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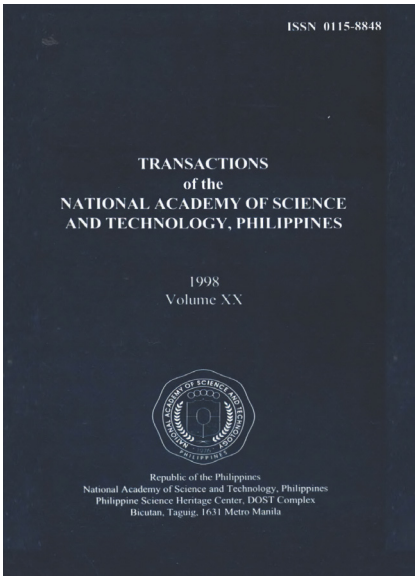

Synthesis of Low Molar Mass and Side-Chain Polymeric Liquid Crystals

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MATHEMATICAL, PHYSICAL, AND ENGINEERING SCIENCES DIVISION

SYNTHESIS OF LOW MOLAR MASS AND SIDE-CHAIN POLYMERIC LIQUID CRYSTALS

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ABSTRACT

Low molar mass liquid-crystalline cholesteryl esters and epoxy-based polymeric liquid crystals were synthesized in the laboratory. Fatty acids obtained from coconut oil were esterified with cholesterol, and the resulting esters were added to commercial nematic E7 to yield cholesteric low molar mass liquid crystals (LCs). These are presently being utilized in researches involving liquid crystals dispersions and thermochromic mixtures. Epoxy-based side-chain polymeric LCs were also synthesized for possible use as matrices in LC/polymer composites. Ring opening reaction of a commercially available epon resin, ethyleneglycol diglicidyl ether (EGDE) with the nematic 4-ω aminohexyloxy)-4'-cyanobiphenyl and the twisted nematic cholesteryl 4-aminobutyrate was carried out in bulk at 100°C for 10 hours. The side-chain copolymers obtained were found to be mesomorphic as observed under the polarizing micoscope. No trend was observed in the transition temperatures of these polymeric systems based on the differential scanning calorimetric (DSC) study. A liquid-crystalline epoxy prepolymer exhibiting monotropic mesomorphism was also prepared by functionalization of the dihydroxyl terminated groups of 4,4'-dihydroxybiphenol with the glycidyl groups of epichlorohydrin. The effect on its mesomorphic properties with the addition of side-chain mesogenic pendant group, 4-(ω-aminohexyloxy)-4'-cyanobiphenyl and varying concentrations of a diamine crosslinker were compared. FTIR and DSC were used to monitor the isothermal cure of the thermosets at different temperatures. Liquid crystallinity of the thermosets were sustained for a 3 wt % crosslinker whereas a highly crosslinked network resulted in the loss in mesomorphic properties.

Key words: Liquid crystals, cholesteric, thermochromic, side-chain liquid crystalline polymers, nematic, epoxy thermosets, curing

INTRODUCTION

Liquid crystals (LCs) are organic materials considered as partially ordered systems between the highly ordered solid and the isotropic liquid. LCs are generally rod-like (calamitic) and hence are anisotropic in form. They may be of low molecular mass or polymeric and may exist in different forms or mesophases. They may exist as nematic, cholesteric (or twisted nematic), or smectic. Molecules (of low molar mass LCs) or macromolecules (of liquid crystal polymers in the nematic phase maintain a parallel or nearly parallel arrangement to each other. The electro-optic properties of the nematic liquid crystal phase play a significant role in various display applications. The cholesteric phase is usually associated with the beautiful colorplay exhibited by thermochronic devices. The cholesterics have a nematic packing in layers with a superimposed twist resulting in a helical structure that is temperature sensitive. Selective reflection properties of short pitch length cholesteric liquid crystals find applications in thermometry, thermal mapping, radiation sensing, decorative and novelty products.[1] Both the low molar mass and the liquid crystal polymers (LCPs) share the above properties but the polymers being more viscous are slower in electro-optic response than the low molar mass LCs. However, LCPs which are characterized by the macroscopic orientation of macromolecules have improved mechanical properties and as such are attractive for use as high tensile stength fibers, extrudates, and reinforced resins. One form of LCPs, the side-chain LCPs, are also potential materials for optical data storage, optical elements and non-linear optics.[2]

The objective of this paper is to present the basic synthetic routes being undertaken to prepare cholesteryl-based low molar mass liquid crystals which may be used in the fabrication of thermo-electro-optic devices and epoxy-based liquid crystal polymers which may have potential use as matrix in special types of display devices and possibly as compatibilizer in polymer blends.

