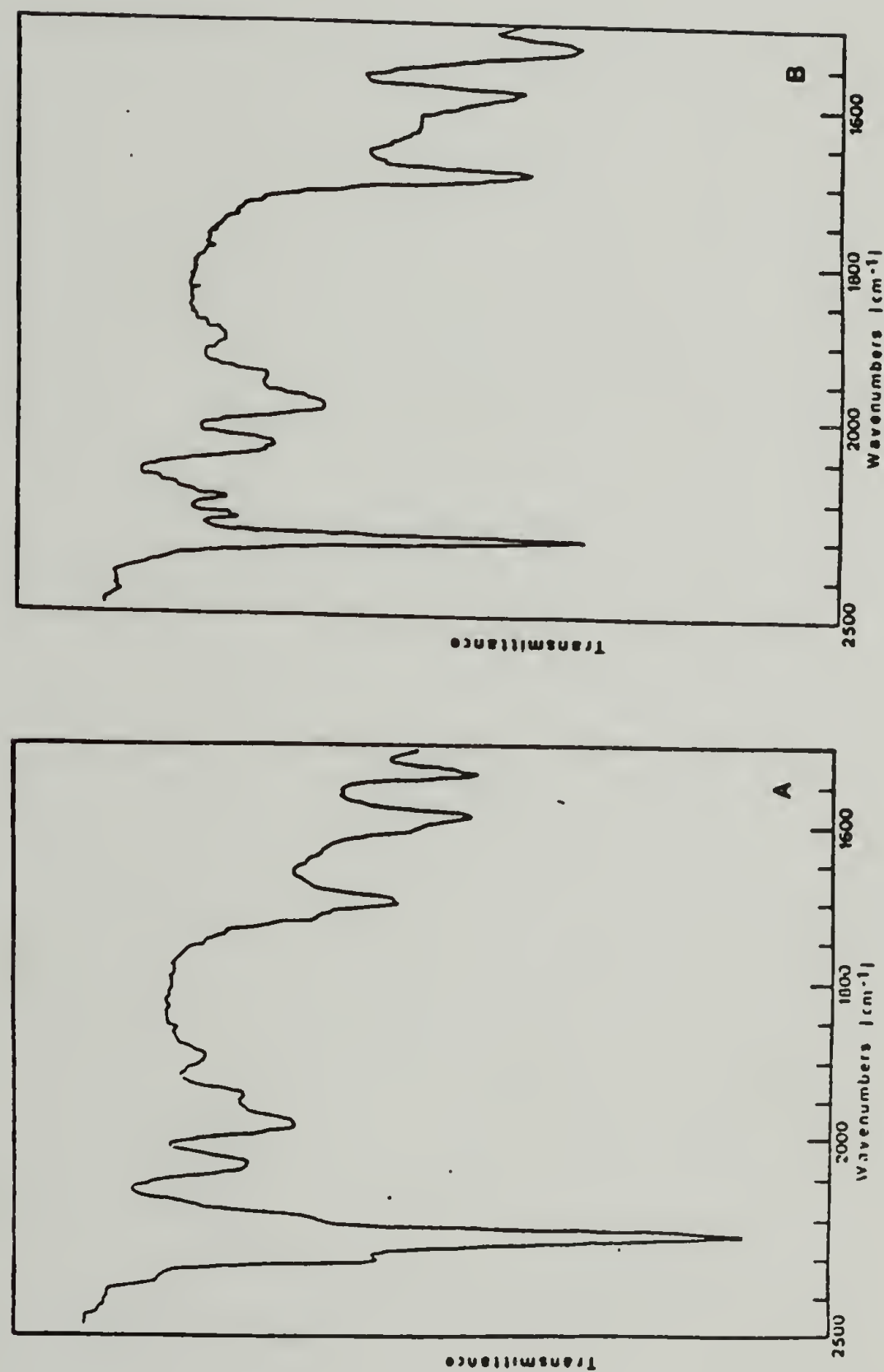
Water is a common impurity in DMSO, and from the spectra in Figure 21 an absorption at 3.3 ppm is seen which was attributed to aromatic amine protons, which are a result of isocyanate hydrolysis. However, these rapidly disappeared and absorptions at 7.8-8.2 ppm appeared which were attributed to an aromatic urea product, as a result of addition of the amine to the available isocyanate. Because 1-carbamoyl benzimidazole is known to hydrolyze rapidly,⁸⁹ it is not known what effect the moisture impurity in the deuterated DMSO plays in the dissociation of the urea link with isocyanate present. The isocyanate obviously reacted with the available moisture but there was still a concurrent dissociation of the urea link, which would seem to indicate that the hydrolysis of the carbamoyl unit was competitive with the hydrolysis of the isocyanate.

An alternate method of examining this effect was by infrared spectroscopy. This same TDI/2(4Th)B adduct was dissolved in DMSO which was previously dried over calcium hydride and distilled under reduced pressure from calcium hydride. Infrared analysis of the solution at 30 minutes and 28 hours is reproduced in Figure 22. At thirty minutes, the carbamoyl carbonyl absorption at

FIGURE 22

Changes in Infrared Spectra of TDI/2(4Th)B Adduct with Time:

A-30 minutes: B-28 hours.



1730 cm^{-1} was present only as a shoulder on the stronger absorption at 1710 cm^{-1} , which was believed to be due to trimer formation. After 28 hours only the trimer absorption was observed. Thus, it appears that a dissociation of the adduct occurred, and not a hydrolysis. DMSO is known to be difficult to dry completely, and if it is assumed that traces of moisture remain and that this moisture does cause a hydrolysis of the carbamoyl functionality, it is interesting to note the strong isocyanate absorption which remained after 28 hours. Hydrolysis alone does not explain the decomposition of the adduct, unless the 1-carbamoyl benzimidazole was more reactive than the isocyanate.

Returning to Figure 21, the NMR analysis clearly indicates the dissociation of the TDI/2(4Th)B adduct when solubilized in DMSO. However, for the purpose of determining the relative amounts of 2(4Th)B and TDI/2(4Th)B adduct in the products isolated from the reactions initially, the relative areas of the thiazolyl protons to tolyl methyl protons is an adequate measure. Chemical shifts change as dissociation occurs, but areas are still related to absolute molar concentrations of all thiazolyl protons and all tolyl methyl protons. For the product isolated from the reaction in the glyme solution, the methyl protons had a total area of 3 and the thiazolyl

protons had a total area of 2, which corresponds to 100% TDI/2(4Th)B adduct. This 100% adduct product is the product used for all subsequent reactions.

One additional comment concerning the TDI/2(4Th)B adduct should be made. In an attempt to observe a melting point for the TDI/2(4Th)B adduct, an apparent decomposition occurred. Thermo gravimetric analysis of it, 2(4Th)B and TDI are displayed in Figure 23, and it is clear that the TDI/2(4Th)B adduct was thermally unstable. At approximately 150 °C, volatilization began. A break in the curve appeared at 210 °C where 2(4Th)B began to sublime after a 47% weight loss, which closely corresponds to the weight percent of TDI in the adduct (46%). Evidently the adduct thermally decomposed back to TDI and 2(4Th)B and each volatilized as the pure compounds do when examined individually.

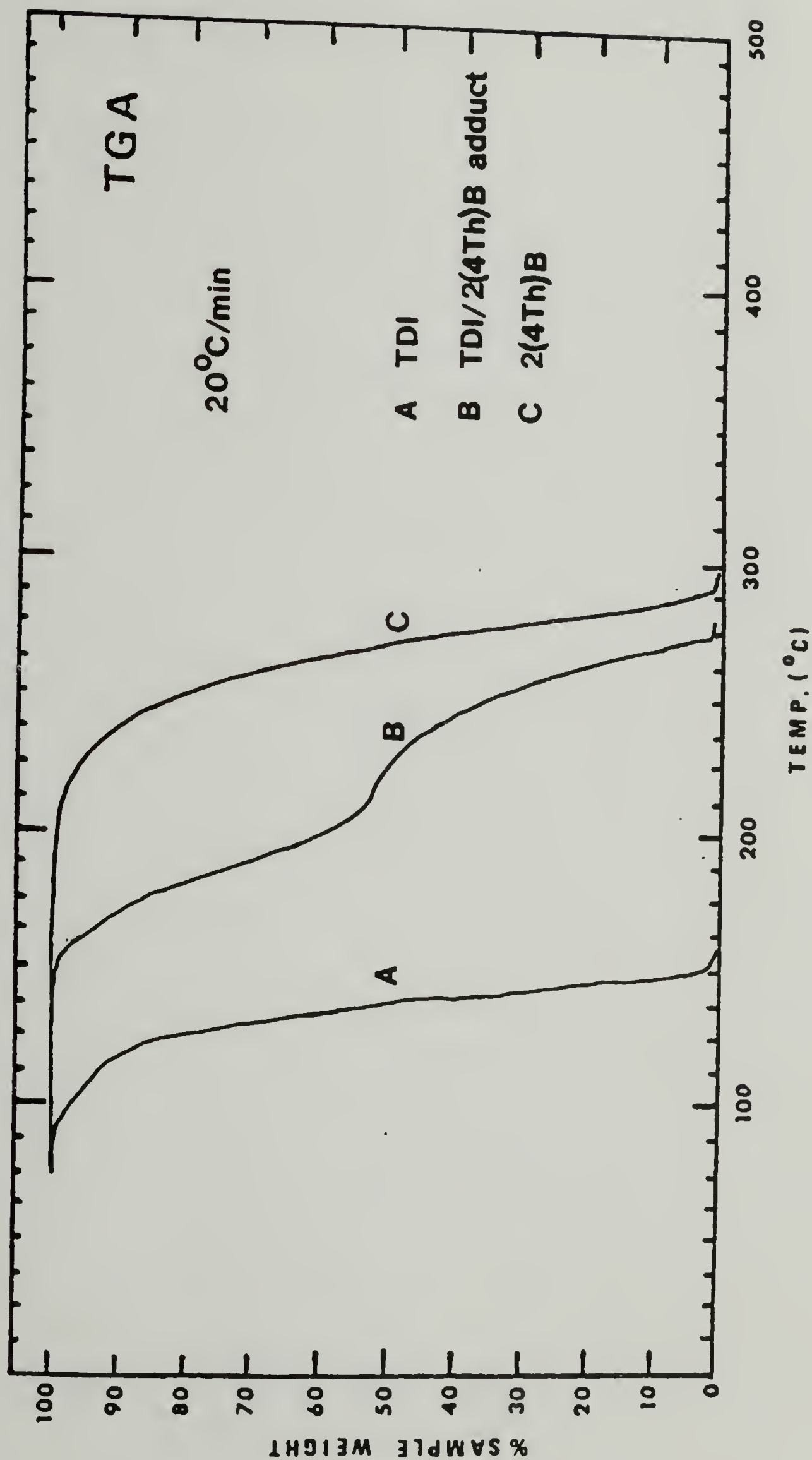
Only one other mention of a thermally unstable 1-carbamoyl benzimidazole was found in the literature and this was reported for 1-(n-butyl carbamoyl)-2-(methylcarbamate)-benzimidazole. Kilgore and White⁹⁸ found that this compound decomposed to 2-(methylcarbamate)-benzimidazole when heated or when dissolved in chloroform.

Reactions of the TDI/2(4Th)B adduct

The reaction of this adduct with a bis-nucleophile

FIGURE 23

TGA Curves of 2(4Th)B, TDI, and TDI/2(4Th)B Adduct



as depicted in Figure 19 was expected to be difficult due to the apparent solvolytic instability. An attempt to react the adduct with 2-hydroxy-1-propylamine by dissolving the adduct in an excess of the amine and exhaustive removal of the amine under vacuum afforded a mixture of 2(4Th)B and the bis-urea product. The presence of 2(4Th)B was verified by its characteristic infrared absorptions in the $3100\text{--}2700\text{ cm}^{-1}$ region and the $900\text{--}740\text{ cm}^{-1}$ region. The infrared spectrum additionally showed no isocyanate absorptions, nor an absorption at 1720 cm^{-1} , typical for a 1-carbamoyl benzimidazole. However, a strong broad band appeared at $1700\text{--}1650\text{ cm}^{-1}$ and this was assigned to the urea functionality by comparison with known absorptions of aliphatic-aromatic substituted ureas in the Sadtler catalogue.⁹² Verification that the product of this reaction was the bis-urea product of an amine and diisocyanate was afforded by $^1\text{H-NMR}$. The tolyl methyl protons ($\delta = 2.09$ ppm, singlet) had a relative area of 3, while the aliphatic methyl protons of the amine residue ($\delta = 1.06$ ppm, doublet) had a relative area of 6.

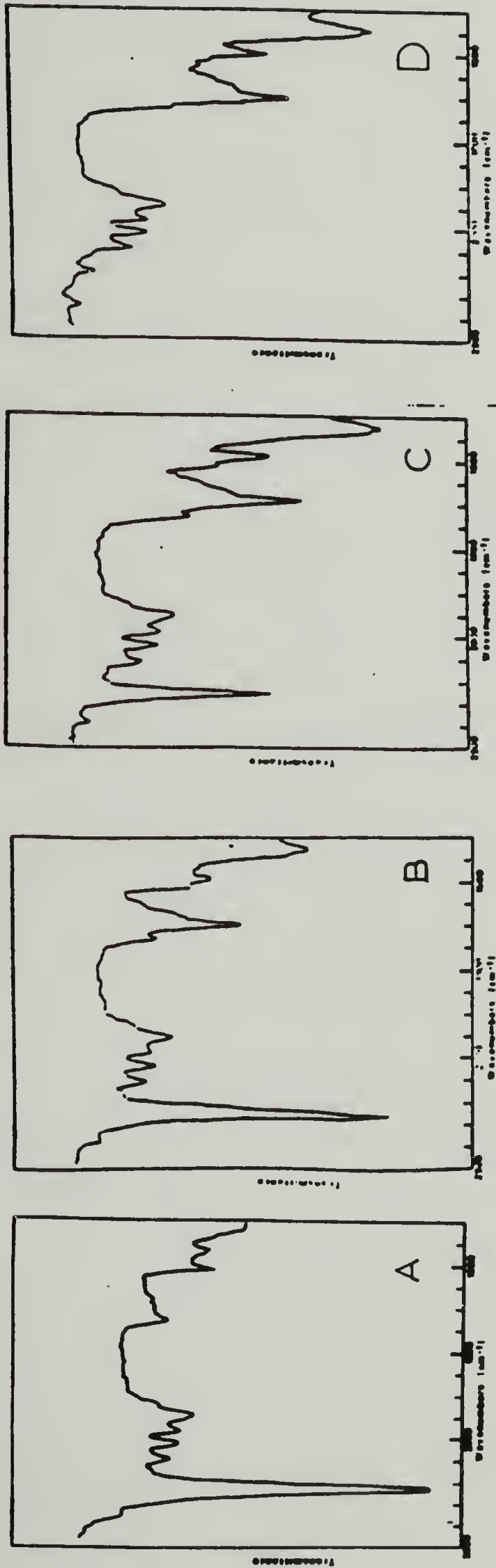
Obviously, this mixture of products could have been formed by addition of amine to the isocyanate function first, followed by nucleophilic addition-elimination at the 1-carbamoyl benzimidazole function. Therefore, a more appropriate synthetic approach would be a titration

of the TDI/2(4Th)B adduct with the addition of the amine stopped when all of the isocyanate had reacted. Thus, the TDI/2(4Th)B adduct was slurried in dry glyme at 0°C and the mixture was titrated with a 2-hydroxy-1-propylamine by injections. The progress of the reaction was monitored by infrared spectroscopy.

Figure 24 displays these infrared spectra. It can be seen immediately from spectrum A, which is prior to addition of any amine, that the carbonyl absorption at 1720 cm^{-1} is significantly smaller than that of the adduct taken in solid form in a KBr pellet. (Spectrum No. 24, Appendix A) Therefore, it is believed that a significant amount of dissociation of the 1-carbamoyl-benzimidazole to TDI and 2(4Th)B had occurred. With the incremental addition of 2-hydroxy-1-propylamine to the heterogeneous mixture up to an equimolar ratio (Spectrum B), a decrease in the isocyanate absorption was observed, with a concurrent formation of a peak at 1700 cm^{-1} (urea carbonyl) and an increase in the peak at 1535 cm^{-1} (urea N-H bond). However, isocyanate still remained and the peak at 1720 cm^{-1} was only a shoulder on the peak at 1700 cm^{-1} . Continued addition of the amine up to a 1.8 molar ratio (Spectrum C, Figure 24) and finally to a 2.1 molar ratio (Spectrum D, Figure 24) showed the continuation of this trend. Exhaustive removal of solvent and the small excess of amine under vacuum

FIGURE 24

IR Analysis of Reaction of TDI/2(4Th)B Adduct with
2-Hydroxy-1-propylamine in Glyme at 25 ° C. Molar
ratio of amine to adduct : A=0, B=1.0, C=1.8, D=2.1



afforded the same product mixture as was obtained from the first reaction of the TDI/2(4Th)B adduct with a 2-hydroxy-1-propylamine - the bis-urea and 2(4Th)B.

Reactions with other nucleophiles capable of adding to the isocyanate function yielded similar results. A reaction with methanol in methanol yielded 2(4Th)B and the bis methyl urethane of TDI. Likewise, ethylene glycol yielded 2(4Th)B; no attempt to isolate the urethane product was made. A reaction with acetic acid in toluene also yielded 2(4Th)B. A reaction of the TDI/2(4Th)B adduct with P(E/MAA) in refluxing toluene afforded unreacted P(E/MAA), probably because of a thermal decomposition of the adduct and subsequently the TDI; hence, no addition to the methacrylic acid functionality was observed.

Final remarks on a 1-carbamoyl-2(4Th)B functionalized P(E/MAA)

The actual bonding of 2(4Th)B to P(E/MAA) by a 1-carbamoyl substituent has not been achieved because of the gross instability of such a substituted benzimidazole. All evidence indicates that the TDI/2(4Th)B adduct readily dissociates back to starting materials in solution, as was seen in DMSO solutions by ^1H -NMR and infrared spectroscopy. This dissociation also appears to have occurred in the heterogenous TDI/2(4Th)B adduct slurry in glyme used for titration by 2-hydroxy-1-propylamine. Also the reaction

of 2(4Th)B with phenyl isocyanate in DMSO, which was monitored by infrared analysis, showed a similar small amount of conversion which did not increase with time.

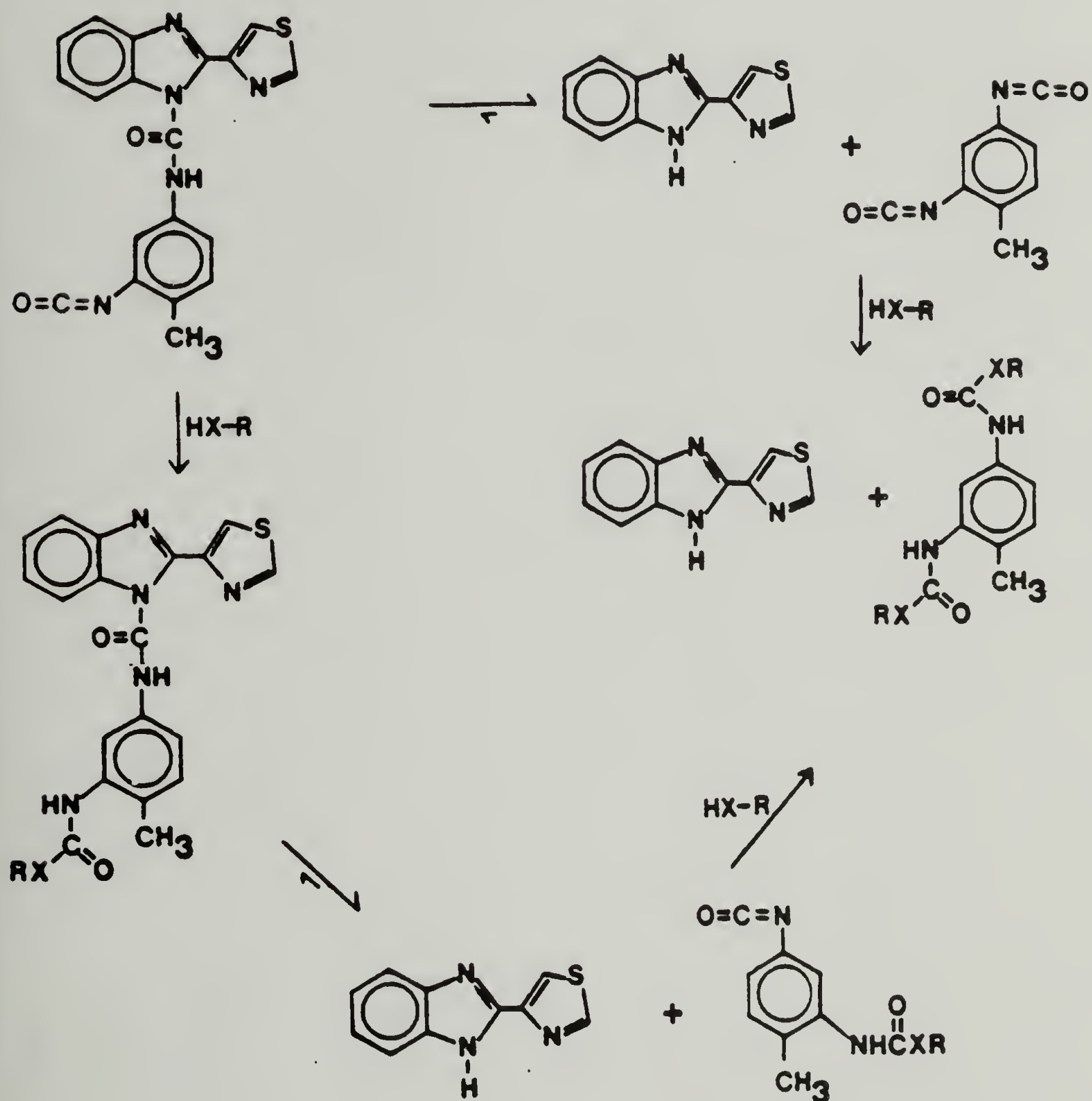
This evidence indicates that the 1-carbamoyl-2(4Th)B unit is extremely labile and when in solution, it readily dissociates. This dissociation appears to be close to 100% as indicated by the very small absorptions noted for the thiazolyl protons of the TDI/2(4Th)B adduct at $\delta = 9.18$ and 8.49 ppm in the ^1H -NMR spectra. It may be that an equilibrium is established between the adduct and the TDI and 2(4Th)B mixture, as was suspected in the case of phenyl isocyanate and 2(4Th)B. The fact that this adduct was isolated at all was due to the synthetic procedures used: large excesses of TDI and precipitation of the adduct.

In Figure 25 is depicted the suspected equilibrium which is believed to be highly favored to the right. Also depicted is what would be expected if a nucleophile was added to such an equilibrium. As can be seen, the ultimate products would be 2(4Th)B and the bis-ureas ($X = \text{NH}$) or bis urathane ($X = \text{O}$) and this is what was observed in the reactions of the adduct with 2-hydroxy-1-propylamine, methanol, and ethylene glycol.

The possibility that the adduct decomposed to these products by nucleophilic attack at the carbonyl of

FIGURE 25

Apparent Equilibria of 2(4Th)B and TDI and
the TDI/2(4Th)B Adduct and Subsequent Reactions



the (1-carbamoyl) benzimidazole is excluded from this scheme for two reasons. First, it is obvious that in solution there was very little of this 1-carbamoyl functionality and an abundance of isocyanate to which a nucleophile would readily add. Secondly, Hegerty and coworkers⁸⁹ clearly showed that the rate determining step in the hydrolysis of 1-phenyl carbamoyl benzimidazole and 1-phenyl carbamoyl imidazole was not a nucleophilic attack of water on the carbamoyl carbon, but a series of proton transfers, followed by dissociation. In addition, Al-Rawi and coworkers invoked a similar elimination-addition mechanism for the hydrolysis of 1-(N-methyl-carbamoyl)imidazoles.⁹⁹ Such proton transfers can readily occur with the TDI/2(4Th)B adduct in DMSO solution or glyme slurry intermolecularly or with the assistance of trace moisture impurity.

Thus, it is not possible to continue the scheme of reactions depicted in Figure 19 and a polymerically bound 2(4Th)B bonding is not possible due to this lability. In addition, the 1-carbamoyl-2(4Th)B bond is not only labile in solution, it is also thermally unstable. Thus, even if bound to a polymer backbone, it would surely regenerate 2(4Th)B during a blending process with N6 which would necessarily be far above its thermal decomposition temperature.

Synthesis of P(E/MAA) functionalized with 1-alkyl-2(4Th)B

As described in Chapter I, some 1-alkyl 2(4Th)B derivatives and 1-alkyl derivatives of other 2-substituted benzimidazoles have shown biological activity. Because the 1-alkyl benzimidazole bond is hydrolytically stable, it is expected that a 1-alkyl-2(4Th)B derivative bound to P(E/MAA) will be a significantly less labile form of bonding.

2(4Th)B was reacted with ethylene oxide in DMSO with triethylamine catalyst to obtain a 9% yield of 1-(2-hydroxyethyl)-2(4-thiazolyl)benzimidazole, (1-2HE-2(4Th)B). Several previous attempts to synthesize this compound in glyme with base catalyst failed. In addition, using strong base catalyst to partially convert the 2(4Th)B to its sodium salt (5%) and subsequent addition of ethylene oxide did not afford the desired derivative as would be expected by comparison of this procedure with that of the addition of ethylene oxide to phenoxide anion.¹⁰¹ This difficulty in synthesizing the ethylene oxide derivative as well as obtaining a low yield in the one successful synthesis was attributed to the inherently low nucleophilic character 2(4Th)B. Although other benzimidazoles have been similarly synthesized, generally low yields are also obtained in these reactions.^{101,102}

The schematic approach to obtain the P(E/MAA) functionalized with this derivative is depicted in Figure 26. P(E/MAA) (5.4 mole % MAA) was first converted to

P(E/MACl) by the oxalyl chloride route and after complete removal of oxalyl chloride, 1-2HE-2(4Th)B was added - 40 mole % of total MACl content - with triethylamine catalyst. The reaction was monitored by infrared analysis of films cast on a sodium chloride plate from the reaction solution and ester formation was observed by the formation of a peak at 1740 cm^{-1} . After no further change in the carbonyl absorptions at 1810 cm^{-1} and 1740 cm^{-1} , methanol was added to obtain a complete conversion of acid chloride to ester.

Absolute conversion of the methacryloyl chloride to the 2(4Th)B derivatized ester in the final product was provided by elemental analysis. Nitrogen content was found to be 0.27 weight % and sulfur content was 0.27 weight %. Thus a value of X and Y in the final compound, were calculated to be $X = 0.052$, and $Y = 0.002$. These values of X and Y represent only a 10% conversion of the available 1-2HE-2(4Th)B. It is suspected that with the excess methanol used, transesterification occurred to some extent, and the resulting percent conversion of methacryloyl repeat units to the 1-2HE-2(4Th)B ester was low.

This mole percent of 1-2HE-2(4Th)B correlates to a total mass percent of 1.9. Considering that 2(4Th)B is effective well below this range, it is conceivable that this polymer bound derivative may have similar activity

given two basic conditions: 1) 1-(2HE)-2(4Th)B is biologically active and 2) that it is active bound to a polymer backbone. As such, these factors have not been analyzed at this time and remain to be studied. In addition, blending properties with N6 have not been studied although because of the small amount of 1-(2HE)-2(4Th)B substituents, its blending properties should be very similar to those of P(E/MAA).

C H A P T E R V

CONCLUSIONS

The overall objectives of this work has been to investigate two polymers as potential supports for a chemical agent in a nylon 6 blend. The polymers were: (1) polyaspartamide derivatives, which were obtained by the ring opening reactions of polyaspartimide, and (2) poly(ethylene)-co-(methacrylic acid). The specific chemical reagent investigated to be bound to either of these different polymeric backbones was 2-(4-thiazolyl) benzimidazole, but only potential methods of bonding it to P(E/MAA) were studied. These investigations and the results obtained emphasize the basic requirements for use of a polymer supported chemical reagent in a binary blend in general, and in particular to a nylon 6 blend.

For a polymer to be used as a support for the reagent, a primary prerequisite which must be met is thermal stability. Polyaspartimide derivatives are unsuitable as the supporting polymer backbone on this account. Ring opening reactions of the polyaspartimide with nucleophiles provides substituted polyamides, which were envisioned to display favorable solubility properties within nylon 6 and, therefore, to provide a more thorough mixing in the blend. However, the ring opening reaction with amines yielded a high ratio of α -aspartamide repeat-

ing units, which were thermally unstable links within the polymer backbone. If used for blending, the resulting polymers would begin to decompose below the melting temperature of nylon 6. A melt mixing of the polymers would necessarily cause significant degradation. As was shown with the PHEA/nylon 6 blend, this degradation also caused a significant drop in the degree of polymerization of nylon 6.

P(E/MAA) has the proven thermal stability to undergo melt mixing with nylon 6, and blending of these two polymers has been previously studied. P(E/MAA) can in principal act as the support for the chemical reagent by bonding the reagent to the methacryloyl repeating unit. The results of the previous study of P(E/MAA) and nylon 6 blends (involving a 10% P(E/MAA) content) indicated that with higher MAA content, improved mixing occurred, and smaller domains of the polyolefin component were obtained as a result of the formation of polyethylene-graft-nylon 6 compatibilizing agents. These grafts were believed to occur by amidation of the methacryloyl unit. It is also conceivable that hydrogen bonding between the methacrylic acid and nylon amide units could also induce a more thorough mixing, but the results of this study clearly deny this possibility. Complete conversion of the methacryloyl repeating unit to ester, amide, or imide functionalities

with subsequent blending resulted in identical morphologies. Also, partial neutralization to the sodium salt resulted in the same blend properties, indicating that only a portion of the methacryloyl functionalities were involved in the graft formation.

Based upon the results from this work and from the previous study,⁷³ it can be concluded that P(E/MAA) is a suitable polymer support for a chemical reagent in a nylon 6 blend. In particular, the properties of the blend can be controlled by the methacryloyl content in P(E/MAA) because of the occurrence of graft formation by an amidation reaction, but the amidation reaction of the methacryloyl function occurred only partially. This result presents an intriguing possibility in that a biocide bound to P(E/MAA) at the MAA repeating unit could be partially released upon blending, while the remainder would remain bound to P(E/MAA) within the polyolefin domain. This behavior would create an immediate biocidal activity in nylon 6 fibers, and also allow for a long term activity if a suitable slow release mechanism is built in to the MAA-biocide bond.

Methods of bonding the biocide, 2(4Th)B, were investigated with attention focused on the reactions of the MAA-2(4Th)B bond. N-acyl and N-carbamoyl bonds of the benzimidazole moiety are known to be hydrolytically unsta-

ble, and such modes of bonding were attempted. A direct amidation of the MAA repeating unit by reaction of its acid chloride with 2(4Th)B failed because of the low nucleophilic character of 2(4Th)B and because of the steric bulk of both reagents. Model acylation reactions demonstrated that the 1-acetyl-2(4Th)B could be synthesized, but the 1-pivalyl-2(4Th)B could not. An attempt was made to synthesize a spacer functionality of either the adipyl or terephthalyl type, but these attempts were not successful. It was concluded that a more appropriate choice may be to use a different copolymer for such an acyl bonding. That is, a copolymer of ethylene and a different monomer with a side chain acid functionality of lower steric constraints may be more suitable.

An attempt was also made to synthesize an N-carbamoyl-2(4Th)B spacer to be linked to the MAA repeat unit, but this carbamoyl substituent was found to be too unstable to be useful. The N-carbamoyl benzimidazole bond is known to be hydrolytically unstable, and it was found in these investigations that it also was readily cleaved in solution to reform the isocyanate function and 2(4Th)B. In addition, the TDI/2(4Th)B adduct was found to be thermally unstable. Hence, this mode of bonding 2(4Th)B to a polymer backbone was not acceptable.

A third mode of bonding 2(4Th)B was studied.

First, 2(4Th)B was reacted with ethylene oxide to form the 1-(2-hydroxyethyl)-2-(4-thiazolyl) benzimidazole intermediate. This intermediate was subsequently bonded in low yield to P(E/MAA) as an ester link by a reaction with P(E/MACl). This method of bonding 2(4Th)B to P(E/MAA) created a more stable link in which the ester group was the weakest link, and partial release by amidation would likely occur in forming a nylon 6 blend. The alkyl benzimidazole is not as likely to be cleaved as the acyl and carbamoyl links. At this time, the biological activity of this 2(4Th)B derivative and the polymer bound derivative is not known.

This work has dealt with methods of bonding 2(4Th)B to a polymeric support, notably P(E/MAA), however other commercial biocides may be applicable and considering the inability to bond 2(4Th)B to P(E/MAA) and still retain a well established release mechanism, such a study with other biocides could be beneficial. P(E/MAA) has been proven to be a suitable support backbone for a chemical reagent in a nylon 6 blend, but it may be concluded from the experimental results that analogous copolymers of ethylene and other carboxylic acid substituted comonomers may also be suitable. Hence, these two concepts embody a frame work for future research involving the study of polymerically supported biocides in a nylon 6 blend.

This dissertation embodies a practical approach to investigating the potential usefulness of a polymeric host as a minor component in a blend. Such an approach must first consider the polymer to which the chemical agent will be bound. High thermal stability, or lack of degradation under blending conditions, must be a prerequisite. The properties of the blended products must be clearly defined and must show no significant detrimental qualities. A suitable chemical reagent with known desired activity must have a viable means of being bound to the polymer support, and if so, the blend properties of such a product should be predictable and verified experimentally. Finally, potential controlled release mechanisms can be established by appropriate methods of bonding the reagent and by choice of blend conditions. Such investigations are, therefore, necessarily complicated and challenging.

C H A P T E R V I

EXPERIMENTAL

Materials

All reagents were obtained from common suppliers, with the exception of P(E/MAA) (Dupont), nylon 6 (Allied), and 6-amino caproic acid (Allied), and most were purified prior to use by accepted procedures.¹⁰³ For materials not listed in this reference, a purification procedure described for a structurally similar compound was utilized. Solvents used in the syntheses were also purified by accepted procedures¹⁰³ with the exception of carbon tetrachloride, cyclohexane, and dimethyl formamide, in which cases spectrophotometric grades were used. Solvents used for polymer precipitation and extraction were reagent grade. Only distilled water was used. All drying agents were used as obtained. Any exceptions to these general rules are noted in the text to follow.

Polymerization of Aspartic Acid

Aspartic acid was mixed thoroughly with fifty weight percent phosphoric acid to form a paste which was spread on a glass petry dish in a thin layer. The mixture was then placed in a vacuum oven preheated to 180°C and a vacuum was applied. Water soon began bubbling out of the pasty mixture and was collected in a dry ice-isopropanol

cooled trap. Water evolution became rapid as the temperature of the mixture approached that of the oven. The mixture formed a viscous foam which eventually solidified into a rigid, porous matrix. After this point, the mixture was kept in the vacuum oven at 180°C, and 0.5-0.1 mm Hg pressure for an additional hour. Total time of reaction was approximately 2 hours. The polyaspartimide/phosphoric acid was removed, allowed to cool and dissolved in dimethyl formamide. A small insoluble fraction was filtered off and the clear, slightly yellow solution was poured slowly with vigorous stirring into distilled water (10:1, H₂O: DMF) to precipitate the polymer. The precipitate was repeatedly washed with distilled water until the filtrate was neutral to pH paper and then dried in a vacuum oven at 100°C under reduced pressure using a water aspirator. This precipitation process was repeated twice to further purify the polyaspartimide, which was then dried at 100°C and 0.1 mm Hg pressure in an Abderhelden over phosphorous pentoxide.

A typical polymerization utilized 25g D,L-aspartic acid or less with yields of 75-85%. Analysis calculated from (C₄H₃NO₂): C, 49.49%; H, 3.11%; N, 14.43%. Found: C, 48.10%; H, 3.13%; N, 13.82%. As discussed in section II, polyaspartimide, PAIm, is difficult to dry completely and moisture tends to be present after drying; hence,

analysis calculated for 97.5% ($C_4H_3NO_2$)/2.5% H_2O : C, 48.26%; H, 3.32%; N, 14.07%. IR spectrum No. 1. 1H -NMR spectrum No. 1. ^{13}C -NMR spectrum No. 1. TGA No. 1.

Synthesis of Poly(aspartic acid) (PAAc)

2.0g (0.020 moles) PAIm was added to a round bottom flask with 50 ml distilled water. A 2N sodium hydroxide solution was prepared and added dropwise, with stirring, monitoring the pH with a pH meter. The pH was not permitted to rise above 9.5 by keeping base addition slow. When the entire polymer was dissolved the pH was brought up to 10.0 and maintained for 1 hour. The solution was then slowly acidified with hydrochloric acid until pH=2 was attained. This solution was then dialyzed against slow flowing distilled water for 3 days. The product was isolated by removal of the water on a rotary evaporator and subsequently dried at room temperature over P_2O_5 under a vacuum of 0.1 mm Hg or less. The product was not soluble in DMF or DMSO as PAIm and other PA derivatives were. IR spectrum (No. 2) indicates a lack of imide structures and is consistent with poly(aspartic acid). Analysis calculated for ($C_4H_5NO_2$): C, 41.75%; H, 4.38%; N, 12.17%. Found: C, 40.99%; H, 4.39%; N, 12.00%. 1H -NMR spectrum No. 2. ^{13}C -NMR spectrum No. 2. TGA No. 2.

Reaction of PAIm with Ethanolamine

Synthesis of poly(2-hydroxyethyl aspartamide)

10g (.10 moles) PAIm was added to a round bottom flask equipped with a nitrogen inlet and a CaCl_2 drying tube. 75 ml spectrophotometric grade dimethyl formamide and a stir bar were added. The flask was flushed with nitrogen while the mixture was magnetically stirred until dissolved (room temperature), 12.8 ml (0.213 moles) ethanol amine was added via syringe and the mixture stirred for 60 minutes. The reaction was terminated by the addition of glacial acetic acid until neutrality was attained (pH paper). The resultant polymer was isolated by first diluting to half the concentration, followed by precipitation in vigorously stirred acetone (10:1, acetone: DMF). The product was air dried and further purified by reprecipitation twice in acetone from dimethyl formamide. The final product, a white powder, was dried at 100°C over phosphorous pentoxide at 0.1 mm Hg pressure in an Abderhalden. Yield of poly(2-hydroxyethyl aspartimide) was 74%. Analysis calculated for $(\text{C}_6\text{H}_{10}\text{N}_2\text{O}_3)$: C, 45.57%; H, 6.37%; N, 17.71%. Found: C, 44.69%; H, 6.39%; N, 16.93%. As with polyaspartimide and the remainder of the amine derivatives, experimental analysis for carbon and nitrogen are lower than theoretical due to the hygroscopic behavior of these materials. IR spectrum No. 3.

^1H -NMR spectrum No. 3. ^{13}C -NMR spectrum No. 3. TGA No. 3.

Syntheses of poly(2-hydroxyethyl aspartamide)-co-(aspartimide)

A series of copolymers with varying ratios of cyclic imide repeat units and linear amide repeat units was synthesized by a similar procedure as that used for the synthesis of poly(2-hydroxyethyl aspartamide). 10g PAIm was dissolved in 60 ml DMF and reacted with varied amounts of ethanol amine as indicated in Table 20. All reactions were terminated after 60 minutes by the addition of acetic acid. The procedure used for the isolation of the polymers were identical to that used for the isolation of poly(2-hydroxyethyl aspartamide). Copolymer composition was determined by IR analysis as discussed in Chapter II. These values are listed in Table 21 as percent conversion to the amide repeat unit and from these values the theoretical analyses were calculated. The IR spectrum of 1-10A through 1-10E are numbered 3 through 7 consecutively. ^1H -NMR for polymers 1-10A through 1-10E are numbered 3 through 7 consecutively, and ^{13}C -NMR of 1-10A and 1-10D are numbered 3 and 4 respectively. TGA curves for 1-10A through 1-10E are numbered 3 through 7 consecutively.

TABLE 20
Synthesis of Poly-(2-hydroxyethyl
aspartamide)-co-(aspartimide): Reaction

Concentrations		
<u>Sample</u>	<u>[PAIm] ($\frac{\text{moles}}{\text{g}}$)</u>	<u>[EA] ($\frac{\text{moles}}{\text{g}}$)</u>
1-10A	1.3	2.8
1-10B	1.6	1.8
1-10C	1.6	1.4
1-10D	1.6	0.90
1-10E	1.6	0.52

TABLE 21

Elemental Analysis for Poly
(2-hydroxyethyl aspartamide)-co-(aspartimide)

<u>Sample</u>	<u>% Conv.</u>		<u>Analysis</u>		
			%C	%H	%N
1-10A	97	Calc'd	45.64	6.31	17.65
		Found	44.69	6.39	16.93
1-10B	78	Calc'd	46.15	5.89	17.23
		Found	46.21	6.40	16.05
1-10C	51	Calc'd	47.01	5.16	16.49
		Found	45.24	6.00	16.56
1-10D	41	Calc'd	47.41	4.84	16.17
		Found	46.18	5.06	15.74
1-10E	28	Calc'd	47.97	4.38	15.70
		Found	46.53	4.66	15.30

Reaction of Polyaspartimide with Amines

General procedure

Polyaspartimide was added to a round bottom flask with a stir bar, serum capped, and flushed with N_2 for at least one hour. Spectrophotometric grade DMF or DMSO was added via syringe and the mixture was stirred until dissolved. The amine was then added via syringe and the reaction was allowed to progress under a nitrogen blanket. The amines used are listed in Table 22 with the reaction variables of stoichiometry and solvent. Reaction conditions of time and temperature and isolation procedures for each are detailed in the subheadings below. All products were dried to constant weight in an Abderhalden at $100^\circ C$ and 0.1 mm Hg pressure over P_2O_5 . Although, all products still contained absorbed water as evidenced by IR, thermal analysis and elemental analysis (lower than theoretical C and N) more vigorous drying was not attempted due to their thermal instabilities. Solution IR analysis (DMSO) was used to determine percent conversions which in turn were used to determine theoretical elemental analysis.

With dicyclohexylamine

The reaction was carried out at room temperature for 18 hours and the polymer precipitated twice. Percent conversion was found to be zero. Calculated analysis for

TABLE 22
Stoichiometry for Reactions of Amines
with Polyaspartimide

<u>Code</u>	<u>Reagent</u>	<u>Moles PAIm</u>	<u>Moles Amine</u>	<u>Vol. DMF</u>
1-14	Dicyclohexylamine	0.062	0.13	50ml DMF
1-15	Phenethylamine	0.062	0.14	50ml DMF
1-19	2(4Th)B	0.021	0.071	50ml DMF
1-20	Amino caproic acid	0.031	0.070	(a)
1-24	Benzylamine	0.031	0.064	25ml DMF
1-24A	Benzylamine	0.031	0.061	25ml DMF
1-25	Aniline	0.031	0.077	50ml DMF
1-30	Methylamine-HCl ^(b)	0.031	0.040	50ml DMF
1-30A	Methylamine-HCl ^(b)	0.031	0.067	50ml DMF
1-31	4-Ethoxy-phenylamine	0.031	0.071	50ml DMF
1-26	Cyclohexylamine	0.031	0.074	50ml DMF
1-32	2-Hydroxypropylamine	0.031	0.071	50ml DMF
1-36	n-hexylamine	0.021	0.038	50ml DMF
1-45A	3-phenylpropylamine	0.021	0.050	25ml DMF

a) solvent amount varied, DMF or DMSO used

b) triethylamine catalyst used

PAIm: C, 49.49%; H, 3.11%, N, 14.43%. Found: C, 48.74%; H, 3.43%; N, 13.84%. IR and ^1H -NMR spectra identical to PAIm.

With phenethylamine

The reaction was carried out at room temperature for 1 hour and the polymer precipitated in ether twice. Percent conversion for the white powder was found to be 80%. Calculated analysis for PPEA - 80%: C, 64.38%; H, 6.13%; N, 12.99%. Found: C, 63.34%; H, 6.06%; N, 12.84%. IR spectrum No. 8. ^1H -NMR spectrum No. 8. ^{13}C -NMR spectrum No. 5. TGA No. 8.

With 2-(4-thiazolyl)benzimidazole

The reaction was carried out at room temperature for 1 hour. IR analysis of the solution showed no conversion. The temperature was gradually raised to 100°C and the solution was periodically checked for conversion by IR analysis. After 45 hours at 100°C, the solution was poured into acetone, precipitating the polymer. The IR and ^1H -NMR spectrum showed PAIm.

With 6-amino caproic acid

The reaction was carried out at room temperature for 18 hours; however its solubility in DMF or DMSO was much too low to effect reaction with PAIm. Using bases such as sodium carbonate and triethylamine or increasing

the temperature to 80°C did not suitably increase its solubility. Therefore, only PAIm was recovered.

