

Synthesis and Properties of New Liquid Crystals as Curing Agents for Epoxy Resins

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Abstract: A novel class liquid crystalline epoxy resins was synthesized by reacting the diglycidyl ether of bisphenol A (DGEBA) with three new liquid crystal diols, 4,4'-di-N-[(6-hydroxy hexoxy)-3-pyridyl methylidene]amino phenyl benzamide, 4,4'- di-N-[(6-hydroxy butoxy)-3-pyridyl methylidene]amino phenyl benzamide, and 4,4'- di-N-[(6-hydroxy etoxy)-3-pyridyl methylidene]amino phenyl benzamide, contain azomethine groups. The new liquid crystals were characterized by Fourier transformed infra-red (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy. Flexibility and adhesion properties were then investigated for the cured resins based on new azomethine mesogenic diols. The cured polymers were found to exhibit high flexibility and good adhesion properties compared to ordinary amine systems.

Keywords: Epoxy Resin, Liquid Crystal, DGEBA, Schiff Base, Azomethine Mesogenic Diol, Synthesis, Characterization, Mechanical Properties

1. Introduction

Epoxyes were widely use in industrial applications such as coatings, automotive primer, printed circuit boards, semiconductor encapsulants, adhesives, and composites. epoxy resins present the attractive characteristics of excellent mechanical strength and toughness; chemical, moisture, and corrosion resistance; good thermal, high adhesive, and superior electrical properties; no volatiles emission and low shrinkage upon cure; and excellent dimensional stability. In industrial, many commercial epoxyes contain aliphatic, cycloaliphatic, aromatic backbones wide used with range of molecular weights. Bisphenol A is one of the most used in the synthesis of epoxyes (>75% of resin sales volume), [1-2].

Several approaches were used in the past to control the crosslink density of an epoxy network. These include varying the epoxy resin curing agent functional group ratio, using a difunctional epoxy prepolymer with a different average chain length, and varying the molecular size of the difunctional curing agent, [3-5].

Liquid crystal thermosets based on this novel chemistry showed excellent combinations of thermal, mechanical, and

chemical properties, unachievable with traditional epoxyes, so many research groups have studied this epoxyes, [6-12].

Lately, many compound of liquid crystalline thermosets with different mesogenic units and reactive end functional groups were prepared by Schiff bases and using in industry as curing agents for epoxyes, [13-14].

Some of the epoxy resins produced showed mesomorphic states when the resins were fully cross-linked after hardening. The length of the mesogenic epoxy compound plays the main function in the appearance of a mesophase, [7], [15-18].

In this article, explores an efficient and economical process for preparing a new class of liquid crystals was described, where this class include Schiff bases. Moreover, we screen their activity as curing agents for synthesis the epoxy resins and using it in diverse applications. Also, we studied the effect of a different chain length methylene groups which prepared for the curing DGEBA and discussion the mechanical properties (flexibility and adhesion) for the cured resins.

2. Experimental

2.1. Materials

4,4'-diaminobenzanilide, ethoxyethane, Sodium carbonate, triethyl amine, butanol-1, DMF, 2-hydroxy-5-formylpyridine, DGEBA, 6-chloro hexanol-1, 4-chloro butanol-1, 2-chloro ethanol-1 were purchased from Sigma-Aldrich USA and used without further purification.

2.2. Preparation of 4,4'-di-N-[(6-Hydroxy Hexoxy)-3-Pyridyl Methylidene]Amino Phenyl Benzamide (I)

2.2.1. Synthesis of 4,4'-di-N-[(6-Hydroxy-3-Pyridyl Methylidene]Amino Phenyl Benzamide (I')

2-hydroxy-5-formylpyridine (4×10^{-3} mol, 0.4924 g) and 4,4'-diaminobenzanilide (2×10^{-3} mol, 0.4544 g) were dissolved in (4)ml of ethanol in a 50 ml round-bottomed flask. A catalytic amount of 4-toluenesulfoic acid in (1)ml ethanol was added dropwise to the flask and the mixture was stirred and refluxed for 6h. The resulting mixture was evaporated under reduced pressure to yield an off white solid, which was washed thoroughly with diethylether and dried under vacuum, (0.7 g) of crystal (m.p 136-137°C, yield: 80%) was obtained, Figure 1.

2.2.2. Synthesis 4,4'-di-N-[(6-Hydroxy Hexoxy)-3-Pyridyl Methylidene]Amino Phenyl Benzamide (I)

(9×10^{-4} mol, 0.0954 g) of anhydrous sodium carbonate and (8×10^{-4} mol, 0.1088 g) of 6-chloro hexanol-1 in (3)ml

DMF were put into a (50)ml three-necked round bottom flask equipped with a mechanical stirrer.

(4×10^{-4} mol, 0.175 g) of 4,4'-di-N-[6-hydroxy-3-pyridyl methylidene] amino phenyl benzamide (I'), respectively was put into (2)ml of DMF, dissolved and added to the reactions flask slowly dropwise using an additional funnel. The reaction mixture was heated for 12h at 130°C, and cooled. The cooled mixture was poured into (25)ml of cold water, then the solid product was filtered by using Buchner funnel.