EXPERIMENTAL

3.1 Materials

Ethyleneglycol diglycidyl ether (EGDE), 1,6-dibromohexane, 5% palladium on activated carbon, tetrabutyl ammonium bromide (TBAB), epichlorohydrin, 4,4' – dihydroxybiphenol, and 1,10-diaminodecane were obtained from Aldrich and were used as received. 4-Bromobutyric acid, N,N-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) were obtained from Sigma and were used as received. Cholesterol from FLUKA was used as received. 4-Hydroxy-4'-cyanobiphenyl (Tokyo Kassei) was generously donated by Professor Sato of Sophia University of Tokyo, Japan.

3.2 Techniques

FTIR spectra of low molar mass intermediates and products, monomers and polymers were obtained using either a Nicolet Series II Magna-IR System 750 spectrometer or a Bio-rad 40 FTS FTIR. Phase transition temperatures of samples were determined using the Shimadzu DSC-50 equipped with a thermal analyzer TA-50WSI. Textures were observed using the Olympus Polarizing Microscope model BH-2 equipped with 100W halogen bulb, crossed polarizers, and camera attachment. Photographs of samples were taken at 200X magnification.

3.3 Synthesis of Low Molar Mass Liquid Crystals

Synthesis of Cholesteryl Esters (CE) is outlined in Figure 1. Extraction of fatty acids from commercial coconut oil (cooking oil) was done via the cold saponification process.[3] The mixture of fatty acids so obtained was reacted with cholesterol using N, N'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) according to standard procedure. The crude product was passed through a silica gel column using hexane:dichloromethane (1:4) as eluent. Fractions with similar R_f values were pooled together and characterized.

3.4 Synthesis of Epoxy-based Side-Chain Polymers with Cholesteryl and Cyanobiphenyl Pendant Groups

The epoxy homopolymers and copolymers were prepared by a ring-opening reaction shown in Figure 2. Equivalent amounts of mixtures of amines ***1*** and ***2*** and EGDE were charged into a polymerization vessel purged with dry N_2. The