With benzlamine

The reaction was carried out at room temperature for 1 hour and the polymer was precipitated in water. The product was redissolved in 20 ml of a 50% DMF, 50% formic acid mixture and then reprecipitated in 250 ml water. IR analysis indicated 70% conversion. Calculated analysis for PBA - 70%: C, 62.12%; H, 5.45%; N, 13.84%. Found: C, 60.72%; H, 5.70%; N, 13.53%. IR spectrum No. 9. ¹H-NMR spectrum No. 9. ¹³C-NMR spectrum No. 6. TGA No. 9.

A second attempt was made for the purpose of obtaining a higher percent conversion by allowing the reaction to progress for a longer period of time (24 hours). Isolation was achieved by precipitation in acetone, and reprecipitating twice from an approximately 20% formic acid/80% DMF solution into water. IR analysis indicated 90% conversion. Calculated analysis for PBA - 90%: C, 63.93%; H, 5.79%; N, 13.75%. Found: C, 59.14%; H, 5.71%; N, 13.03%. IR spectrum No. 10. ¹H-NMR spectrum No. 10. ¹³C-NMR spectrum No. 7. TGA No. 10.

With aniline

The reaction was carried out for 48 hours at 98°C. Solution IR analysis indicated no conversion. The precip-

itated product (methanol) had a IR spectrum identical to PAIm with no additional amide carbonyls.

With Methylamine Hydrochloride

Triethylamine was added to neutralize the acid salt and liberate methylamine. The reaction was carried out at room temperature for 24 hours and polymer was precipitated in methanol twice. IR analysis indicated 53% conversion. Analysis calculated for PMA - 53%: C, 47.92%; H, 5.02%; N, 18.88%. Found: C, 44.66%; H, 5.72%; N, 18.33%. IR spectrum No. 11. ^1H -NMR spectrum No. 11. TGA No. 11.

A second attempt was made to achieve a higher conversion by using a larger amount of methylamine hydrochloride and triethylamine and allowing a longer time for the reaction. After two reprecipitations the product was further purified by dialysis against slow flowing distilled water for 48 hours. The dialyzed product was finally isolated by removal of water under reduced pressure using a rotary evaporator and then dried as the other derivatives were. The IR analysis indicated 92% conversion. Analysis calculated for PMA - 92%: C, 47.03%; H, 6.10%; N, 21.40%. Found: C, 44.91%; H, 6.71%; N, 20.08%. IR spectrum No. 12. ^1H -NMR spectrum No. 12. ^{13}C -NMR spectrum No. 8. TGA No. 12.

With phenetidine

The reaction was carried out at 98°C for 48 hours and the polymer was precipitated in water/1% acetic acid twice. IR analysis indicated 34% conversion. Analysis calculated for PEtPA 34%: C, 56.16%; H, 4.73%; N, 13.06%. Found: C, 54.16%, H, 5.24%; N, 12.78%. IR spectrum No. 13. ¹H-NMR spectrum No. 13. ¹³C-NMR spectrum No. 9. TGA No. 13.

With cyclohexylamine

The reaction was carried out at room temperature for 24 hours and the polymer was precipitated in water/1% acetic acid. The product isolated was reprecipitated from a 60 ml DMF/10 ml formic acid solution into 800 ml water, and then again from a 60 ml DMF/3 ml formic acid solution into 800 ml water. The IR analysis indicated 90% conversion. Analysis calculated for PcHA - 90%: C, 61.20%; H, 8.22%; N, 14.27%. Found: C, 53.24%; H, 7.16%; N, 13.24%. IR spectrum No. 14. ¹H-NMR spectrum No. 14. ¹³C-NMR spectrum No. 10. TGA No. 14.

With 2-hydroxypropylamine

The reaction was carried out at room temperature for 24 hours and was terminated by the addition of acetic acid. The solution was diluted to twice its volume with distilled water. This solution was dialyzed against slow

flowing distilled water for 36 hours and the final dialyzed product was isolated by removing the water under reduced pressure on a rotary evaporator. The product was then dried as usual. IR analysis indicated 70% conversion. Analysis indicated 70% conversion. Analysis calculated for PHPrA - 70%: C, 48.96%; H, 6.26%; N, 15.91%. Found: C, 45.46%; H, 7.16%; N, 14.58%. IR spectrum No. 15. ^1H -NMR spectrum No. 15. ^{13}C -NMR spectrum No. 11. TGA No. 15.

With n-hexylamine

The reaction was carried out at room temperature for 15 hours and the polymer was precipitated twice in water/1% acetic acid. The IR analysis indicated 96% conversion for the white powder obtained. Analysis calculated for PnHA - 96%: C, 60.36%; H, 9.03%; N, 14.14%. Found: C, 58.58%; H, 9.02%; N, 13.79%. IR spectrum No. 16. ^1H -NMR spectrum No. 16. ^{13}C -NMR spectrum No. 12. TGA No. 16.

With 3-phenyl propylamine

The reaction was carried out at room temperature for 2 hours and the polymer was precipitated twice in water/1% acetic acid. The IR analysis indicated a 89% conversion for the white powder. Analysis calculated for PPPrA - 89%: C, 66.35%; H, 6.75%; N, 12.18%. Found:

C, 63.41%; H, 7.08%; N, 11.67%. IR spectrum No. 17.
 ^1H -NMR spectrum No. 17. ^{13}C -NMR spectrum No. 13. TGA
No. 17.

Reaction of PAIm with Methanol

Spectrophotometric grade methanol was used as obtained. The same general procedure used for amines was used here also: 3.0g (0.031 moles) PAIm, 50 ml DMF, 10 ml methanol and 1.0 ml triethylamine were utilized. Stirring was maintained for 24 hours, and the solution was then poured slowly into water (10:1- H_2O /DMF) to precipitate the polymer. The white powder was reprecipitated twice from DMF solution into water. After a preliminary drying under a vacuum of 0.1 mm Hg over P_2O_5 in a dessicator, the product was further dried over P_2O_5 at 100°C and 0.1 mm Hg in an Abderhalden for 24 hours. The IR analysis indicates a zero conversion to the methyl ester. IR spectrum and ^1H -NMR spectrum are identical to that of PAIm.

Synthesis of Poly-ethylene-co-methacryloyl chloride from Poly-ethylene-co-methacrylic acid

Thionyl chloride method

In the first procedure, 10g poly-ethylene-co-methacrylic acid (5.4 mole % MAA, 0.017 moles MAA) was added to a round bottom flask equipped with the following: thermometer; a 10 inch Vigreux column with a nitrogen

outlet adaptor connected with tubing to a three way stopcock, then to a drying tube filled with sodium hydroxide; a Claisen adaptor with a serum cap for nitrogen inflow and solvent addition via syringe needles, and a stopcock adaptor with serum capped outlet for removal of samples to monitor the progress of the reaction by infrared spectroscopy. 200 ml xylene was added via transfer needle. The system was flushed with nitrogen while the mixture was brought to 130°C and magnetically stirred until the copolymer completely dissolved. The solution was cooled to 70°C and maintained while 4.0 ml (0.0206 moles) thionyl chloride was syringed into the solution. After 1 hour a sample was removed by glass pipette through the stopcock and a film on a sodium chloride plate was made. The Infrared spectrum (No. 18) shows an absorption at 1800 cm^{-1} and none at 1700 cm^{-1} , indicating complete conversion to acid chloride. Excess thionyl chloride was then removed by bringing the solution to a gentle reflux and increasing the nitrogen flow. Complete removal of thionyl chloride and gaseous hydrochloric acid by product was ensured by maintaining the gentle reflux 1 hour after the nitrogen outflow through the 3-way stopcock appears neutral to moist pH paper. This solution of poly-ethylene-co-methacryloyl chloride was used for subsequent reactions without isolation of the polymeric acid chloride.

Oxalyl chloride method

1.10g Poly-ethylene-co-methacrylic acid, (5.4 moles % MAA, 0.0019 moles), was added to a round bottom flask equipped with the following: mechanical stirrer; thermometer; nitrogen flow inlet; a stopcock adaptor with serum cap for removal of samples; a potassium hydroxide trap in a liquid/liquid extractor with a reflux condensor above it and a nitrogen outlet leading to an oil bubbler. The system was thoroughly flushed with nitrogen and 125 ml carbon tetrachloride, was added via transfer needle. The mixture was brought to a vigorous reflux with stirring, with the condensate passing through the potassium hydroxide trap, thus removing residual moisture. After complete solvation (hazy solution), the temperature was lowered to 60-65°C and 2.0 ml (0.024 moles) oxalyl chloride was added slowly via syringe. The solution initially gelled due to mixed anhydride formation and soon afterward became a clear homogenous solution. A small sample was then removed through the stopcock via pipette and a film was made on a sodium chloride crystal. The infrared spectra (No. 18) showed a strong absorption at 1800 cm^{-1} and none at 1700 cm^{-1} , indicating a complete conversion to the acid chloride functionality. The excess oxalyl chloride was then removed by bringing the solution to a vigorous reflux. The condensate passed through the potassium

hydroxide trap, thus consuming the excess oxalyl chloride, which forms CO and CO₂ with KOH. The absence of bubbling in the condensate, indicated the absence of oxalyl chloride. This solution of poly-ethylene-co-methacryloyl chloride was then used for subsequent reactions without isolation of the polymeric acid chloride.

Attempted isolation of poly-ethylene-co-methacryloyl chloride.

An attempt was made to isolate this product (formed by the oxalyl chloride route) by precipitating the carbon tetrachloride solution in spectrophotometric grade acetone (10:1). Attempts to redissolve the white, fibrous polymer in carbon tetrachloride at reflux or in xylene at reflux failed. A portion was then dried at 62°C at 0.1 mm Hg pressure over P₂O₅ for 22 hours in an Abderhalden. Analysis calculated for (C₂H₄) .946 (C₄ClH₅O) .054: C, 78.43%; H, 12.66%; Cl, 5.93%. Found: C, 79.35%; H, 13.08%; Cl, 5.20%.

Conversion of P(E/MAA) TO P(E/MMA)

P(E/MAA) was converted to P(E/MACl) via the oxalyl chloride method and to this refluxing carbon tetrachloride solution was added a two fold molar excess of methanol based on initial MAA content. The copolymer was precipitated in methanol and impurities extracted with methanol

for 20 hours in a Soxlet. Hence, P(E/MAA) with 5.4 mole percent MAA was converted to P(E/MMA) with 5.4 mole percent MMA. Analysis calculated for P(E/5.4 MMA): C, 81.36%; H, 13.22%. Found: C, 81.24%; H, 13.50%. IR spectrum No. 19. Likewise P(E/MMA) with 1.3 mole percent MMA was synthesized and P(E/MMA) with 5.8 mole percent MMA was synthesized.

A series of four P(E/MAA/MMA) copolymers with varying MMA content was synthesized by partial conversion of P(E/MAA) (5.4 mole % MAA) to P(E/MACl), utilizing a less than molar equivalence of oxalyl chloride, and subsequently reacting this with excess methanol. Each polymer was then precipitated in methanol and impurities extracted with methanol for at least 15 hours in a Soxlet extractor. IR analysis (Chapter III) confirmed the structure.

Conversion of P(E/MAA) to P(E/MAA/NaMA) with
Varying MAA/NaMA Ratios

6g P(E/MAA) (5.4 moles % MAA, 0.013 moles MAA) was added to a round bottom flask equipped with an addition funnel, an adaptor for nitrogen inflow and a reflux condensor with a calcium chloride drying tube. 250 ml tetrahydrofuran was added via transfer needle and brought to a reflux. Five separate solutions were thus made up and a 5% sodium hydroxide solution was added in varied

amounts to vary the molar ratio of base added, and the heterogenous mixture was refluxed for varied lengths of times as follows: 1) .0025 moles NaOH, 6 hours; 2) .0050 moles NaOH, 14 hours; 3) .0075 moles NaOH, 16 hours; 4) .010 moles NaOH, 18 hours; 5) 0.013 moles NaOH, 20 hours. All copolymers were isolated by precipitation in 600 ml methanol and impurities extracted with methanol for at least 8 hours in a Soxhlet extractor. Conversion was determined by IR analysis (Chapter III).

Synthesis of P(E/nHMAM)

7.0g P(E/MAA) (5.4 moles % MAA, 0.012 moles MAA) was converted to the P(E/MACl) via the oxalyl chloride route and 5 ml n-hexyl amine was syringed into the refluxing solution. After 1 hour, complete conversion to the n-hexyl methacryloyl amide was observed by IR analysis of a film cast on a sodium chloride plate (No. 20). The copolymer was precipitated in 1 liter of acetone and reprecipitated in acetone from carbon tetrachloride, and dried at 0.1 mm Hg pressure and room temperature for 18 hours. Analysis calculated: C, 81.93%; H, 13.59%; N, 2.08%. Found: C, 81.81%; H, 13.84%; N, 2.04%.

Synthesis of P(E/N-MACap)

P(E/MACl) was synthesized by the oxalyl chloride

method and to this solution was added a solution of 6-caprolactam and triethylamine in carbon tetrachloride by syringe. After refluxing for 2 hours, IR analysis of a film cast on a sodium chloride plate indicated no acid chloride remaining. The copolymer was precipitated in acetone and reprecipitated in acetone from carbon tetrachloride. The final product was dried at 0.1 mm Hg pressure and 62°C for 20 hours. Hence, P(E/N-MACap) with 5.4 mole percent N-MACap was synthesized. Analysis calculated for P(E/5.4N-MACap): C, 80.34%; H, 12.77%; N, 2.04%. Found: C, 80.34%; H, 12.87%; N, 1.91%. IR spectrum No. 21. Also P(E/N-MACap) with 1.3 mole percent N-MACap was synthesized. Analysis calculated for P(E/1.3N-MACap): C, 84.26%; H, 13.74%; N, 0.60%. Found: C, 83.96%; H, 14.44%; N, 0.54%. IR spectrum same as No. 21 with the exception of smaller carbonyl absorptions at 1710 cm^{-1} and 1680 cm^{-1} .

Attempted Syntheses of P(E/MAA)-graft-Nylon 6

3.75g P(E/N-MACap) (5.4 mole % N-MACap, 0.0055 moles N-MACap) and 10.127g (0.0895 moles) 6-caprolactam were charged into a 100 ml reaction kettle equipped with a mechanical stirrer, a reflux condensor with nitrogen outlet adaptor leading to an oil bubbler, and a Claisen adaptor with one neck serum capped and the other capped

with a ground glass tube with a 50° bend which was stoppered. After flushing the apparatus with nitrogen for one hour, 45 ml xylene was added via transfer needle. The mixture was brought to a gentle reflux by heating in an oil bath and stirred until completely dissolved (Temperature = 135°C). In a glove bag under nitrogen, 0.26g (0.011 moles) NaH and 2.509g (0.0222 moles) 6-caprolactam were charged into a Shlenk tube with a side arm adaptor and serum capped. 5 ml xylene was added to the Shlenk tube via transfer needle and nitrogen was continuously flushed through (inflow from side arm, outflow through 2 syringe needles through septum) while this mixture was gently heated. When complete solvation was achieved and the sodium hydride had completely reacted, the solution was heated in the oil bath for five minutes to bring its temperature nearer to that of the P(E/N-MACap)/6-caprolactam solution. The nitrogen flow was greatly increased in both the Shlenk and the kettle. The septum was removed from the Shlenk, which was quickly attached to the angled glass tube on the kettle apparatus. The sodium 6-caprolactam solution thus flowed into the kettle and the nitrogen flow was slowed. After one minute the mixture set, freezing the stirrer; however the temperature was maintained at 130-135°C for one hour. The contents were then poured into ethanol and filtered. The slightly

Yellow product was placed in a Soxhlet and impurities were extracted with 95% ethanol for 24 hours. The white product was then dried at 55-60° C in a vacuum oven at 0.2 mm Hg pressure for 24 hours. Yield: 13.76g. Analysis found: C, 67.54%; H, 10.64%; N, 8.89%. The stoichiometry for this reaction and five others, similarly run with P(E/N-MACap) (5.4 mole % N-MACap) are summarized in Table 23 with the yields and analysis found in Table 24. Also a series of reactions were run by the same procedure using P(E/N-MACap) with 1.3 mole % N-MACap. The stoichiometry and yields are indicated in Table 25 with the analyses found in Table 26.

Attempted Synthesis of Poly(ethylene)-co-
(1-methacryloyl-2-(4-thiazolyl)
benzimidazole) (PE/MA4ThB)

Several attempts were made to synthesize this material by addition of 2-(4-thiazolyl benzimidazole) to the apparatus containing the freshly prepared solution of P(E/MACl) (5.4 moles % MACl) synthesized via the thionyl chloride route or the oxalyl chloride method. In all cases contact of the solution with atmosphere was minimized and the progress of the reaction was monitored by removing small aliquots by syringe or pipette through the stopcock adaptor and forming a film on a sodium chloride plate for IR analysis. Specific methods, analyses and

TABLE 23
 Stoichiometry of Attempted Graft-N6
 Syntheses from P(E/5.4% N-MACap) (a)

<u>Code</u>	<u>Mass(g) of P(E/N-MACap)</u>	<u>Moles N-MACap</u>	<u>Vol.(ml) Xylene</u>	<u>Yield(g)</u>
G-1	3.75	0.0055	50	13.76
G-2	1.70	0.0024	50	11.65
G-3	0.785	0.0011	50	1.33
G-4	0.388	0.00057	50	0.44
G-5	0.375	0.00055	25	2.39
G-6	0.365	0.00054	10	0.83

(a) 12.4g (0.113 moles) 6-caprolactam
 0.26g (0.011 moles) NaH
 1 hour reaction time

TABLE 24

Analysis Found For Attempted
Graft-N6 Syntheses From P(E/5.4 mole % N-MACap)

<u>Code</u>	<u>%C</u>	Analysis Found <u>%H</u>	<u>%N</u>
G-1	67.54	10.64	8.89
G-2	66.18	10.31	10.00
G-3	69.01	11.51	6.19
G-4	72.04	12.08	4.84
G-5	65.59	10.35	10.36
G-6	65.81	10.32	10.38

TABLE 25

Stoichiometry for Attempted Graft-N6
Syntheses from P(E/1.3 % N-MACap) (a)

<u>Code</u>	<u>Mass(g) of P(E/N-MACap)</u>	<u>Moles of N-MACap</u>	<u>Yield</u>
G-7	0.51	2.2×10^{-4}	0.54
G-8	1.26g	5.5×10^{-4}	1.35
G-9	2.50g	11×10^{-4}	3.30
G-10	5.00g	22×10^{-4}	12.44g

a) 12.5g (0.113 moles) 6-Caprolactam
0.26g (0.011 moles) NaH
30ml xylene
1 hour reaction time

TABLE 26

Analysis Found for Attempted Graft-N6
Syntheses from P(E/1.3 % N-MACap)

<u>Code</u>	<u>%C</u>	Analysis Found <u>%H</u>	<u>%N</u>
G-7	73.91	12.24	0.58
G-8	80.48	13.28	1.06
G-9	78.90	13.19	3.01
G-10	70.23	11.33	8.16

isolation are given below.

Attempts by P(E/MACl) from thionyl chloride route

5.81g (0.0289 moles) 2(4Th)B was added to the xylene solution (200 ml) of P(E/MACl) containing 0.017 moles MACl and temperature maintained at 110°C for 18 hours. Solution heterogenous due to low solubility of 2(4Th)B. Periodic IR analysis showed no change in carbonyl at 1800 cm^{-1} . Precipitation in methanol and extraction with methanol for 15 hours in a Soxhlet, afforded P(E/MMA). IR showed strong carbonyl absorption at 1740 cm^{-1} , none at 1800 cm^{-1} . Analysis found: C, 81.24%; H, 13.50%; N, < 0.1%. A repeat at higher dilution affords a homogenous solution but IR analysis again showed no reaction.

In a glove bag, under nitrogen, 2.01g (0.0100 moles) 2(4Th)B and 0.23g (0.010 moles) sodium hydride are charged into a Shlenk tube which was then capped with a stopcock adaptor. 75 ml toluene and 50 ml DMF were added by transfer needle. This mixture was heated gently (60°C oil bath) until complete solvation and complete conversion of 2(4Th)B to its sodium salt. Under strong nitrogen flow the Shlenk tube was attached to an addition funnel attached to the apparatus containing the P(E/MACl) solution. The solution of the 2(4Th)B anion was then added slowly to the P(E/MACl) solution (.0044 moles MACl

in 175 ml xylene) causing the precipitation of the P(E/MACl). After addition, the mixture was stirred for 16 hours at 70°C under a nitrogen blanket. The mixture was then poured into 1 liter of methanol and the precipitate placed in a Soxlet extractor and extracted with methanol for 24 hours. Product dried at 62°C over P_2O_5 at 0.1 mm Hg for 18 hours. Elemental analysis found: N, < 0.10%.

2.10g (0.0104 moles) 2(4Th)B was dissolved in dimethyl acetamide with 1.0 ml (0.0065 moles) triethylamine and the solution was transferred dropwise to the P(E/MACl) solution, (0.0044 moles MACl in 175 ml xylene), with vigorous stirring. P(E/MACl) precipitates slowly. The mixture was brought to a gentle reflux and maintained for 15 hours, poured into 800 ml methanol, and the precipitate was placed in a Soxlet and extracted with methanol for 8 hours. Analysis found: C, 80.77%; H, 13.59%; N, < 0.1%. Infrared analysis showed a strong methyl ester carbonyl absorption (1740 cm^{-1}) and a weak acid chloride carbonyl absorption (1800 cm^{-1}).

Attempts by P(E/MACl) from oxalyl chloride route

2.24g (0.0111 moles) 2(4Th)B was added to the refluxing P(E/MACl) solution (0.0044 moles MACl, 200 ml carbon tetrachloride) and 1.0 ml (0.0065 moles) triethylamine was syringed in. Periodic IR analysis of the heterogeneous mixture showed no change in carbonyl at 1800 cm^{-1}

over the next 15 hours. Mixture poured into methanol and precipitate was extracted with methanol for 48 hours in a Soxlet. IR analysis shows a strong carbonyl absorption at 1740 cm^{-1} and weak absorption at 1800 cm^{-1} indicating near complete conversion to the methyl ester. Analysis found: C, 80.60%; H, 13.75%; N, < 0.1%.

Two more attempts were made to convert the P(E/MACl) to P(E/MAThB) by first synthesizing the P(E/MACl) by the oxalyl chloride route and then adding this solution to an addition funnel under nitrogen blanket. This was subsequently added dropwise to a solution of the sodium salt of 2(4Th)B. In the first, the 2(4Th)B and sodium hydride were dissolved in a 50/50 toluene/DMF solution at 60°C forming the anion. In the second, a 50/50 benzene/DMSO solution at 60°C was used. In both cases, the P(E/MACl) product precipitates out of solution. After isolation of the polymeric material by precipitation in acetone and extracting with acetone for 24 hours in a Soxlet, elemental analysis indicated that neither product contained nitrogen.

Attempted synthesis of P(E/MAThB) from P(E/MAA) and 2(4Th)B

27.0g P(E/MAA) (3.1 moles % MAA, 0.0282 moles MAA) and 13.0g (0.0647) 2(4Th)B are added to a Brabender Blending Apparatus preheated to 200°C and mixed for 5 hours at 30 rpm under a nitrogen blanket. The material was

removed and cooled quickly on dry ice. A sample was dissolved in refluxing toluene and a film on a sodium chloride plate was made. Infrared analysis showed no change in the carbonyl absorption at 1700 cm^{-1} . All other peaks were attributed to the P(E/MAA) or 2(4Th)B. (IR spectrum of 2(4Th)B: No. 22.)

Attempted synthesis of P(E/MATHB) from P(E/MMA)

P(E/MMA) synthesis and isolation was described previously. 4.00g P(E/MMA) (1.3 moles % MMA, 0.00185 moles ester), 0.410g (0.00204 moles) 2(4Th)B and 0.0142g (7.47×10^{-5} moles) p-toluenesulfonic acid monohydrate were charged into a round bottom flask equipped with a mechanical stirrer, septum for nitrogen inflow and a reflux condensor with an adaptor for nitrogen outflow leading to an oil bubbler. 100 ml xylene was added by transfer needle and the mixture was brought to a reflux with stirring. The homogenous mixture was monitored by infrared analysis by removing a small aliquot and forming a film on a sodium chloride plate. After 4 days, no change was observed. P(E/MMA) was recovered by precipitation in methanol.

Synthesis of 1-Acetyl-2(4-thiazolyl) benzimidazole

Attempts from the lithium salt of 2(4Th)B

0.500g (0.00249 moles) 2(4Th)B was added to round

bottom flask equipped with a septum for nitrogen inflow and reagent addition, thermometer and reflux condensor with a nitrogen outlet connected to a bubbler. The system was flushed vigorously with nitrogen while flamed out. After cooling the nitrogen flow was slowed and 60 ml glyme was added via transfer needle under nitrogen pressure. The mixture was stirred and heated to 60°C until complete solvation. 1.5 ml of a 1.6 M n-butyl lithium in hexane (0.024 moles n-BuLi) was syringed into the mixture slowly, with the solution turning yellow as the lithium salt was formed. Ten minutes after addition, 0.18 ml (0.025 moles) acetyl chloride was syringed into the solution slowly. After one hour the mixture was allowed to cool to room temperature and the solvents were removed under reduced pressure. The reddish oil that remained was dissolved in ether and washed twice with water. After drying over magnesium sulfate, the ether was allowed to evaporate. The residue was recrystallized from ethanol, yielding 0.373g off-white crystals. Infrared analysis (KBr) and ^1H -NMR analysis (No. 18) showed the product to be unreacted 2(4Th)B: 75% recovery.

A repeat was made using tetrahydrofuran as the solvent and the following conditions: 0.0049 moles 2(4Th)B, .0050 n-butyl lithium, 150 ml THF, 0.018 moles acetyl chloride, 60°C, and 8 hours. Upon slow cooling

after the 8 hours, a yellow product was isolated by filtration. This proved to be Lithium 2(4Th)B in 85% recovery. Removal of the solvent from the filtrate afforded a reddish viscous oil, which upon trituration with a 50/50 acetone/hexane solution yielded a yellow powder. IR analysis showed this to be 2(4Th)B. Total recovery: 90%.

A third attempt using the same procedure and dimethyl acetamide as the solvent was made. Conditions: 0.00998 moles 2(4Th)B, 100 ml DMAc, .010 moles n-butyl lithium, .012 moles acetyl chloride, 60°C, 16 hours. After cooling to room temperature, 100 ml ether and 50 ml water were added and the ether layer was removed. The aqueous layer was washed 5 times with 50 ml portions of ether. After drying the ether over magnesium sulfate and removing the ether under reduced pressure, a 10% recovery of 2(4Th)B was obtained. After several days crystals formed in the aqueous layer. Isolation by filtration yielded more and in total, an 80% recovery was obtained.

Synthesis from 2(4Th)B directly

0.500g (0.00249 moles) 2(4Th)B was added to a round bottom flask equipped with a stopcock adaptor with outlet capped with a septum. The set up was flamed out while vigorously flushing with nitrogen. After cooling, the nitrogen flow was slowed and 100 ml benzene was added

by transfer needle under nitrogen pressure. The heterogenous mixture was stirred at room temperature. 0.35 ml (0.0025 moles) triethylamine and 0.18 ml (0.0025 moles) acetyl chloride were syringed into flask and the stopcock was closed. After 50 hours, the heterogenous mixture was filtered. Mass of air dried solid product: 0.4005g. IR and ^1H -NMR analysis indicated this product was predominately triethylamine hydrochloride, with a small fraction of unreacted 2(4Th)B. Removal of the solvents from the filtrate under reduced pressure yielded 0.3417g crude 1-Acetyl-2-(4Th)B after air drying. Product was recrystallized once from a 50/50 benzene/cyclohexane mixture to obtain a final yield of 0.1682g (28%) pure material. M.P. = 125°C(d). Analysis calculated for $\text{C}_{12}\text{H}_9\text{N}_3\text{OS}$: C, 59.21%; H, 3.73%; N, 17.34%. Found: C, 59.24%; H, 3.81%; N, 17.14%. IR spectrum No. 23. ^1H -NMR spectrum No. 19.

Attempted Synthesis of 1-Pivalyl-
2(4-thiazolyl) benzimidazole

The procedure was the same as that used successfully to synthesize 1-Acetyl-2(4-thiazolyl)benzimidazole, however a 99% recovery of 2(4Th)B was obtained (Identified by IR and ^1H -NMR). In addition, no triethylamine hydrochloride was formed. A repeat at higher dilution and higher temperature (80°C) under which conditions the

2(4Th)B was completely soluble, again afforded a 99% recovery of 2(4Th)B.

One additional study of this reaction was conducted. 0.0025 moles 2(4Th)B was placed in two separate flasks, serum capped and flamed out while flushing with nitrogen. 15 ml DMSO was added to each. To one was added 0.0029 moles triethylamine and 0.0025 moles pivalyl chloride was added via syringe. To the second was added 0.0024 moles n-butyl lithium dissolved in hexane and 0.0025 moles pivalyl chloride via syringe. Both are monitored periodically over the next 20 hours by infrared analysis of the DMSO solutions in a sodium chloride liquid IR cell. Both indicated no change in the carbonyl absorption of pivalyl chloride at 1810 cm^{-1} .

Attempted Synthesis of 1-(Monochloro adipyl)-2-
(4-thiazolyl) benzimidazole

2.013g (0.0100 moles) 2(4Th)B was added to a 250 ml round bottom flask equipped with a thermometer, a septum for addition of nitrogen and reagents by syringe, and a condensor with a nitrogen outlet leading to a bubbler. Glassware was flamed out while flushing with nitrogen. 200 ml glyme and 1.6 ml (0.012 moles) triethylamine were added and the mixture was brought to reflux with stirring. 30 ml adipyl chloride was added by syringe slowly. A white precipitate soon began forming. After 1

hour the mixture was allowed to cool and was then filtered under a nitrogen atmosphere in ground glass filtering apparatus. The white precipitate proves to be triethylamine hydrochloride by its IR spectrum. Most of solvent was removed from the filtrate under a nitrogen atmosphere of reduced pressure and 100 ml cyclohexane was added. This reddish solution was set aside and later cooled to -15°C in a ice/salt bath to effect crystallization of the desired product. None was obtained.

A second attempt utilizing benzene as the solvent with similar stoichiometry was made. This reaction was run at room temperature for 48 hours. Again triethylamine hydrochloride was isolated by filtration. Again solvents were removed under reduced pressure and an attempt was made to distill unreacted adipyl chloride from the residue under vacuum. Some adipyl chloride was isolated but the residue which might contain the desired product blackened and became a very viscous tar.

A third attempt was made using a similar procedure with toluene as the solvent. In this case, after 49 hours reaction time at room temperature, the reaction solution was washed three times with a 10% potassium carbonate solution. A product insoluble in the organic and aqueous phase was isolated by filtration and found to be predominantly 2(4Th)B by IR analysis with some adipic acid

(C=O at 1700 cm^{-1} , very weak). The aqueous extracts were slowly acidified with hydrochloric acid and one-third of the water was removed by heating. Crystals formed on cooling. IR (KBr) and ^1H -NMR analysis of the isolated, air dried crystals indicate that it was adipic acid free of aromatic impurities. The toluene fraction was dried over magnesium sulfate, filtered and the toluene was removed under reduced pressure. The residue was analyzed by IR (KBr) and ^1H -NMR indicating that it was 2(4Th)B. No carbonyl absorptions are observed in the infrared spectrum. Hence, approximately 80% of the 2(4Th)B was recovered.

Attempted Synthesis of 1-(Monochloro
terephthalyl)-2-(4-thiazolyl) Benzimidazole

1.021g (0.00508 moles) 2(4Th)B and 10.0g terephthalyl chloride were placed in a round bottom flask equipped with a side arm adaptor which is serum capped for nitrogen inflow and a condensor with an adaptor for nitrogen outflow to an oil bubbler. The system was flushed vigorously with nitrogen and heated gently with a flame. After cooling, 150 ml toluene was added by transfer needle, and 1.0 ml (0.0072 moles) triethylamine was added by syringe. The heterogenous mixture was refluxed gently for 4 hours and filtered hot. The precipitate was washed

three times with cyclohexane and air dried. IR (KBr) analysis shows the product to be triethylamine hydrochloride, with a small amount of 2(4Th)B present. The filtrate was allowed to cool under a nitrogen blanket. Cooling to -15°C did not induce any crystallizations as anticipated.

This procedure was repeated using glyme as a solvent. Triethylamine hydrochloride was isolated as before and the glyme was removed from the filtrate under a nitrogen atmosphere at reduced pressure. 100 ml cyclohexane was added to the residue, minimizing contact with the atmosphere, and brought to a gentle reflux under nitrogen to dissolve the excess terephthalyl chloride. This hot mixture was then filtered under a nitrogen atmosphere and the white solid quickly transferred to tared vial and dried at 0.1 mm Hg pressure over calcium chloride in a dessicator. Yield: 0.807g. The IR spectrum showed two strong carbonyl absorptions at 1790 cm^{-1} and 1730 cm^{-1} . ^1H -NMR analysis showed aromatic hydrogens but no thiazolyl protons.

Reaction of 2(4Th)B with Succinic Anhydride

1.00g (0.00498 moles) 2(4Th)B and 0.62g (0.0062 moles) succinic anhydride were charged into a round bottom flask equipped with a side arm adaptor for nitrogen inflow

and a reflux condensor with an adaptor for nitrogen outflow leading to an oil bubbler. After flushing with nitrogen for one hour, 150 ml toluene was added and the mixture was brought to a reflux with stirring. After 44 hours, the homogenous solution was cooled slowly and crystals filtered (0.654g). IR analysis showed it to be 2(4Th)B with no carbonyl containing impurities. Solvents were removed under reduced pressure using a vacuum pump and avoiding contact with moisture. The final residue was analyzed by IR. All peaks could be attributed to succinic anhydride (carbonyls at 1790 and 1700 cm^{-1}) and 2(4Th)B. Adding 10 ml of chloroform, stirring and filtering leaves 0.301 2(4Th)B free of succinic anhydride (IR shows no carbonyls). 96% recovery 2(4Th)B.

Reaction of 2(4Th)B with Phenyl Isocyanate

0.506g (0.00252 moles) 2(4Th)B was added to round bottom flask and serum capped. The flask was flushed with nitrogen for 30 minutes and 100 ml benzene was added by transfer needle. 1.0 ml (0.0092 moles) phenyl isocyanate. (Aldrich, taken from a freshly opened bottle) was added by syringe. The heterogenous mixture was stirred for 2 days at room temperature and filtered. The white powder was washed twice with cyclohexane and dried at 0.1 mm HG pressure at 35°C over P_2O_5 for 20 hours. Yield of 0.407g.

The IR spectrum indicated that it was 2(4Th)B. No carbonyl or isocyanate absorptions were observed. The ^1H -NMR spectrum showed it to be identical to 2(4Th)B. 81% recovery of 2(4Th)B.

A repeat of this experiment was made using 2.0231g (0.01005 moles) 2(4Th)B, 2.0 ml (0.018 moles) phenyl isocyanate, and 0.75 ml (0.0048 moles) triethylamine as catalyst. 200 ml refluxing glyme was used as the solvent to completely dissolve the 2(4Th)B. The solution was periodically monitored by IR analysis. It is clear that the isocyanate remains with only a small absorption at 1705 cm^{-1} . After 44 hours, there was no change.

Another attempt was made using approximately equimolar amounts of 2(4Th)B, triethylamine and phenyl isocyanate in a 4% 2(4Th)B in DMSO solution at room temperature. Again this was monitored by infrared analysis indicating that after 48 hours most of the phenyl isocyanate remained (2330 cm^{-1}), however a carbonyl absorption at 1710 cm^{-1} was present. A further IR study of the reaction of phenyl isocyanate in DMSO was conducted by making up three solutions with reagent concentrations at 0.1M - 1) phenyl isocyanate; 2) phenyl isocyanate and 2(4Th)B; 3) phenyl isocyanate and triethylamine. Products were not isolated. IR spectra discussed in Chapter IV.

Syntheses of 1-(3-Isocyanato-4-methyl phenyl
carbamoyl)-2-(4-thiazolyl) benzimidazole

0.502g (0.00250 moles) 2(4Th)B was added to a round bottom flask equipped with a serum capped reflux condensor and flushed with nitrogen for 30 minutes. 200 ml benzene was added by transfer needle and the mixture was brought to a reflux until complete solvation. The mixture was allowed to cool causing partial crystallization into a fine white powder which was adequately dispersed by stirring. 10.0 ml (0.0703 moles) toluene diisocyanate (technical grade, 80% 2,4-isomer, 20%, 2,6-isomer) was syringed into mixture. The mixture was stirred for 48 hours and then filtered under reduced pressure through a fritted glass filter funnel attached directly to the round bottom flask to minimize contact with the atmosphere. The white powder was washed quickly twice with dry benzene and then dried under a vacuum of 0.1 mm Hg pressure for two hours. Yield of 0.7768 g. Analysis calculated: C, 60.79; H, 3.49; N, 18.66. Found: C, 60.29; H, 3.48; N, 18.27. IR spectrum No. 24. ^1H -NMR spectrum No. 20.

Several repetitions were made using similar heterogeneous conditions and products were analyzed by IR, ^1H -NMR spectroscopy and elemental analysis. All showed an isocyanate absorption at 2290 cm^{-1} and a carbonyl absorp-

tion at 1720 cm^{-1} in the IR. The ^1H -NMR spectra were similar to that of Spectrum No. 20 with the integrations of the peaks being slightly different due to variations in conversion as discussed in Chapter IV.

Using glyme at reflux as the solvent to create a homogenous solution, 46% of the initial 2(4Th)B was initially recovered by the filtration, but addition of cyclohexane to the filtrate (1/3 total) afforded a fine white powder. After drying at 0.1 mm Hg pressure and ambient temperature for 20 hours, this product had a ^1H -NMR spectrum similar to the product just described. Integration indicated that it was the desired product only. Analysis calculated: C, 60.79%; H, 3.49%; N, 18.66%. Found: C, 60.73%; H, 3.52%; N, 18.50%. IR spectrum similar to IR spectrum No. 24. This is the product used for subsequent reactions.

Reactions of the TDI Adduct of 2(4Th)B

With 2-hydroxy-propylamine (2H-PrA)

0.502g (0.00134 moles) TDI adduct of 2(4Th)B was added to a round bottom flask equipped with a septum. 20 ml 2H-PrA was syringed into the flask and contents stirred until complete solvation (5 hours). The 2H-1PrA was distilled out under vacuum leaving a pasty mixture, which after failed crystallization attempts was placed in

a tared vial and dried under a vacuum of 0.1 mm Hg at 62°C for 24 hours over P_2O_5 . The IR spectrum No. 25 showed no isocyanate absorptions nor carbonyl absorptions at 1720 cm^{-1} ; however, absorptions between 1700 cm^{-1} and 1650 cm^{-1} were present. Alternately, DMSO or glyme were used as solvents and in both cases, the product isolated displayed the same strong IR absorptions.

With methanol

0.5321g (0.00142 moles) of the TDI adduct was added to a round bottom flask with 50 ml spectrophotometric grade methanol and stirred until dissolved. The solvent was removed under reduced pressure leaving a white residue. Yield: 0.5446g. IR spectrum No. 26. 1H -NMR spectrum No. 21.

With ethylene glycol

0.512g (0.00137 moles) of the TDI adduct was stirred into 40 ml ethylene glycol until dissolved (5 hours). The mixture is then poured into water (10:1) and the precipitate collected. This proved to be predominantly 2(4Th)B by IR analysis, with a small amount of the urethane by-product.

With acetic acid

0.501g (0.00134 moles) of the TDI adduct was stirred in 100 ml toluene and 5 ml glacial acetic acid

until dissolved (2 hours). The solvents were removed under reduced pressure leaving a pasty white material, which was triturated with acetone resulting in 0.3967g white powder. IR spectrum No. 27.

With P(E/MAA)

1.51g P(E/MAA) (1.3 mole %, 0.00070 moles) was dissolved in 75 ml toluene at reflux and 0.261g (0.000697 moles) of the TDI adduct was added. The mixture became homogenous, but after 24 hours of stirring under nitrogen, it was yellow and heterogenous and was precipitated in acetone. The polymer was redissolved in toluene and a film was cast on a sodium chloride plate and IR analysis indicated it to be unreacted P(E/MAA).

Synthesis of 1-(2-hydroxyethyl)-2-
(4-thiazolyl) benzimidazole

A clean dry 100 ml graduated cylinder was serum capped and then flamed out with a nitrogen flow. Upon cooling 60 ml DMSO was added via transfer needle and 2.0 ml (0.014 moles) triethylamine was syringed in. Ethylene oxide (Eastman, stored under nitrogen) was transferred from its storage flask to a 1.0 ml volumetric flask in a ice bath, filled to the mark and subsequently transferred to the above DMSO solution by transfer needles. Approximately 1 ml increase is noticed in the DMSO solution.

2.005g (0.00998 moles) 2(4Th)B was charged into a 100 ml Parr pressure reactor. The DMSO solution was quickly added, and the reactor was closed and pressurized with nitrogen to 200 psi. The mixture was heated to 50°C and stirred for 16 hours, after which time it was cooled to room temperature and the pressure was released. The DMSO solution was poured into 200 ml water and the precipitate was filtered. ^1H -NMR showed it to be 2(4Th)B - 84% recovery. After several hours, crystals formed in the aqueous solution. Isolation and drying at 62°C over P_2O_5 at 0.1 mm Hg pressure yielded a white powder: 0.295g, 9%. Analysis calculated for $\text{C}_{12}\text{H}_{11}\text{N}_3\text{S}$: C, 58.77%; H, 4.52%; N, 17.13%. Found: C, 58.26%; H, 4.42%; N, 17.17%. IR spectrum No. 28. ^1H -NMR spectrum No. 23.

Similar procedures using glyme as the solvent and pyridine or triethylamine as the base catalyst gave no conversion. Procedures using dimethyl acetamide or DMSO as the solvent, and sodium hydride or n-butyl lithium to partially convert the 2(4Th)B to its anion, which in turn acts as the base catalyst, also showed no conversion.

Reaction of 1-(2-hydroxyethyl)-2-(4-thiazolyl)
benzimidazole with P(E/MACl)

1.00g P(E/MAA) (1.3 mole % MAA, 0.0017 moles MAA) was converted to P(E/MACl) by the oxalyl chloride method

using 125 ml toluene. The temperature was brought to 60°C from 110°C (reflux) and, with the nitrogen flow vigorous, 0.152g (6.64×10^{-4} moles, 39% of MACl) 1-2HE-2(4Th)B was added. After 1 hour 0.5 ml (0.005 moles) triethylamine was added and the system was brought to a gentle reflux. After 5 hours a small aliquot was removed and a film was cast on a sodium chloride plate. IR analysis showed a strong carbonyl absorption at 1805 cm^{-1} indicative of the P(E/MACl) and a smaller absorption at 1735 cm^{-1} typical of esters. The solution was then cooled to 60°C and 10 ml methanol was added. After stirring for one hour, the hot solution was poured slowly into 500 ml methanol. The precipitate was filtered, redissolved in toluene, and reprecipitated in methanol, and then dried at 0.1 mm Hg pressure and room temperature for 24 hours. Yield: 0.894g. Analysis found: C, 77.83%; H, 13.76%; N, 0.27%; S, 0.27%. IR spectrum now appears to be very similar to P(E/MMA) (No. 19).

Polymer Blending and Conditioning

All blends were prepared by mixing the components in a Brabender mixing head for 20 minutes at 250°C at 30 RPM. The blending was performed under a nitrogen atmosphere to prevent oxidative degradation. The resultant blend was pressed to uniform thickness at 250°C and

20,000 psi for at least 6 minutes between Teflon sheets using a Pasadena press. The films were cut into Dumbbell shaped strips, ASTM specification No. D.638, to perform the mechanical tests.

The strips were placed in boiling water for 3 hours and stored under 2 different conditions. One involved sealing the strip in a polyethylene envelope for at least five days to mimic 50% relative humidity conditions. The second involved storing in a jar above a saturated ammonium sulfate solution, which creates a relative humidity of 80%. Water absorption was determined by measuring the mass lost after drying a film at 105°C for 24 hours under a vacuum of 0.1 mm Hg pressure.

Measurements and Analyses

Spectroscopic Analyses

Infrared spectra were recorded on a Perkin Elmer Model 283 Grating Infrared Spectrometer. Solids were run as KBr pellets. Polymers were run as films cast from solution. Solutions were run in a NaCl cell with a matching reference containing the pure solvent.

NMR spectra were recorded on a Varion T60 ^1H -NMR spectrometer, a Perkin Elmer Model R-32 90 MHz spectrometer, a Varion CFT-20 100 MHz spectrometer, or a Varion XL-200 spectrometer. Spectra run on the Varion XL-200

were run at 50°C. DMSO-d₆ was the most commonly used solvent. D₂O and CDCl₃ were also used.

Elemental Analyses

Elemental Analyses were performed by the Micro-analysis Laboratory of the University of Massachusetts.