The solid product was washed by water and dried at 70°C under vacuum for 24h. After drying, it was recrystallized in mixture of DMF and butanol-1 (1:1). The crystallized product was washed by ethyl ether and dried at 90°C under vacuum for an additional 24h. (0.1784g, m.p 101-102°C, yield: 70%, off white solid), Figure 1.

FT-IR (KBr, cm^{-1}): 3560 cm^{-1} (O-H), 3430 cm^{-1} (N-H), 2890 cm^{-1} and 2950 cm^{-1} (C-H aliphatic), 1660 cm^{-1} (C=O), 1620 cm^{-1} (C=N), 1270 cm^{-1} and 1180 cm^{-1} (C-O). δ_{H} (400 MHz, *d*-DMSO) δ : 9.33 (s, 1H), 9.24 (s, 2H), 8.26 (d, 2H, *J* = 4.0 Hz), 7.95 (s, 2H), 7.85 (d, 2H, *J* = 8.0 Hz), 7.53 (dd, 4 H, *J* = 4.0 Hz, *J* = 12.0 Hz), 7.43 (d, 2H, *J* = 4.0 Hz), 6.64 (d, 2H, *J* = 8.0 Hz), 4.34 (t, 4H, *J* = 8.0 Hz), 3.75 (s, 2H), 3.65 (t, 4H, *J* = 8.0 Hz). δ_{C} (100 MHz, *d*-DMSO) δ : 166.34, 164.12, 158.78, 147.85, 145.97, 139.24, 137.73, 136.69, 128.05, 127.82, 122.11, 121.15, 105.15, 104.30, 104.01, 75.42, 60.48, figure 5.

Elem. Anal. Calcd.(%) for $\text{C}_{37}\text{H}_{43}\text{N}_5\text{O}_5$: C, 69.68; H, 6.08; N, 10.98; Found: C, 69.55; H, 6.11; N, 10.95.

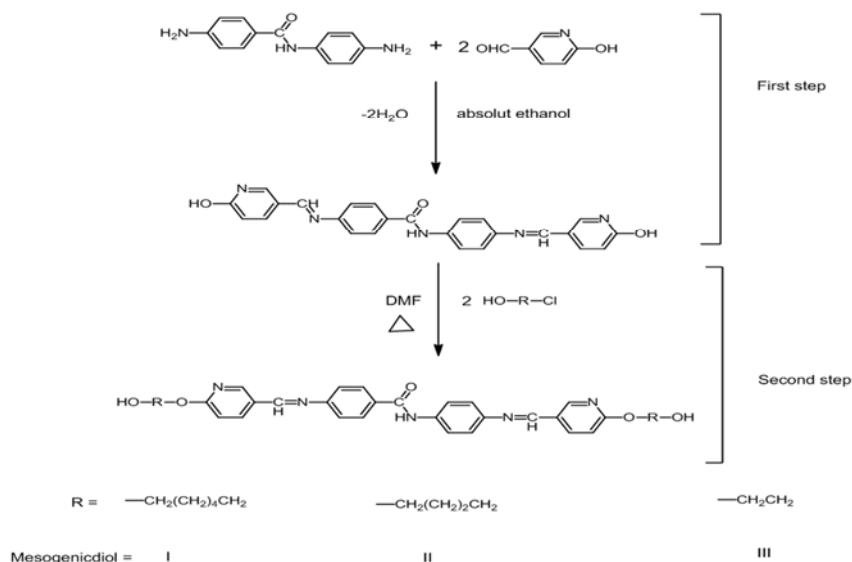


Figure 1. Synthesis of liquid crystals (I)(II)(III).

2.3. Preparation of 4,4'-di-N-[(6-Hydroxy Butoxy)-3-Pyridyl Methylidene]Amino Phenyl Benzamide (II)

(9×10^{-4} mol, 0.0954 g) of anhydrous sodium carbonate and (8×10^{-4} mol, 0.1011 g) of 4-chloro butanol-1 (86%) in (3) ml DMF were put into a (50)ml three-necked round bottom flask equipped with a mechanical stirrer.

(4×10^{-4} mol, 0.175 g) of 4,4'-di-N-[6-hydroxy-3-pyridyl methylidene]amino phenyl benzamide (I'), respectively was

put into (2)ml of DMF, dissolved and added to the reactions flask slowly dropwise using an additional funnel. The reaction mixture was heated for 12h at 130°C, and cooled. The cooled mixture was poured into (25)ml of cold water, then the solid product was filtered by using Buchner funnel.

The solid product was washed by water and dried at 70°C under vacuum for 24h. After drying, it was recrystallized in mixture of DMF and butanol-1 (1:1). The crystallized

product was washed by ethyl ether and dried at 90°C under vacuum for an additional 24h. (0.1278 g, m.p 109°C, yield: 55%, off white solid), Figure 1.

