

Synthesis of Phenetidine-Based Telechelics and Subsequent Reactions with Water-Based Curing Reagents

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ABSTRACT: The development of soluble telechelics based on aniline are highly desirable due to numerous applications that are possible, especially in the coatings and adhesive industry. Control of molecular length and ease of synthesis lends *o*-ethoxyaniline to be an ideal candidate for the synthesis of amino-terminated telechelic oligomers. Combined with the higher solubility and reactivity, curing of these functionally reactive oligomers has been accomplished using aqueous formaldehyde, as well as water-dispersed epoxy resins. Spectroscopic studies have been done to characterize the prepolymer, as well as the cured materials. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1811–1817, 1998

Key words: telechelics; phenetidine; thermosets; conducting polymers

INTRODUCTION

Much research attention has been focused on the uses of conducting polymers, such as polyaniline and its derivatives.^{1–4} Polyanilines and substituted polyanilines are known to be more stable than other conducting polymers, are lower in cost to produce, and may be synthesized in an aqueous environment. Solution processability is a highly desirable characteristic that is not readily attainable by most conducting polymers due to their rigid conjugated backbone structure.⁵

Polyaniline by itself has marginal solubility in some solvents, but the solubility of polyaniline can be improved by substitutions on the benzene ring. However, substituted polyanilines are somewhat less conducting than unsubstituted polyanilines.⁵ Poly(*o*-ethoxyaniline) however, has been shown to exhibit higher solubility without great sacrifice in conductivity compared to polyaniline.⁶ If reactive polyaniline telechelics are desired, the pres-

ence of an alkoxy group in the ortho position of the aniline monomer should also increase the nucleophilicity of the terminal amino groups toward reactive electrophiles used during the subsequent reactions involving these functional groups. It has been found that phenylenediamine can be used as a radical initiator in the polymerization of aniline, yielding a product with an amine functionality at each terminus.^{1–3} The molecular weight of polyaniline can be controlled by varying the molar ratios of phenylenediamine and aniline.⁴ This feature is useful for other reactions, particularly the reaction with epoxy resins to produce coatings with polyconjugated blocks in the backbone. The focus of this article is to report on work done on the reaction of *o*-phenetidine (*o*-ethoxyaniline) with phenylenediamine in 2 : 1 and 4 : 1 ratios and the curing reactions of the products with aqueous formaldehyde and epoxy resins. Figure 1 shows the synthetic scheme used for the preparation of a telechelic based on phenetidine and phenylenediamine. Figures 2 and 3 show proposed reactions with formaldehyde and bisphenol A epoxy.

EXPERIMENTAL

Phenetidine (*o*-ethoxyaniline) and *p*-phenylenediamine were purchased from Aldrich Chemical

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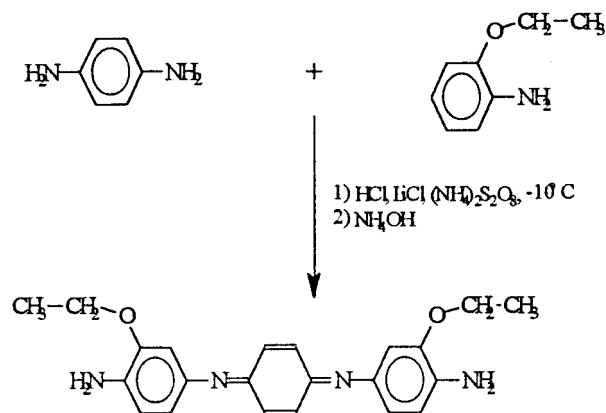


Figure 1 Preparation of diamine oligomer from phenylene diamine and phenetidine.

Co. Phenetidine was distilled prior to use. Phenylenediamine was recrystallized from ethanol. All other reagents were used as received.