Thermal Analyses

A Perkin Elmer Differential Scanning Calorimeter, Model DSC-2, was used to determine all glass transition temperatures and all melting transitions of the polymers and the polymer blends. Sample sizes of 5 - 15 mg were used and nitrogen atmosphere was maintained during analyses. A heating rate of 20°C per minute was utilized unless otherwise specified.

X-ray diffraction analysis

X-ray diffraction analysis was conducted using a Statton II camera on powdered samples with the film approximately 2 inches from the sample. All polyaspartamide derivatives failed to show crystallinity.

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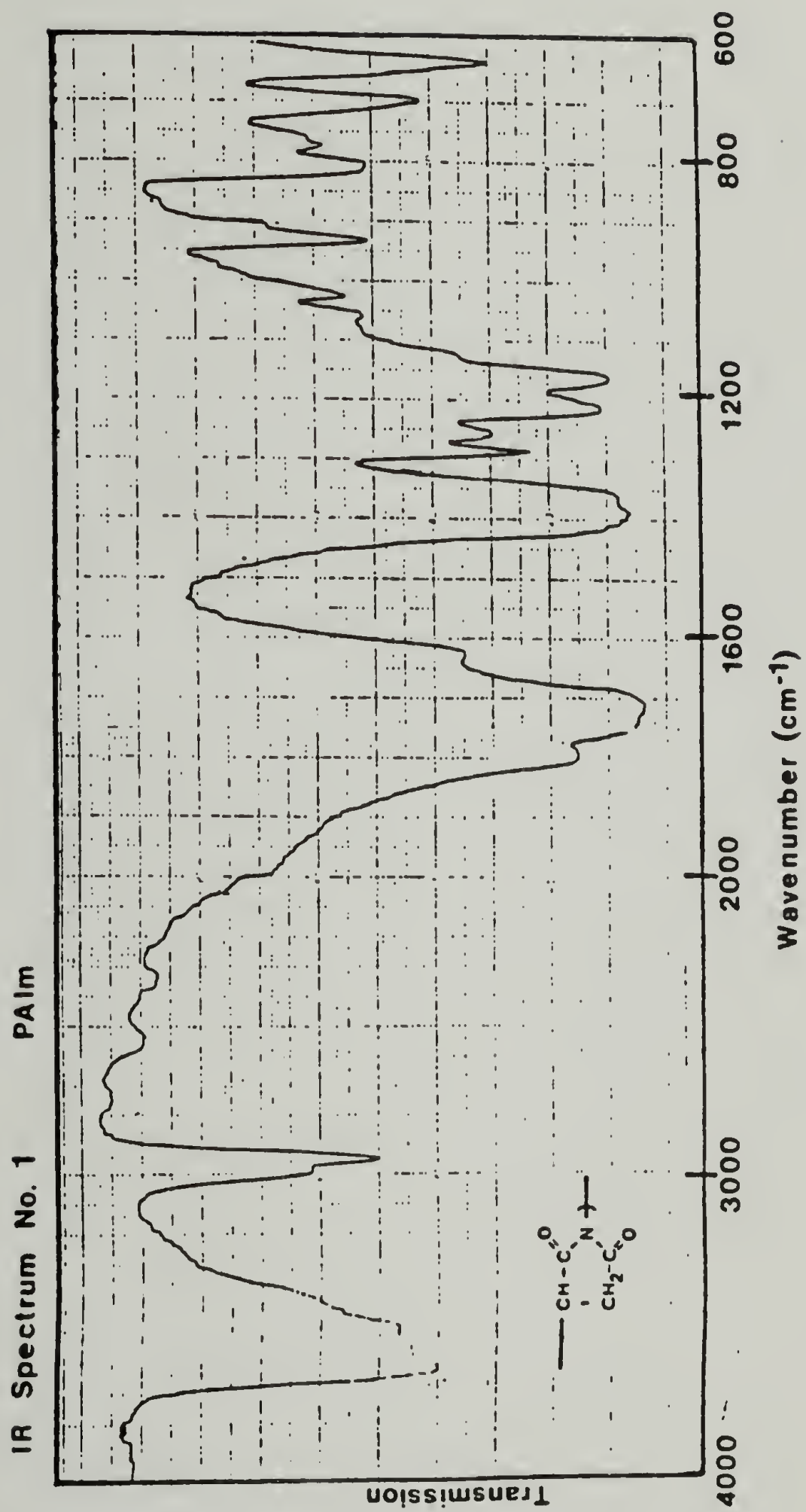
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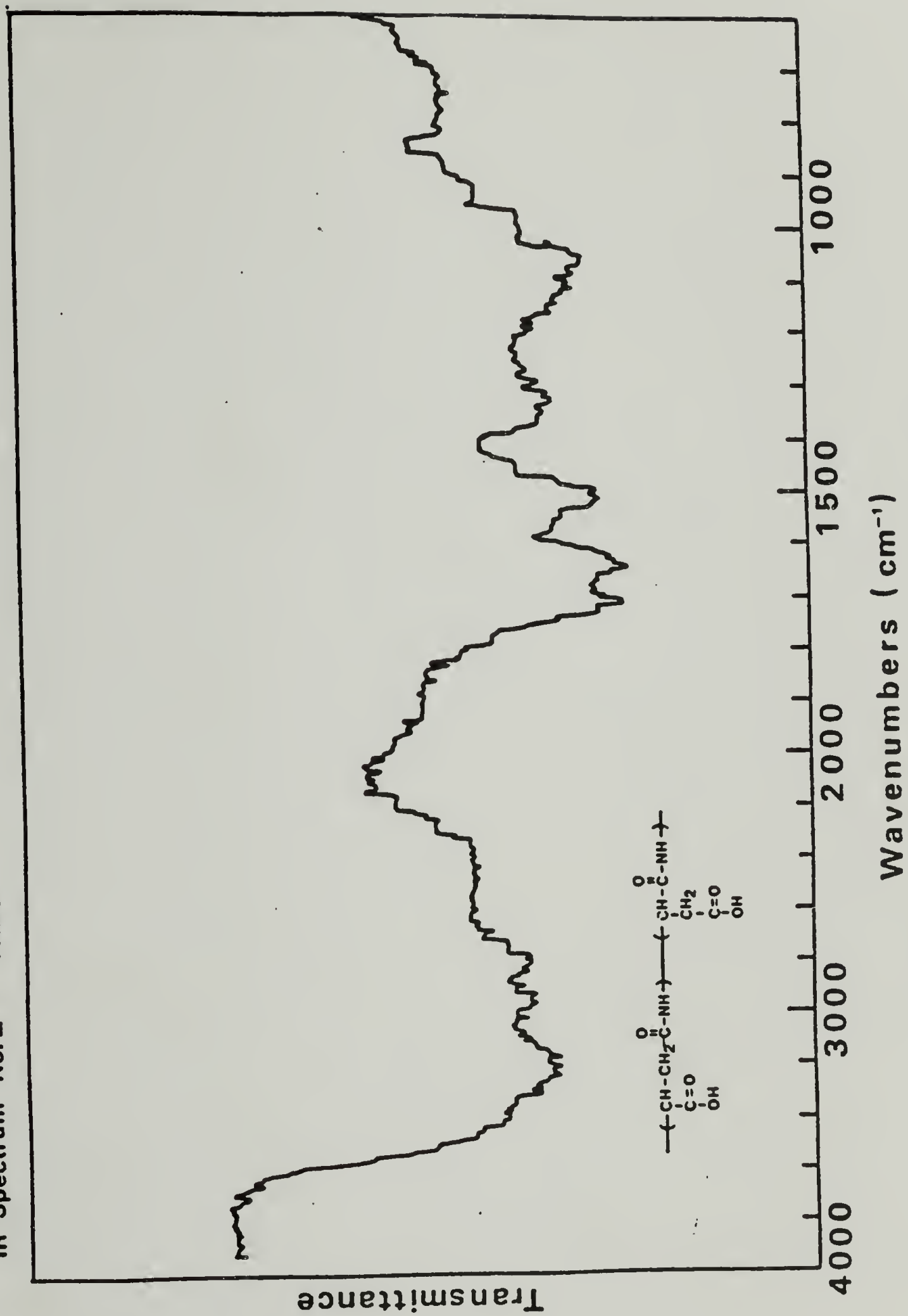
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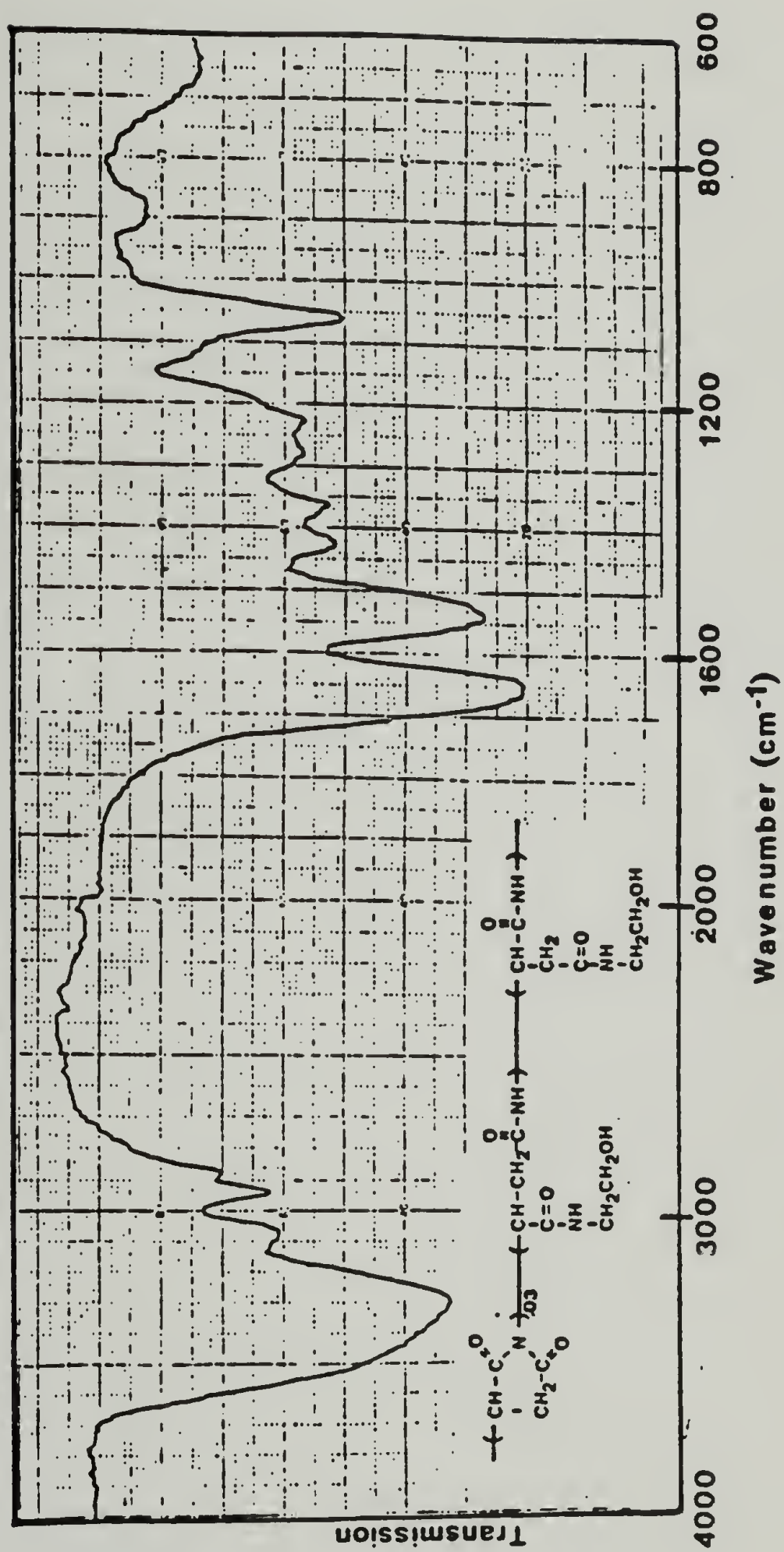
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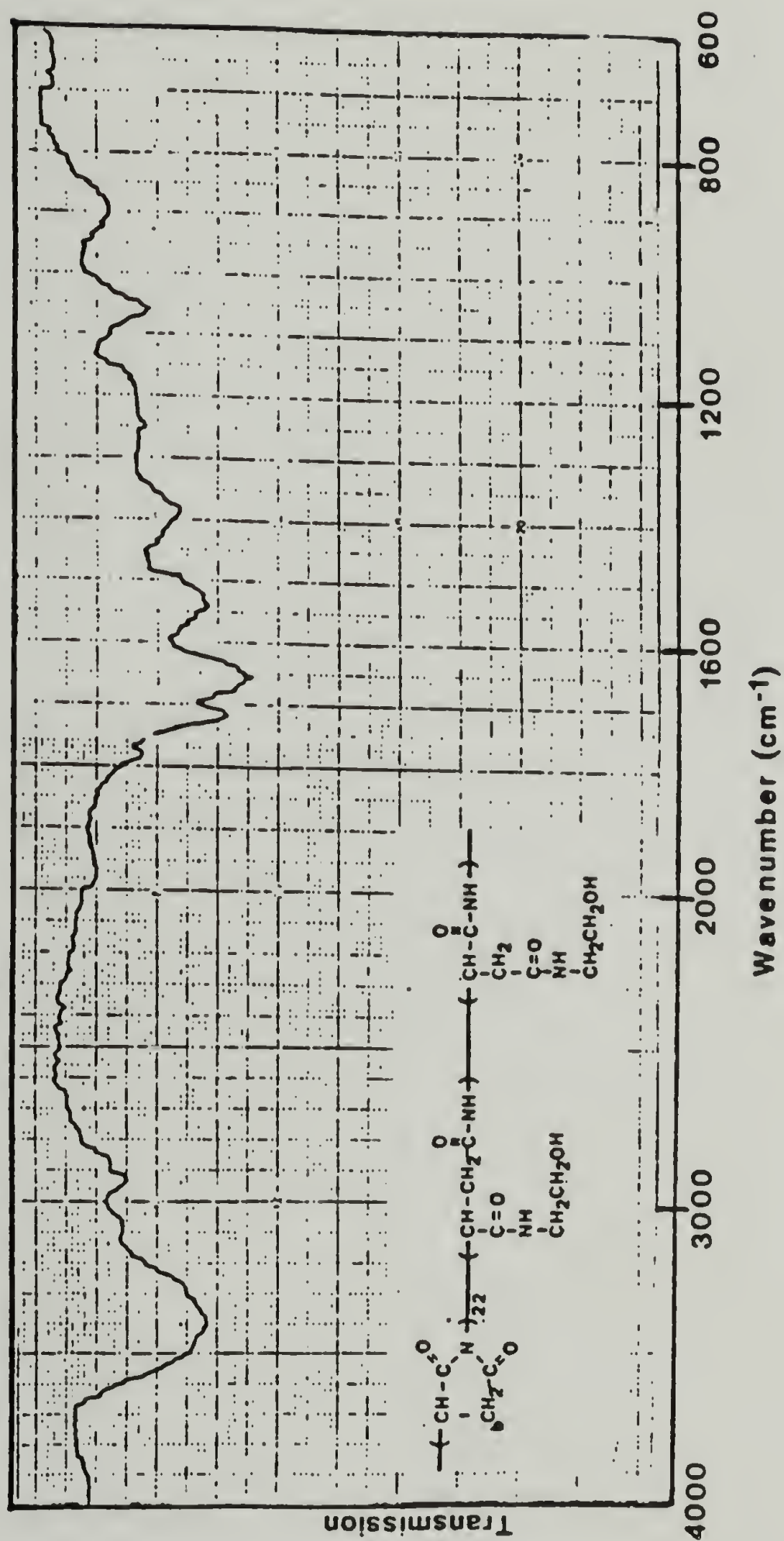
IR Spectrum No.2 PAAC