FT-IR (KBr, cm^{-1}): 3510 cm^{-1} (O-H), 3400 cm^{-1} (N-H), 2870 cm^{-1} and 2960 cm^{-1} (C-H aliphatic), 1660 cm^{-1} (C=O), 1625 cm^{-1} (C=N), 1280 cm^{-1} and 1190 cm^{-1} (C-O). δ_{H} (400 MHz, *d*- DMSO) δ : 9.14 (s, 1H), 9.13 (s, 2H), 8.55 (s, 2H), 8.25 (d, 2H, $J = 4.0$ Hz), 7.85 (d, 2H, $J = 8.0$ Hz), 7.57 (dd, 4H, $J = 4.0$ Hz, $J = 12.0$ Hz), 7.39 (d, 2H, $J = 4.0$ Hz), 6.85 (d, 2H, $J = 8.0$ Hz), 4.24 (t, 4H, $J = 8.0$ Hz), 3.65 (s, 2H), 3.45 (t, 4H, $J = 8.0$ Hz), 1.68-1.76 (m, 4H), 1.34-1.58 (m, 4H). δ_{C} (100 MHz, *d*- DMSO) δ : 166.69, 164.12, 159.78, 148.85, 147.22, 142.73, 138.82, 137.15, 131.73, 131.69, 126.32, 124.61, 123.15, 112.30, 112.22, 66.34, 60.73, 22.61, 21.12, figure 6.

Elem. Anal. Calcd.(%) for $\text{C}_{33}\text{H}_{35}\text{N}_5\text{O}_5$: C, 68.14; H, 6.07; N, 12.04; Found: C, 68.06; H, 6.01; N, 11.98.

2.4. Preparation of 4,4'-di-N-[(6-Hydroxy Etoxy)-3-Pyridyl Methylidene]Amino Phenyl Benzamide (III)

(9 X 10^{-4} mol, 0.0954 g) of anhydrous sodium carbonate and (8 X 10^{-4} mol, 0.0645 g) of 2-chloro ethanol-1 in (3)ml DMF were put into a (50)ml three-necked round bottom flask equipped with a mechanical stirrer.

(4 X 10^{-4} mol, 0.175 g) of 4,4'- di-N-[6-hydroxy-3-pyridyl methylidene] amino phenyl benzamide (I),

respectively was put into (2)ml of DMF, dissolved and added to the reactions flask slowly dropwise using an additional funnel. The reaction mixture was heated for 12h at 130°C, and cooled. The cooled mixture was poured into (25)ml of cold water, then the solid product was filtered by using Buchner funnel.

The solid product was washed by water and dried at 70°C under vacuum for 24h. After drying, it was recrystallized in mixture of DMF and butanol-1 (1:1). The crystallized product was washed by ethyl ether and dried at 90°C under vacuum for an additional 24h. (0.1365g, m.p 124°C, yield: 65%, off white solid), Figure 1.

FT-IR (KBr, cm^{-1}): 3540 cm^{-1} (O-H), 3480 cm^{-1} (N-H), 2870 cm^{-1} and 2950 cm^{-1} (C-H aliphatic), 1660 cm^{-1} (C=O), 1620 cm^{-1} (C=N), 1270 cm^{-1} and 1190 cm^{-1} (C-O). δ_{H} (400 MHz, *d*- DMSO) δ : 9.28 (s, 1H), 9.18 (s, 2H), 8.58 (s, 2H), 8.27 (d, 2H, $J = 8.0$ Hz), 7.87 (d, 2H, $J = 4.0$ Hz), 7.61 (dd, 4H, $J = 4.0$ Hz, $J = 12.0$ Hz), 7.40 (d, 2H, $J = 8.0$ Hz), 6.91 (d, 2H, $J = 8.0$ Hz), 4.26 (t, 4H, $J = 8.0$ Hz), 3.65 (s, 2H), 3.46 (t, 4H, $J = 8.0$ Hz), 1.78-1.86 (m, 4H), 1.33-1.42 (m, 12H). δ_{C} (100 MHz, *d*- DMSO) δ : 168.30, 166.30, 162.34, 154.85, 153.22, 147.11, 139.82, 137.15, 132.36, 131.96, 125.77, 123.44, 122.53, 112.63, 112.16, 66.60, 60.36, 28.32, 27.69, 22.53, 21.41, figure 7.

Elem. Anal. Calcd.(%) for $\text{C}_{29}\text{H}_{27}\text{N}_5\text{O}_5$: C, 66.27; H, 5.18; N, 13.33; Found: C, 66.21; H, 5.23; N, 13.24.