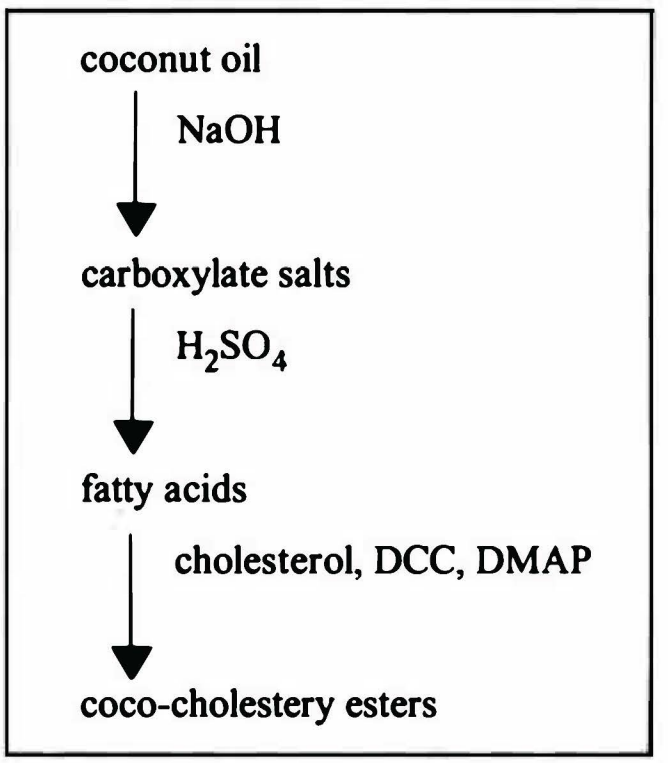

Figure 1. Preparation of cholesteryl esters from coconut oil

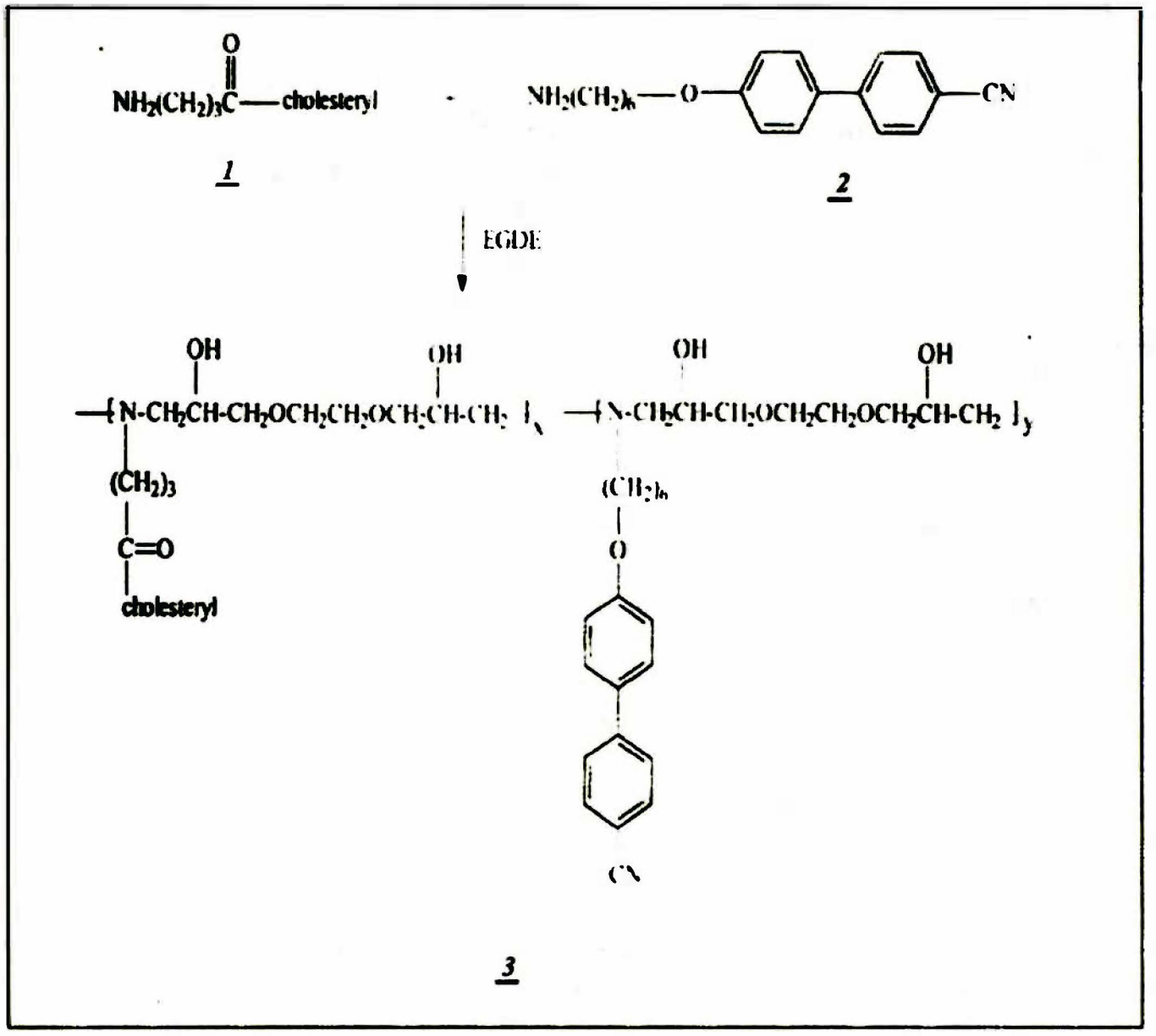

Figure 2. Synthesis of copolymers bearing cholesteryl and cyanobiphenyl groups

reaction vessel was sealed and heated in an oil bath at 100°C for 16 hours. The obtained polymers were purified by multiple precipitation from a THF solution into cold petroleum ether. The polymers were dried in vacuum dessicator for 48 hours.