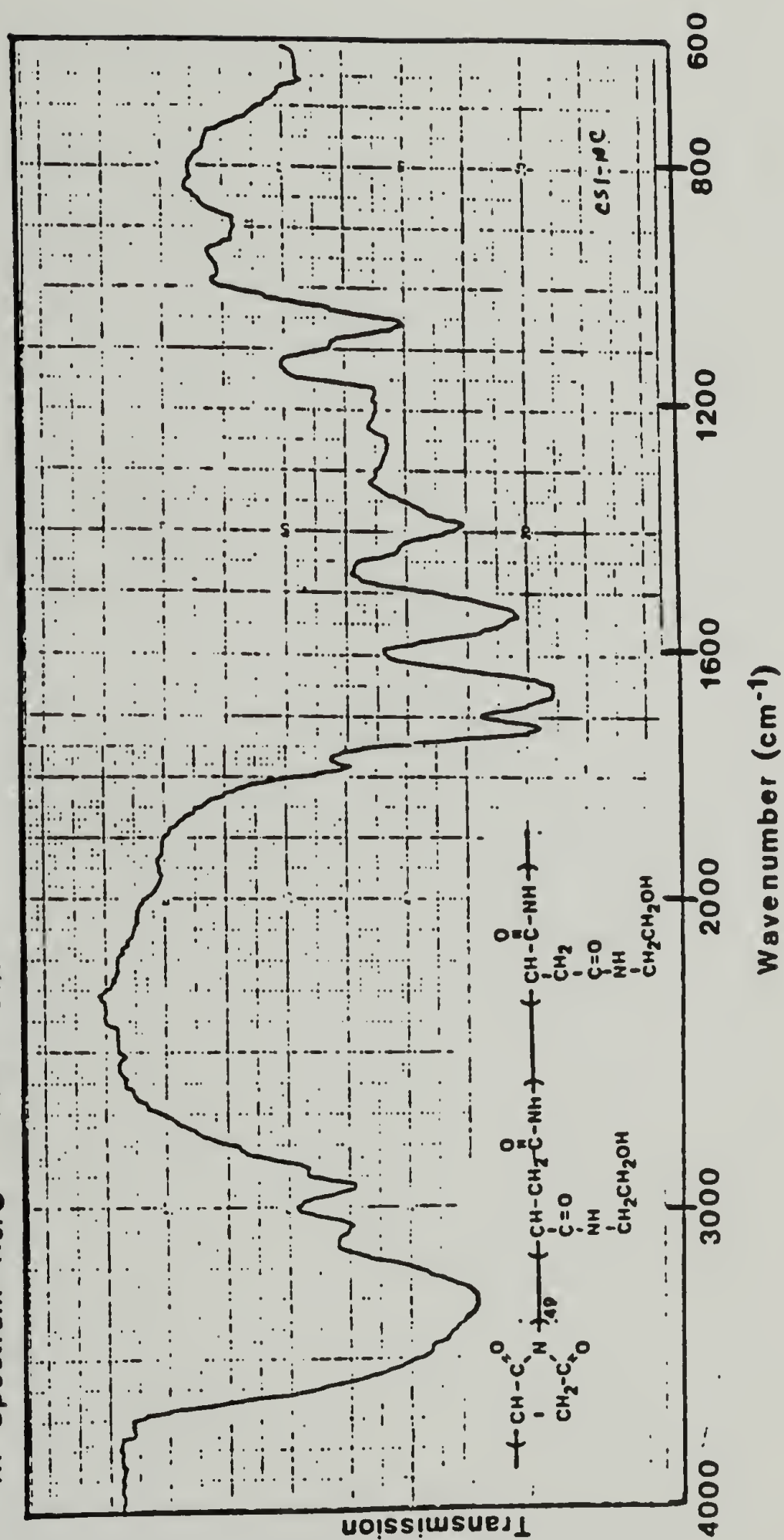
IR Spectrum No.3 PHEA - 97%



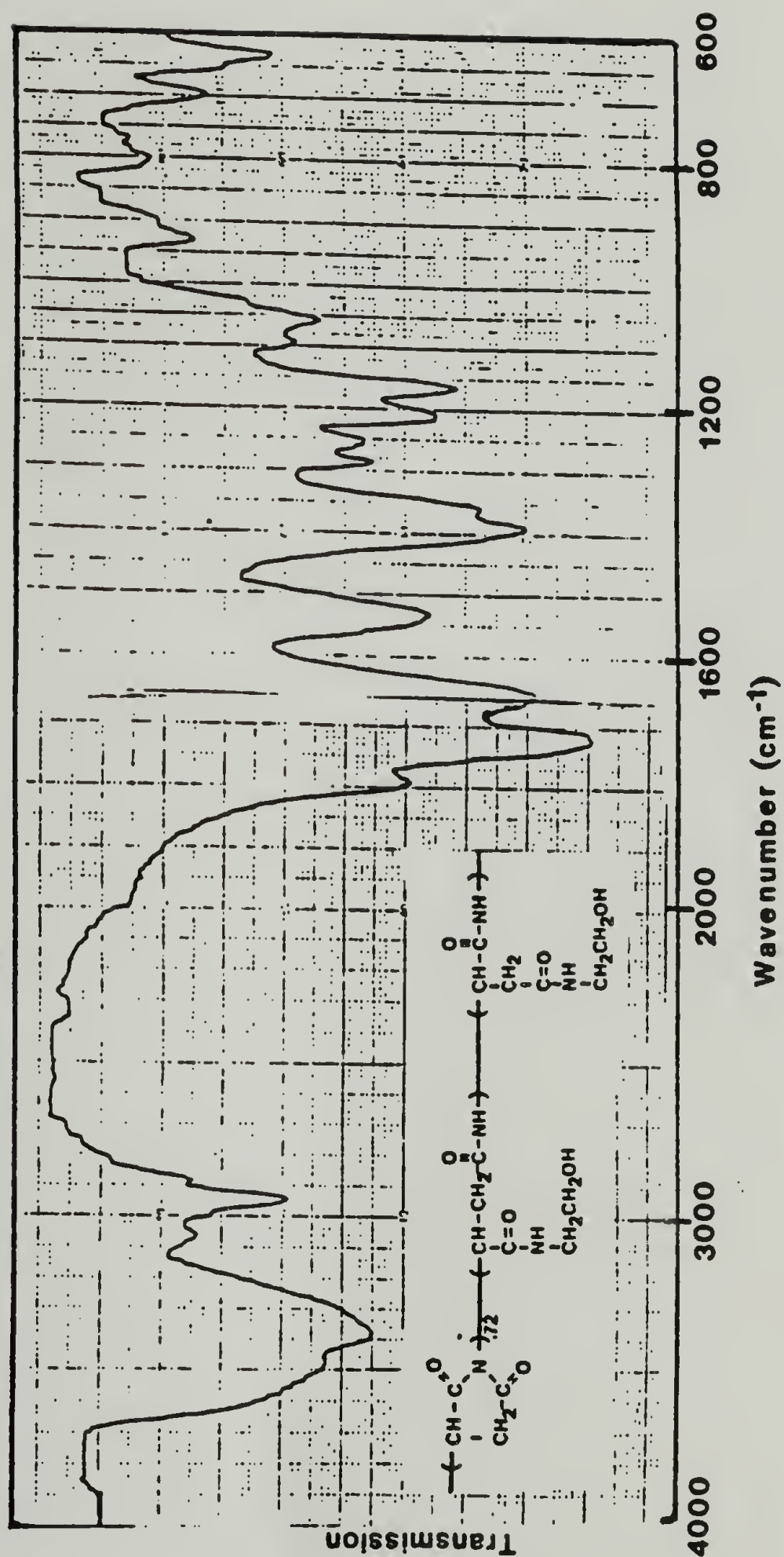
IR Spectrum No. 4 PHEA-78%



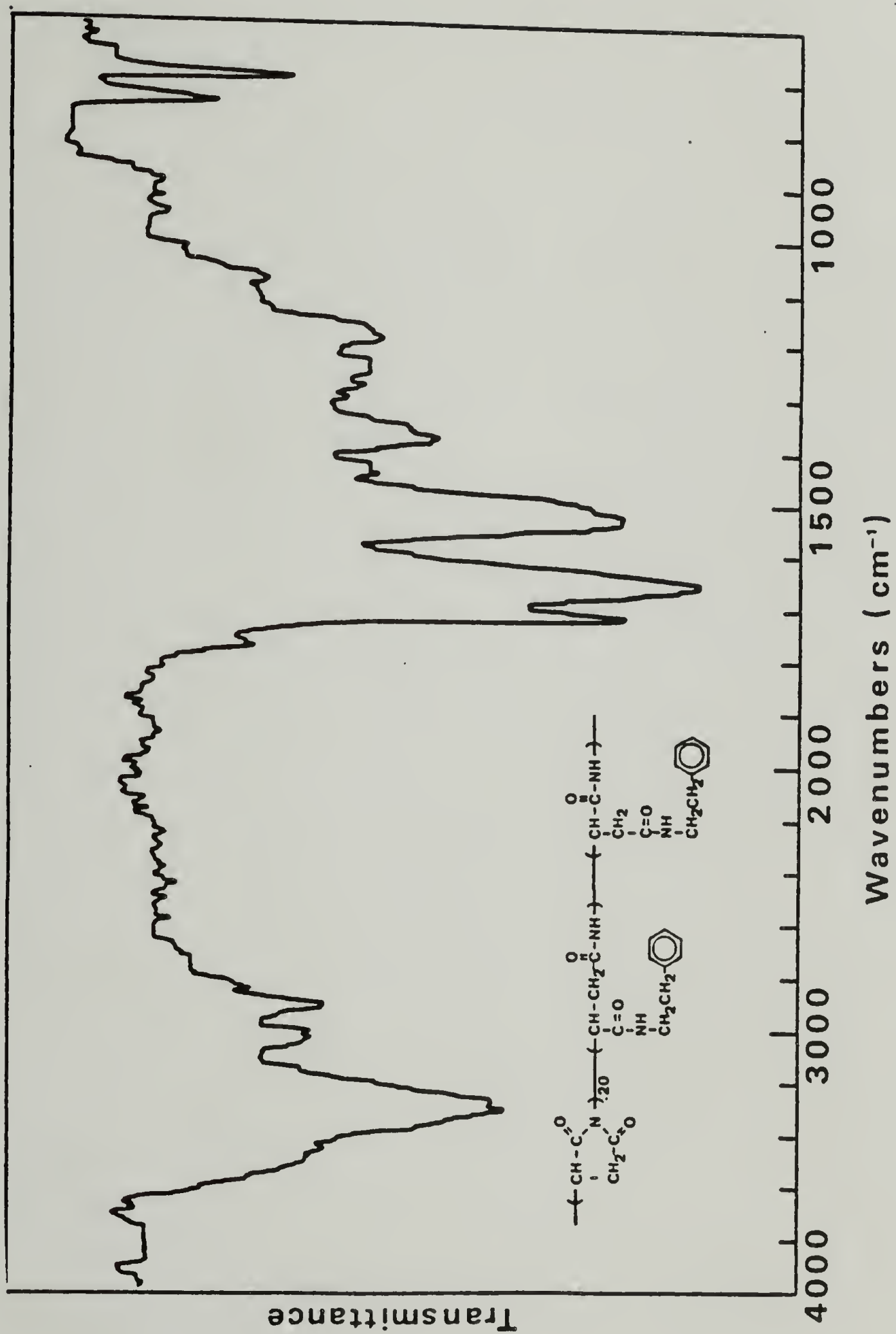
IR Spectrum No.5 PHEA -51%



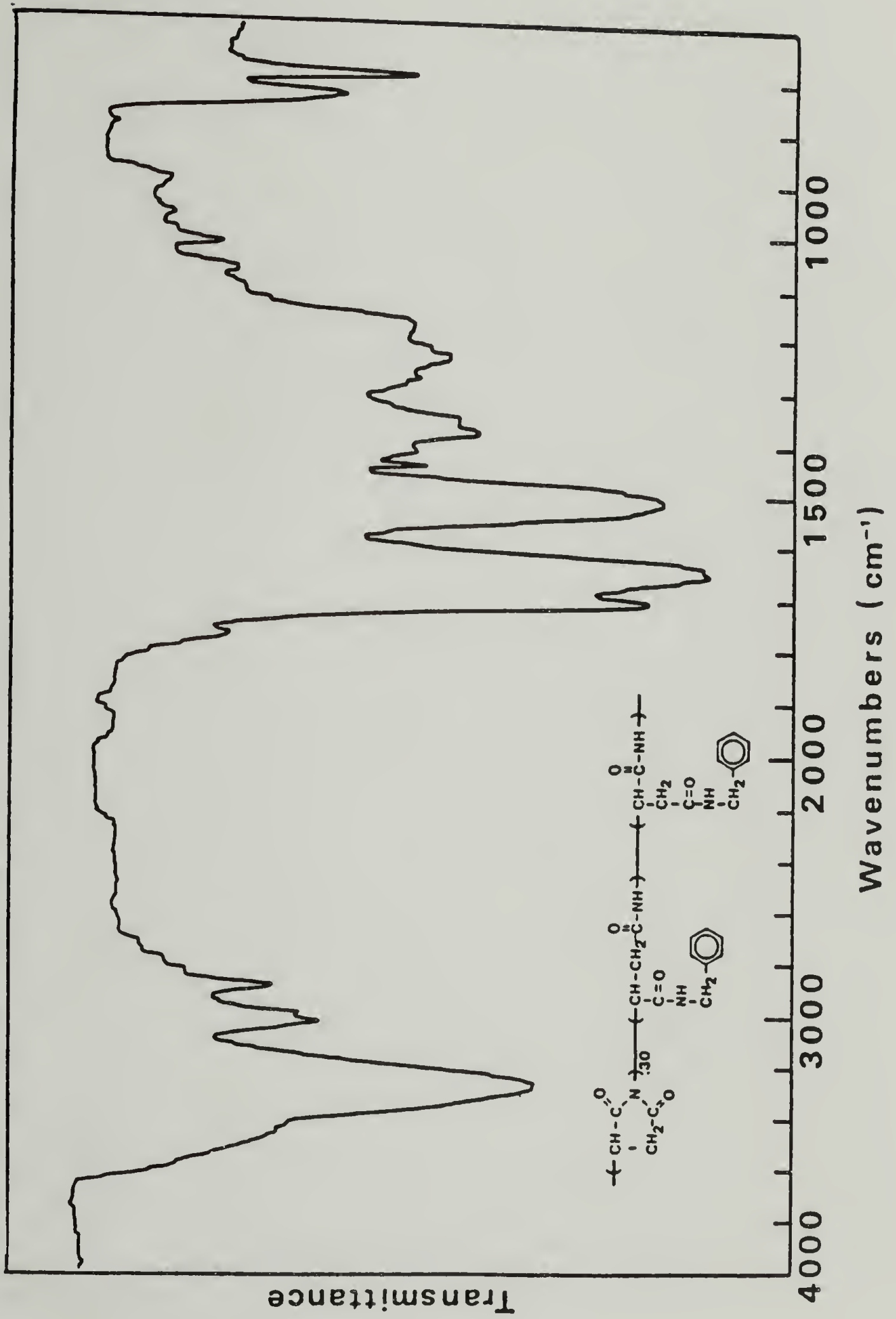
IR Spectrum No.7 PHEA - 28%



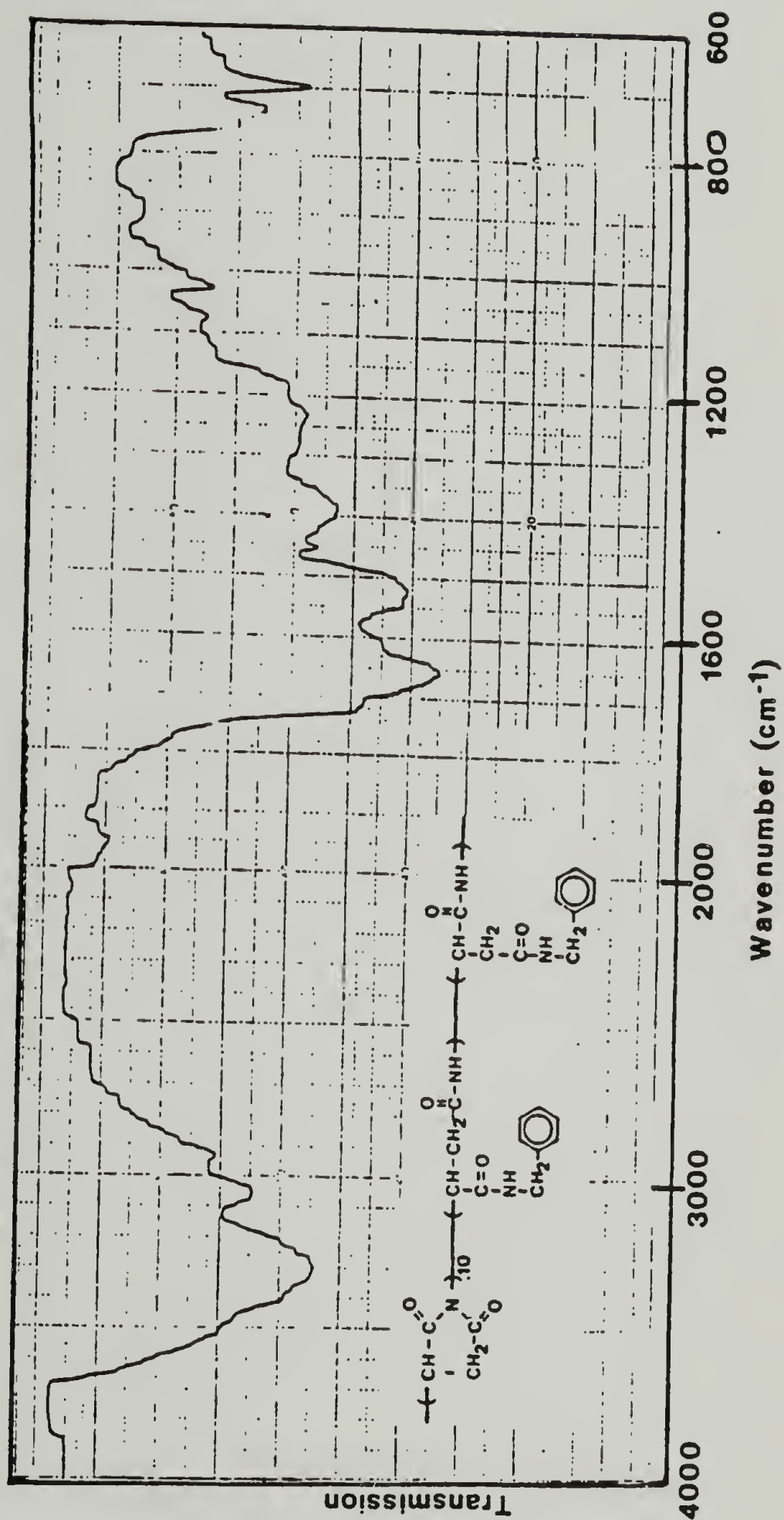
IR Spectrum No.8 PPEA-80%



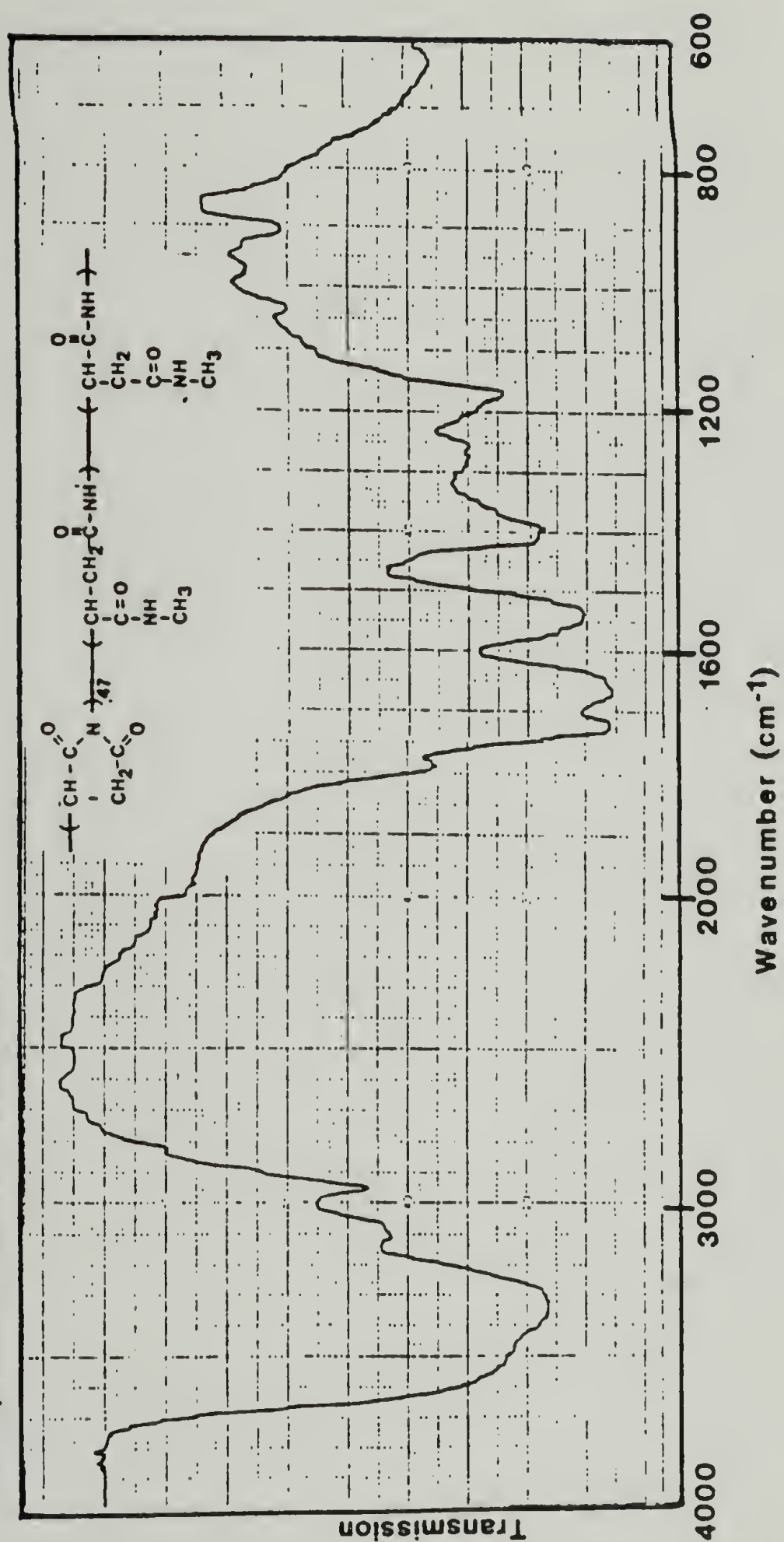
IR Spectrum No. 9 PBA - 70%

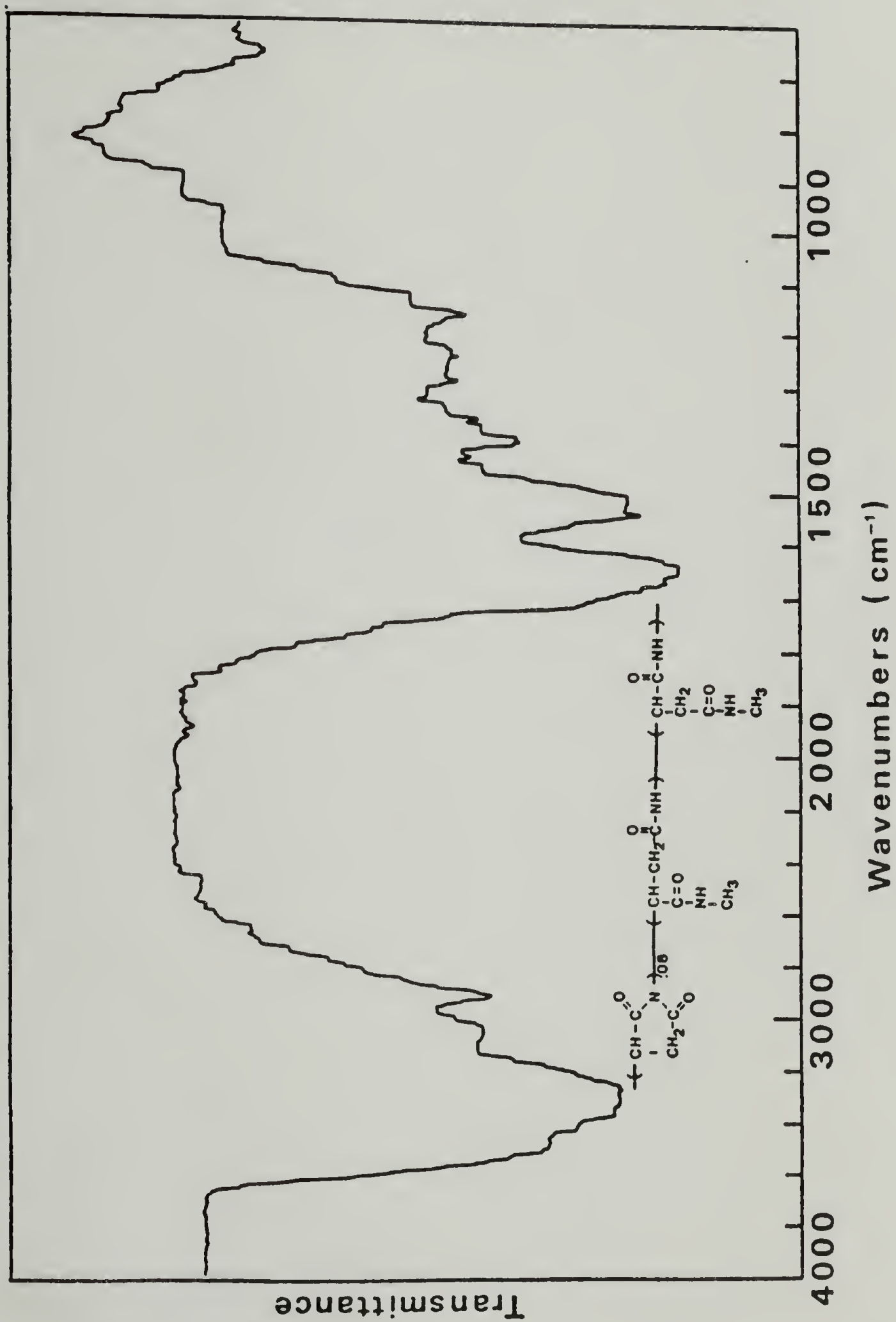


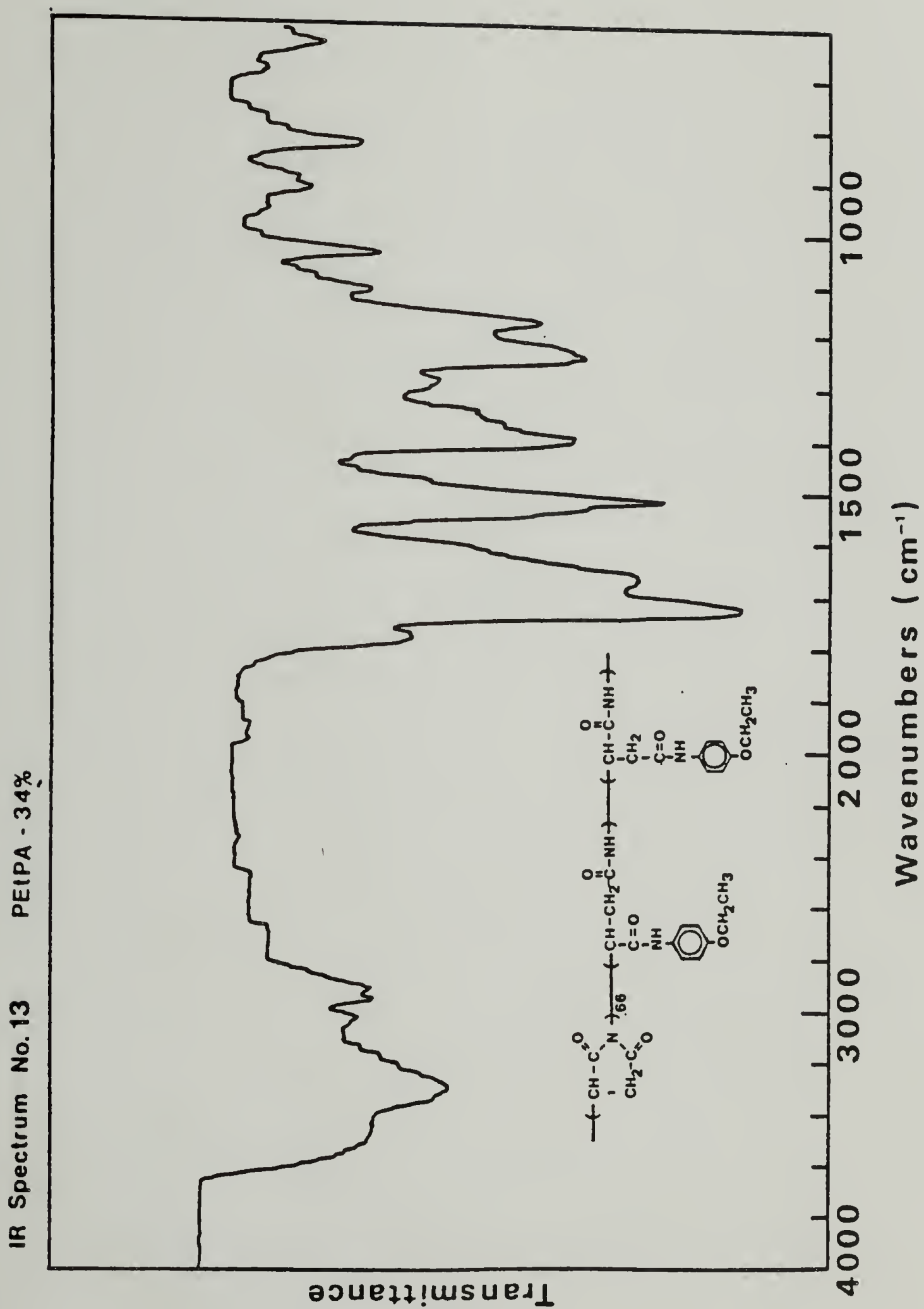
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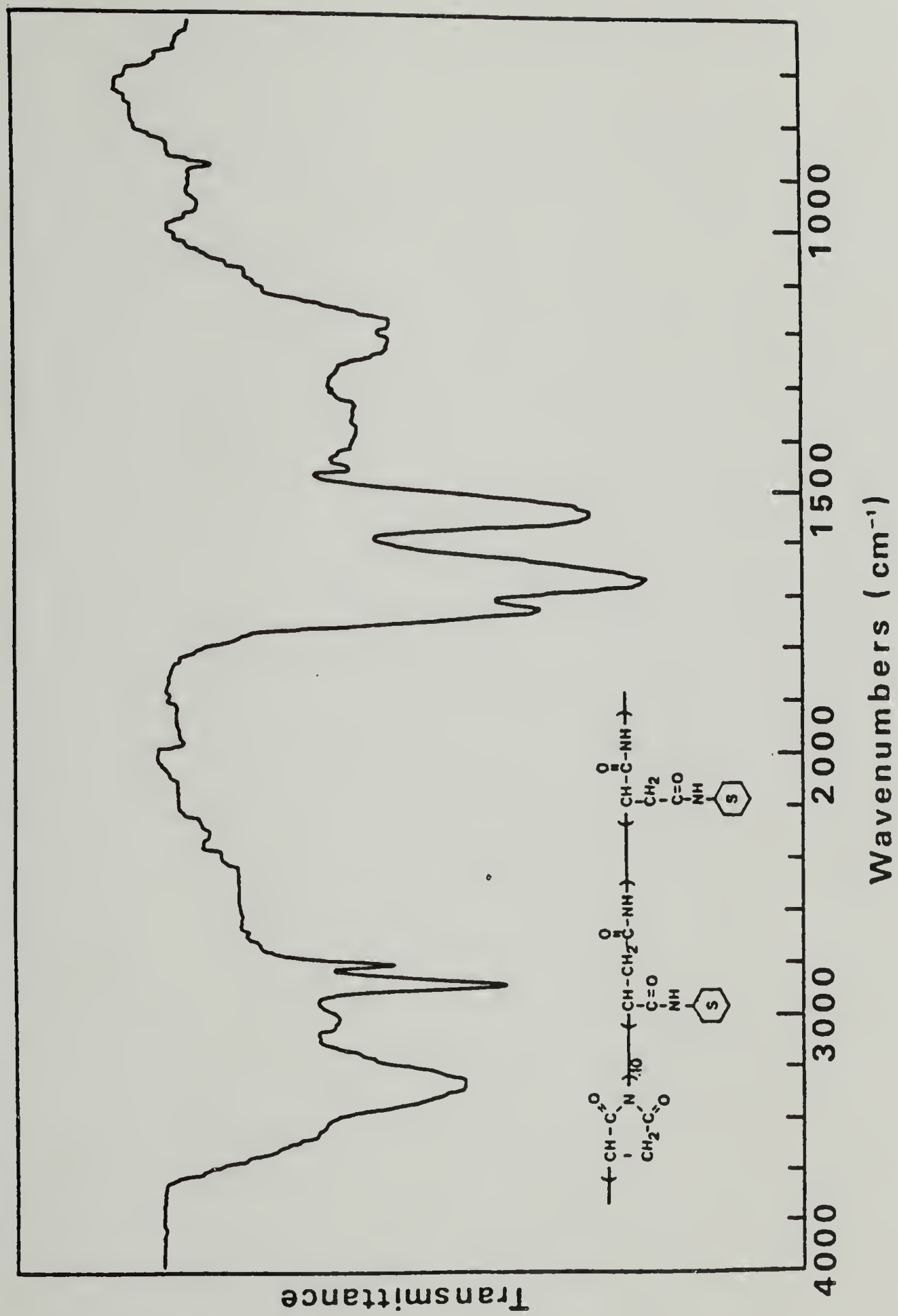
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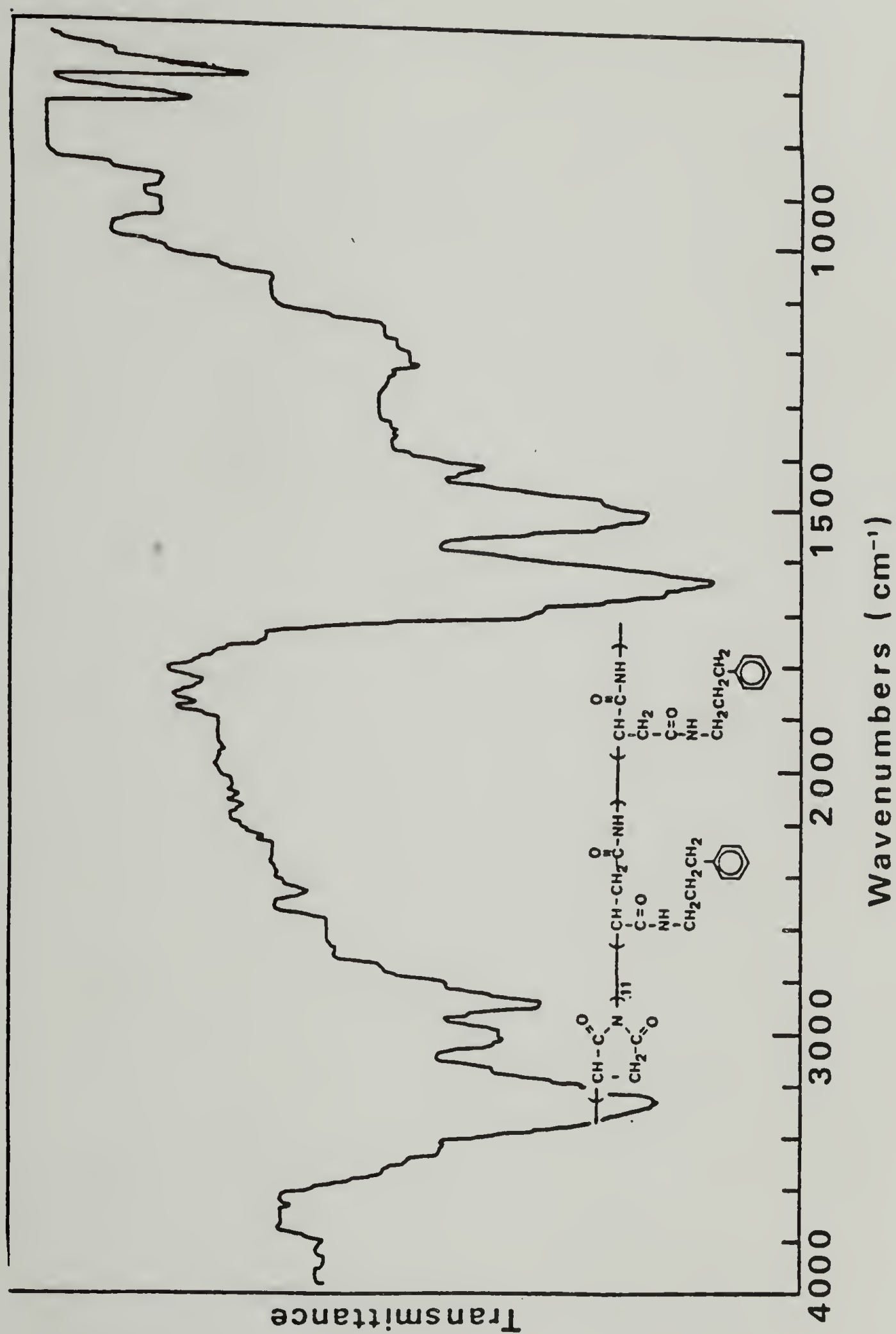




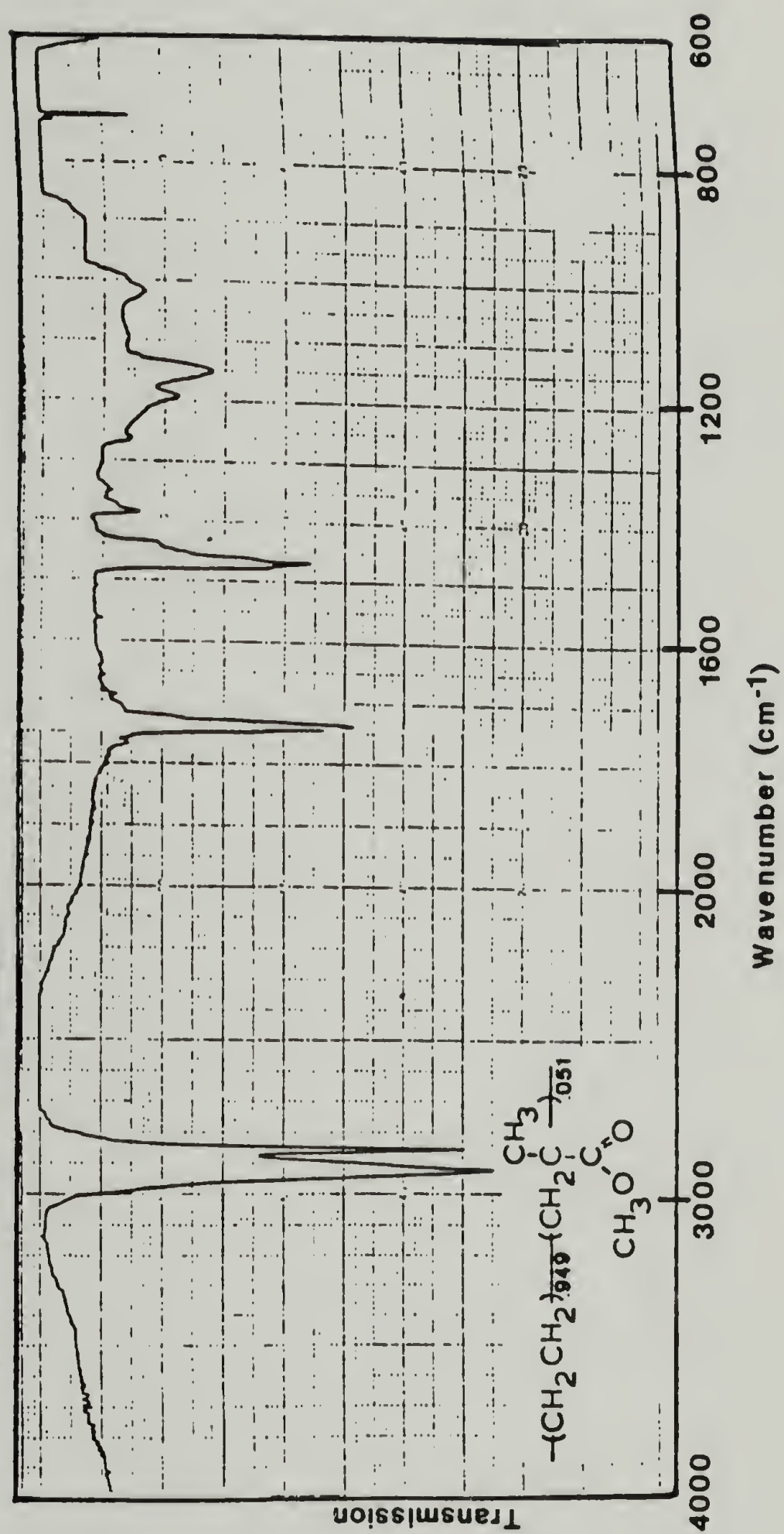


IR Spectrum No.14 PcHA - 90%

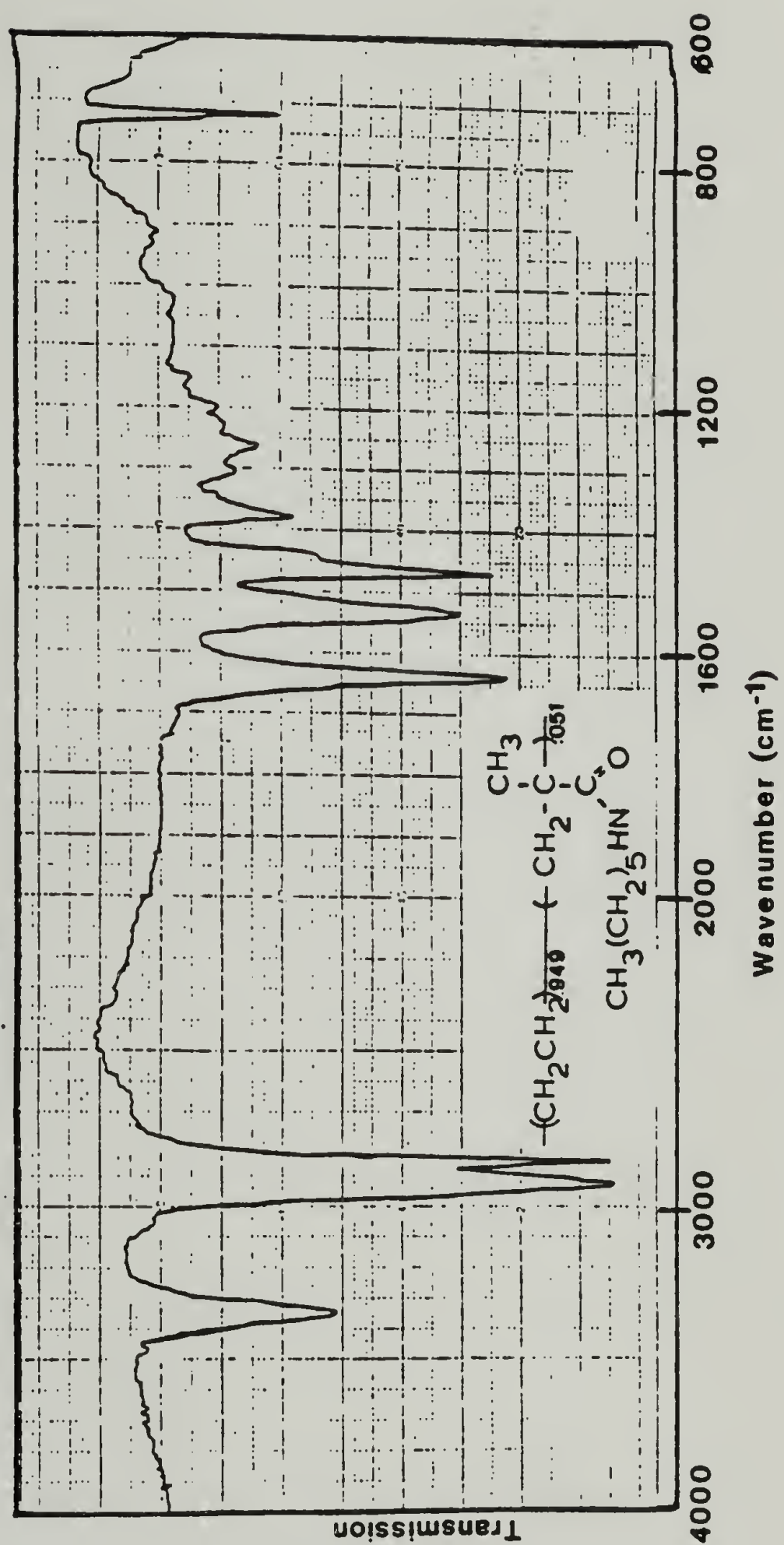




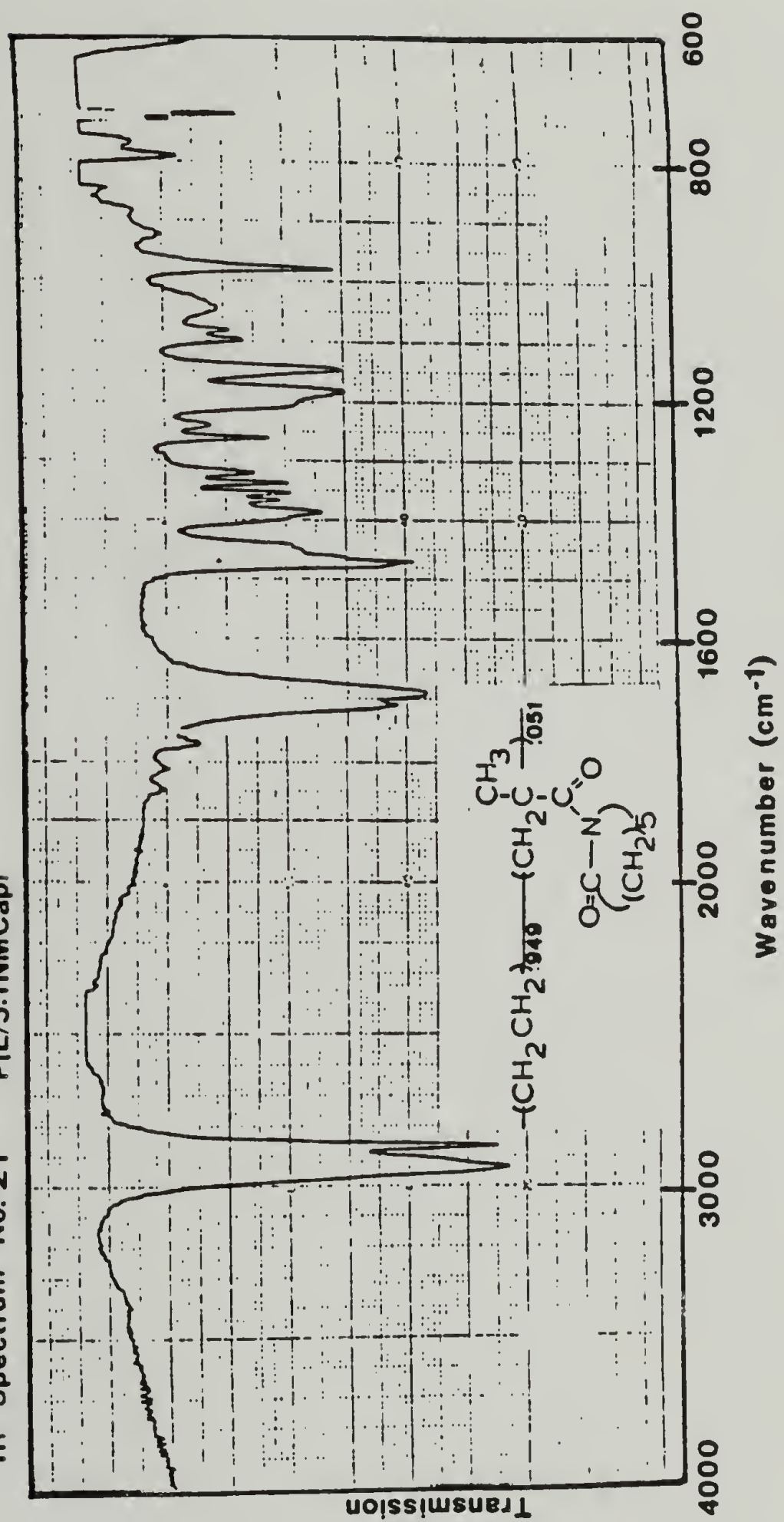
IR Spectrum No.19 P/E/5.1MMAI



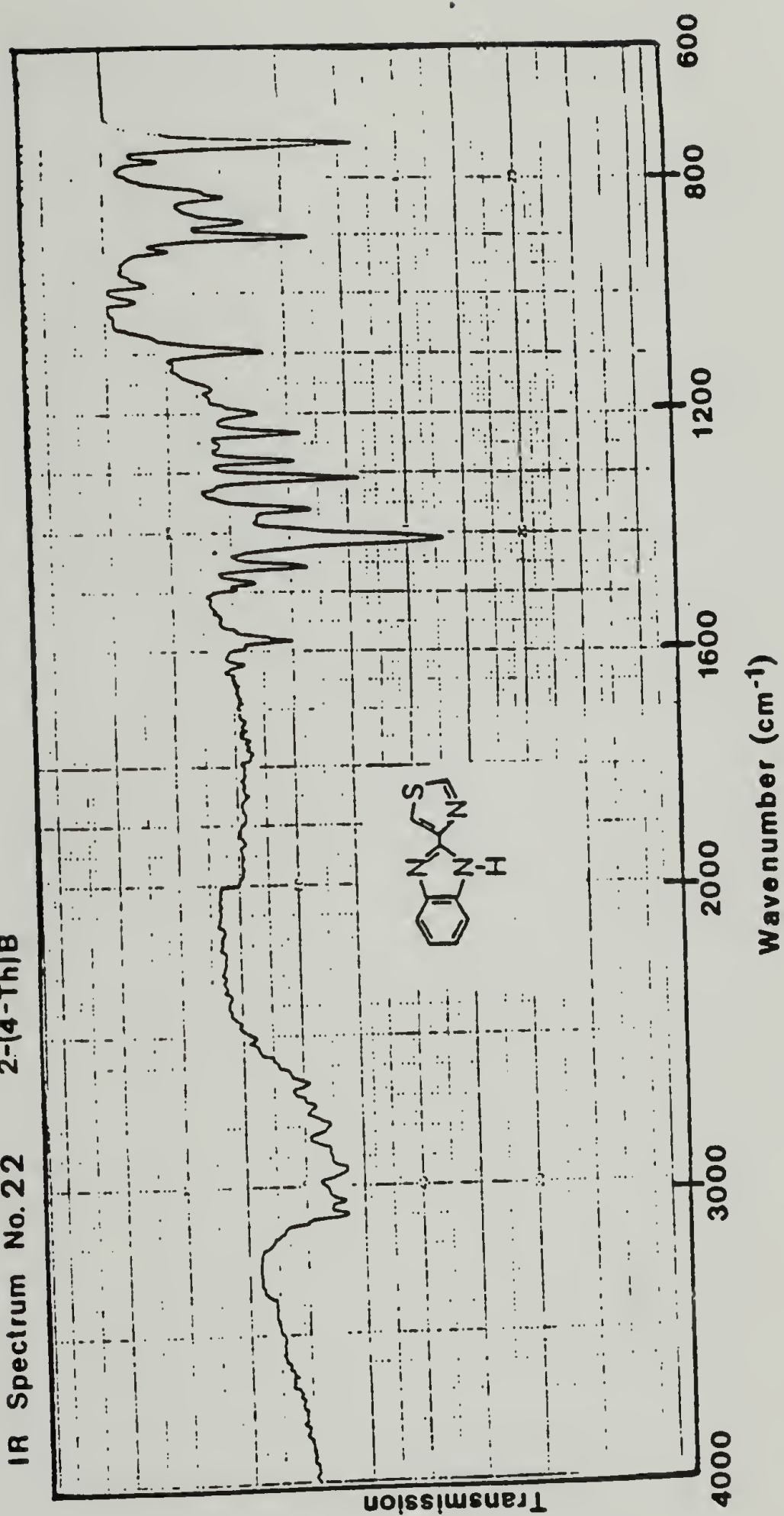
IR Spectrum No. 20 P/E/5.1nHMAI



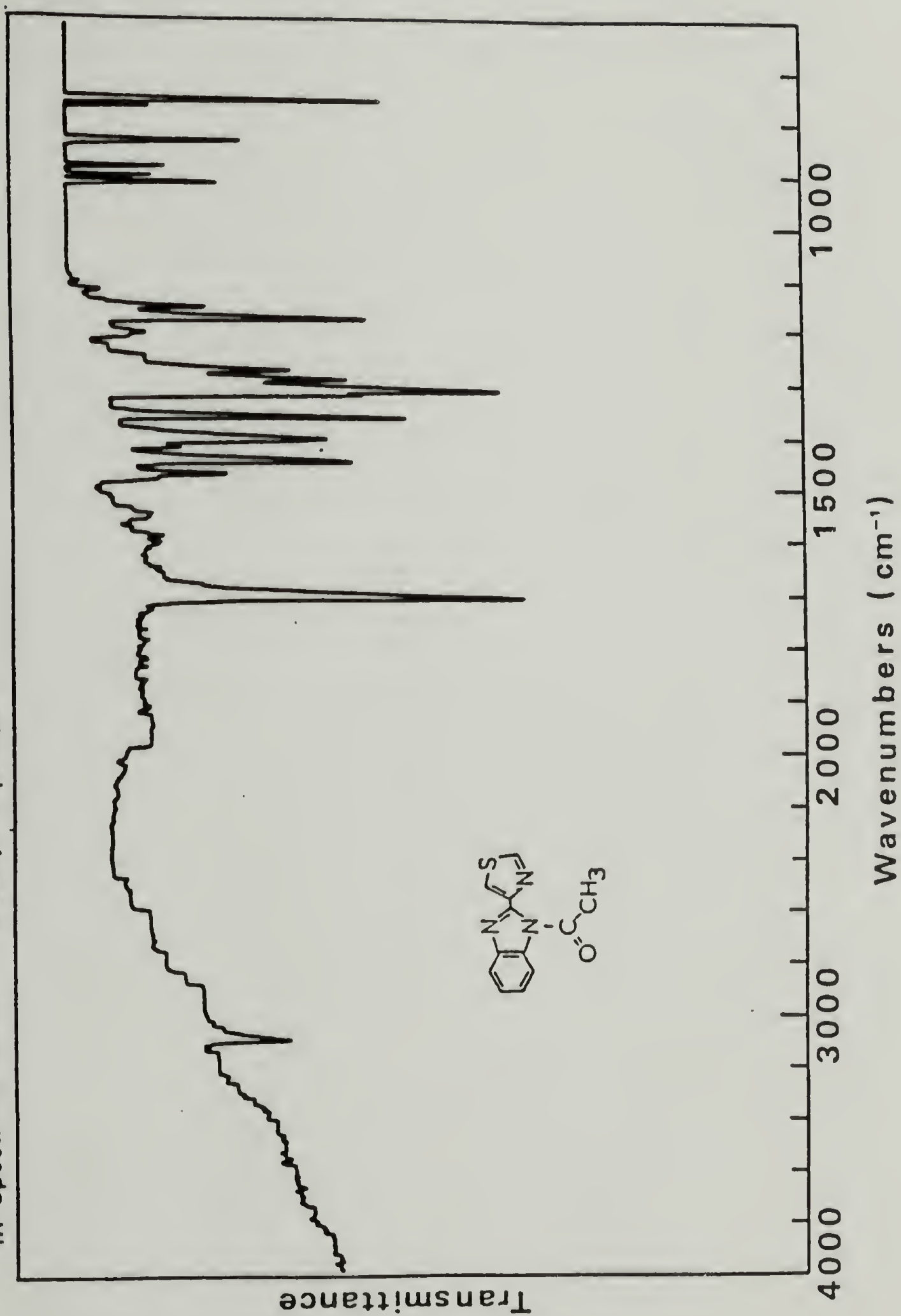
IR Spectrum No. 21 P/E/5.1NMCapI



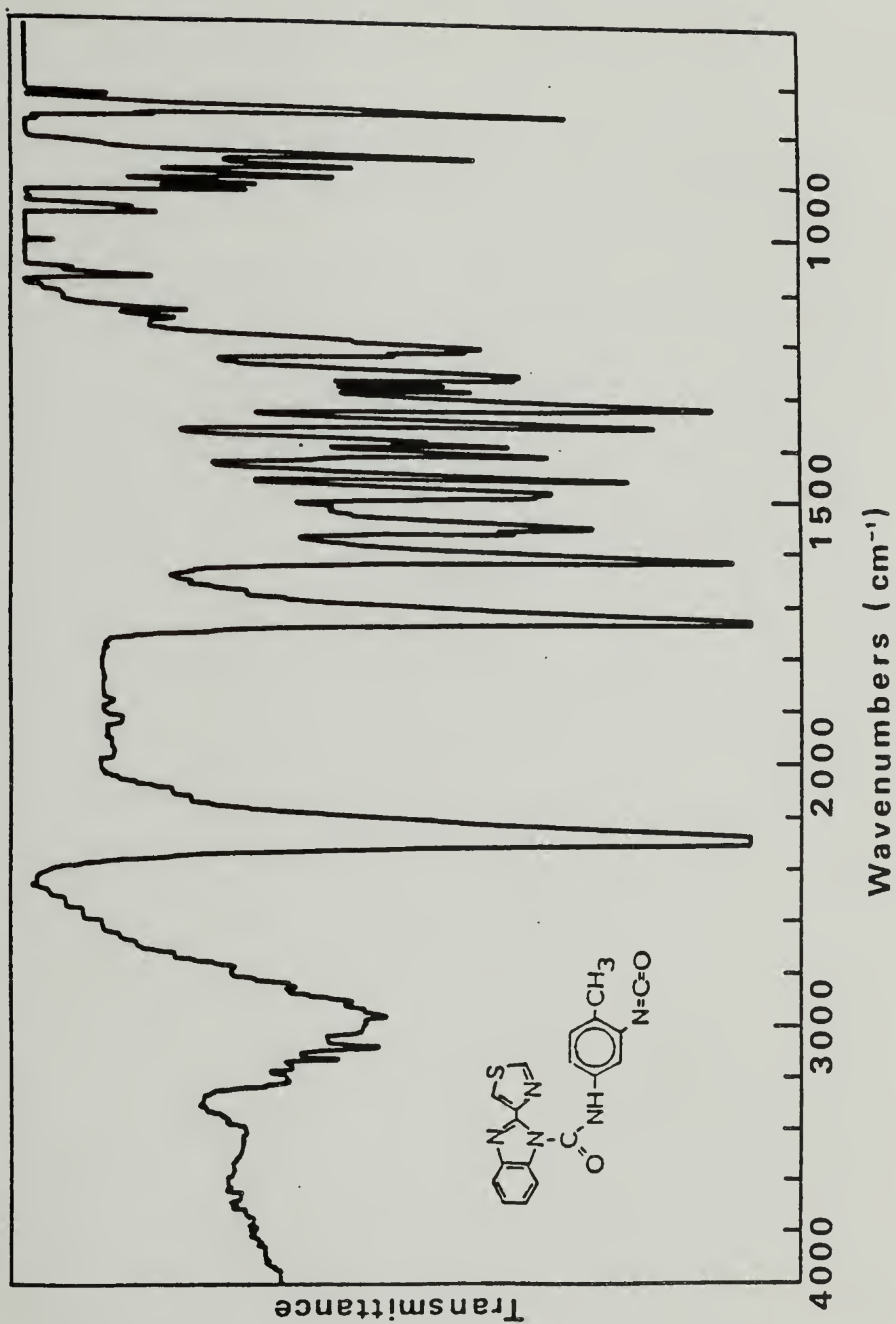
IR Spectrum No. 22 2-(4-Th)B



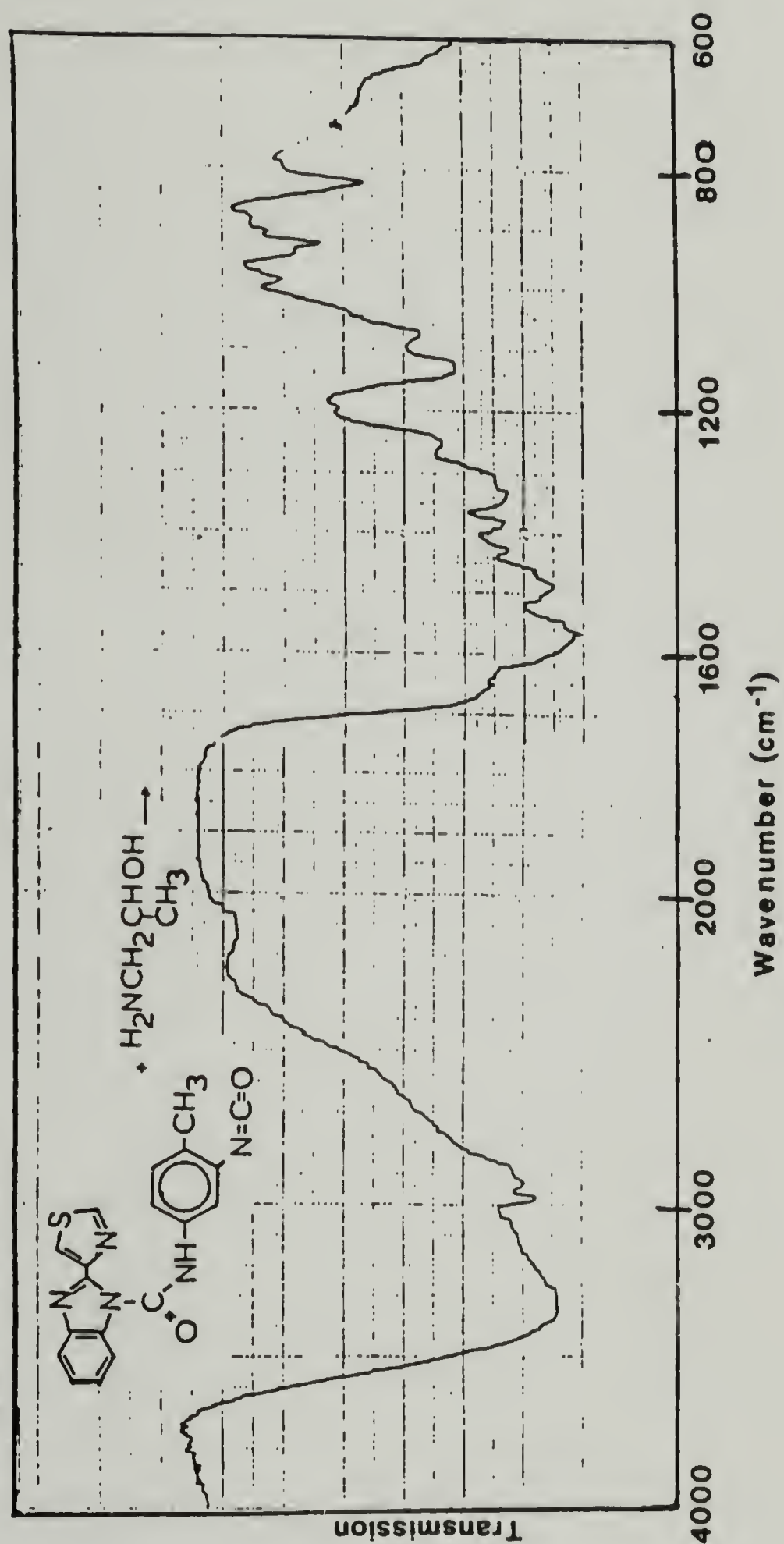
IR Spectrum No. 23 1-Acetyl-2-(4-Th)B



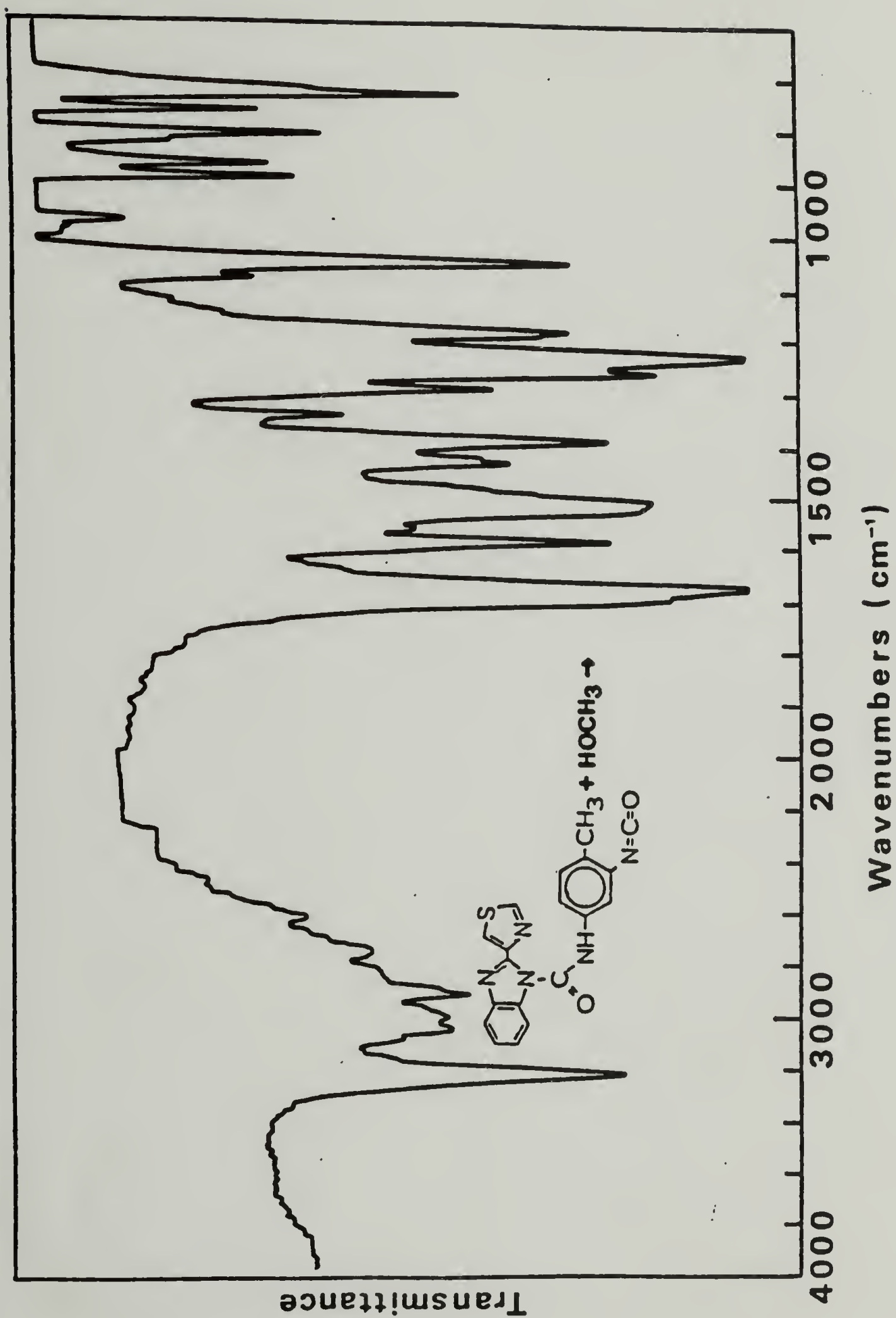
IR Spectrum No. 24 TDI/2-(4-Th)B Adduct



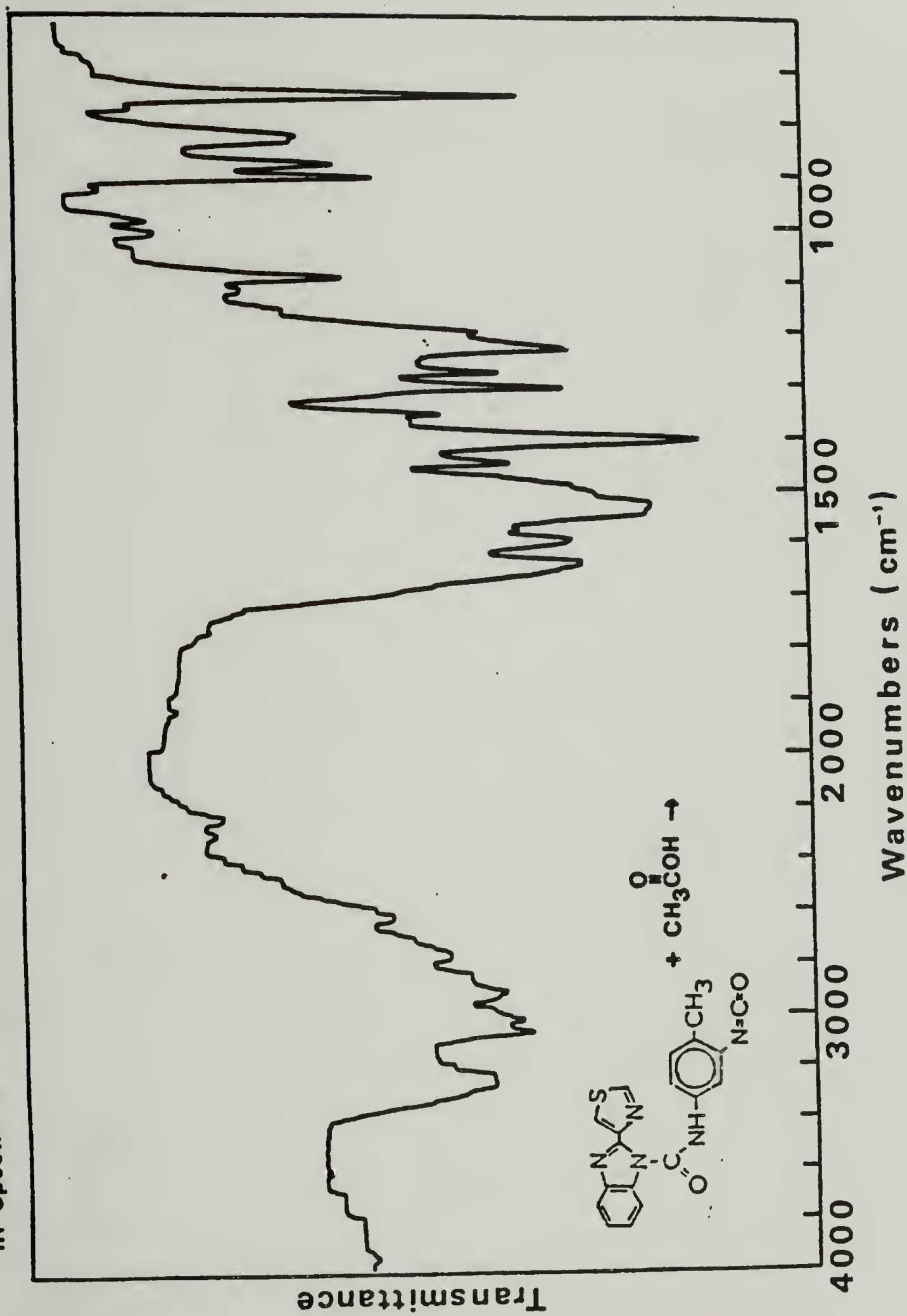
IR Spectrum No. 25

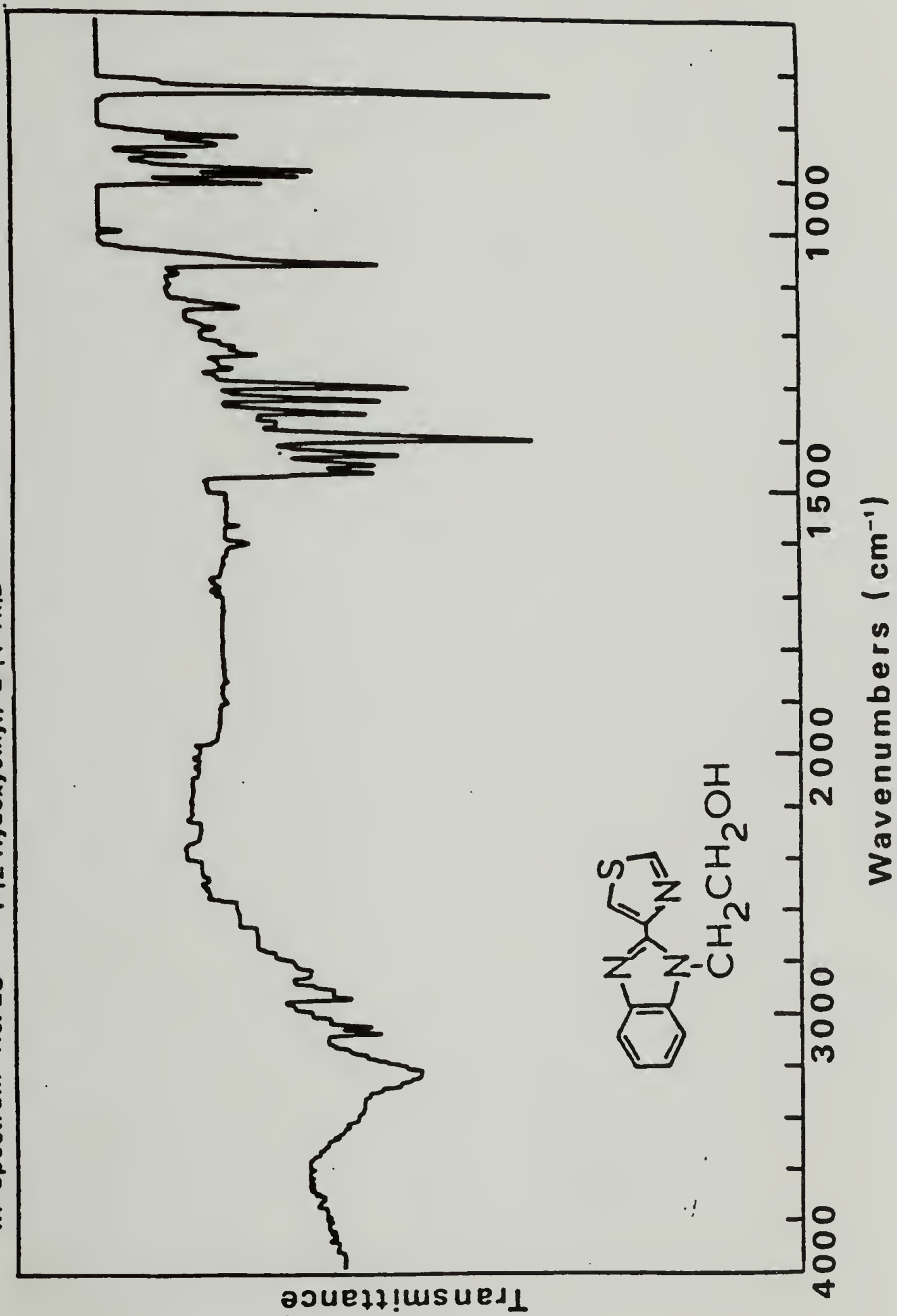


IR Spectrum No. 26

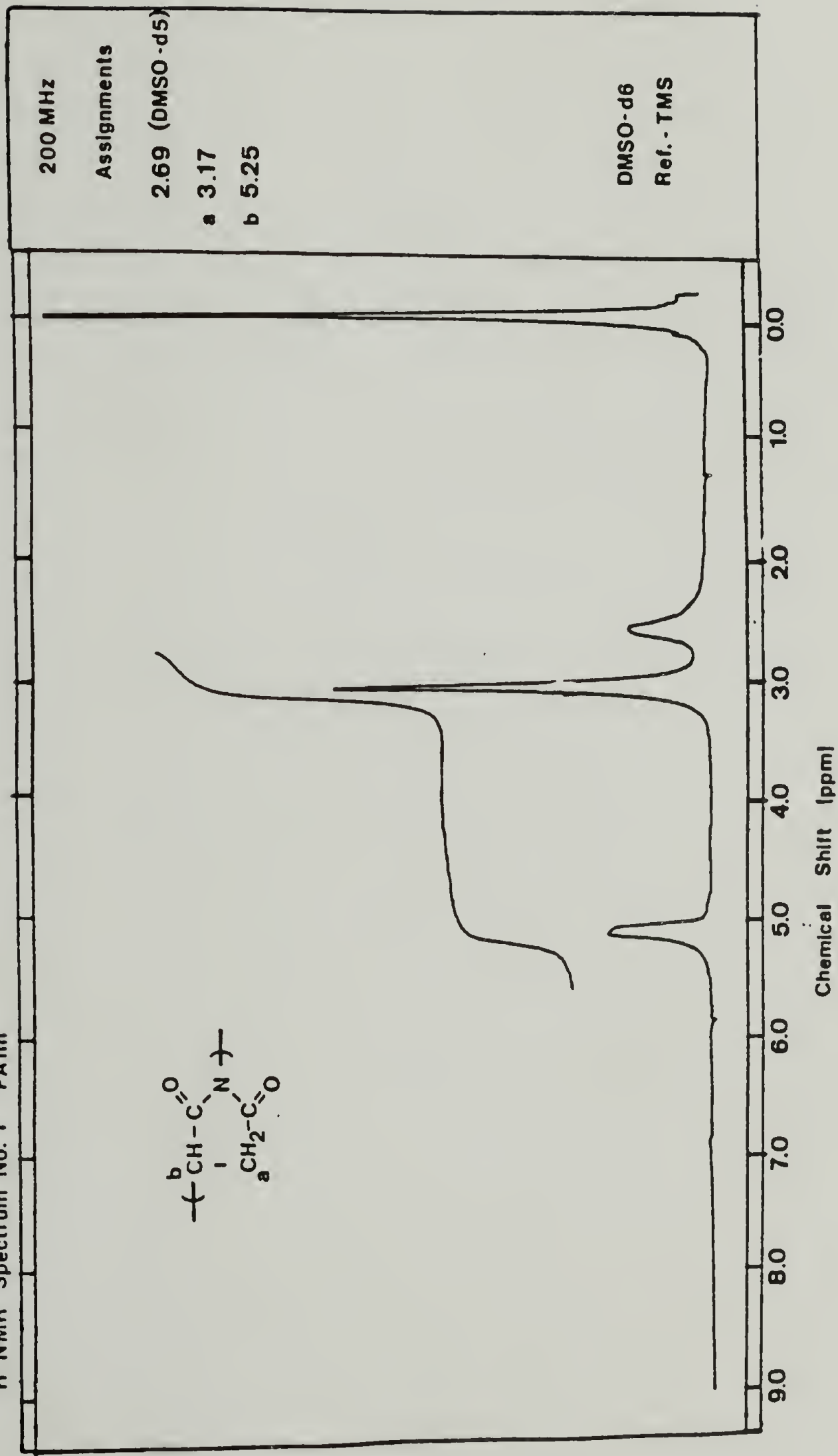
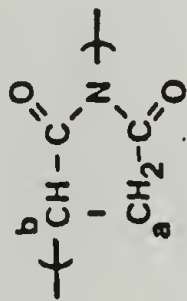