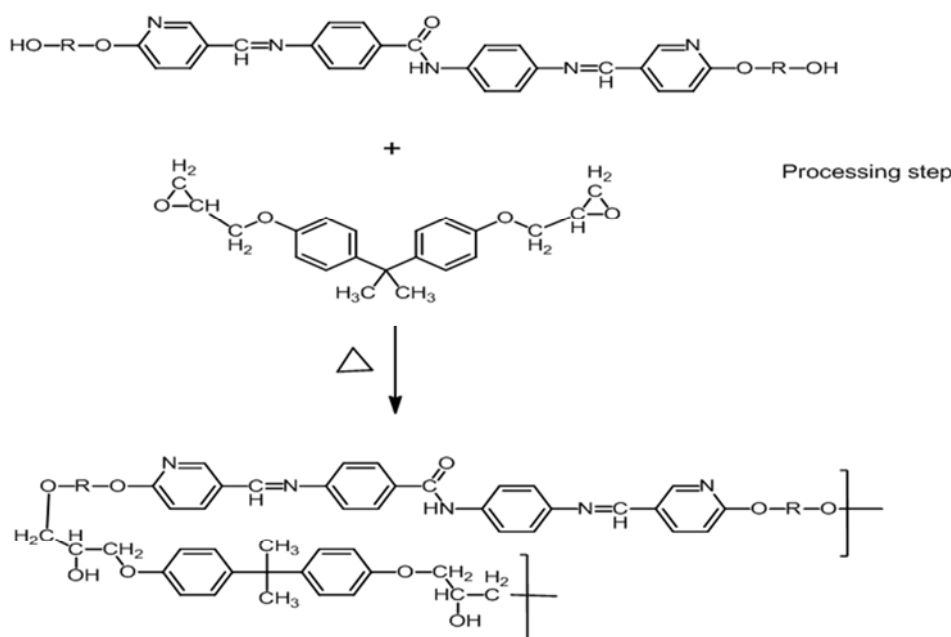


Figure 2. Cure reaction between DGEBA and liquid crystals (I)(II)(III).

2.5. Cure Reaction Between DGEBA and Liquid Crystals Diols

The cure reaction between epoxy resin DGEBA and liquid crystals was carried out with the mole ratio (1:1) of DGEBA to liquid crystal. To start the cure reaction, appropriate quantities of DGEBA and liquid crystal were mixed well in an aluminum panel (5X10cm), and (3%) triethylamine, with

respect to the weight of the liquid crystal, was then also added to the panel. The panel was placed in an air-circulated oven at 150°C for 1h. The cure resins were then used for mechanical studies, Figure 2.

2.6. Instrumentation

NMR spectra were recorded on a Bruker-Avance 400-MHz spectrometer. The residual solvent protons (^1H) or the solvent

carbon (^{13}C) were used as internal standards. CDCl_3 was used as the solvent and TMS as the internal reference. Infrared (IR) spectra were recorded on a Vertex 80/80v (FT-IR) spectrometer using samples in KBr pellets.

2.7. Mechanical Studies

2.7.1. Coating Flexibility Test

This test method (ASTM D4145-83 Reapproved 2002) describes a procedure for determining the flexibility and adhesion of organic coatings (paints) on metallic substrates that are deformed by bending when the sheet is fabricated

into building panels or other products. The metal substrate must be passing this test without fracturing and with no excessive grain development. Preprinted panels are bent 180 around progressively more thicknesses of metal or larger diameter dies, the end point being when failures no longer occur. The panels are examined at low magnification (5X10cm) after each bend for fracture of the coating (cracking) and for loss of adhesion pickoff, by means of a tape pull-off test, figure 3. This test is a means of evaluating the ability of a coating system to withstand the stresses of fabrication [19].