Infrared (IR) spectroscopy was obtained using a Nicolet Magna 500 Fourier transform infrared (FTIR) on KBr pellets. All measurements were carried out under atmospheric conditions. Nuclear magnetic resonance (NMR) was obtained using a Bruker AC-200F FT-NMR. Samples were dissolved in deuterated dimethyl sulfoxide (DMSO) using a tetramethylsilane (TMS) internal standard. Ultraviolet–visible (UV–vis) spectroscopy (frequency range 190 to 900 nm) of solutions in quartz cuvettes were obtained using a Perkin–Elmer Lambda Array 3840 UV–vis spectrophotometer. Mass spectrometry (MS) was performed using a LaserTech time-of-flight instrument using an accelerating voltage of 26,000 V. Thin-layer chromatography (TLC) was performed on silica gel plates (60 Å pore size) purchased from Aldrich Chemical Co. using methanol as eluent, and the spots were visualized using a hand-held UV lamp.

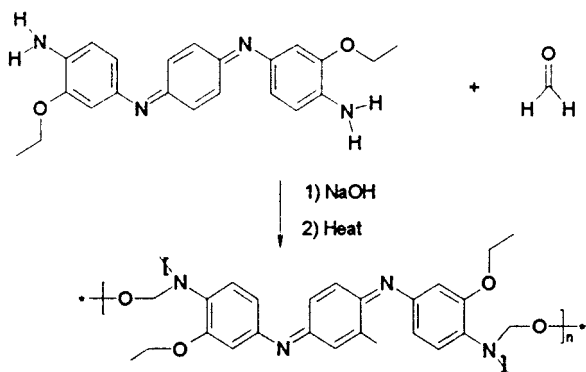


Figure 2 Crosslinking of diamine oligomer by reaction with formaldehyde.

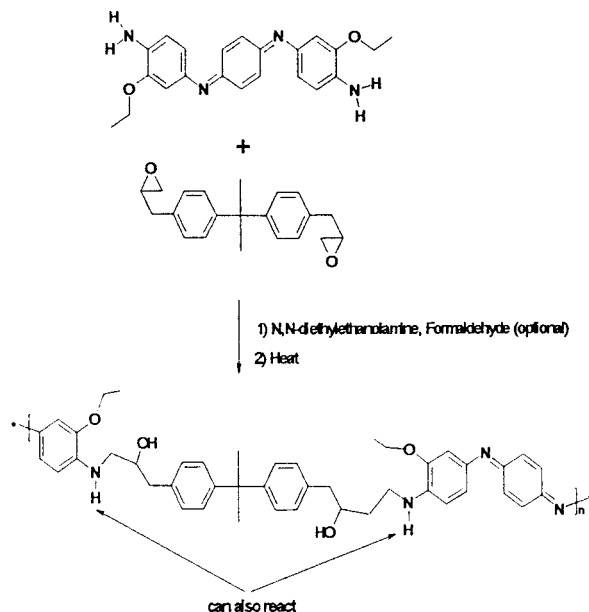


Figure 3 Curing reaction of diamine oligomer with bisphenol A.

Preparation of Diamine Oligomer

Synthesis of the 2 : 1 oligomer was carried out in a 1000 mL three-necked round-bottomed flask equipped with a magnetic stirrer, a vacuum adapter, and a thermometer. To 500 mL, 1M HCl, 2.49 g (23.1 mmol) *p*-phenylenediamine was added. Then, 29.79 g (702 mmol) LiCl was added. The solution was constantly stirred as it was chilled to -10°C in a salt–ice bath. Then, 10.93 g (47.9 mmol) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was dissolved in 40 mL distilled H_2O and added to the phenylenediamine solution. After each addition of reactants, the flask was evacuated under low vacuum and stirred for a few minutes. After 10 min, a color change from light brown to dark brown was observed. At this time, 6.0 mL (46.0 mmol) *o*-phenetidine was added. The mixture was constantly stirred, and the temperature was maintained below 0°C as it was allowed to react for 6 h. The temperature was allowed to rise to room temperature, and the reaction was allowed to continue for

Table I Wavelengths of Maximum UV Absorption (λ_{max}) of the Phenetidine Telechelics Undoped and Doped States

| Associated Structure | λ_{max} (nm) Undoped | λ_{max} (nm) HCl Doped |
|----------------------|-------------------------------------|---------------------------------------|
| Benzenoid | 310 | 310, 430 |
| Quinoid | 570 | 550, 860 |