IR Spectrum No. 27

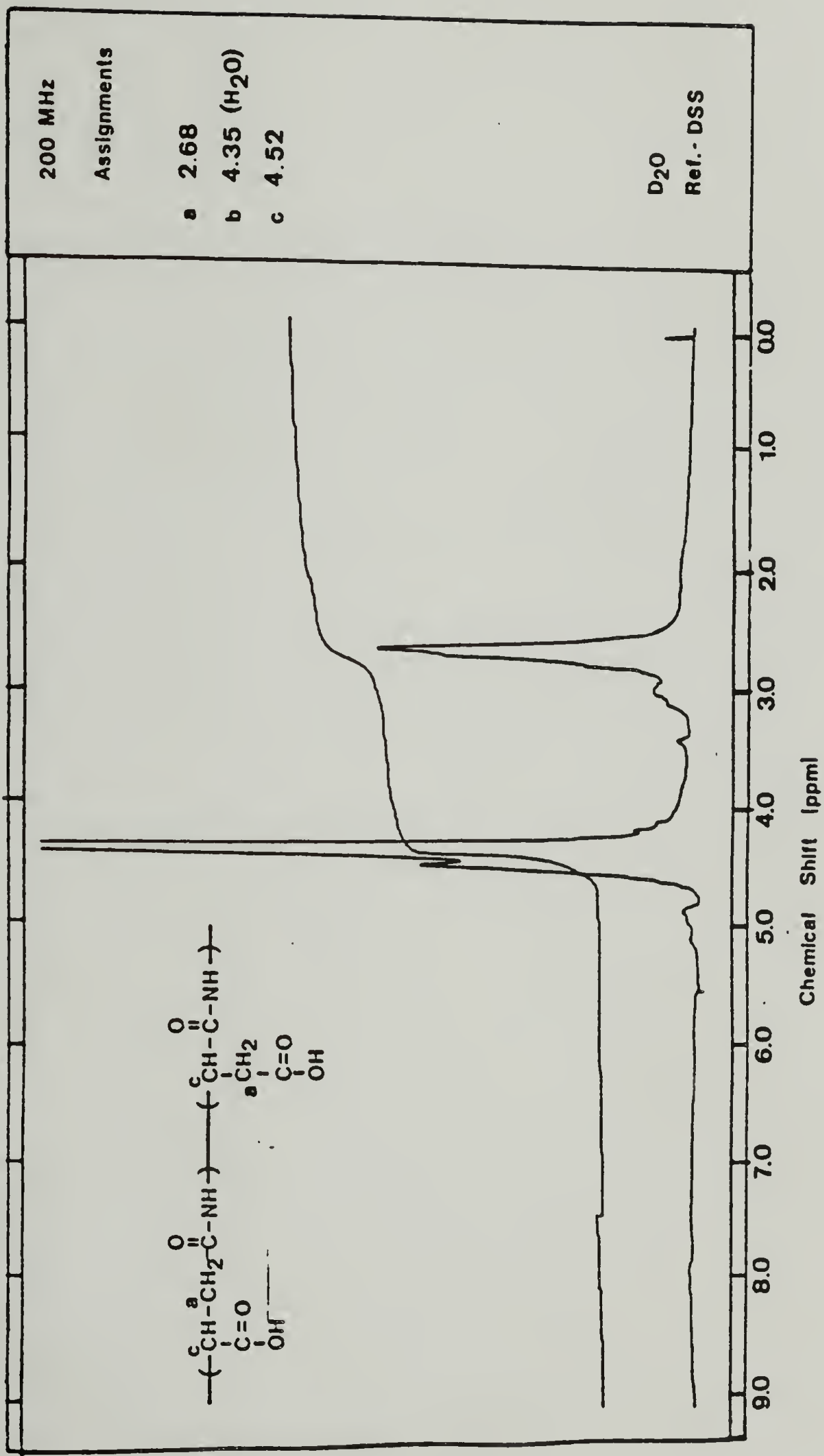




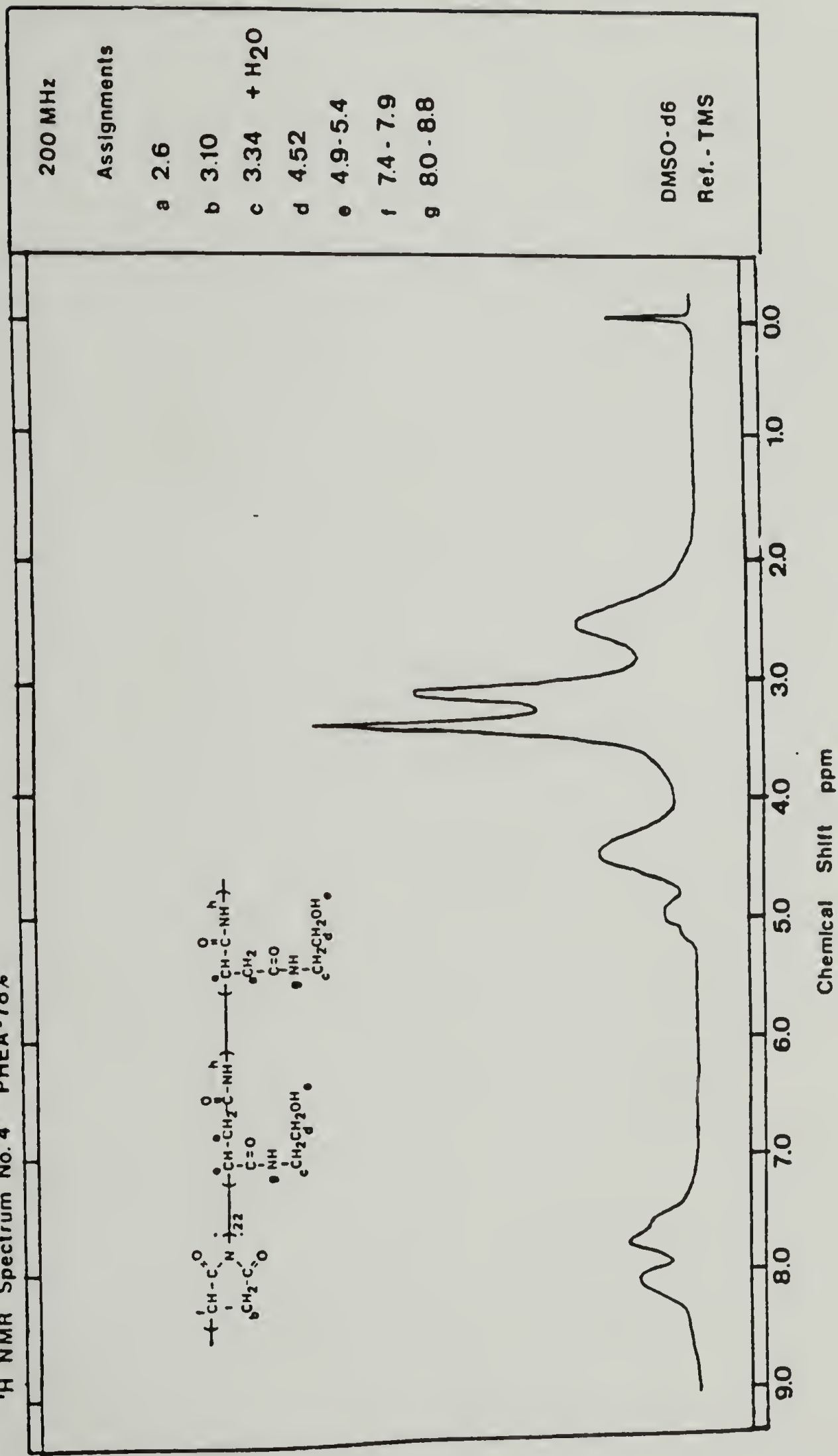
¹H NMR Spectrum No. 1 PAIm



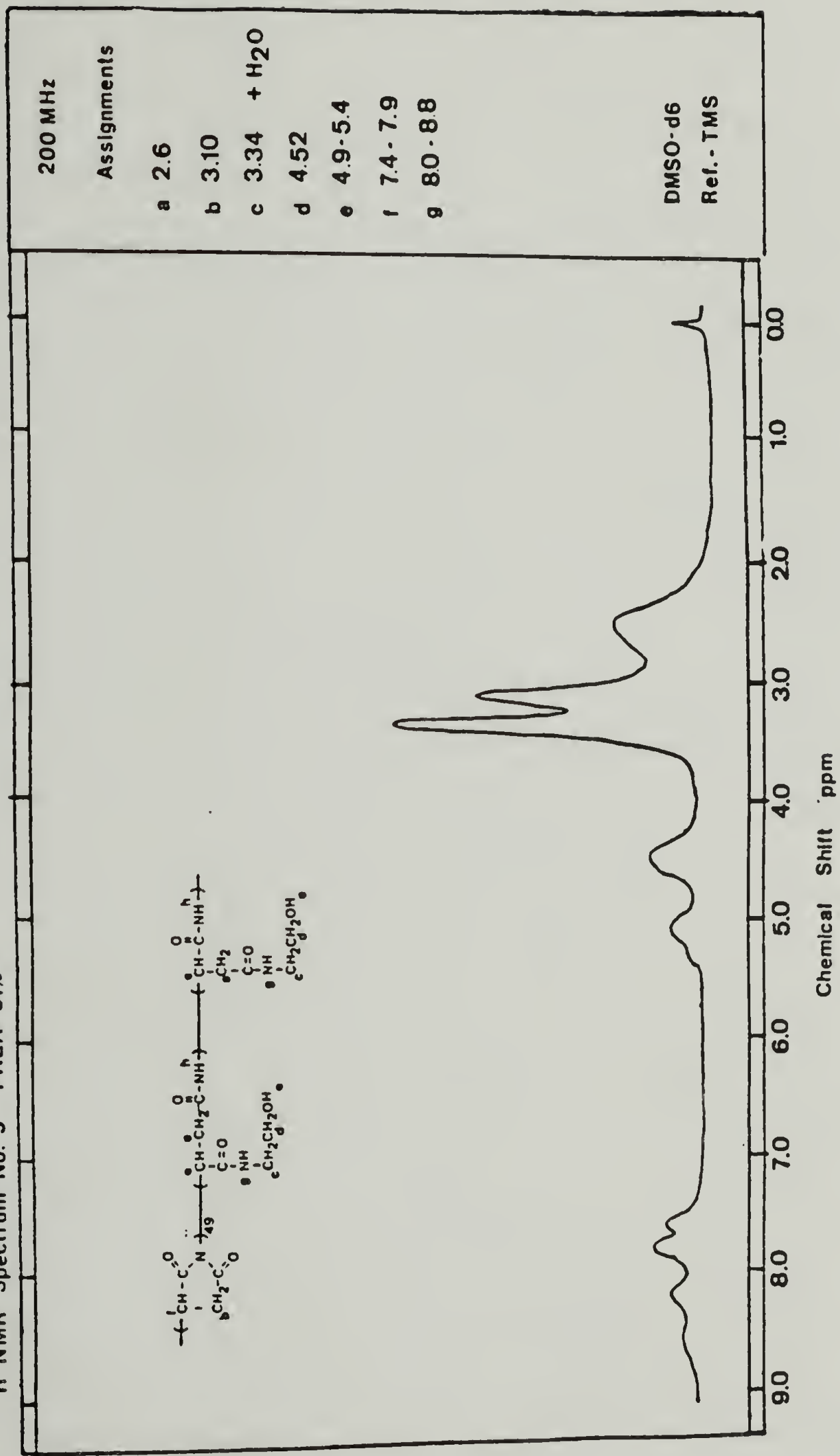
¹H NMR Spectrum No. 2 PAAC

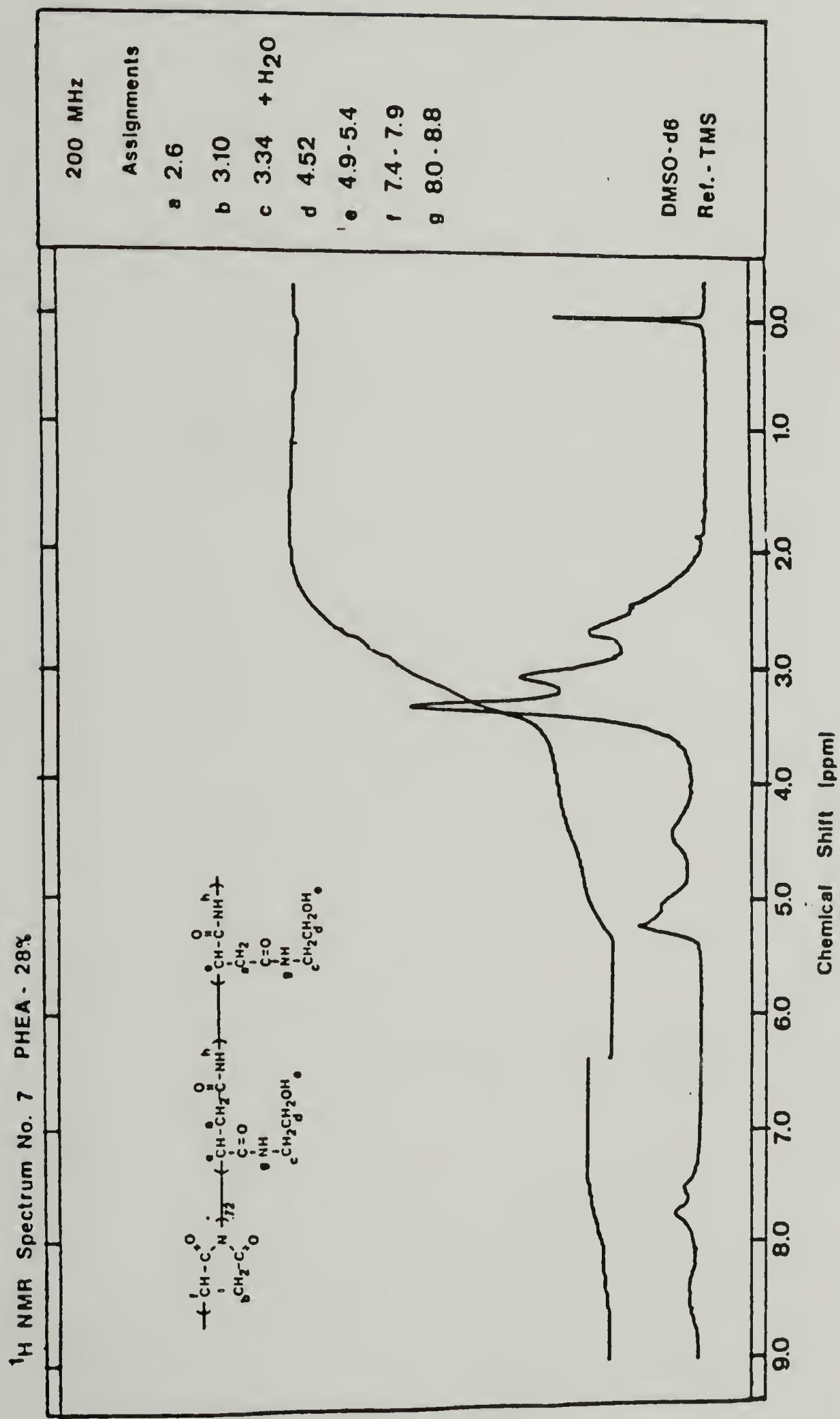


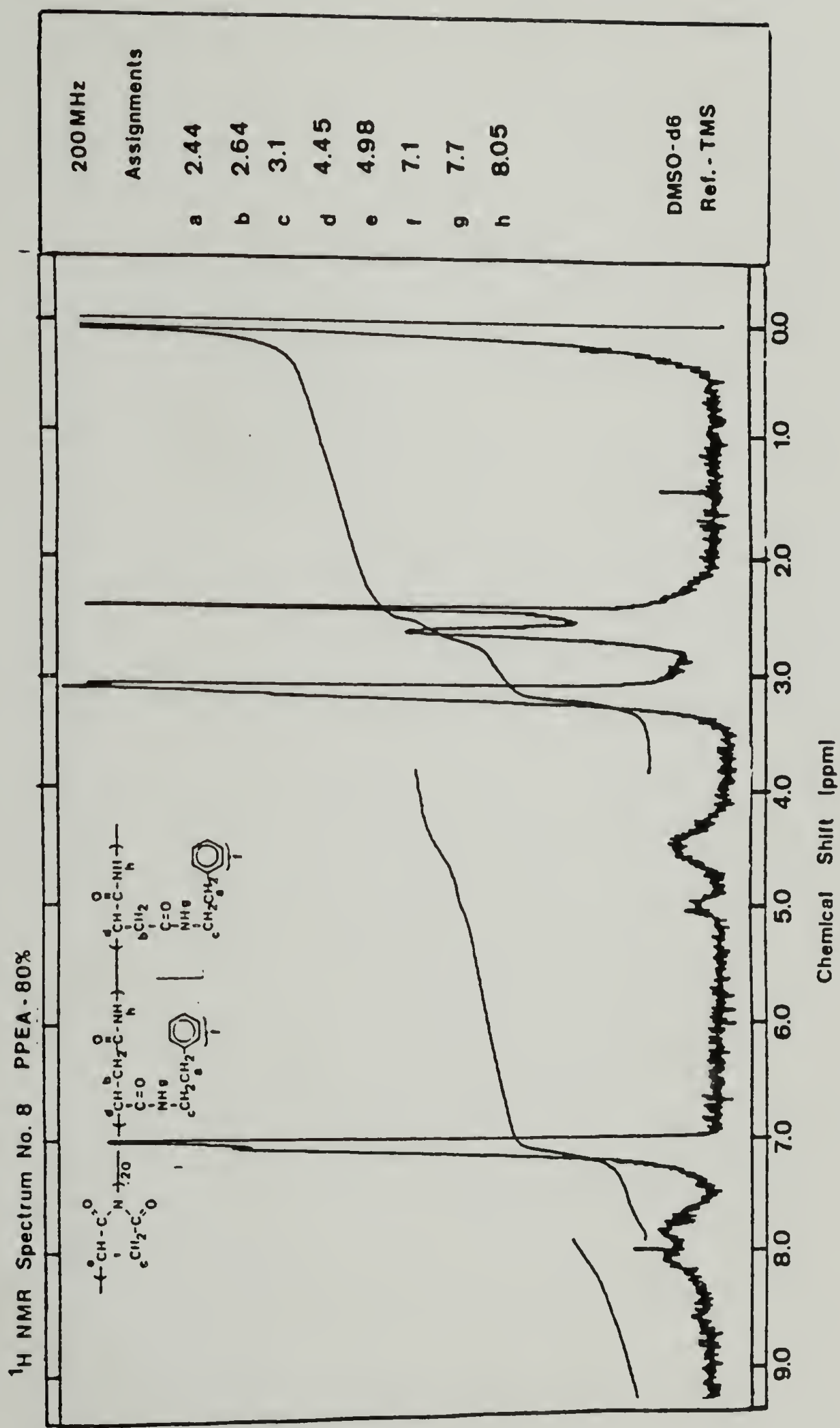
¹H NMR Spectrum No. 4 PHEA-78%



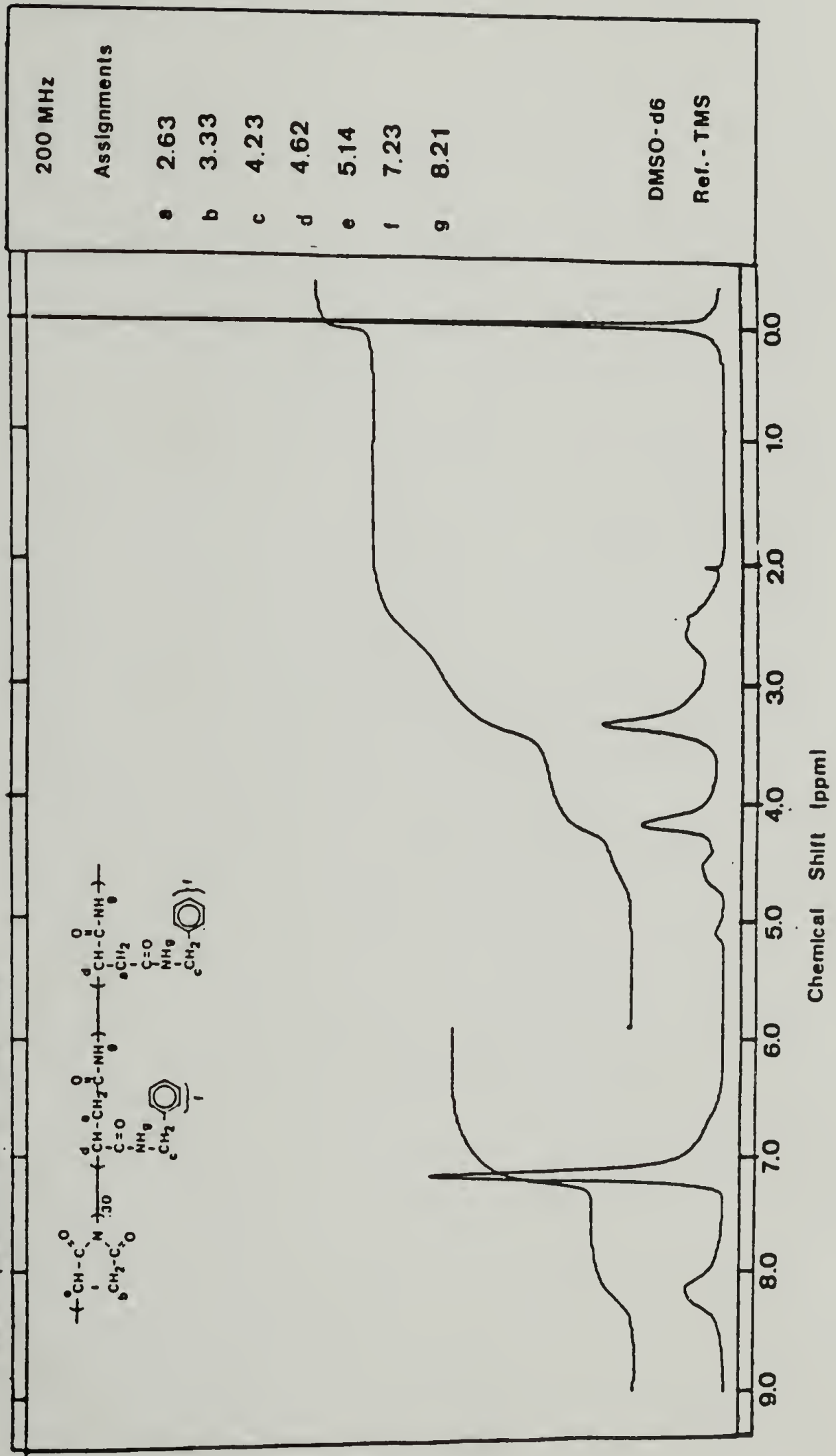
¹H NMR Spectrum No. 5 PHEA - 51%



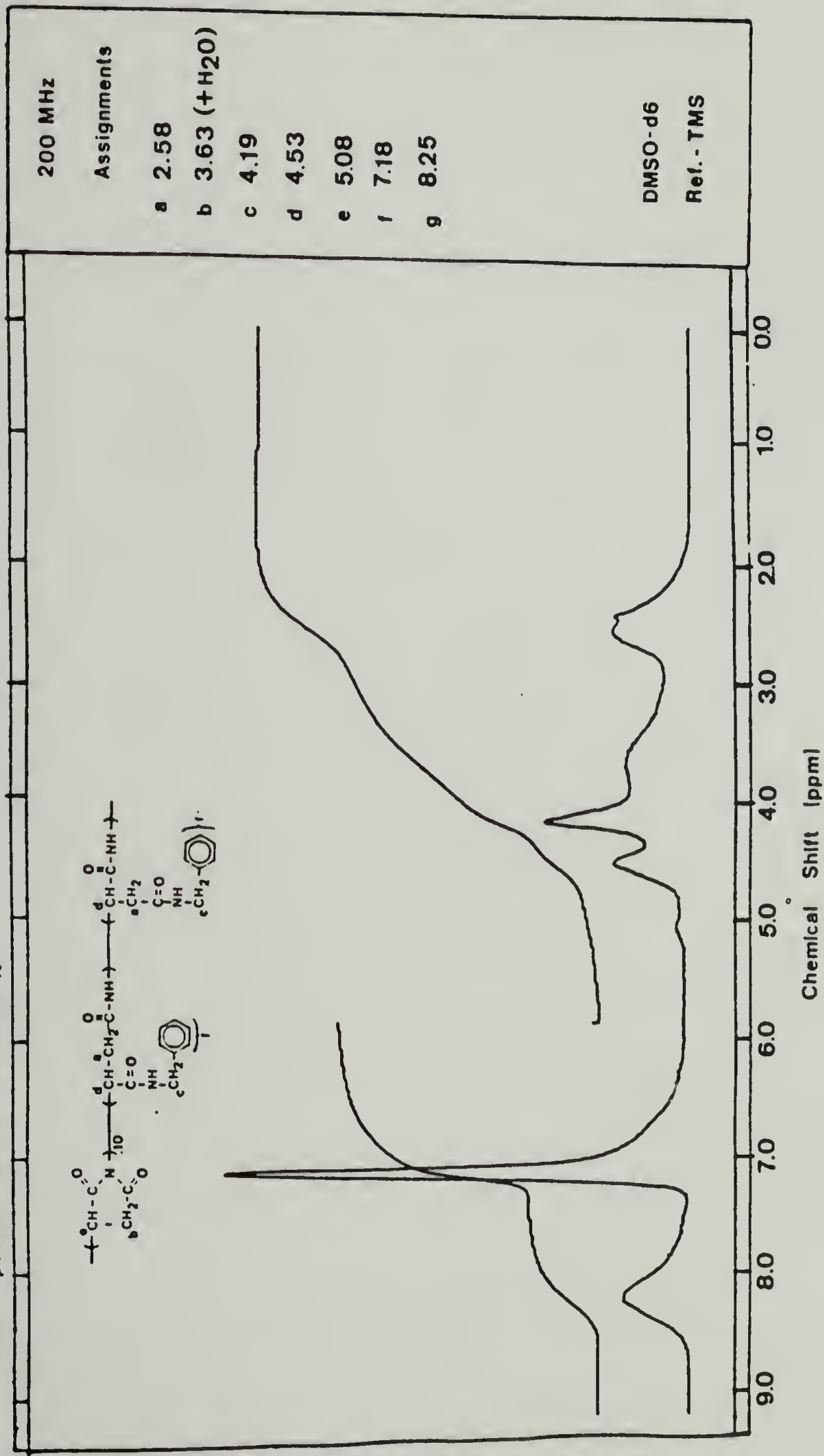


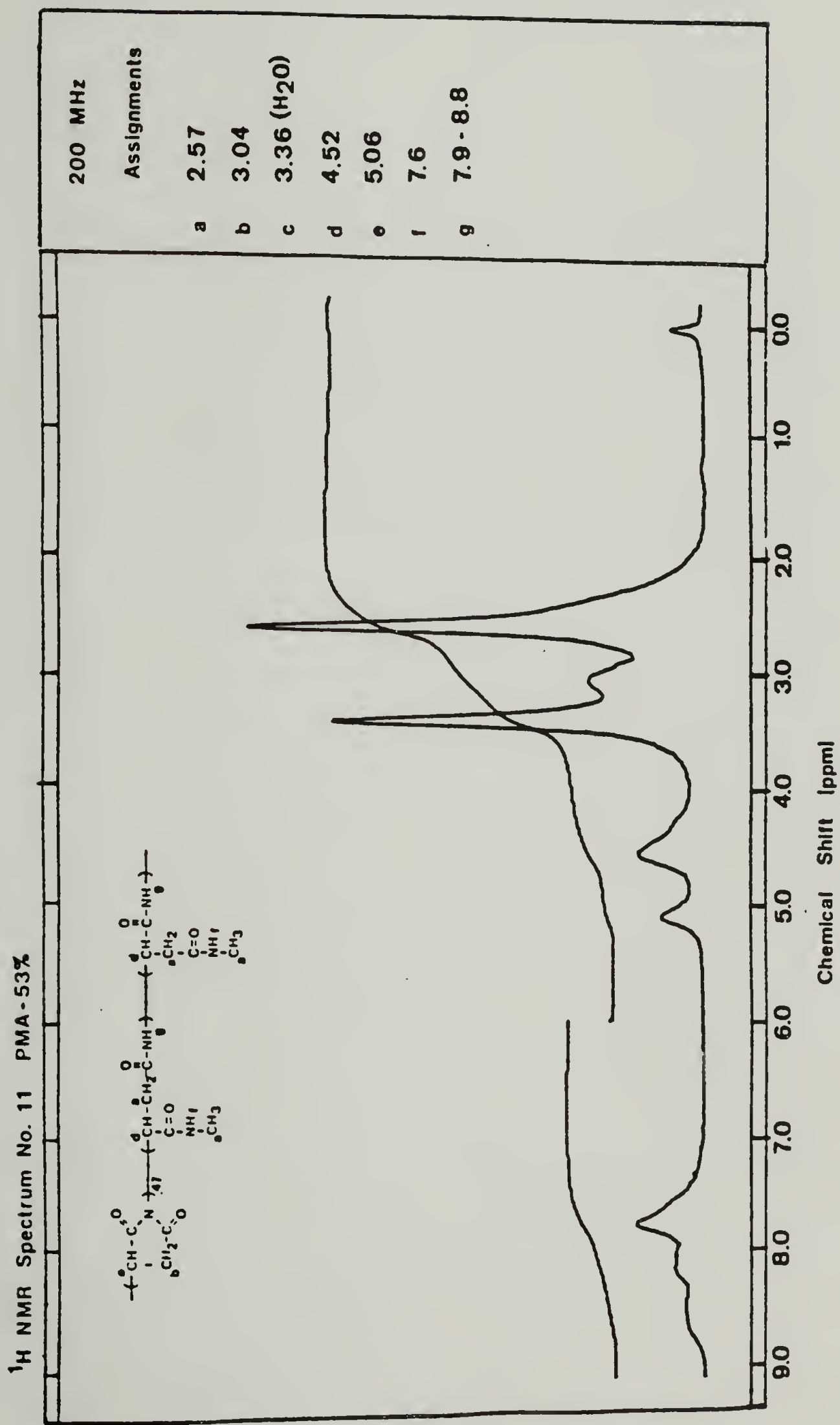


¹H NMR Spectrum No. 9 PBA - 70%

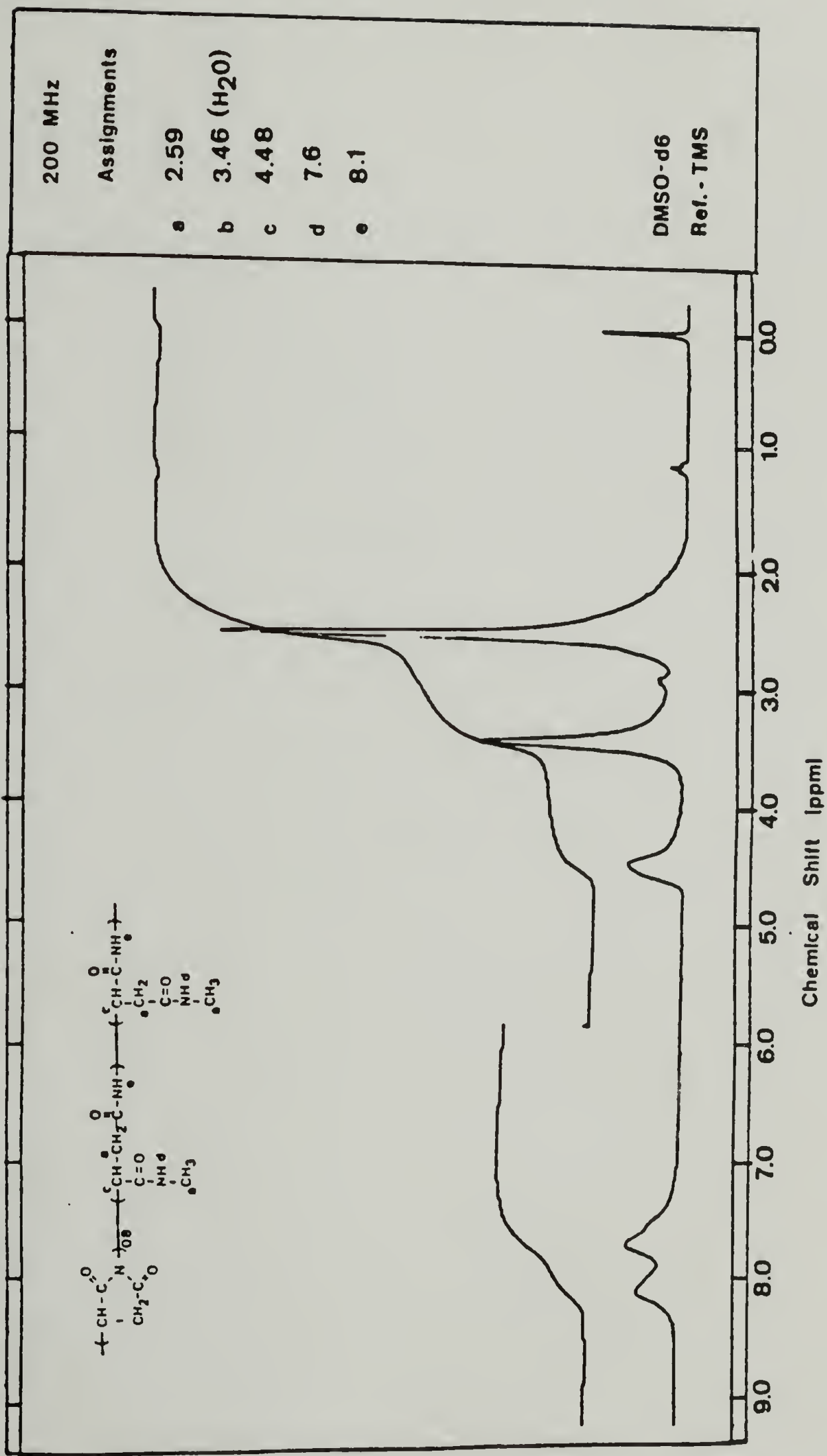


¹H NMR Spectrum No. 10 PBA-90X

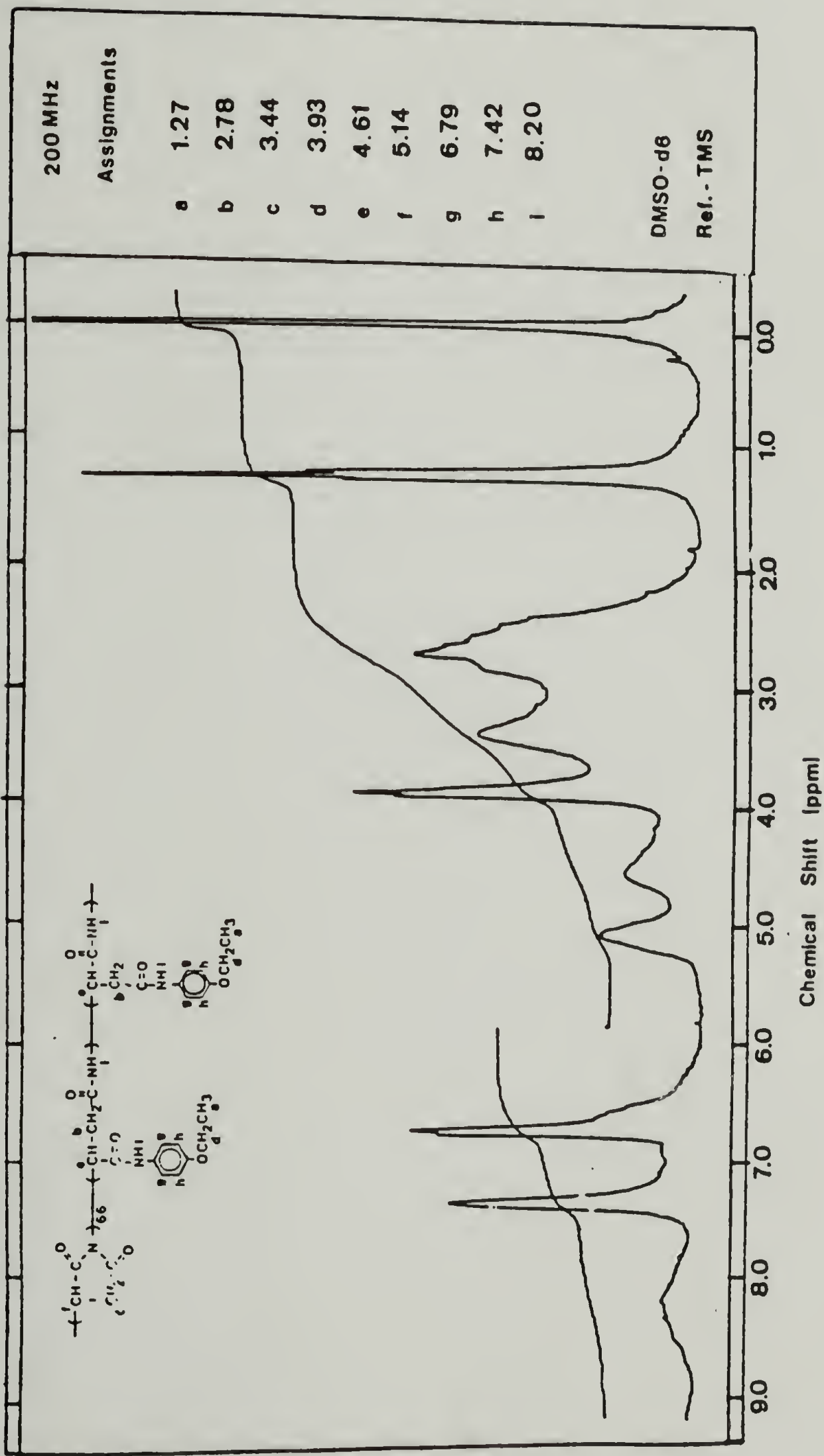




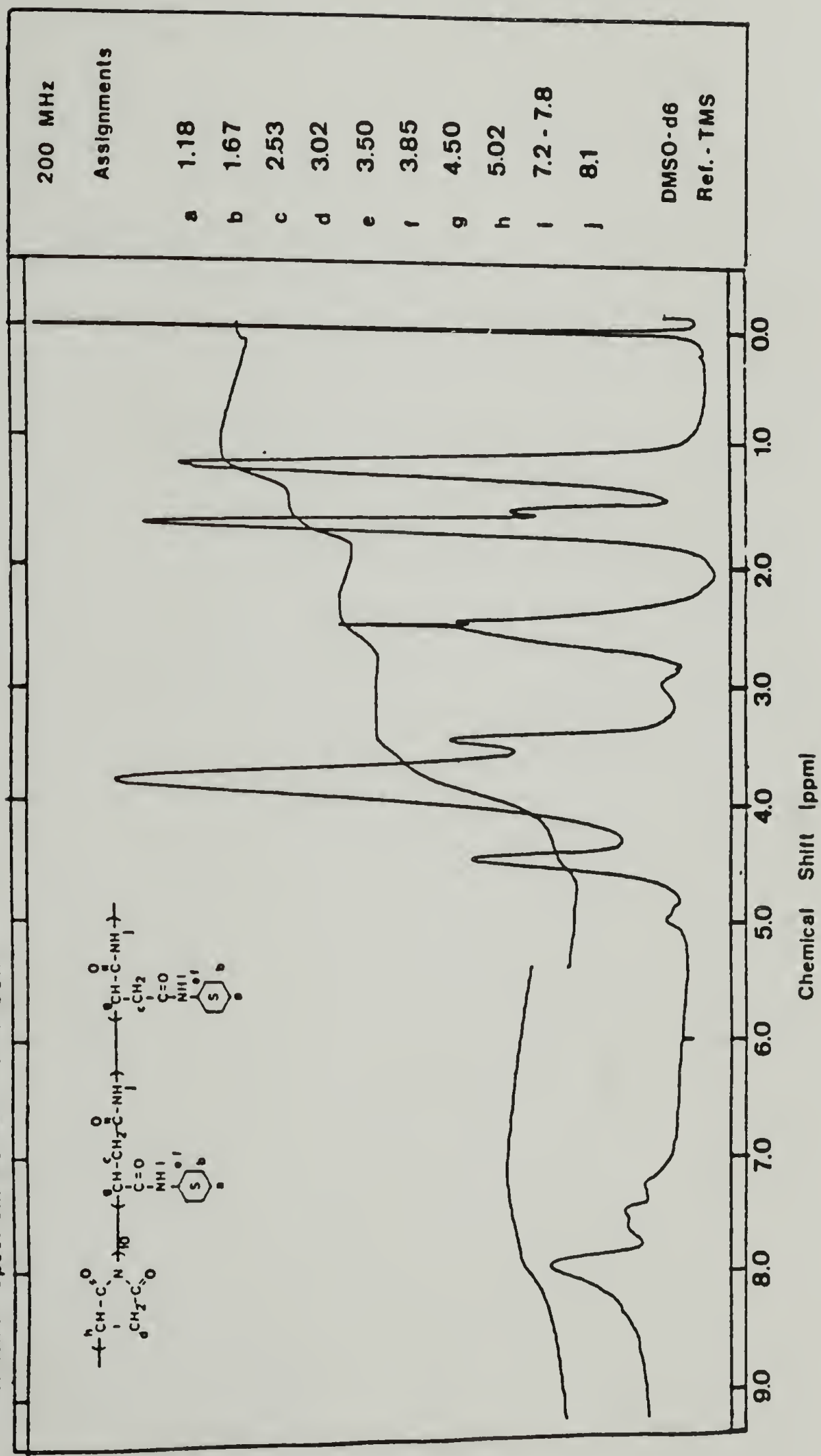
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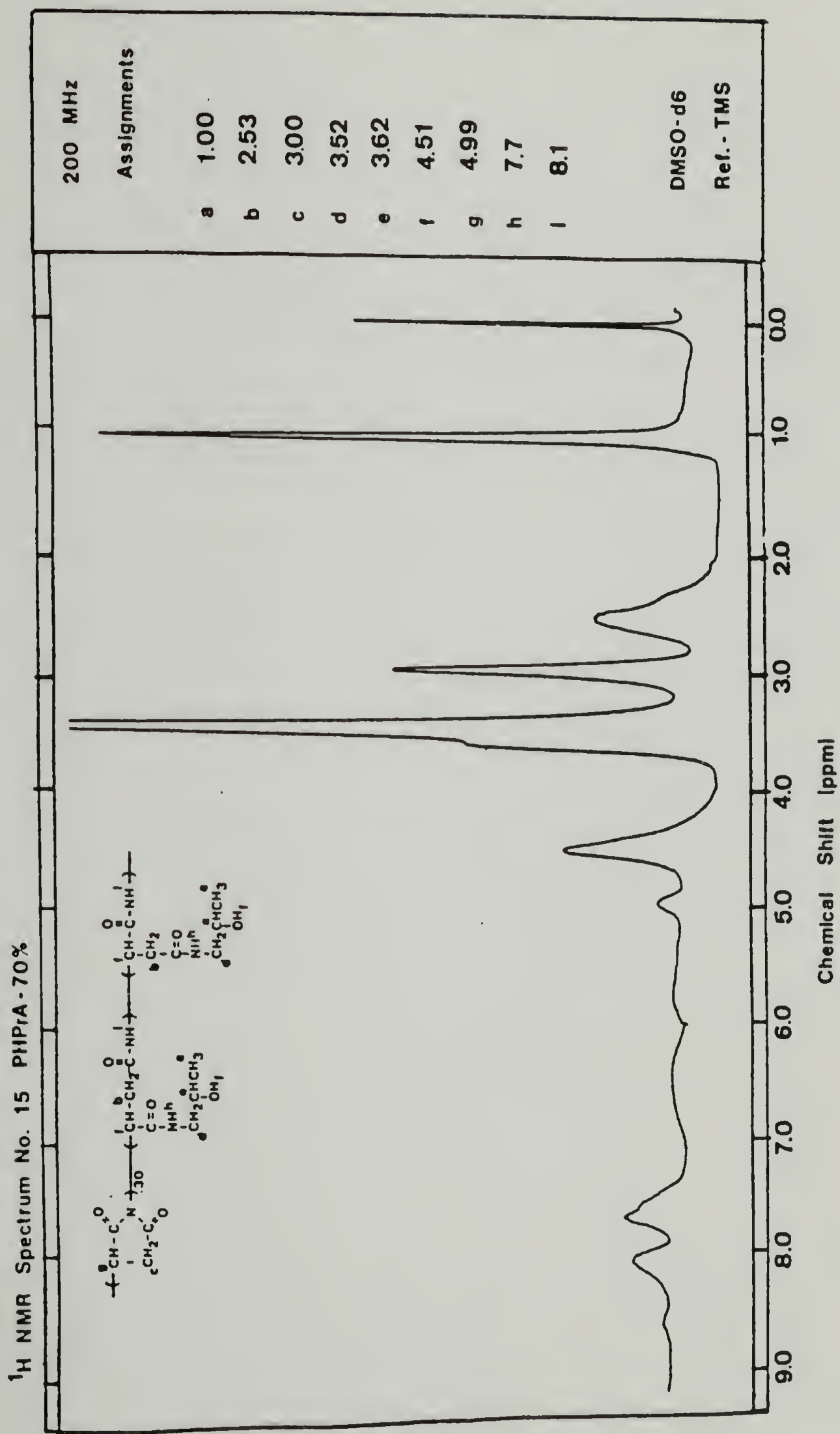