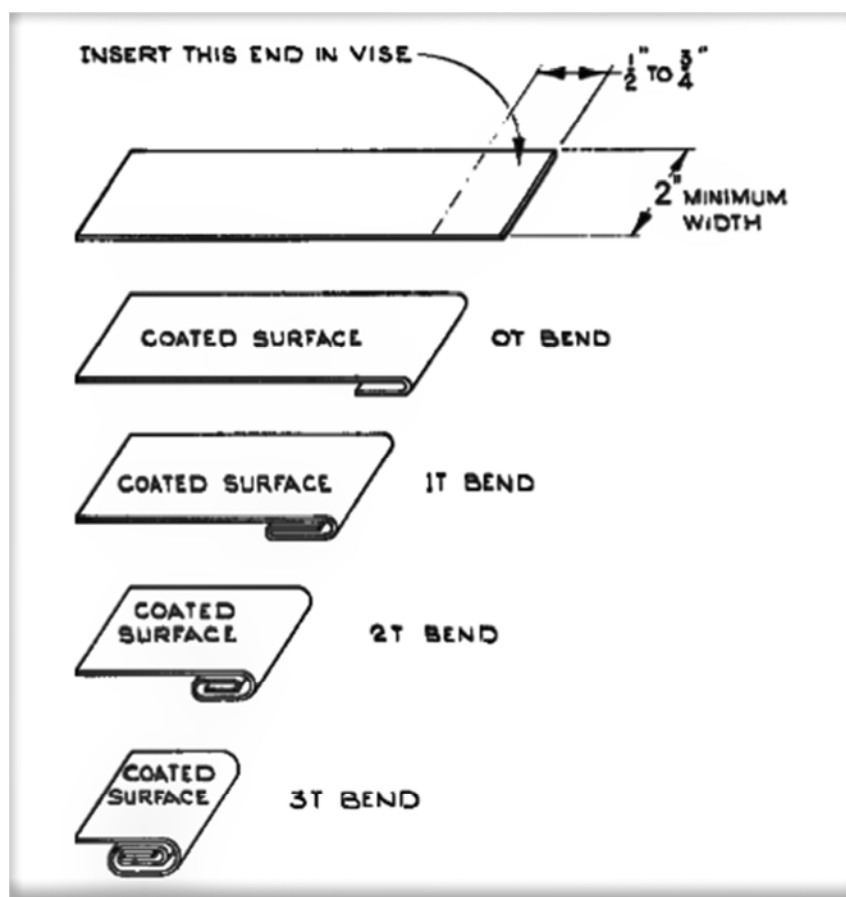


Figure 3. Coating Flexibility Test.

2.7.2. Coating Adhesion Test

These test method (ASTM D 3359-97-B) procedures for assessing the adhesion of coating films to metallic substrates by applying and removing pressure-sensitive tape over cuts made in the film. These test methods are used to establish whether the adhesion of coating to a substrate is at a

generally adequate level. Test Method-A lattice pattern with either six or eleven cuts in each direction is made in the film to the substrate, pressure-sensitive tape is applied over the lattice and then removed, figure 4. and adhesion is evaluated by comparison with descriptions and illustrations, [20].

Surface of cross-cut area from which flaking has occurred. (Example for 6 parallel cuts)	None						Greater than 65%
Classification	5	4	3	2	1	0	

5: none, 4: (< 5%), 3: (5-15%), 2: (15 to 35%), 1: (35-65%), 0: (>65%).

Figure 4. Coating Adhesion Test.