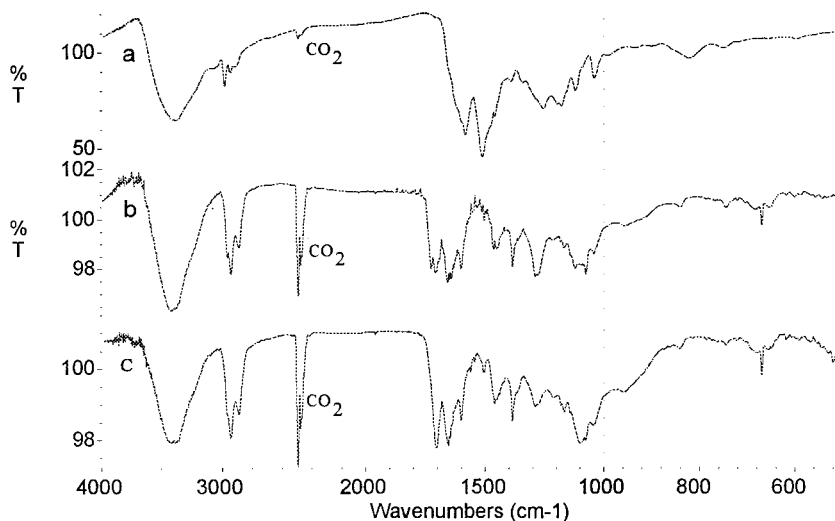


Figure 4 (a) Infrared spectrum of diamine oligomer. (b) After reaction with formaldehyde. (c) Upon heating for 1.5 h.

14 h. The total reaction time was 20 h, all under vacuum. A dark green precipitate was collected by suction filtration in a Buchner funnel. The precipitate was washed with 200 mL 1M HCl, followed by washing with 200 mL distilled H₂O, 200 mL 1M NH₄OH, and 200 mL distilled H₂O. The precipitate was dried overnight in a vacuum. A total of 1.74 g of the product was collected, which corresponds to a 20% yield.

For the synthesis of the 4 : 1 oligomer, a 1.0M acetic acid solution was used instead of hydrochloric acid since *o*-phenetidine was observed to have

a greater solubility in the former. The synthesis of the oligomer was carried out in a 500 mL round-bottomed flask fitted with a vacuum adapter, thermometer, and stir bar, as described earlier. In the flask, 0.42 g (4 mmol) of 1,4-phenylenediamine was dissolved in 150 mL 1M acetic acid, and the solution was degassed for 10 minutes under low vacuum with constant stirring. The solution was then chilled to -5°C in a salt-ice bath with constant stirring. After chilling, 3.6 g (16 mmol) (NH₄)₂S₂O₈ was mixed and stirred until the solution became dark brown in color. At this time,

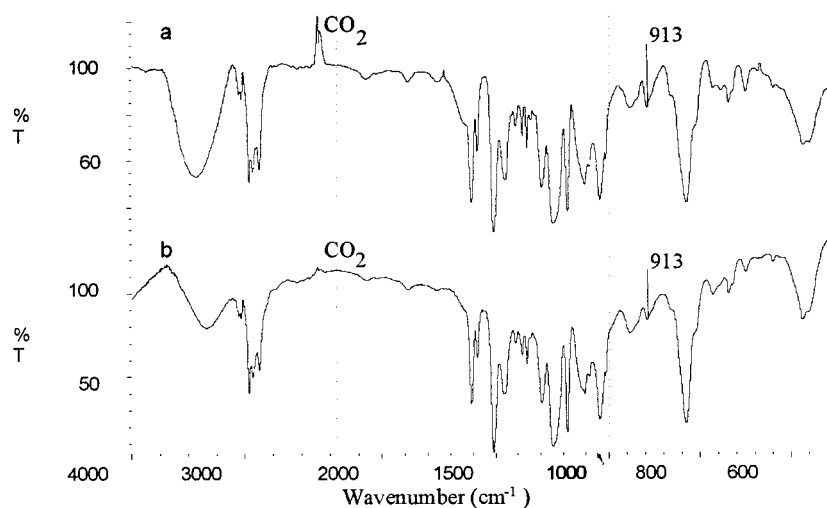


Figure 5 (a) Infrared spectroscopy of Beckopox EP384W water-dispersed bisphenol A resin; (b) Beckopox EP384W cured with diamine oligomer.