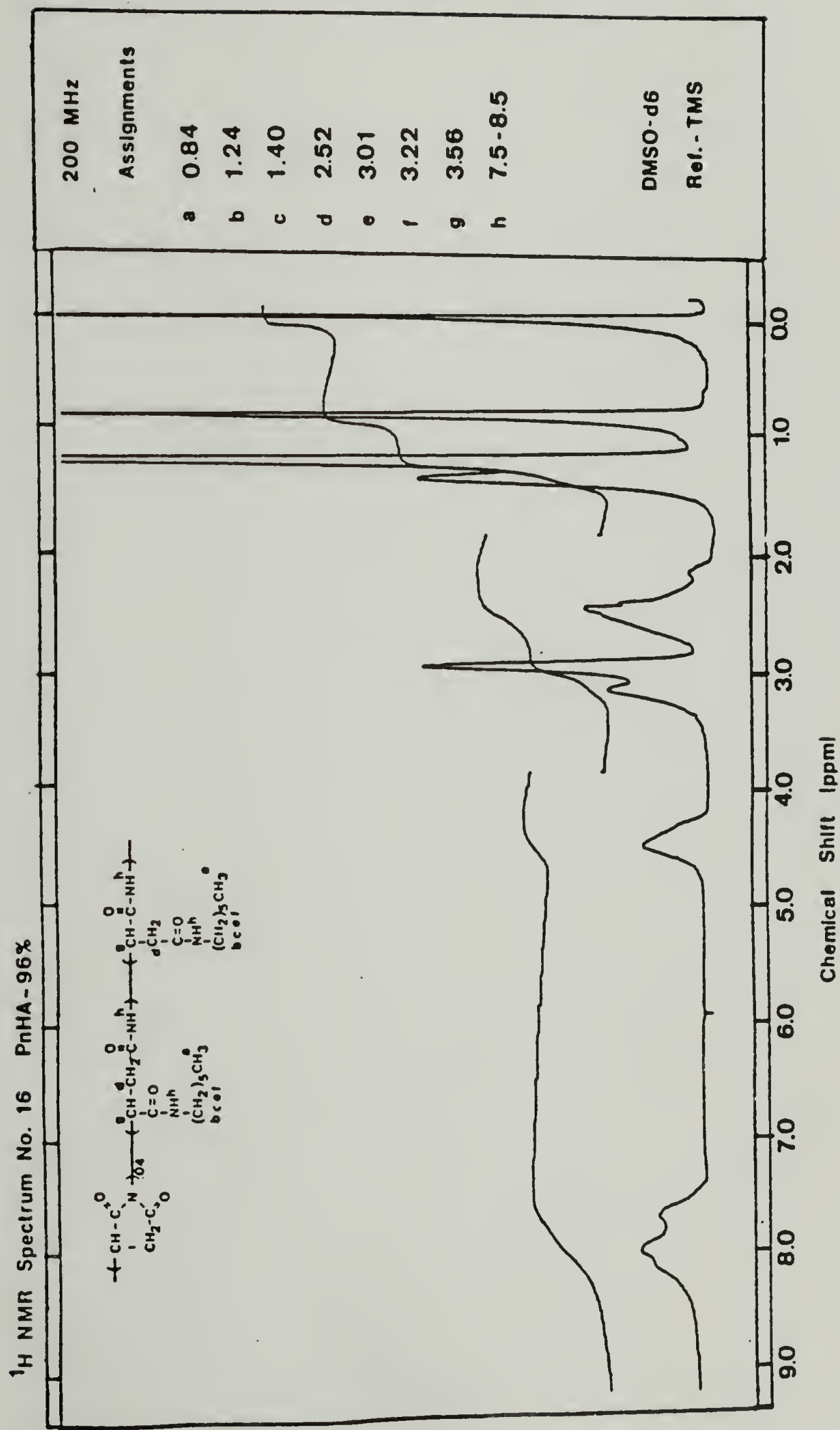
¹H NMR Spectrum No. 13 PEIPA - 34%

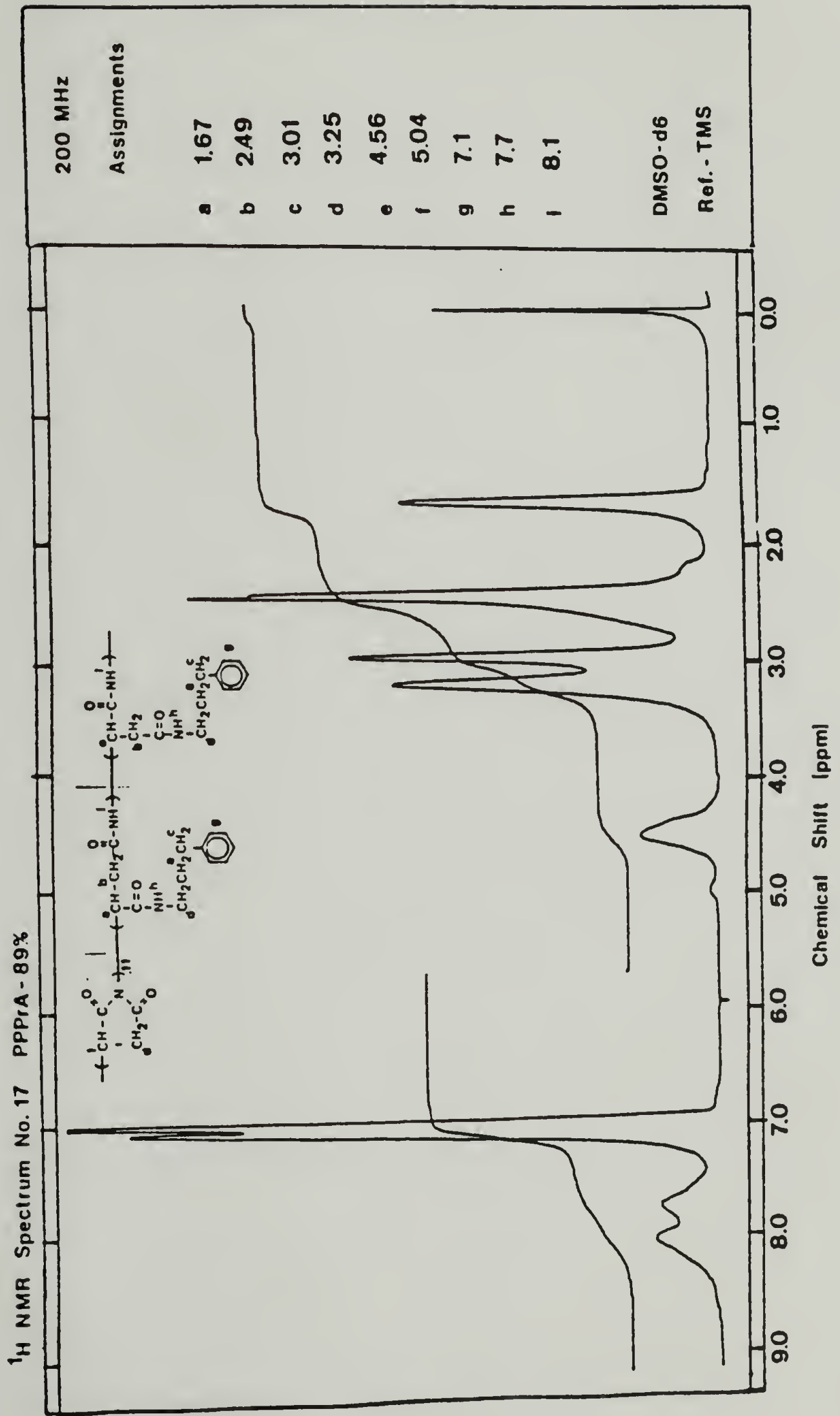


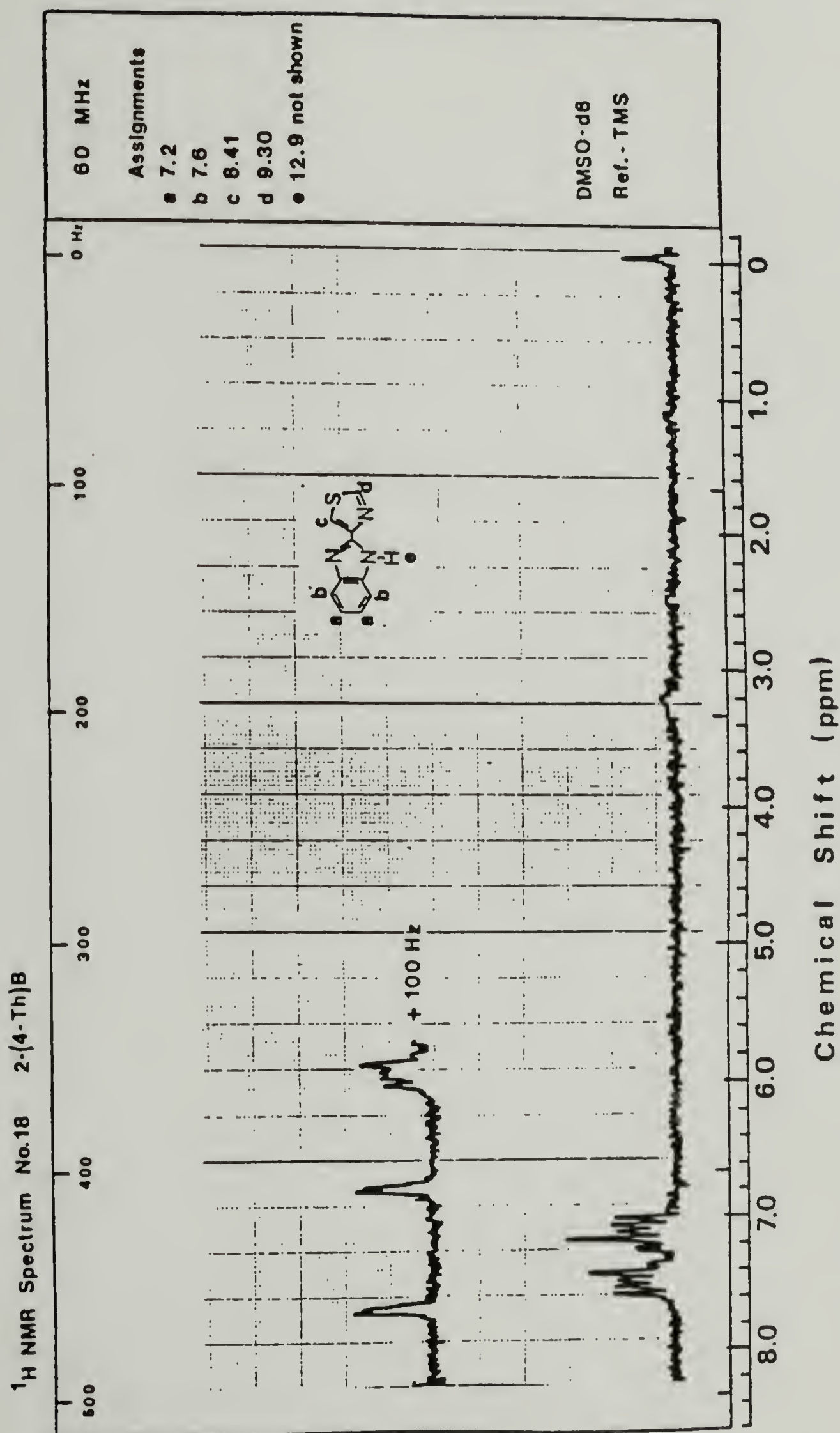
¹H NMR Spectrum No. 14 PcHA - 90%

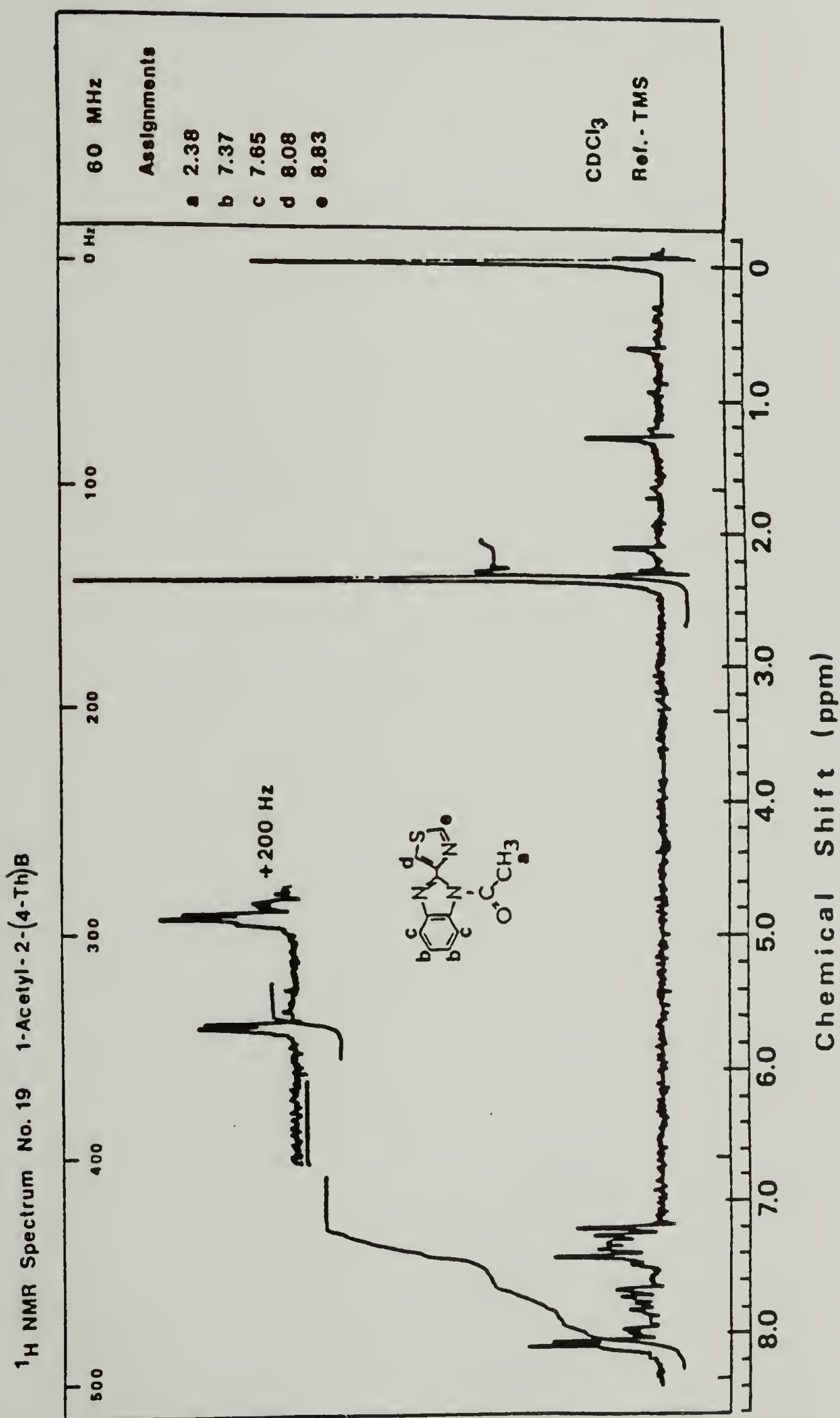




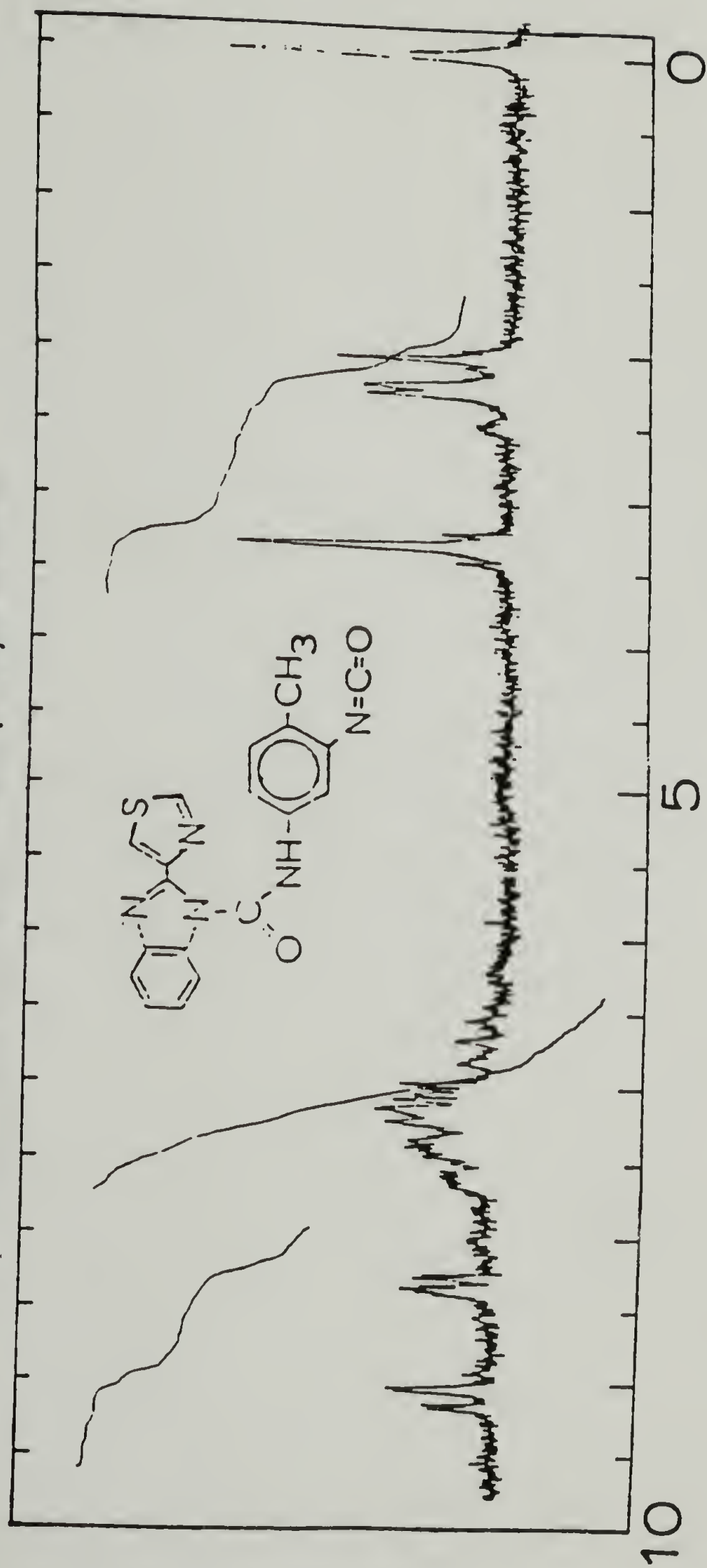




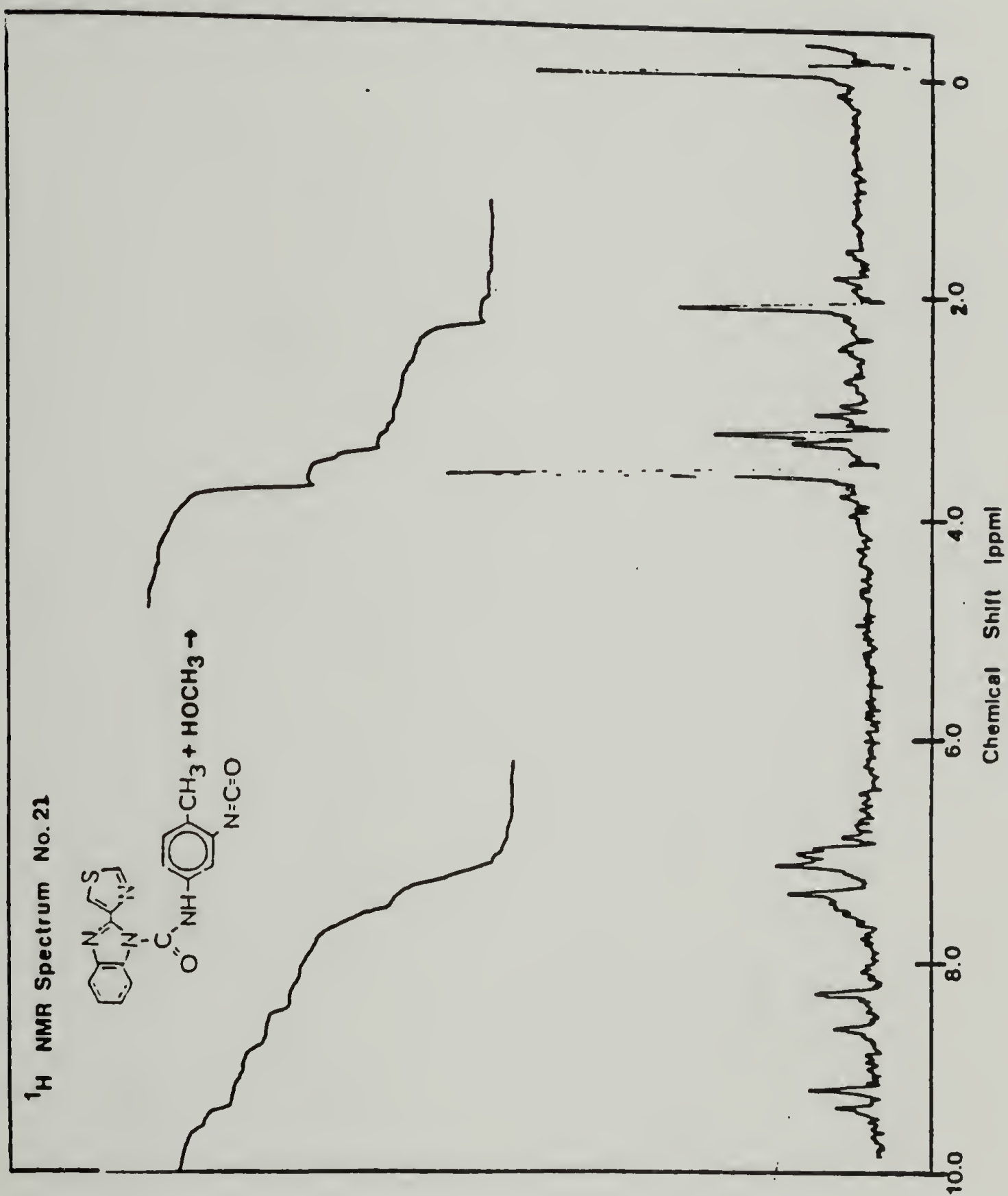


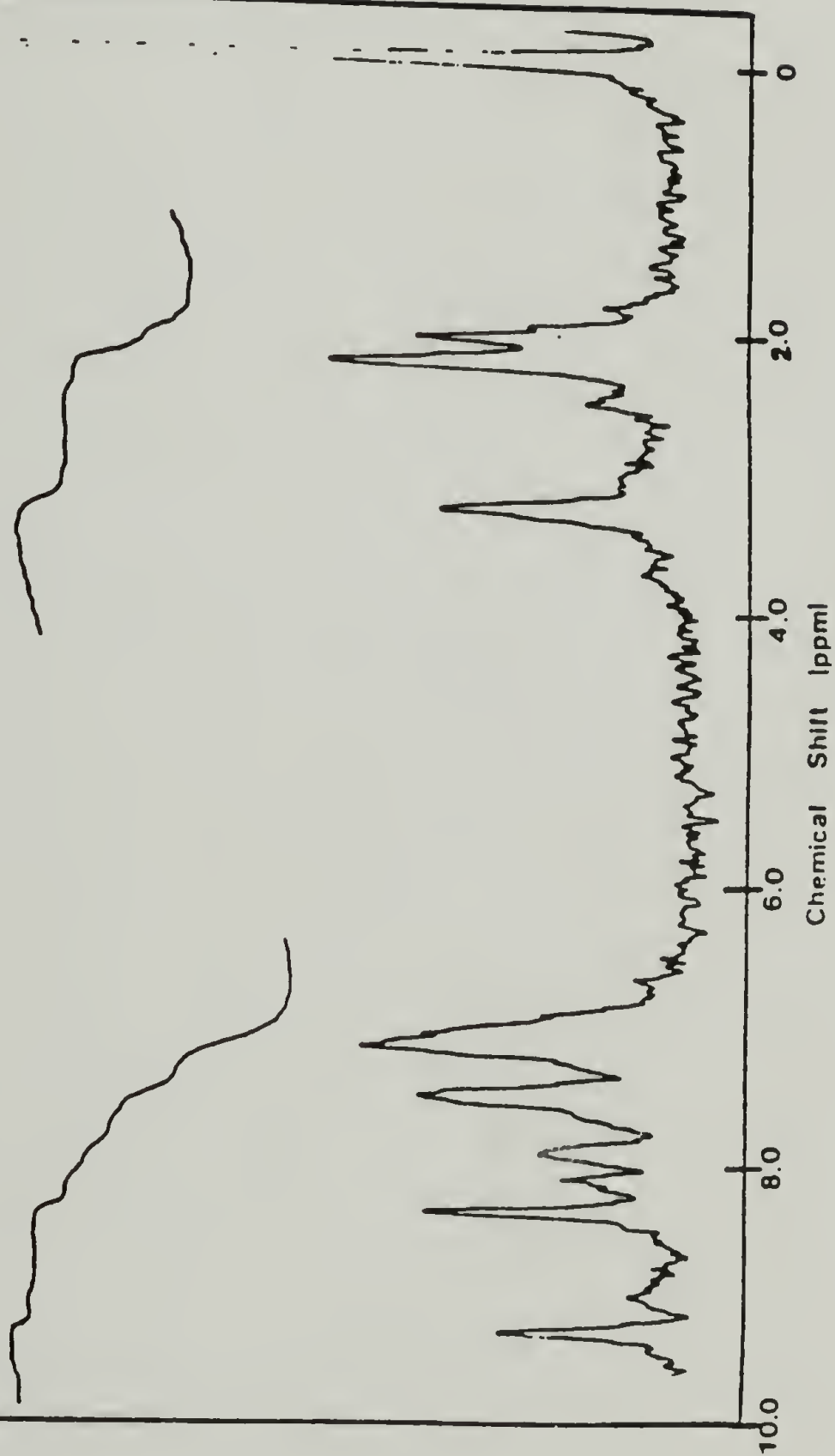
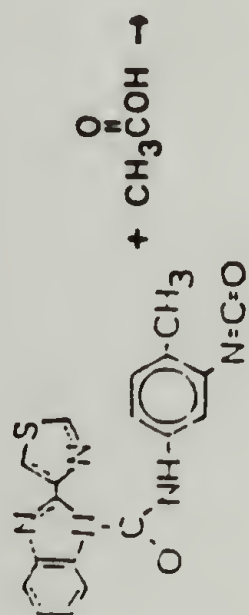


^1H NMR Spectrum No. 20 TDI/2-(4-Th)B Adduct



Chem. shift (ppm)

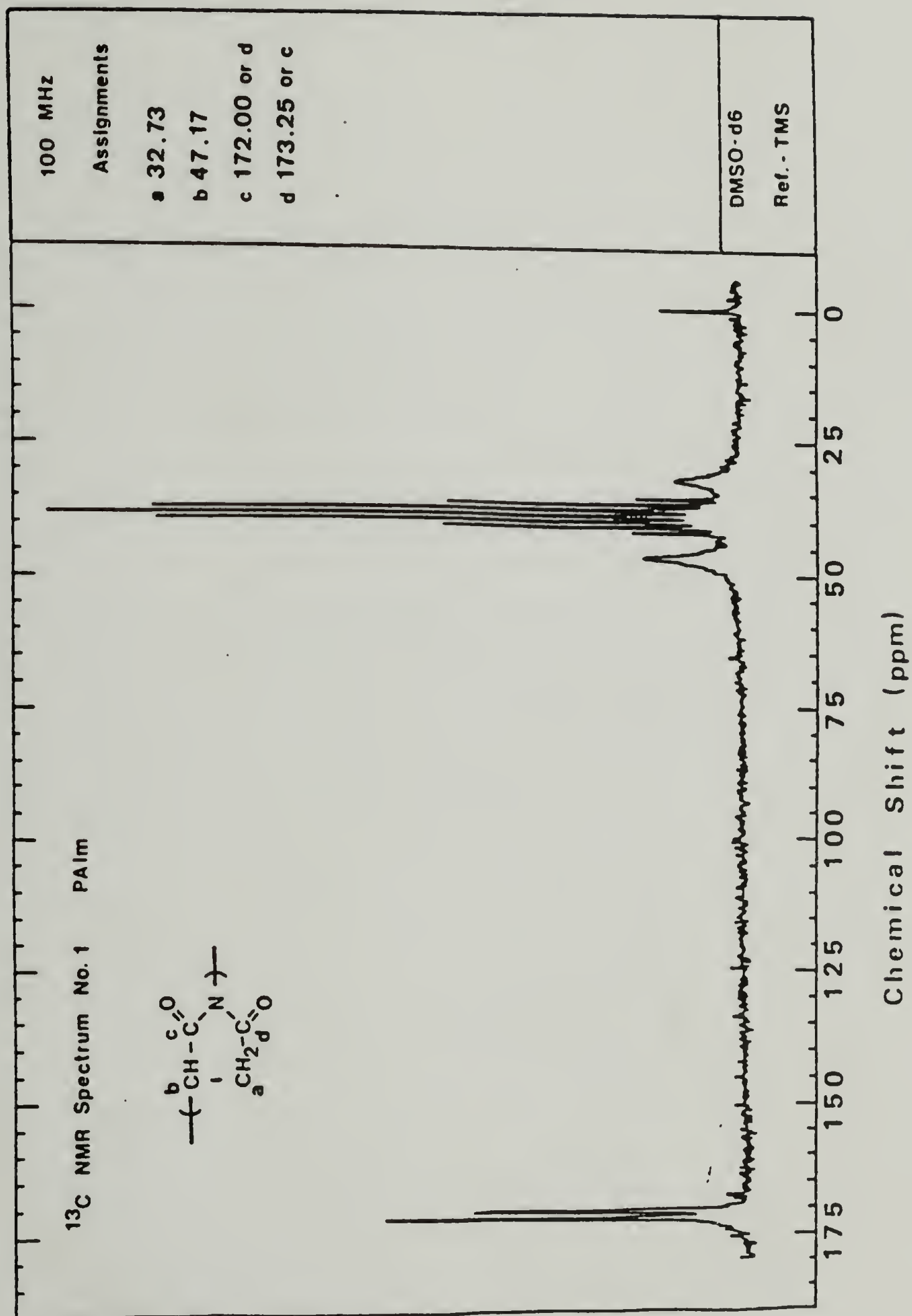


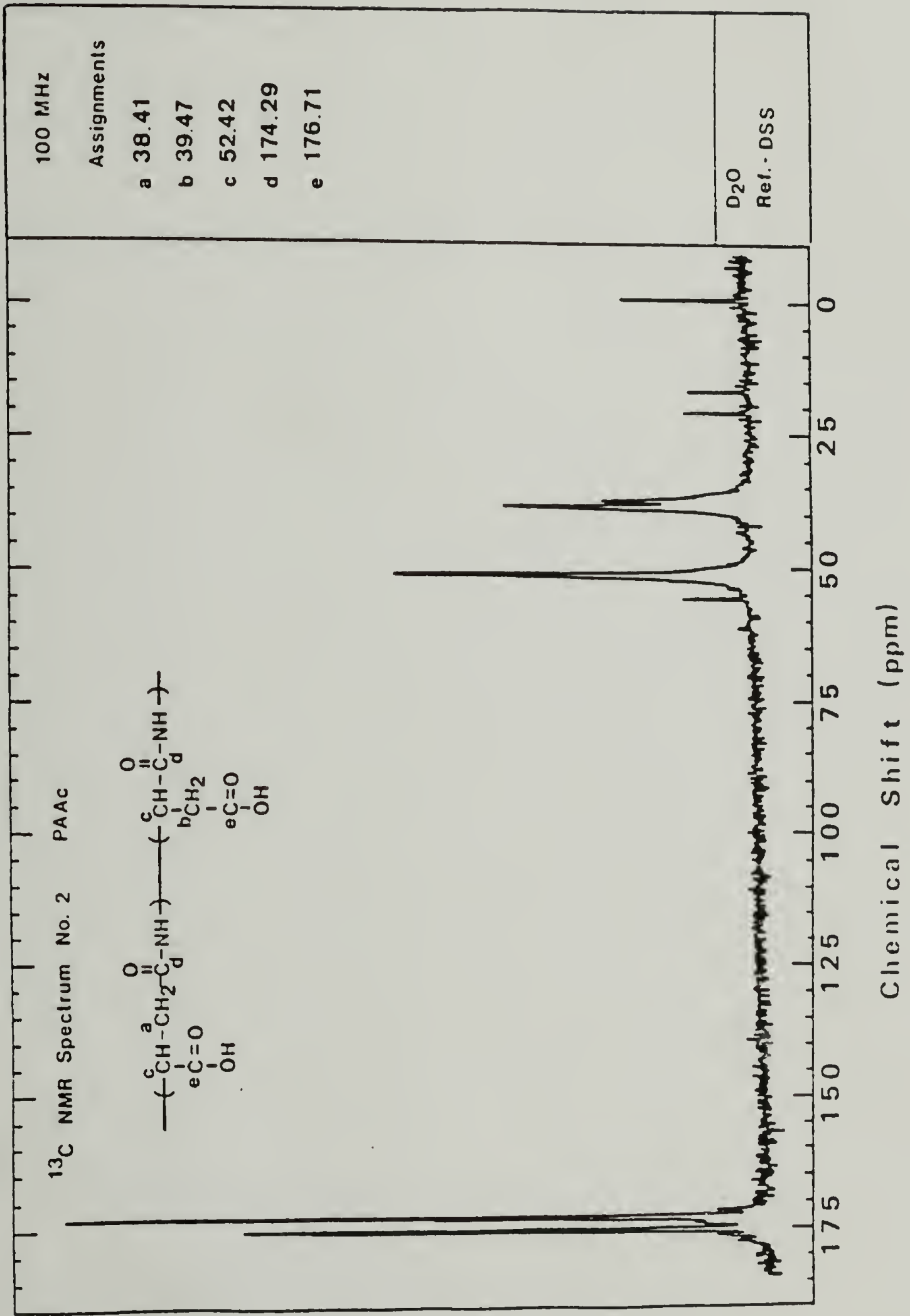
^1H NMR Spectrum No. 22

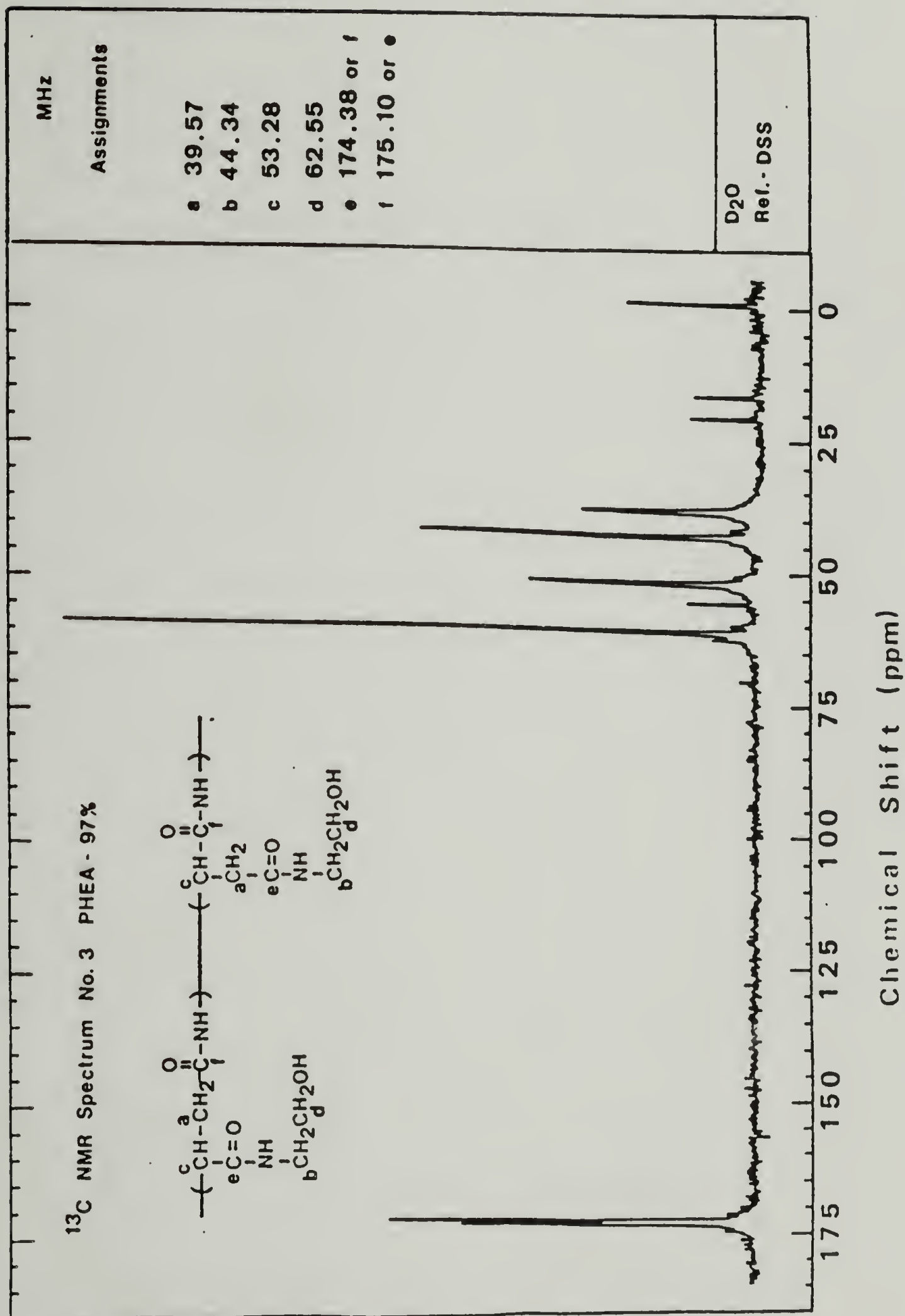
¹H NMR Spectrum No. 23 1-(2-Hydroxyethyl)-2-(4-Th)B