3. Results and Discussions

3.1. Synthesis and Characterization of Mesogenic Diols I, II, III

3.1.1. Spectra of 4,4'-di-N-[(6-Hydroxy Hexoxy)-3-Pyridyl Methylidene]Amino Phenyl Benzamide (I)

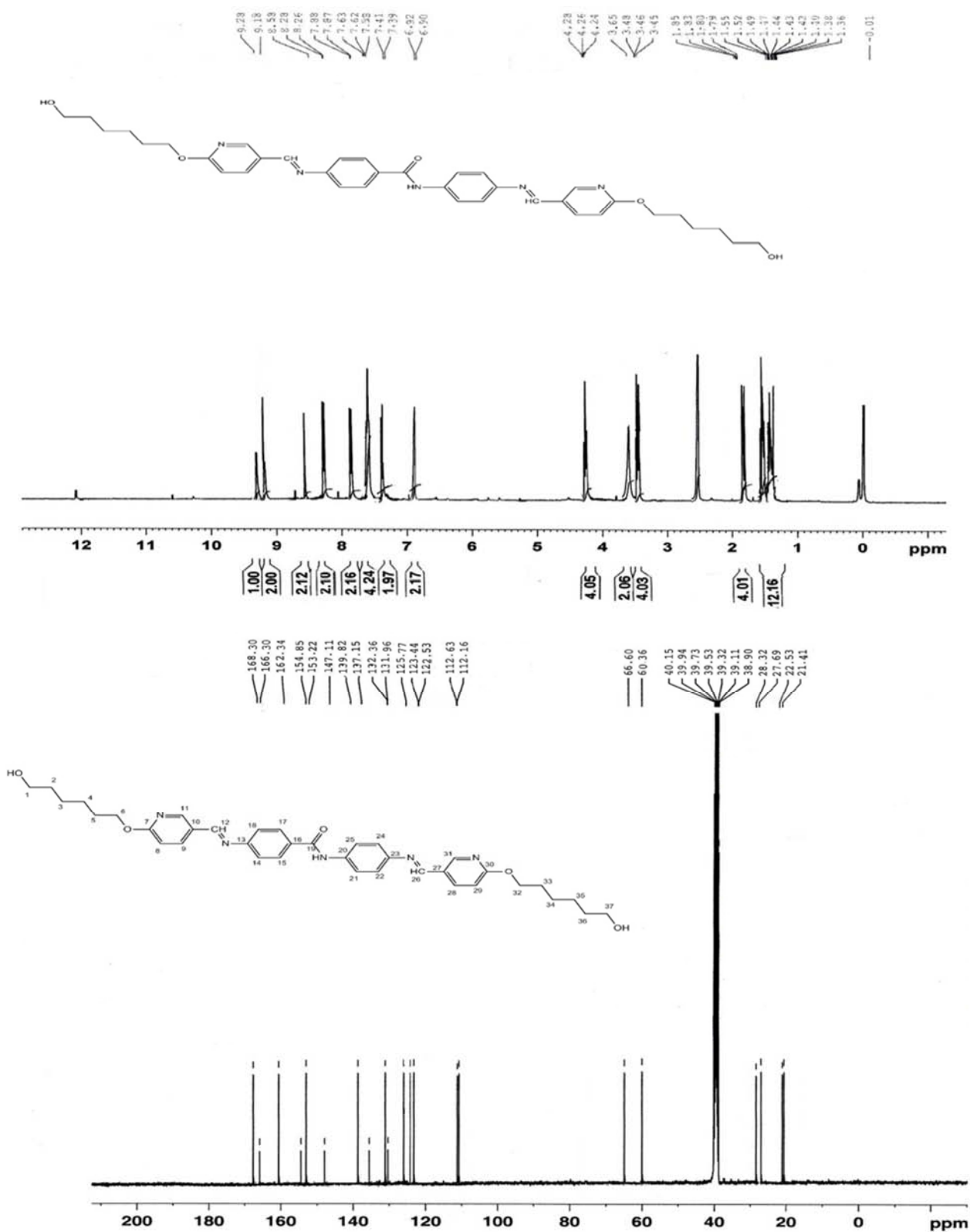


Figure 5. Spectra of (I).

3.1.2. Spectra of 4,4'-di-N- (6-Hydroxy Butoxy)-3-Pyridyl Methylidene]Amino Phenyl Benzamide (II)

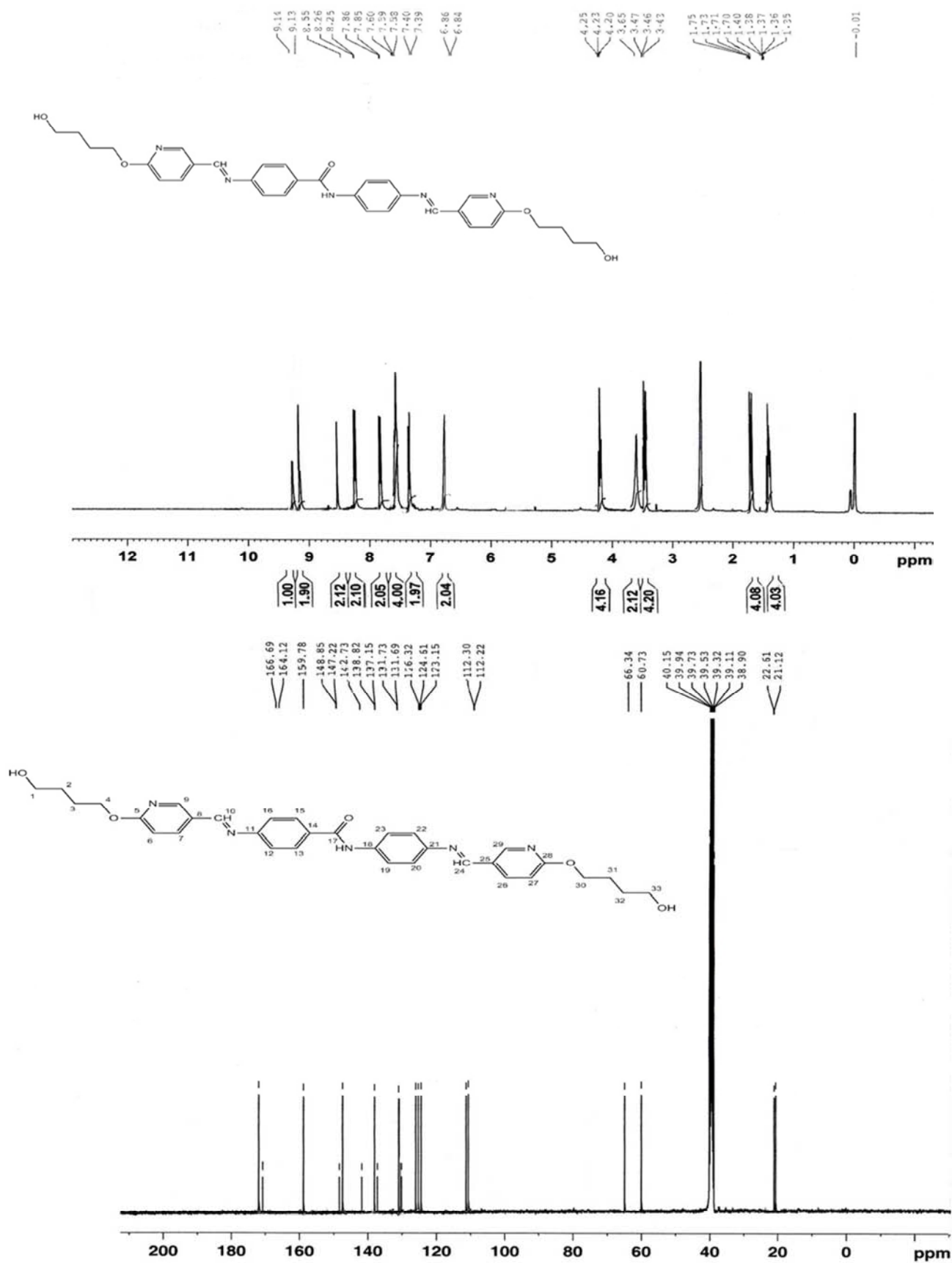


Figure 6. Spectra of (II).