LaserTec Time-of-Flight Mass Spectrometry

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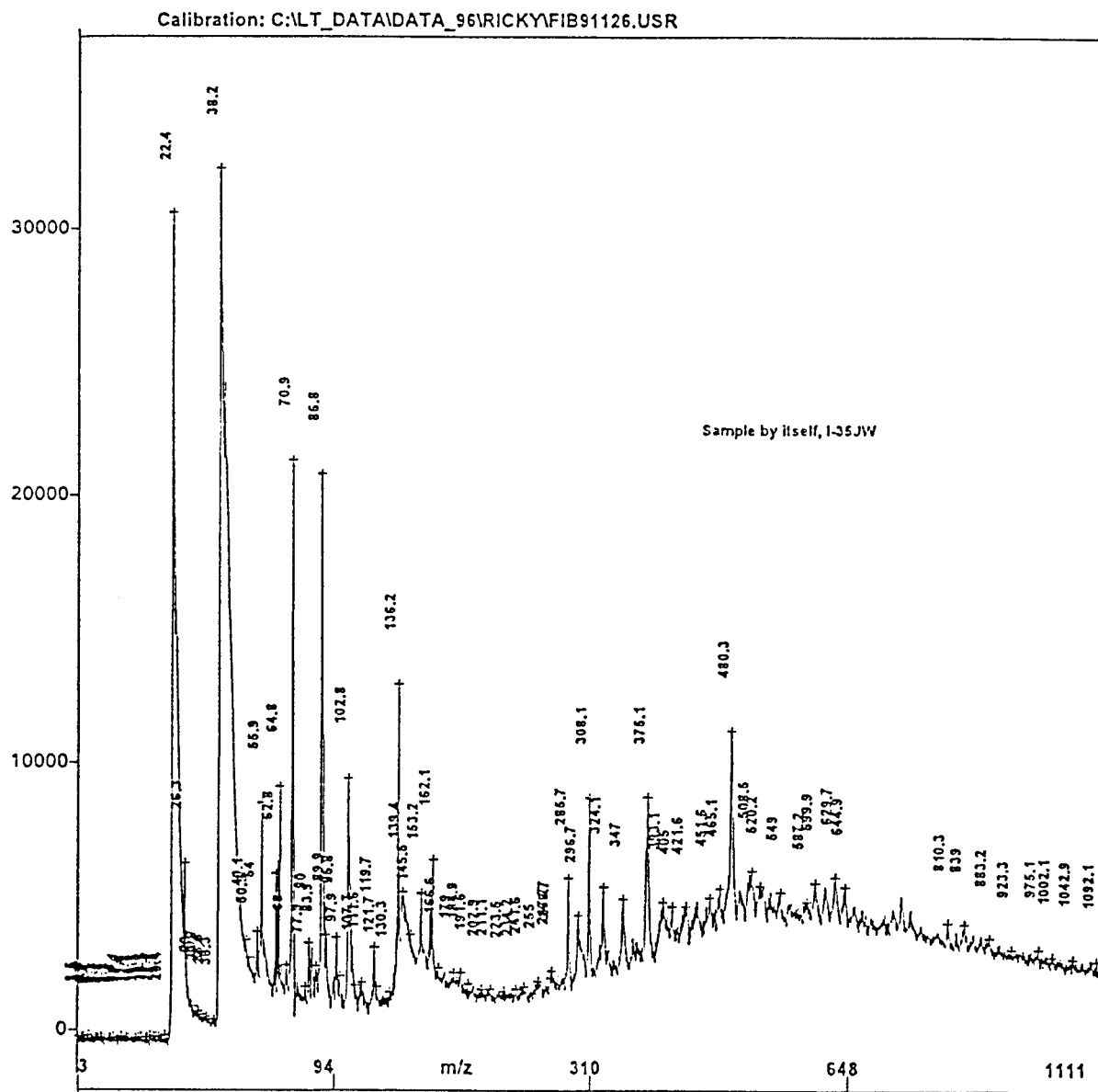