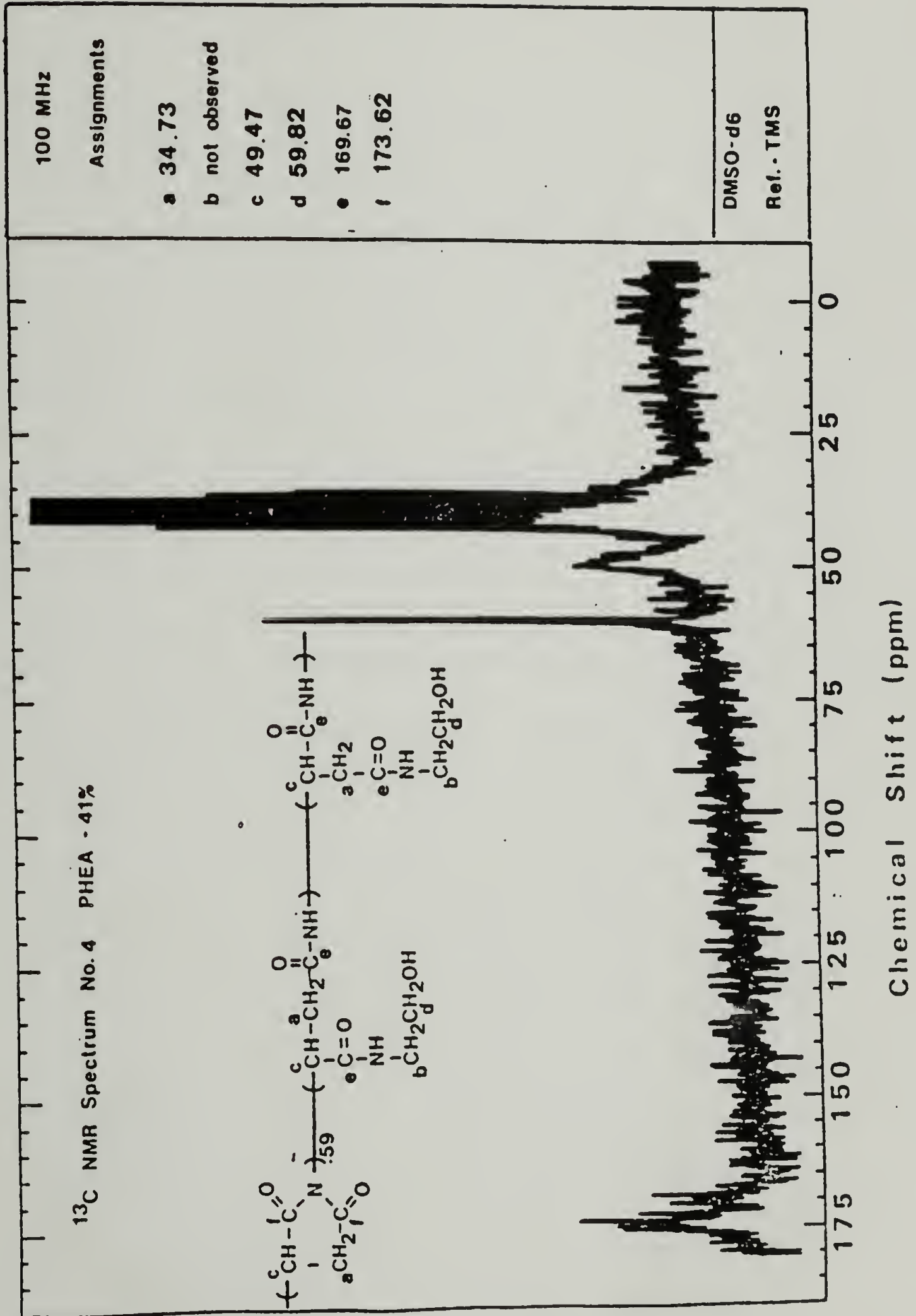


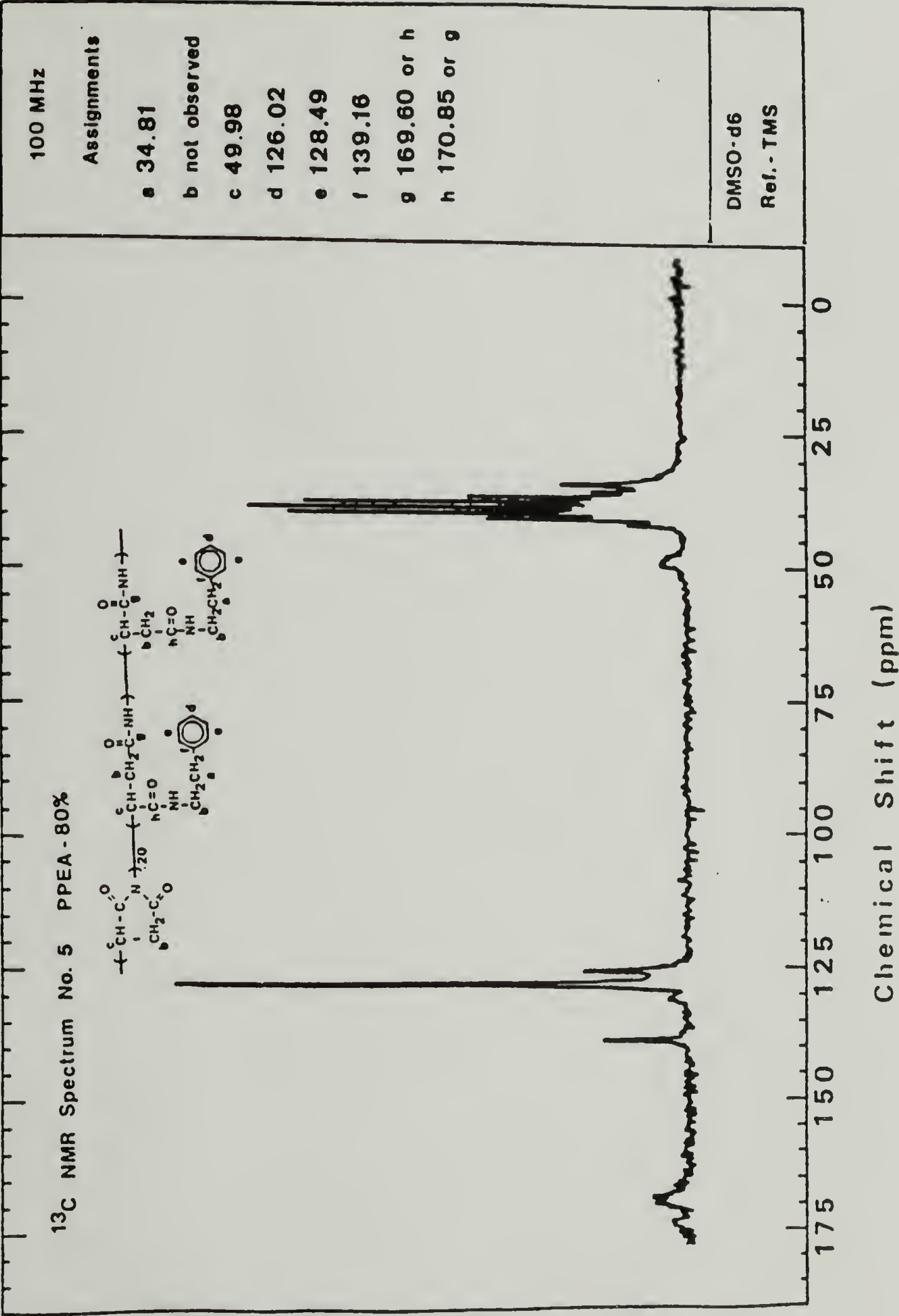
Chemical Shift (ppm)

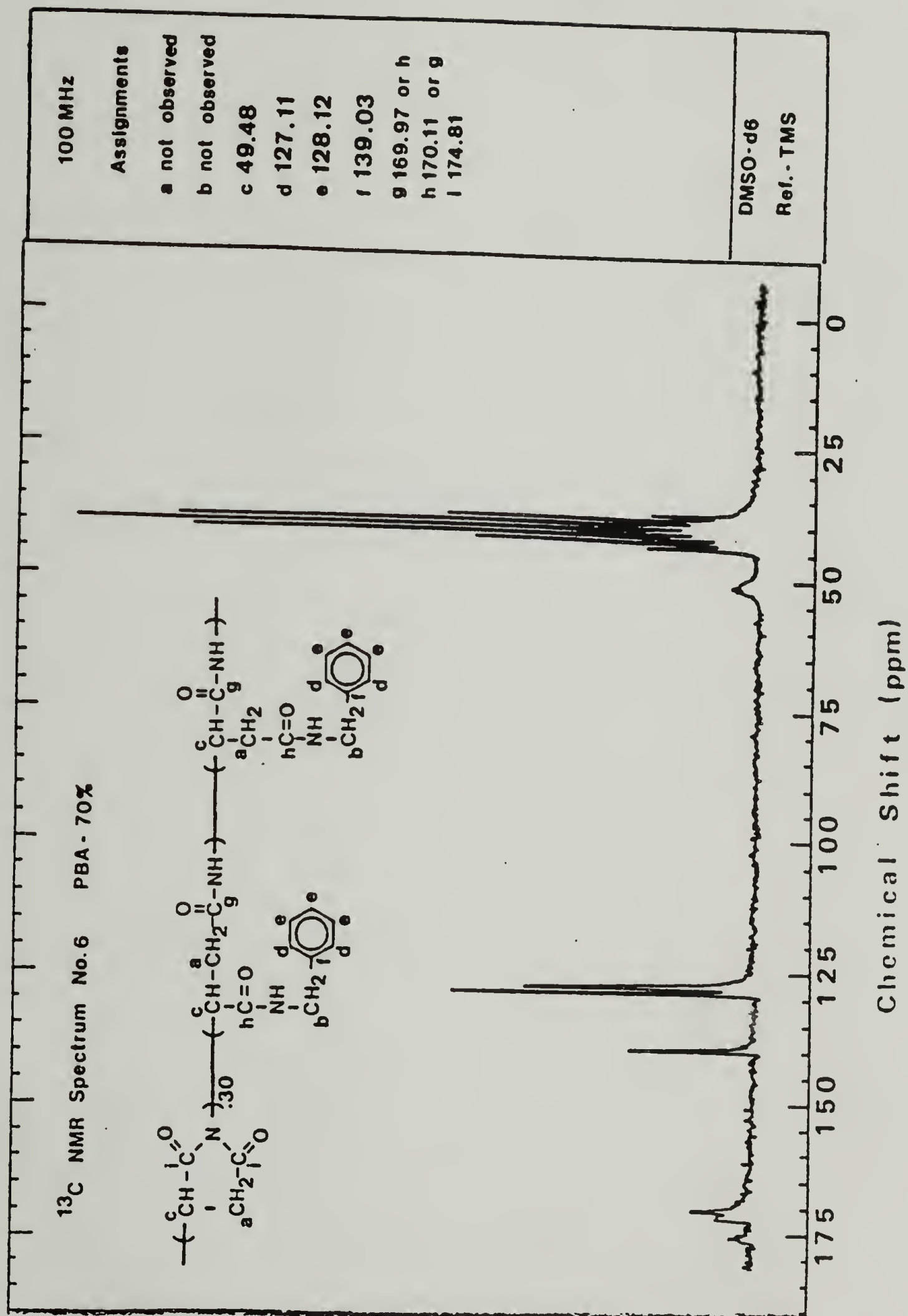


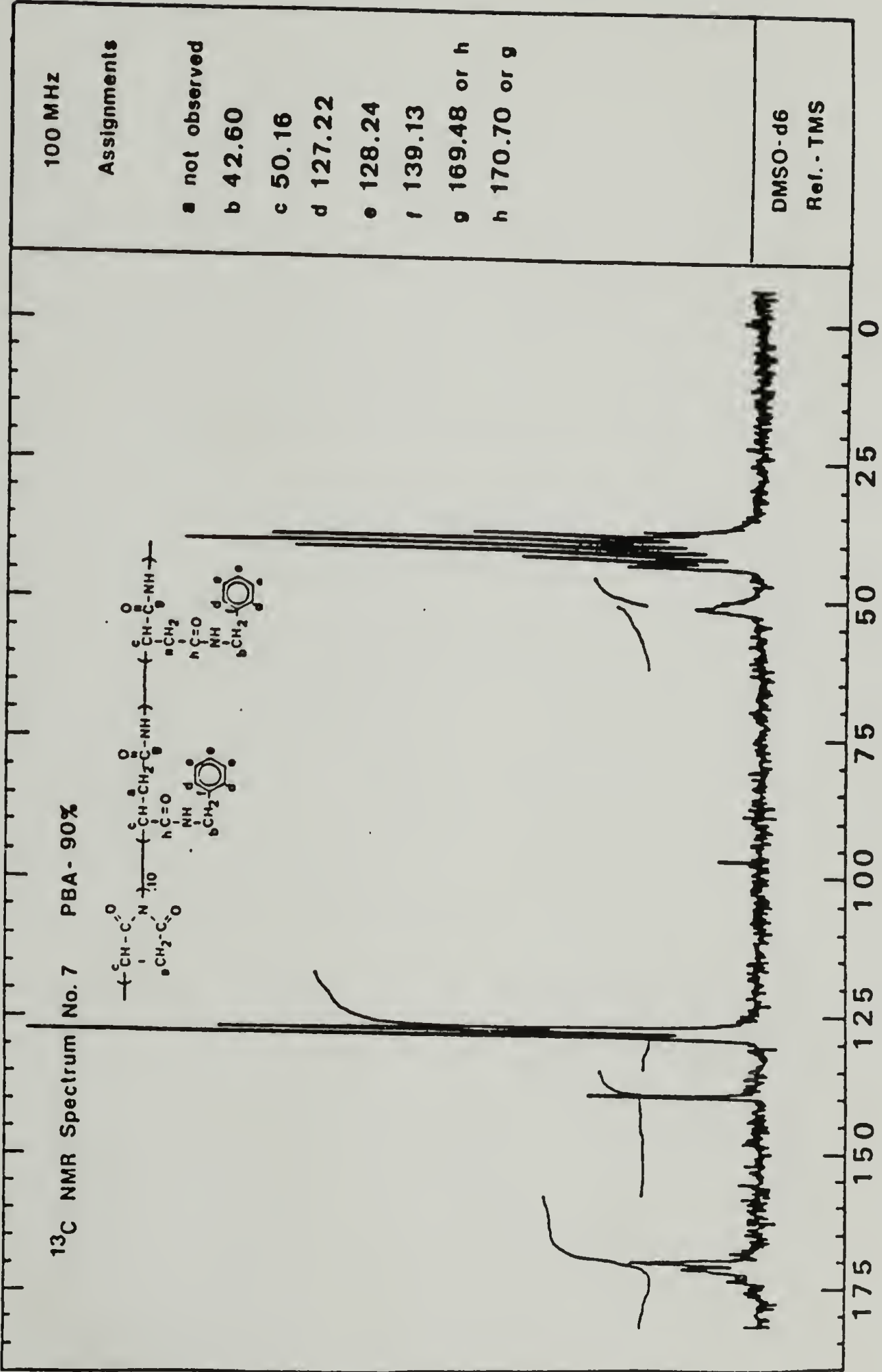




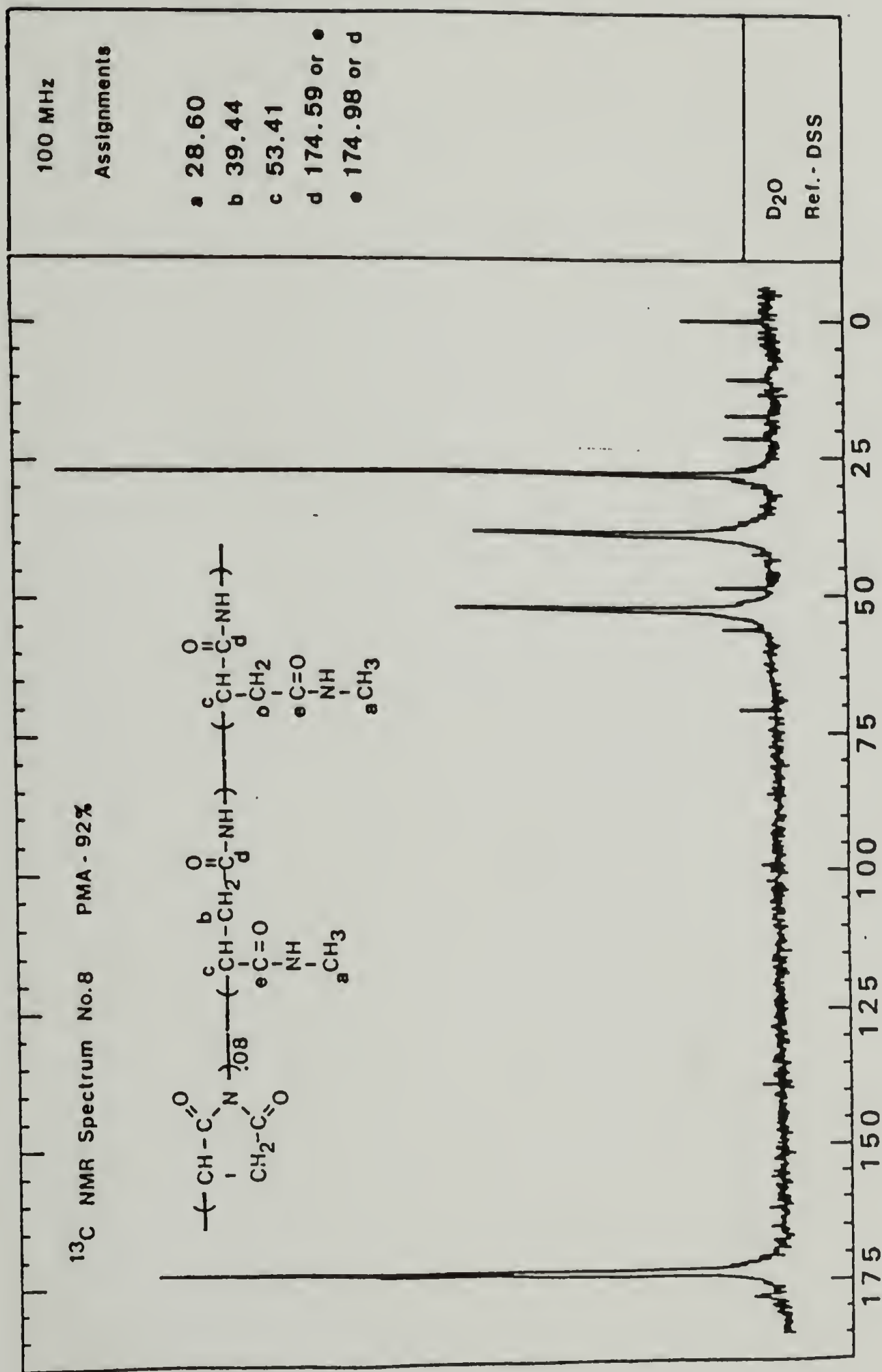


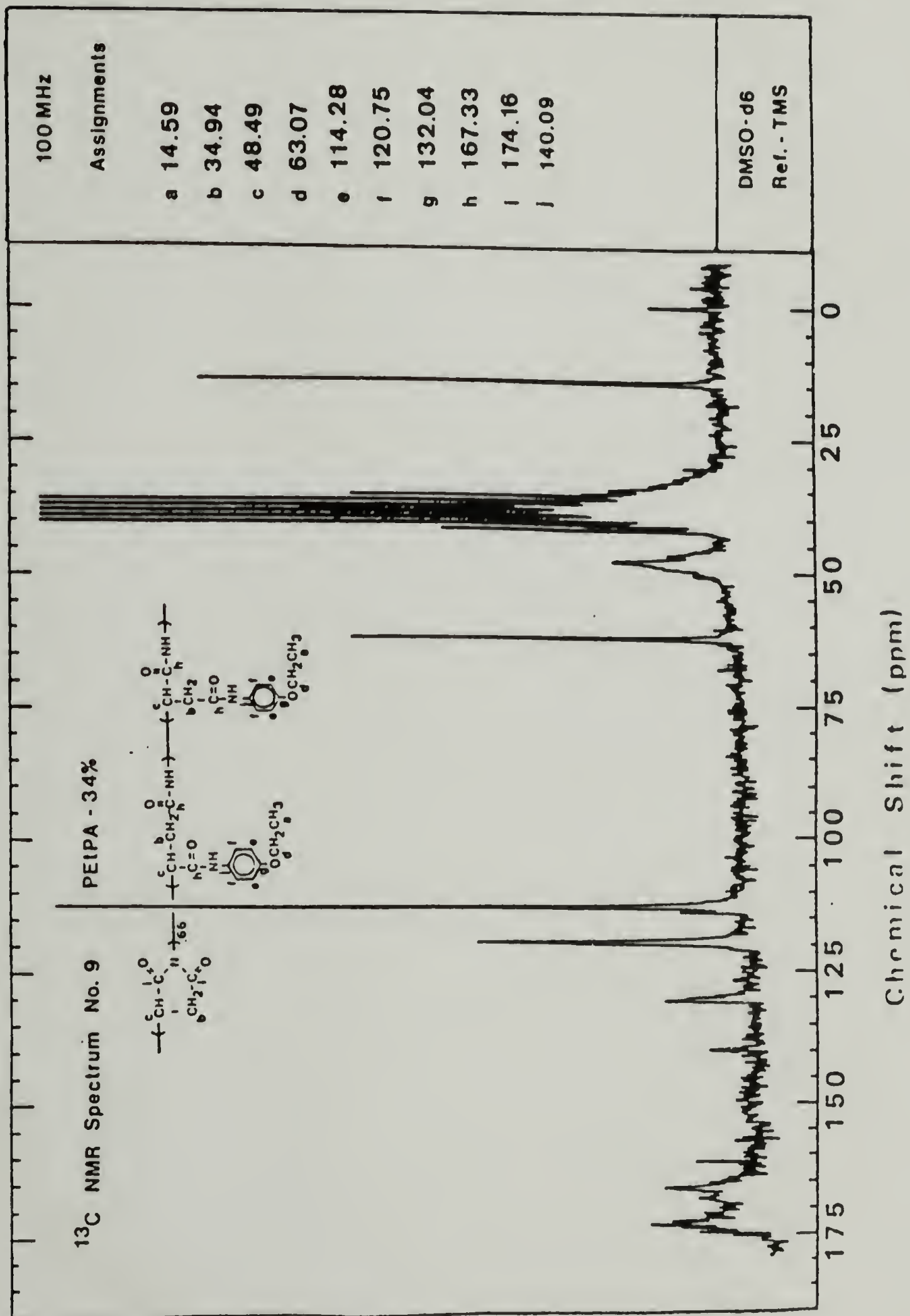


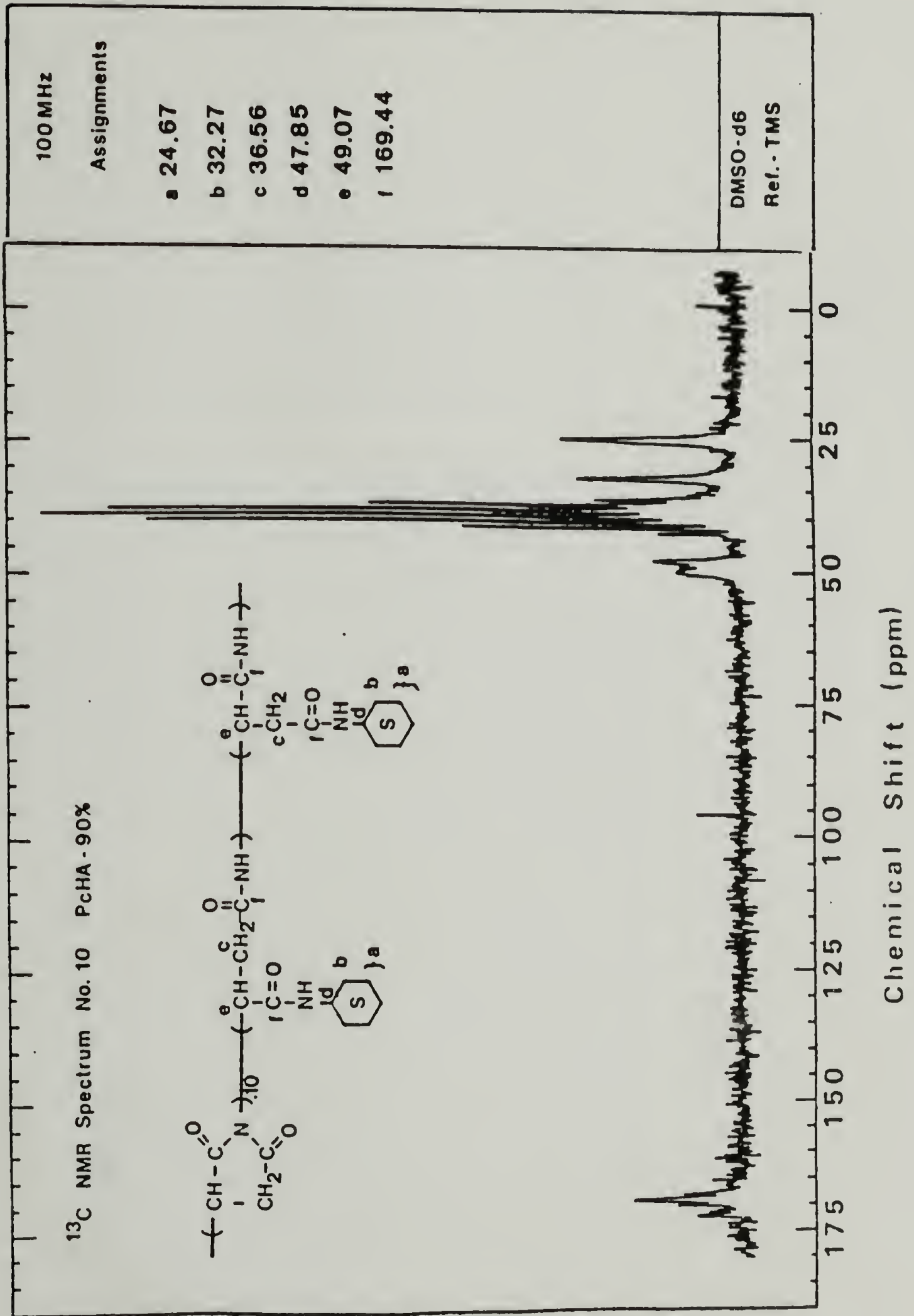


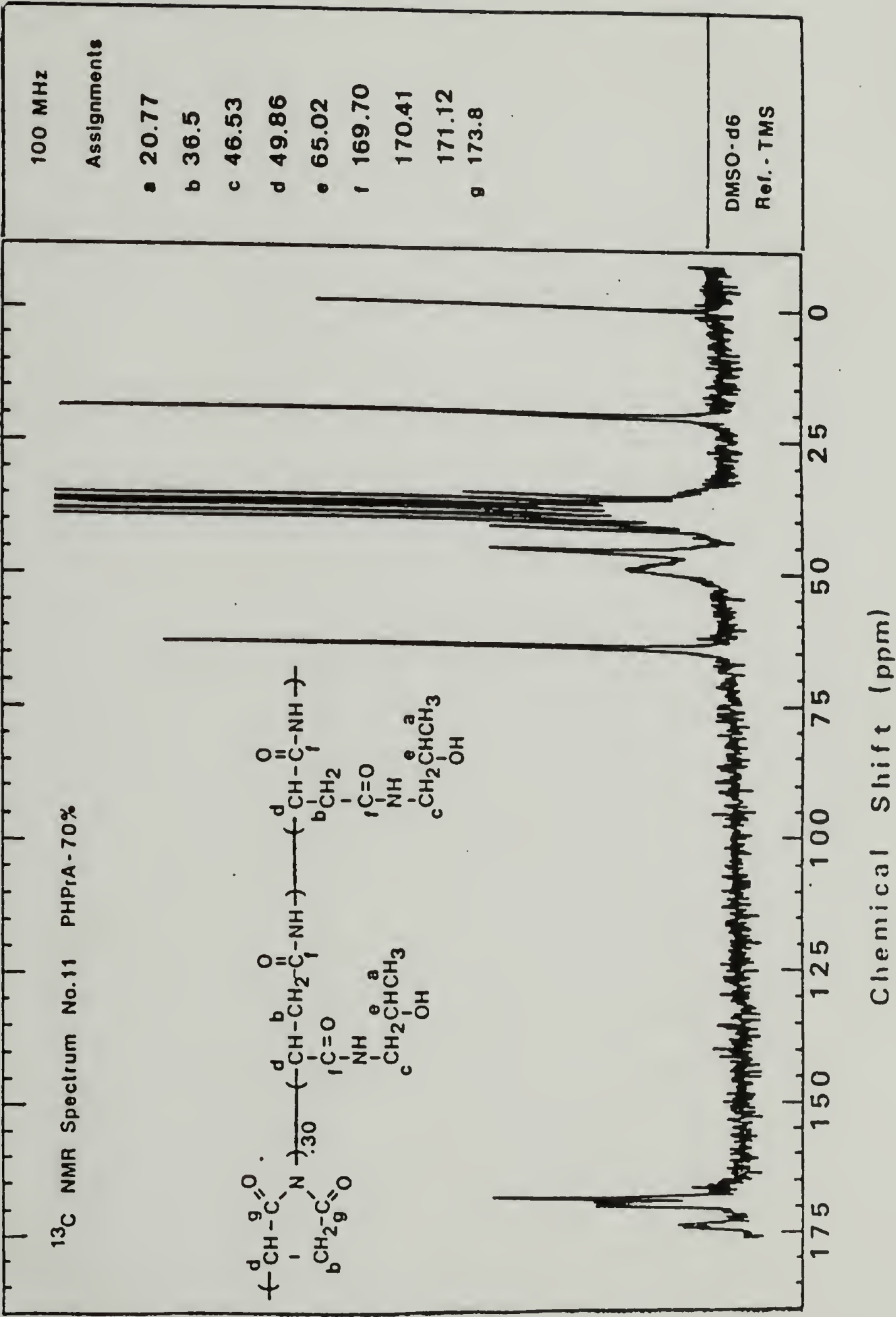


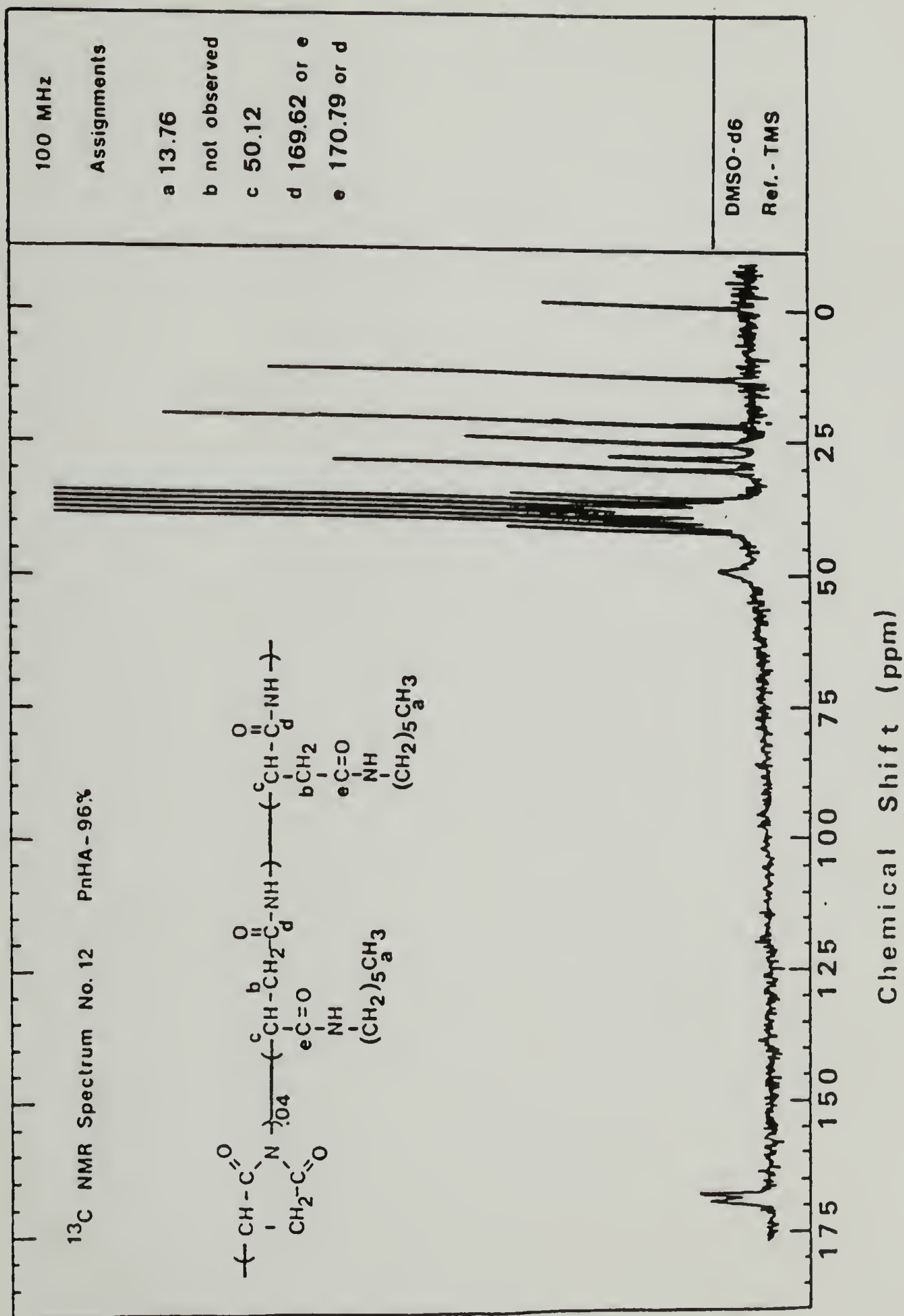
Chemical Shift (ppm)

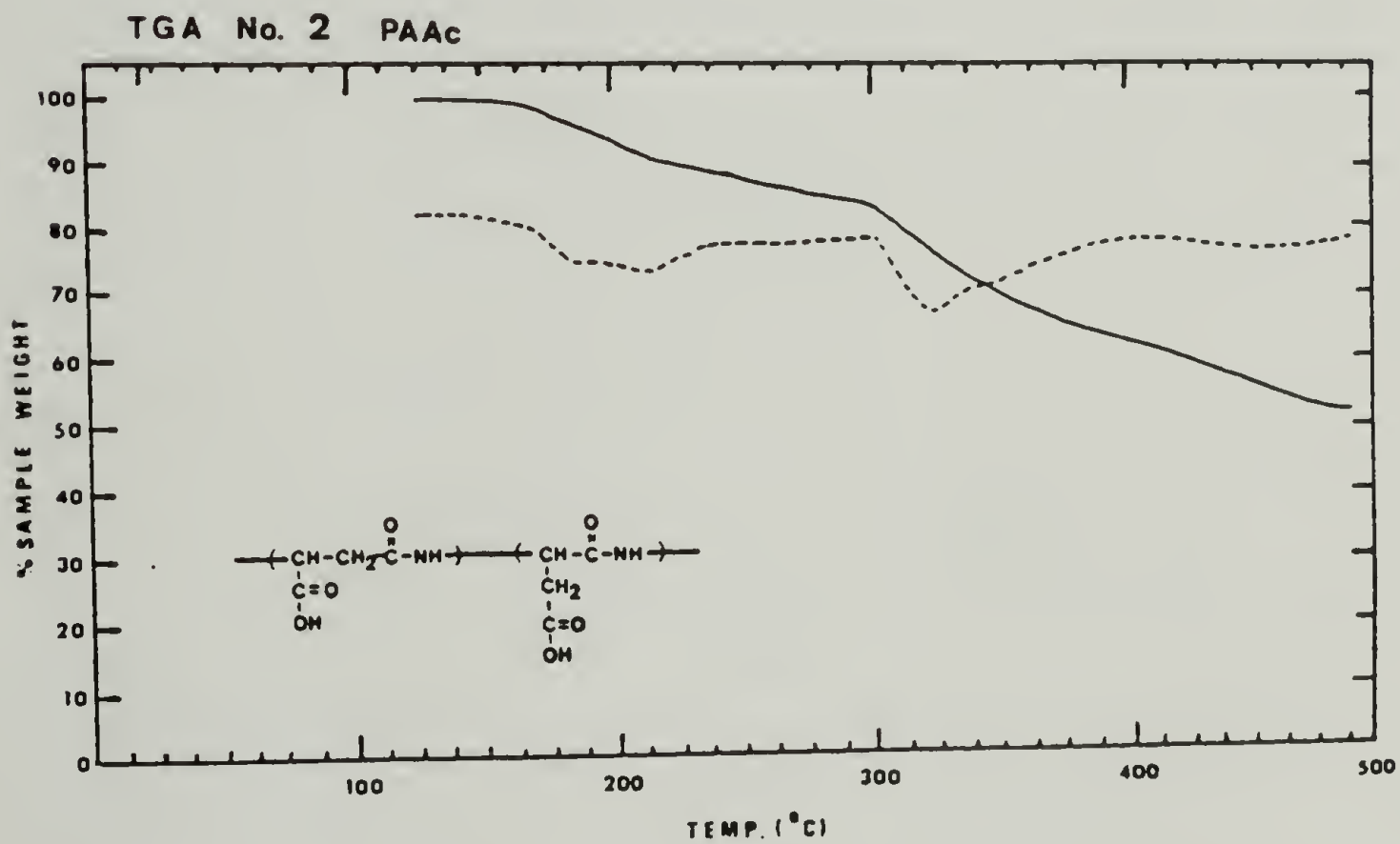
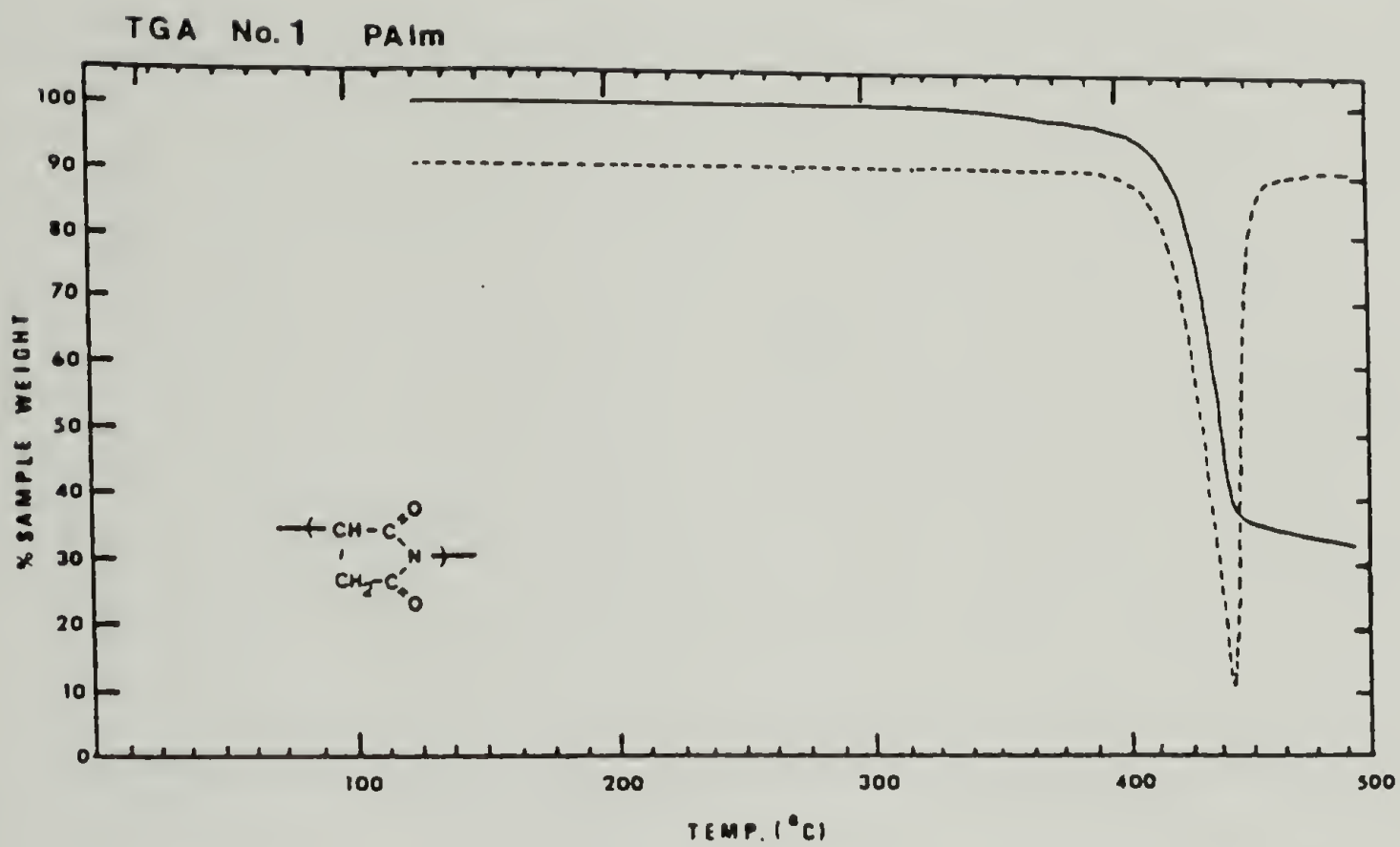