3.1.3. Spectra for 4,4'-di-N-[(6-Hydroxy Etoxy)-3-Pyridyl Methylidene]Amino Phenyl Benzamide (III)

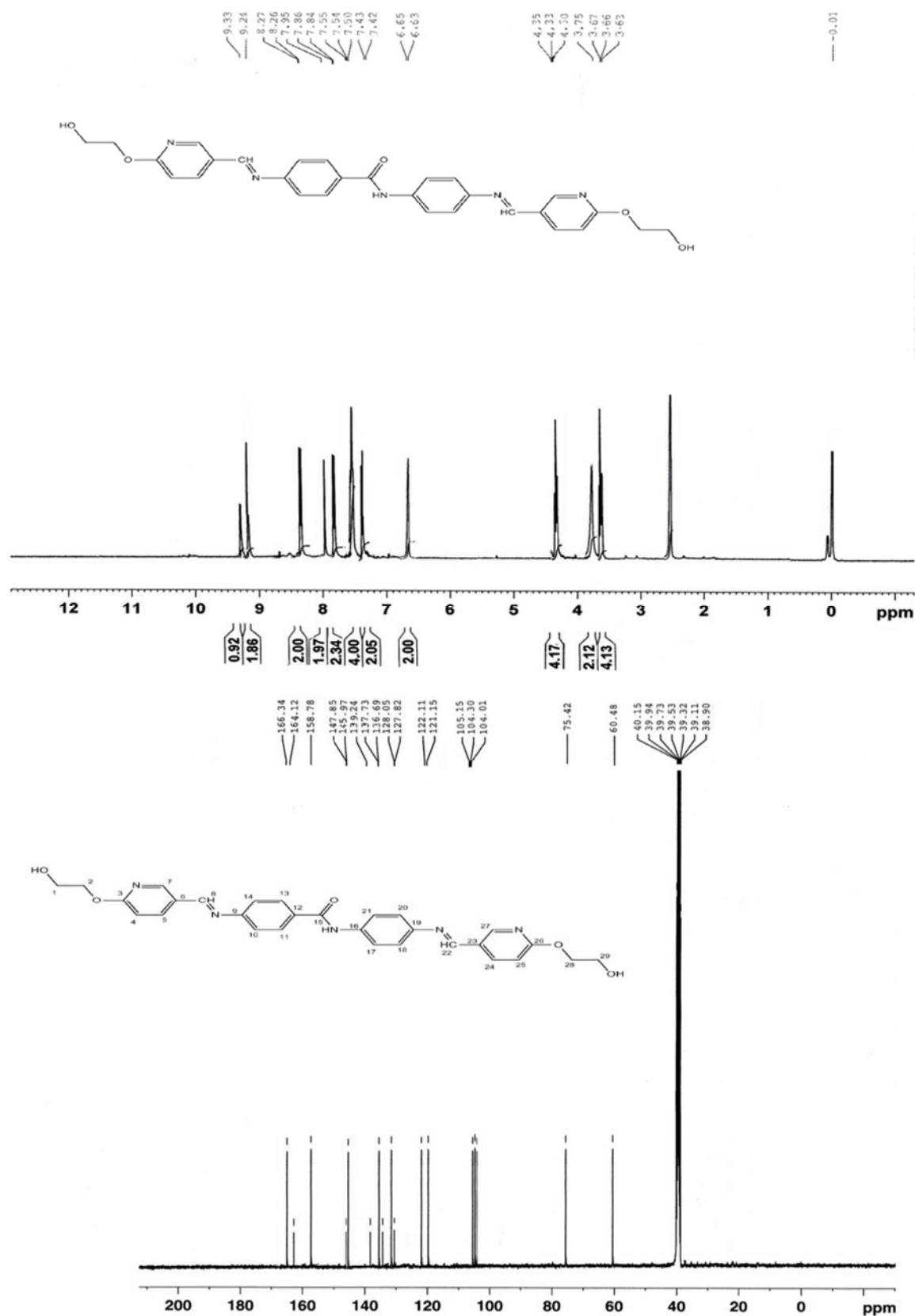


Figure 7. Spectra of (III).