3.5 Synthesis of Liquid Crystalline Epoxy Resin

Liquid crystalline epoxy prepolymer *6* (4,4'-diglycidyloxydiphenyl resin, DIF) was synthesized according to the scheme outlined in Figure 3. A 500-mL 3-neck flask equipped with a reflux condenser, a thermometer, and a powerful stirrer was charged with epichlorohydrin *5* (1.34 mol), 4,4'-dihydroxyphenol *4* (0.13 mol), water, and a portion of NaOH (0.25 mol), and then stirred. The reaction mixture was heated to a pot temperature of 80°C. The temperature of the heated mixture rose to 100°C. When the temperature dropped to 80°C, another portion of NaOH was added. Addition was repeated until all of the NaOH pellets were used up. The mixture was cooled to 70°C. Enough benzene was added to

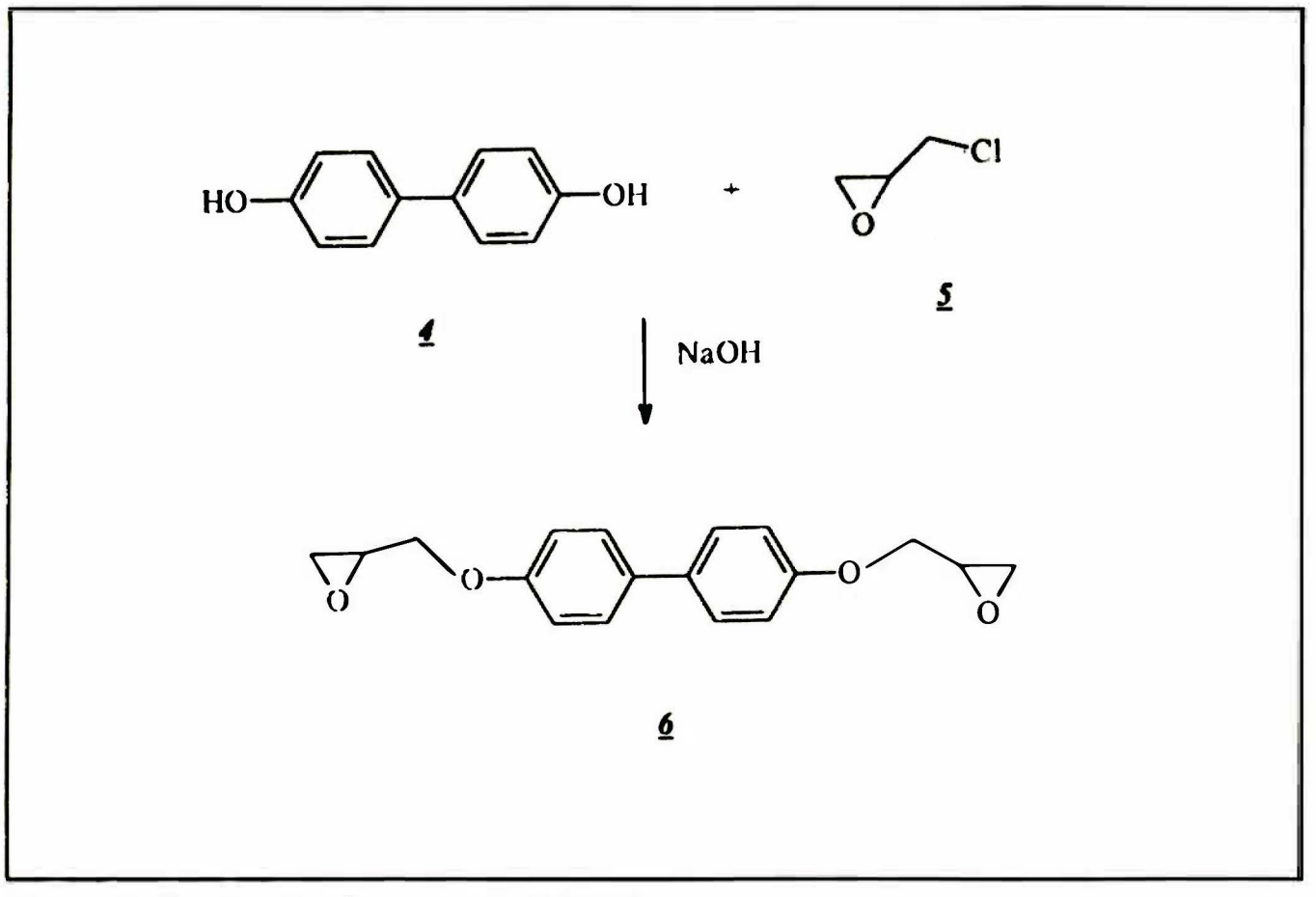

Figure 3. Synthesis of epon resin DIF (6)

precipitate the salt from the reaction. The reaction mixture was filtered, the salt washed with benzene and this washing added to the filtrate. The filtrate was evaporated in vacuo. The product was recrystallized in cold petroleum ether (ten times the volume).

3.6 Synthesis of Epoxy Coplymers and Thermosets

The epoxy thermosets were prepared by a ring-opening reaction shown in Figure 4. The crosslinker diaminodecane 7, the epoxy resin 6, and the mesogenic amine 2 were charged into a polymerization vessel purged with dry N_2 gas. The reaction vessel was sealed and heated in an oil bath at 100°C for 10 hours. The obtained thermoset was washed with THF and vacuum-dried for 48 hours.

4. RESULTS AND DISCUSSION

4.1 Mesomorphic Properties of Cholesteryl Esters

The coco-cholesteryl esters were found to be liquid crystalline, with the following phase transition temperatures: a solid to smectic phase transition at 44.5°C, a smectic to cholesteric phase change at 66.5°C, and isotropization at 78.2°C. The presence of cholesteric and smectic mesophases were confirmed using the polarizing microscope.