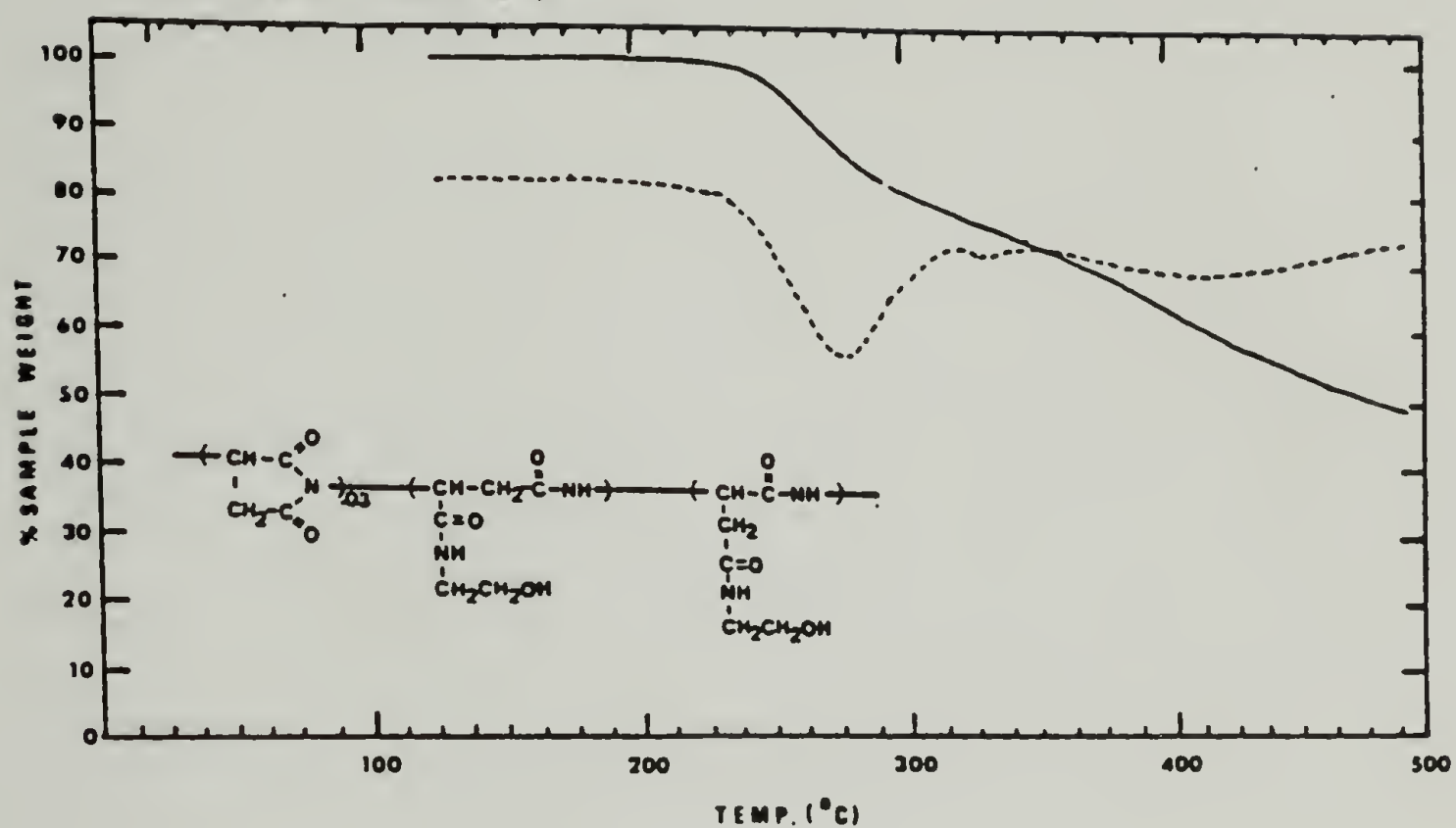




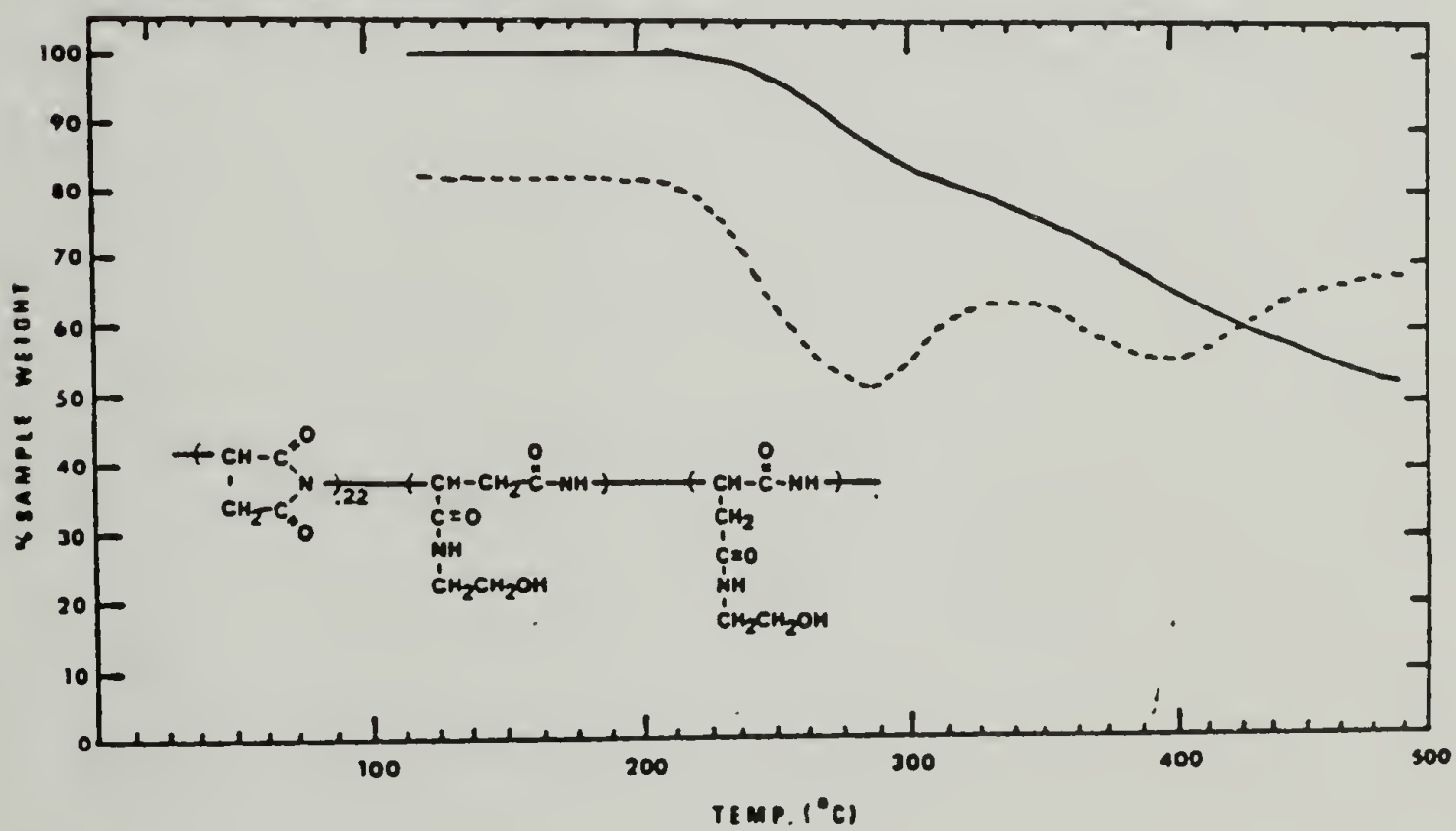


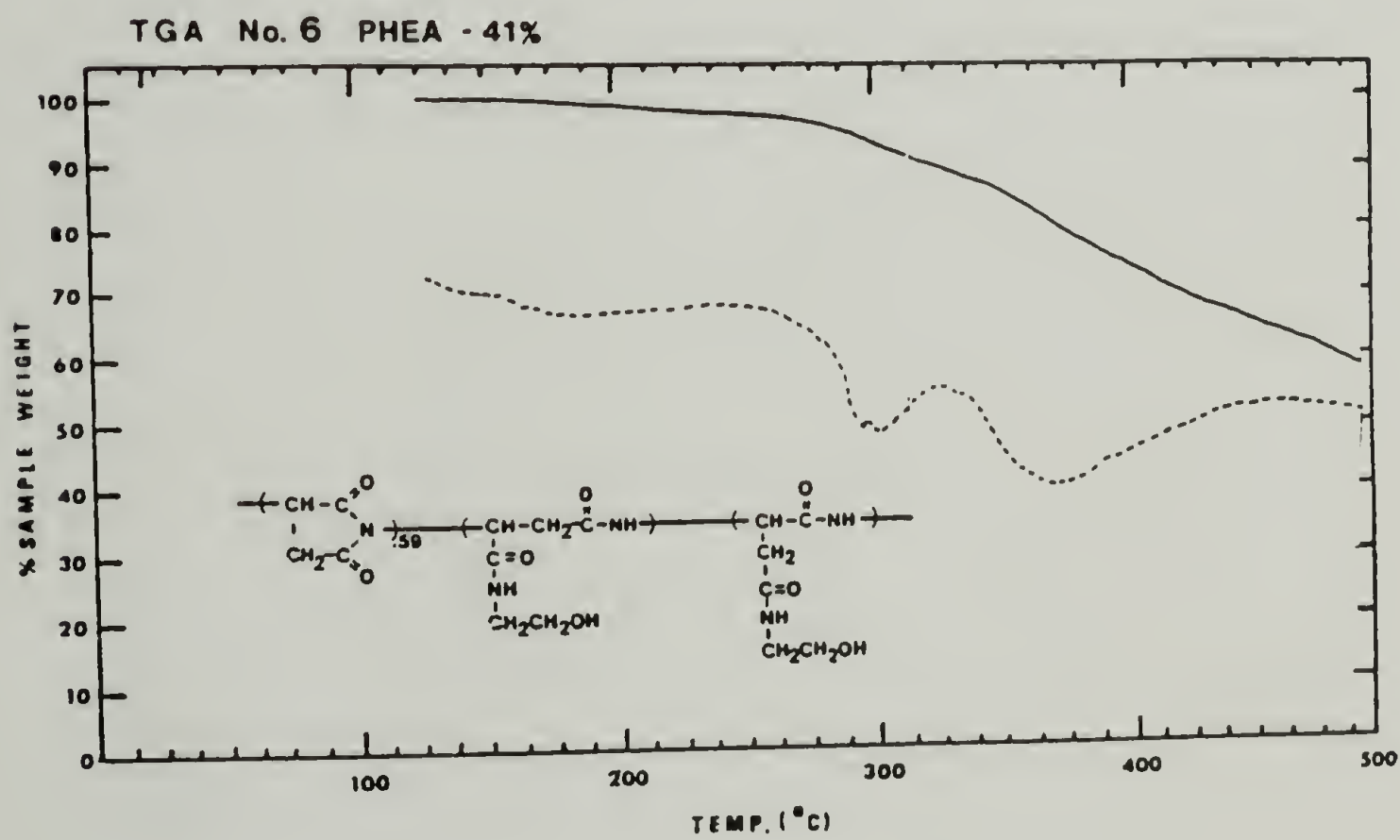
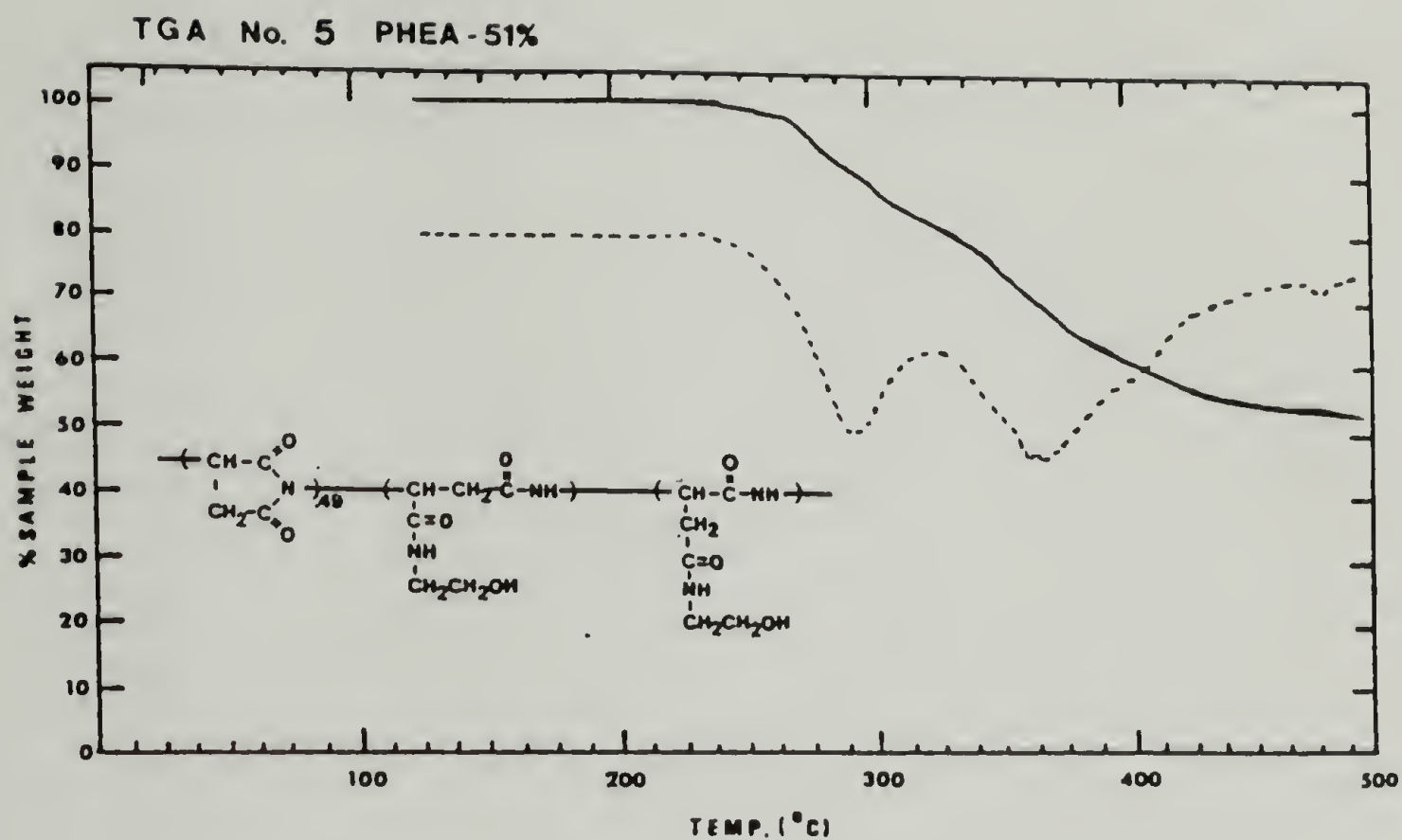


TGA No. 3 PHEA-97%

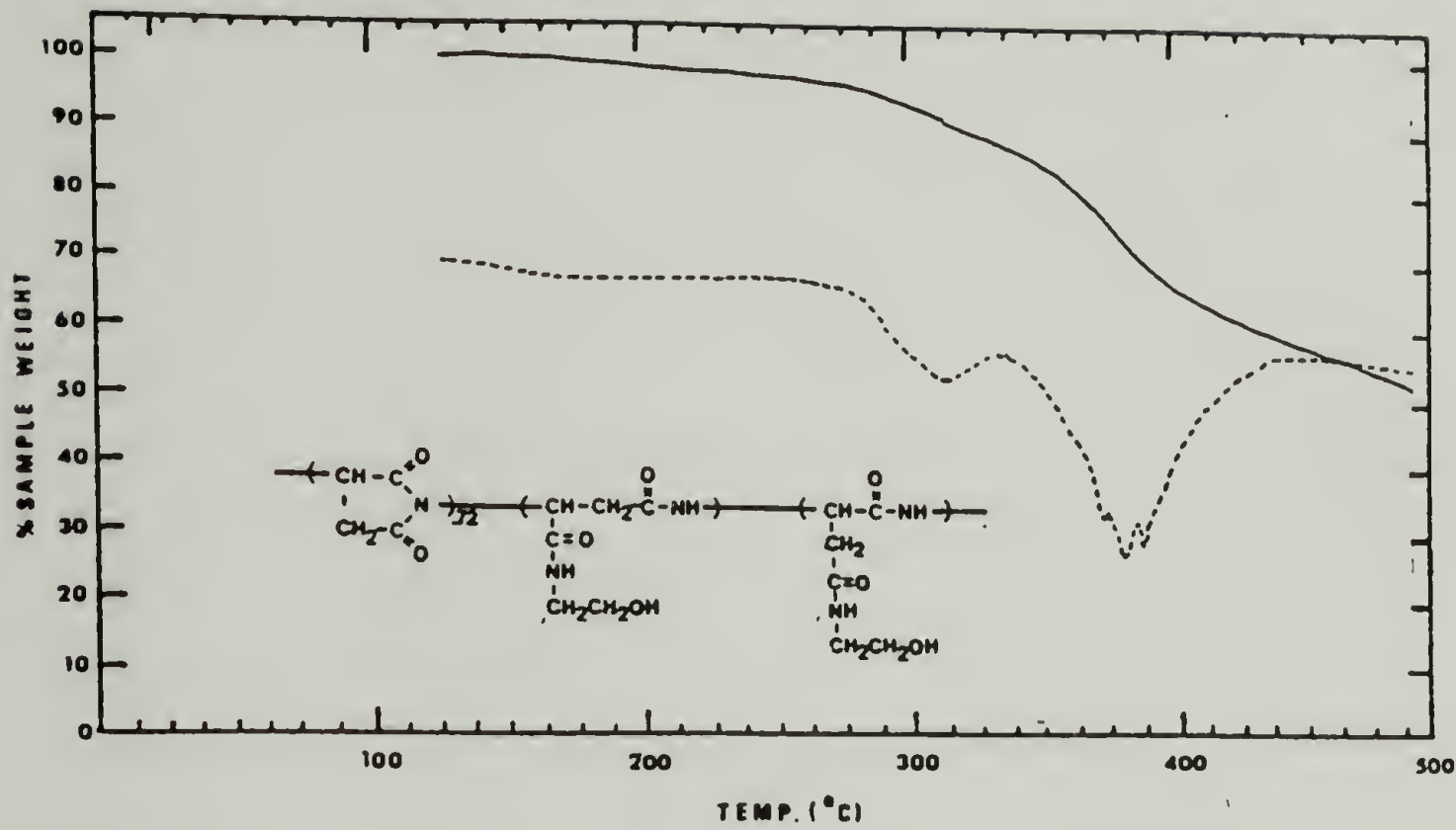


TGA No. 4 PHEA-78%

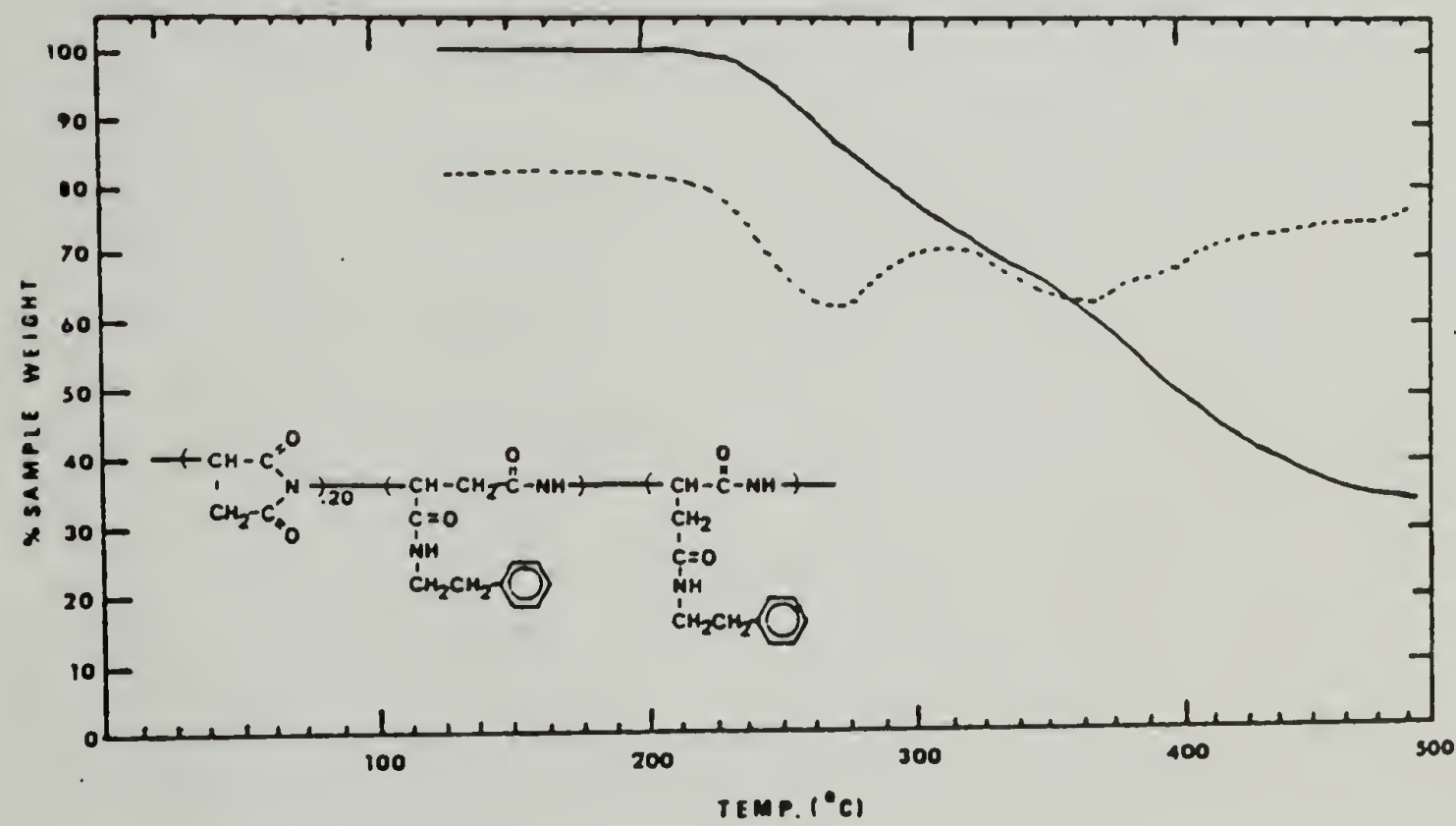




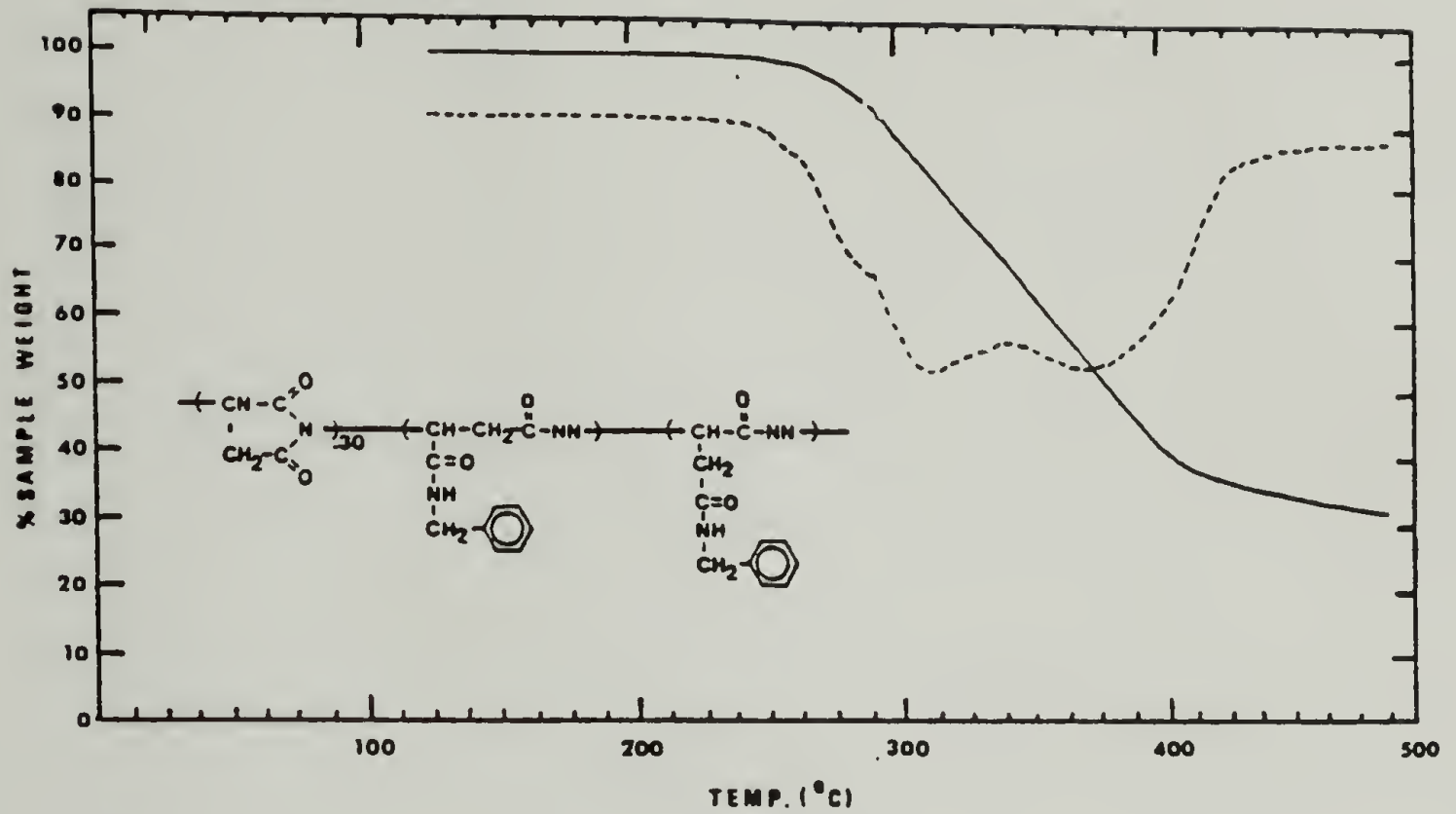
TGA No. 7 PHEA - 28%



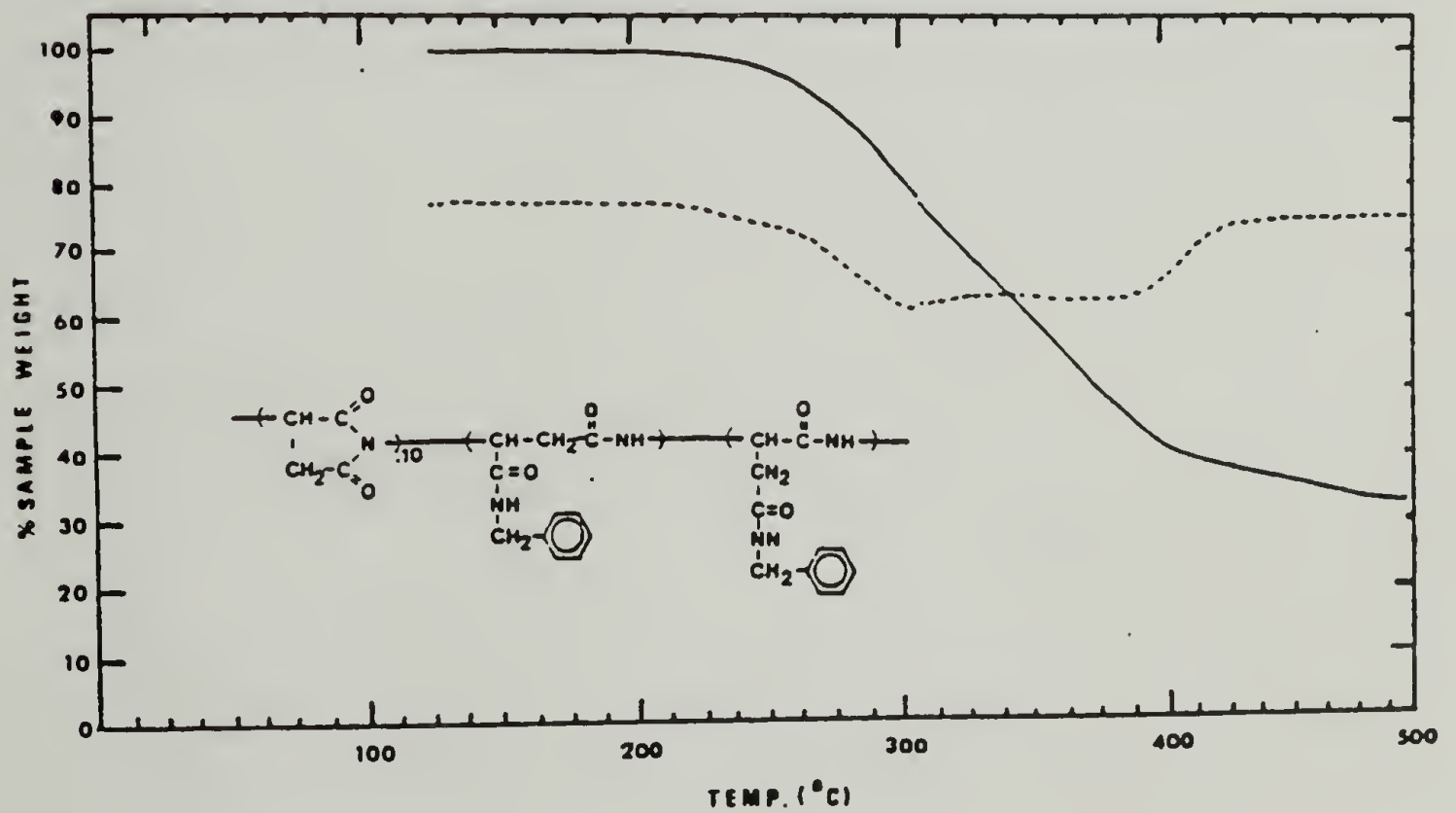
TGA No. 8 PPEA - 80%



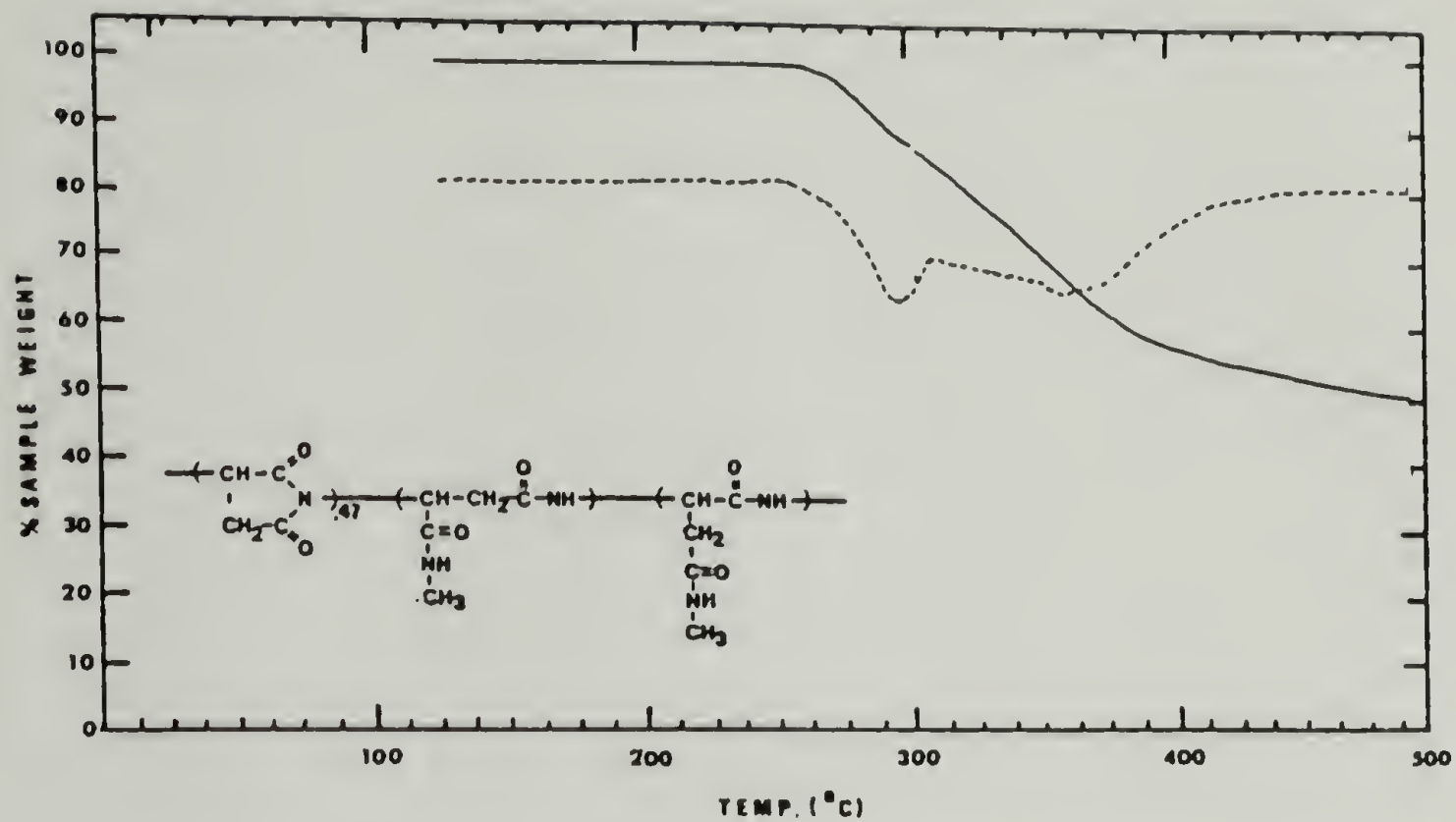
TGA No. 9 PBA-70%



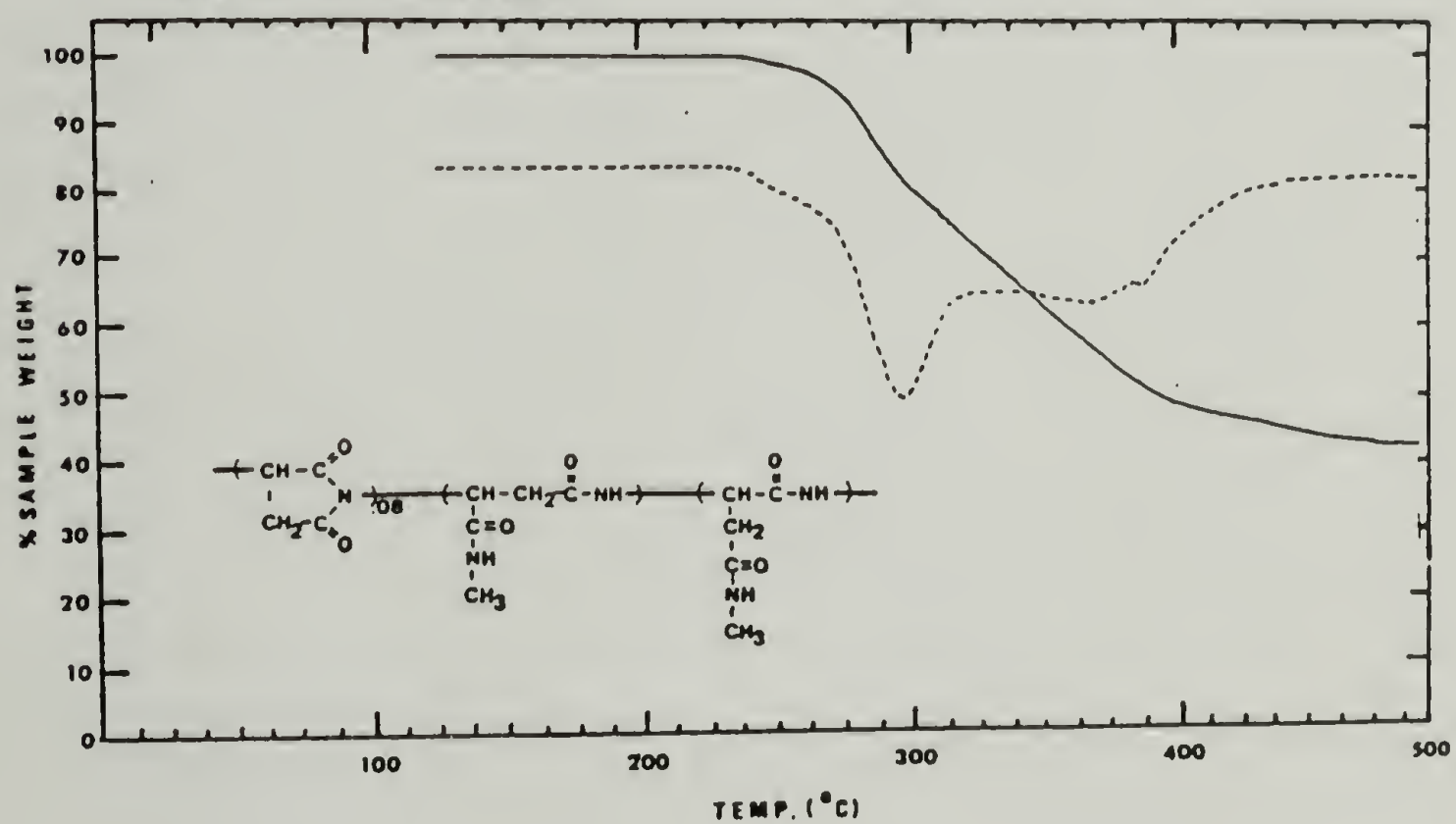
TGA No. 10 PBA-90%

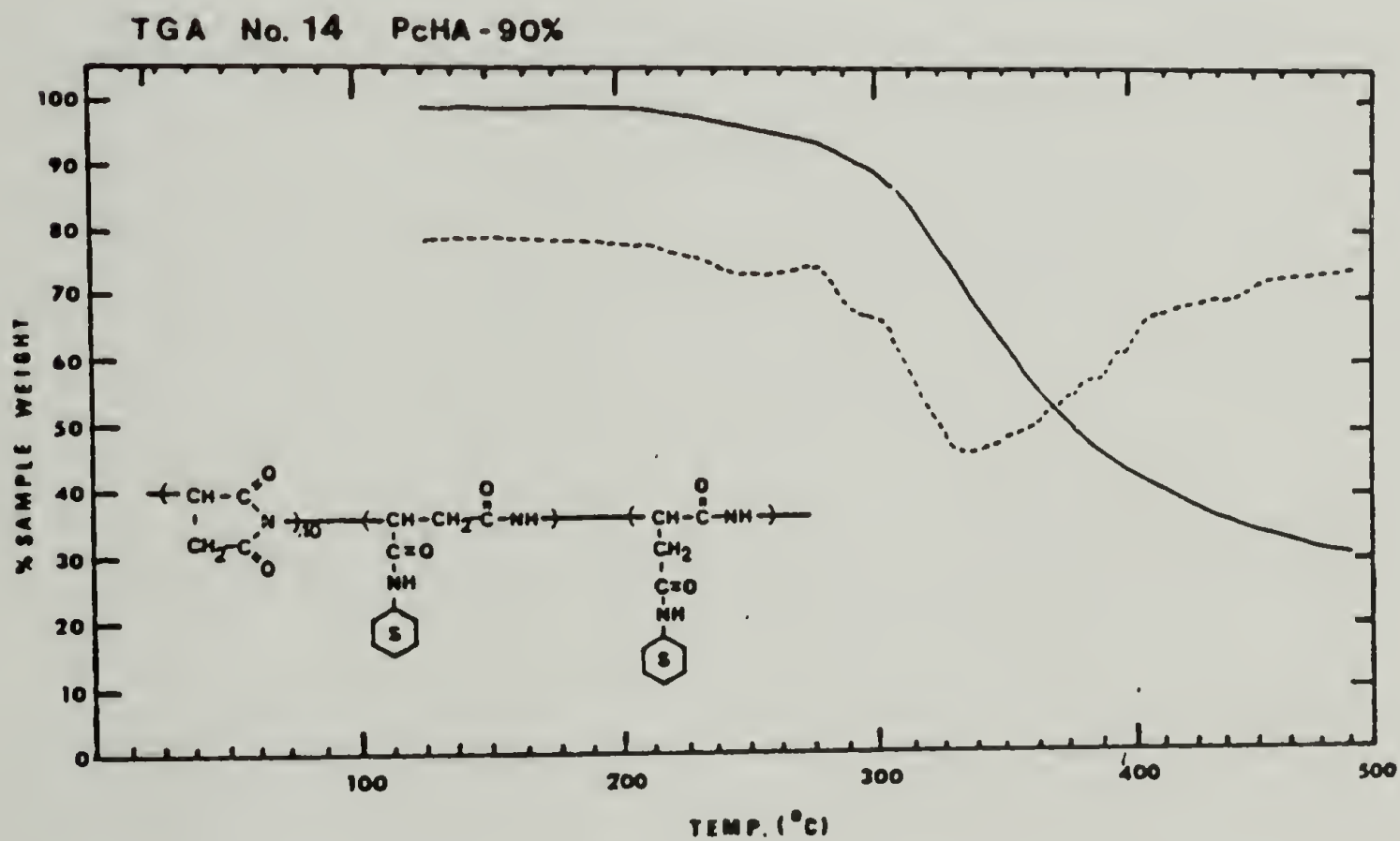
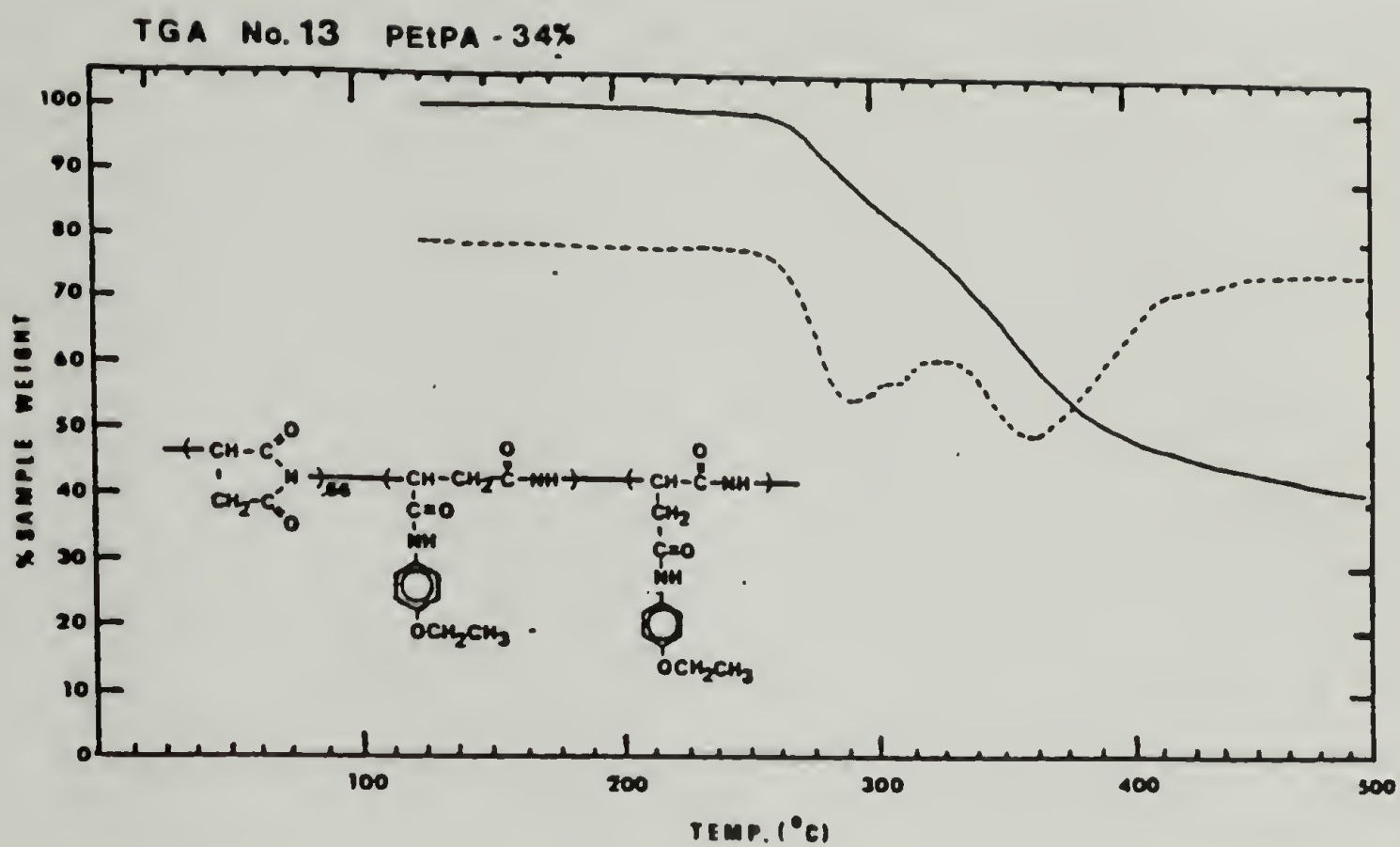


TGA No. 11 PMA-53%

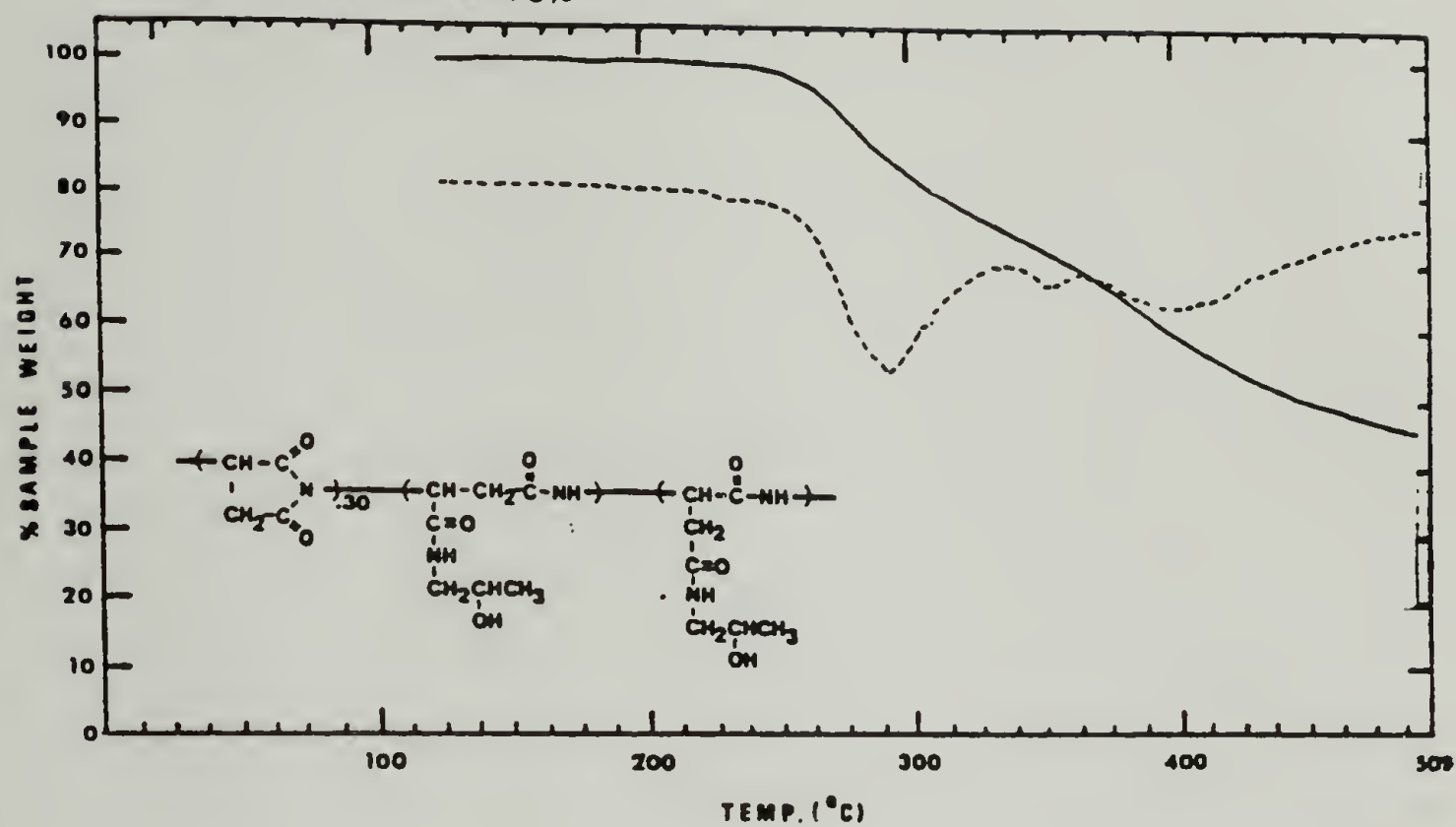


TGA No. 12 PMA-92%





TGA No. 15 PHPrA-70%



TGA No. 16 PnHA-96%