Figure 6 Time-of-flight mass spectrum of phenetidine-phenylenediamine telechelic.

2.0 mL (16 mmol) of *o*-phenetidine dissolved in a small amount of the acetic acid solution was added. All other steps were similar to the one described for the preparation of the trimer.

Reaction of Diamine Oligomer with Formaldehyde

A 0.0035 g (0.0093 mmol) sample of the diamine oligomer was dissolved in about 10 drops of acetone. Five milliliters of formalin (37% formalde-

hyde in H₂O) (0.067 mmol HCHO) and seven drops (0.35 mmol) of 1M NaOH were then added and heated. A color change from dark purple to medium brown was observed with concomitant precipitation. After centrifugation, a sticky brownish-orange precipitate was found at the bottom of the test tube. This was dissolved in methanol and evaporated on a KBr plate for IR spectroscopy. The plate was then heated at 89°C for 1.5 h. Another IR spectrum was obtained at this stage.

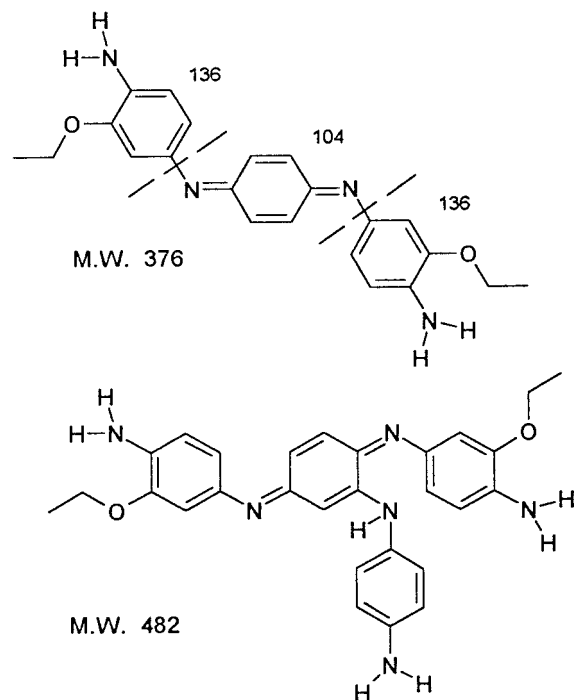


Figure 7 Proposed structures of telechelics from mass spectral data.

Curing of Epoxy Resin

The resin used was Beckopox EP384W (Hoechst-Celanese®), which is a water-dispersed bisphenol A epoxy resin. It consists of a 53% solution of (chloromethyl)oxirane, 4,4-(1-methylethylidene) bisphenol copolymer in water-methoxypropanol (40/7%). It has an epoxy value (solid resin) of 0.18–0.20/1000 g. This resin was cured both with and without formaldehyde-modified phenetidine-telechelic.

Without Formaldehyde Modification

A 0.004 g (0.016 mmol) sample of the diamine was mixed with about four drops (0.0015 mmol) of *N,N*-diethylethanolamine (base). About eight drops (0.44 g, 0.005 mmol equivalent of epoxy groups) of Beckopox EP384W were then added. The mixture was stirred well and was then coated on a KBr plate. The coating began to cure within 15 min, evidenced by a color change from light purple to dark purple around the edges. After curing, the entire coating was dark purple. When heated, the color of the coating was observed to change from dark purple to dark red. After curing, air small pockets were observed in the coating. IR spectroscopy was obtained for the samples at different stages of curing.