3.1.4. IR Spectra for 4,4'-di-N-[(6-Hydroxy Hexoxy)-3-Pyridyl Methylidene]Amino Phenyl Benzamide (I)

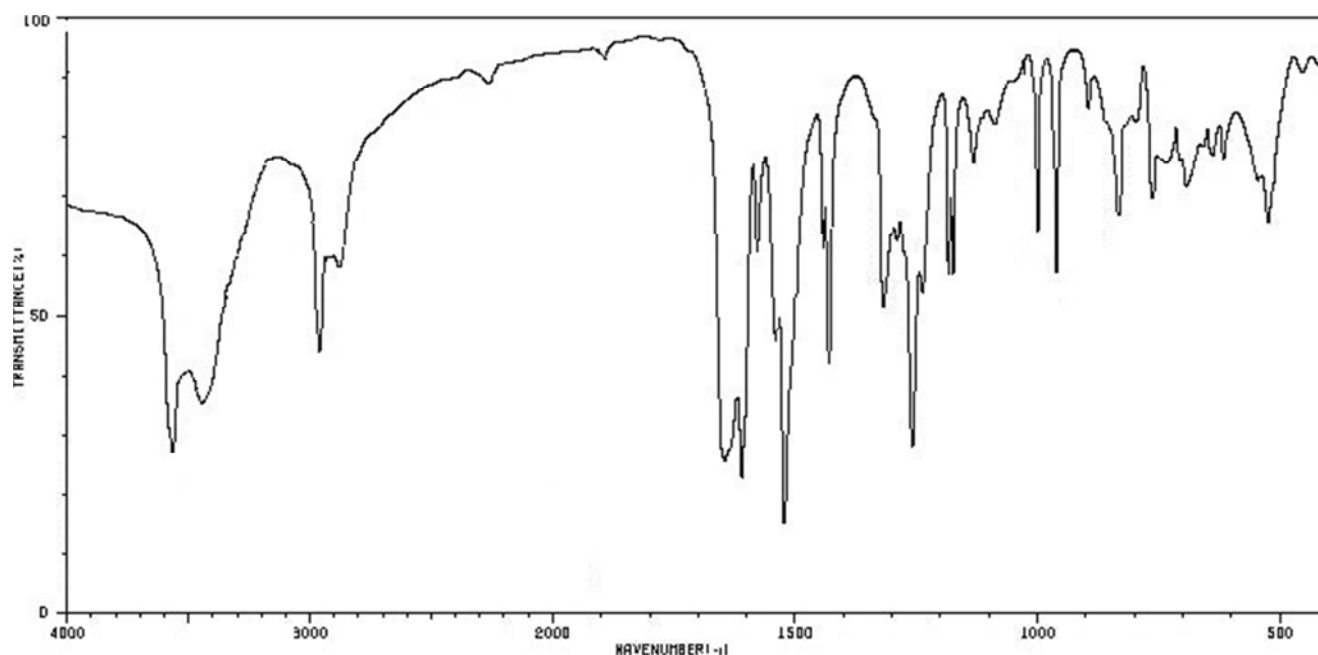


Figure 8. IR Spectra of (I).

The FT-IR spectra of liquid crystal (I) is given in figure 8, which shows the absorption band at 1620 cm^{-1} , indicating the presence of a ($-\text{CH}=\text{N}-$) group. The peaks at 1540 cm^{-1} and 1580 cm^{-1} were assigned to aromatic ring ($-\text{C}=\text{C}-$) stretching. In addition, the ($\text{C}=\text{O}$) was positioned at 1660 cm^{-1} , and the ($-\text{OH}$) stretching band at 3560 cm^{-1} . The absorption bands at 2890 cm^{-1} and 2950 cm^{-1} were assigned to aliphatic group ($\text{C}-\text{H}$). The absorption bands at 1020 cm^{-1} and 1270 cm^{-1} indicating the presence of a ($\text{C}-\text{O}$) group. The ^1H NMR spectra of azomethine liquid crystals I, II and III are shown in figure 5, figure 6 and figure 7, respectively. Figure 5 shows the presence of a peak at 9.18 ppm that confirmed the existence of the azomethine group ($-\text{CH}=\text{N}$). Two characteristic peaks centered at 3.65 and 4.26 ppm corresponded to ($-\text{OH}$) and ($-\text{CH}_2-\text{O}$), respectively, further confirming the formation of the desired azomethine liquid crystal.

3.2. Mechanical Properties

3.2.1. Coating Flexibility Test

The result revealed that the cured resin films exhibited high flexibility compared to amine curing systems. The cured resin with liquid crystals (III) Was cracked at (3T), but with liquid crystal (II) and liquid crystal (I) weren't cracked at (3T), this flexibility was attributed to the incorporation of chain length methylene groups in the liquid crystals (II) and (I).

3.2.2. Coating Adhesion Test

The cured resin DGEBA with liquid crystal diol (I), (II) and (III) showed high adhesion properties compared to ordinary amine systems, the result of all cured resin tests were (5).

4. Conclusions

New liquid crystals that can be used as curing agents for epoxy resin (DGEBA) were successfully Prepared and characterized by means of NMR and FT-IR spectra. The flexibility and adhesion properties of cured polymers were studied by test methods of ASTM D4145-83 and ASTM D3359-97-B. These cured resins were found to exhibit high flexibility, electrical properties, low shrinkage upon cure, dimensional stability and good adhesion properties. These products could use in wide applications: semiconductor encapsulants, printed circuit boards and aerospace composites.

In the future, we will prepare new types of liquid crystal by using the heterocyclic rings and studying their thermal, mechanical, and chemical properties.

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