With Formaldehyde Modification

A 0.004 g (0.016 mmol) sample of the diamine was mixed with about four drops of *N,N*-diethylethanolamine. About four drops of formalin were added, followed by eight drops of Beckopox EP384W (~ 0.005 mmol equivalent of epoxy groups). The mixture was stirred well and was then coated on a KBr plate. The coating began to cure within 15 min, evidenced by a color change from light purple to dark purple around the edges. After curing, the entire coating was dark purple. When heated, the color of the coating was observed to change from dark purple to dark red. The coating area was observed to shrink as the coating cured; however, the coating did not have the pockets that were observed in the coating without formaldehyde.

RESULTS AND DISCUSSION

First attempts to synthesize this diamine oligomer at low temperatures and with short reaction times resulted in poor yields (about 5% or less). The yield was improved to about 20% by increasing the reaction time to 20 h, allowing the temperature of the system to rise to room temperature after 6 h at -10°C , and by carrying out the reaction under vacuum. Allowing the entire reaction to occur at room temperature for a reaction time of 20 h under vacuum gave a yield of about 10%.

The diamine oligomer was found to be soluble in acetone, methanol, THF, methylene dichloride, formalin, ethylacetate, and DMSO. Thin layer chromatography on a silica gel plate was done with the diamine oligomer using acetone for spotting and methanol as an eluent. After development, both the preparations appeared to be composed of essentially only two components with very close R_f values. A trace amount of a compound was also found at the origin.

Results obtained using UV-vis spectroscopy of the 2 : 1 preparation in water with a few drops of DMSO added are shown in Table I. The λ_{max} at 310 nm corresponds to π to π^* transition of the (undoped) benzenoid, and that at 570 nm corresponds to π to π^* transition of the (undoped) quinoid structure. The addition of 1M HCl led to a partial protonation and produced two additional absorptions. The λ_{max} at 430 nm corresponds to π to π^* transition of the (doped) benzenoid, and the λ_{max} at 860 nm corresponds to π to π^* transition of the (doped) quinoid structure. This phenome-

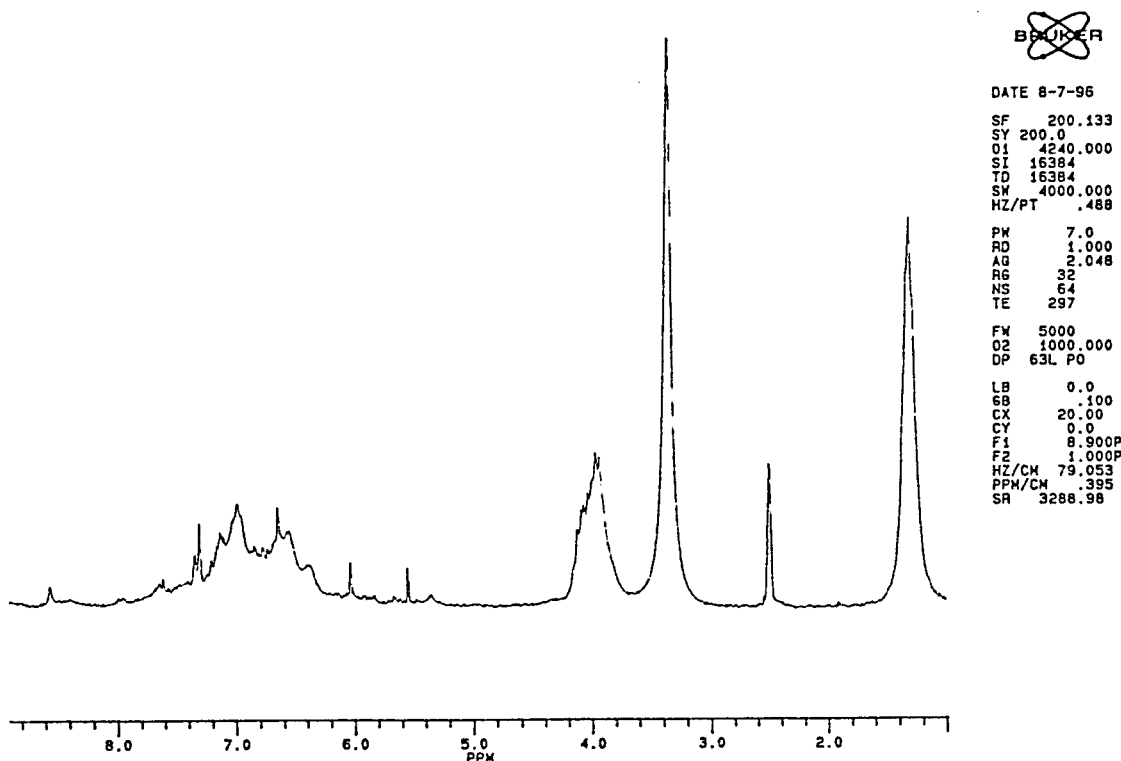


Figure 8 Nuclear magnetic resonance spectroscopy of diamine oligomer in d_6 -DMSO.

non is generally indicative of doping of the polyaniline chain.

Infrared spectroscopy was obtained on a KBr pellet containing the telechelic [Fig. 4(a)]. The large absorption peak at 3390 cm^{-1} due to H_2O masks the two NH_2 stretches that would be observed for terminal amino groups. Peaks are seen between 2979 and 2897 cm^{-1} that are due to the vibrational modes of the ethoxy functional group, and a peak is seen at 822 cm^{-1} due to C—H stretching of a 1,2,4-trisubstituted benzene ring.

Upon reaction with formaldehyde, an increase can be seen in the intensity of the OH peak at 3443 cm^{-1} [Fig. 4(b)], which reduced in intensity as the resin was heated [Fig. 4(c)]. As it is heated, the solubility of the resin decreases, which implies that crosslinking is occurring. An increase in intensity at 2930 cm^{-1} is indicative of an increase in methylene content as a result of the reaction with formaldehyde.

Reaction with Water-Dispersed Epoxy Resin

Beckopox EP 384 W contains 51% (chloromethyl)oxirane, 4,4'-(1-methylethylidene) bisphenol copolymer, 7% methoxypropanol, 3% benzyl alcohol, 3% polyethylene glycol, diglycidyl bisphenol A polymer, and 36% water. The spectrum of Beck-

opox EP 384 W [Fig. 5(a)] was very similar to the diamine cured resin [Fig. 5(b)]; however, the peak representing the oxirane ring at 913 cm^{-1} decreases upon reaction with an amine and is representative of spectra of other cured bisphenol A epoxy resins.⁷

Mass Spectrometry

Figure 6 shows the results obtained by time-of-flight spectrometry of the 2 : 1 phenetidine : phenylenediamine product. An analysis of the data reveals the presence of two different phenetidine telechelics, whose structures are consistent with the ones shown in Figure 7. The first is that of the expected trimer (MW 376), and the other is that of a branched tetramer (MW 481). The fragmentation pattern is consistent with those arising from these two structures. For example, the peak at 104 AMU is ascribed to ionized phenylenediamine, and the one at 137 AMU is ascribed to fragmentation at the phenetidine–phenyldiamine bond.

Nuclear Magnetic Resonance

The nuclear magnetic resonance (NMR) of the 2 : 1 diamine (trimer) (Fig. 8) is consistent with a

mixture containing the structures of a trimer and a tetramer shown in Figure 7. The peak at 1.3 ppm is due to $-\text{CH}_3$, at 4.0 ppm due to $-\text{CH}_2-$, at 5.5 ppm and 6.0 ppm due to terminal amine groups, and at 8.5 ppm due to an imino hydrogen. So far, we have been unable to purify the components by gel permeation chromatography using silica gel (different mesh sizes) using different eluents, both polar and nonpolar. This may be attributed to possible degradation (oxidation) of the compound on the column, very high affinity of the diamines for the stationary phase, or other factors. In any event, it should be noted that both products will react with either formaldehyde or epoxy resins and will covalently bond to the cured product.

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