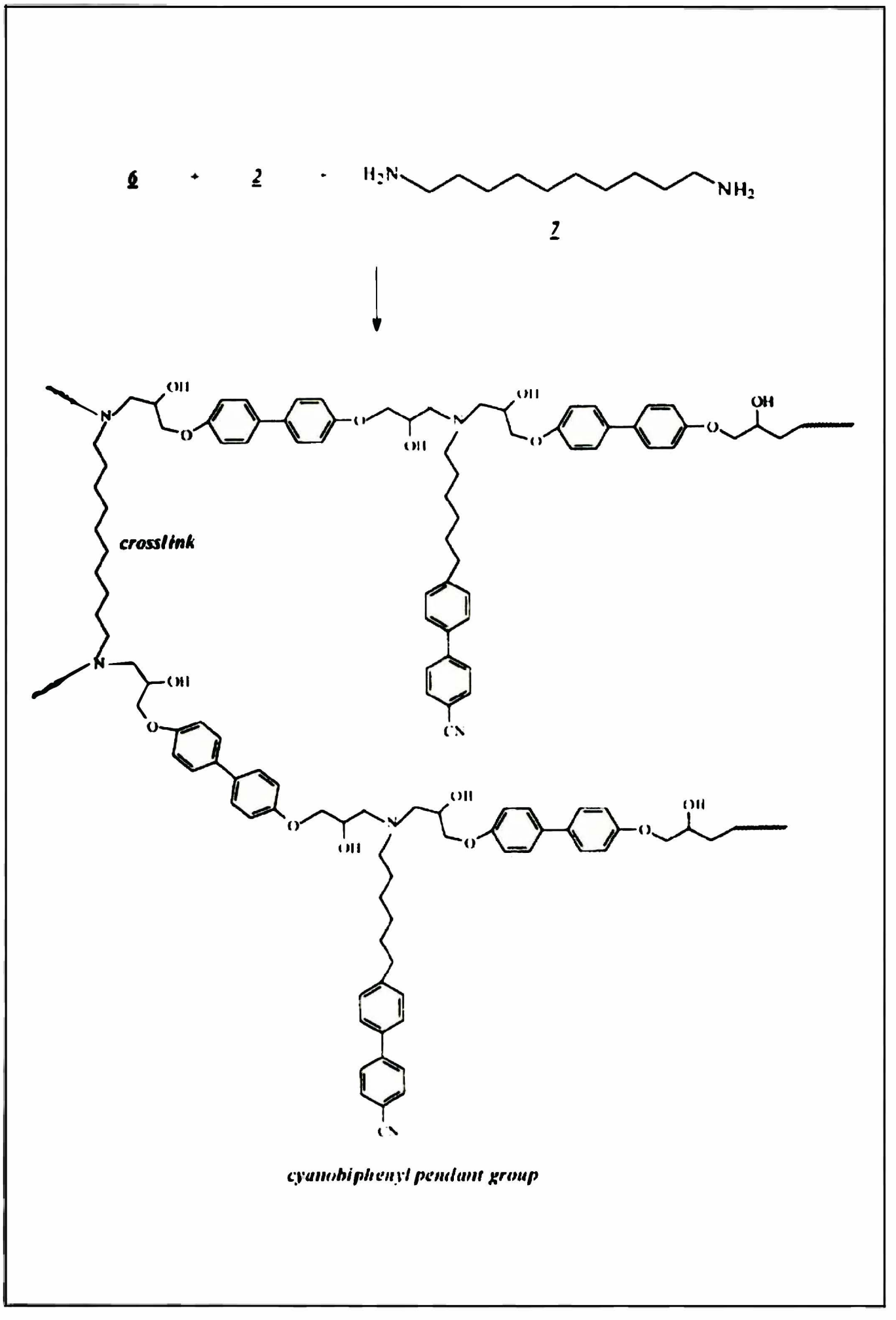

Figure 4. Synthesis of DIF-based thermoset

The effects of the prepared coco-cholesteryl esters on nematic E7 were examined. DSC studies reveal an increase in theisotropization temperature of the E7 mixture upon addition of coco-cholesteryl esters. E7 mixtures with low percentage weight of cholesteryl esters (not more than 30%) are turbid and exhibit the planar texture at room temperature. Higher concentrations yielded waxy formulations at room temperature, and were observed to change colors upon cooling from isotropic state (Table 1).

4.2 Mesomorphic Properties of Polymers Bearing the Cholesteryl and the Cyanobiphenyl Moieties

The cholesteryl-containing amine ***1*** which exhibits the cholesteric phase and the nematic cyanobiphenyl-containing amine ***2***, when attached as pendant groups to an epoxy backbone yield random side-chain liquid-crystalline epoxy polymers, some of which are cholesteric. The transition temperatures of select polymeric systems are shown in Table 2. The listed transition temperatures showed no significant trend. This may be attributed to the unpredictable extent of the destabilizing effect on the mesophase due to the intermolecular/intramolecular hydrogen-bonding of the OH groups in the polymer backbone which tends to disrupt the mesomorphic packing of the side groups.[4]

Since the nature of the polycondensation reaction does not provide a good control of molecular weights, completely random copolymers are expected from the comonomer pair of ***1*** and ***2***. It is known that when two monomers copolymerize, the tendency of each monomer to enter the chain can differ markedly.[5] Although the kinetic schemes for polycondensation reaction of epon resins and amines are known[6], no published report was found on the curing kinetics for side-chain liquid-crystalline epoxy polymers. Hence, reactivity ratio for the mesogenic

Table 1. Properties of some mixtures of cholesteryl esters and E7

Weight ratio of cholesteryl esters and E7 (esters: E7)	Clearing temperature (°C)	Physical state at room temperature	Colors observed after heating and as the temperature decreases
5:95	58.30	turbid	no color
30:70	60.22	turbid	no color
50:50	62.09	waxy	blue→green→ yellow→orange→
70:30	67.15	waxy	violet→yellow→ orange
90:10	69.77	waxy	drastic color change

Table 2. Phase transition temperatures (mesogen to isotropic phase change) of the copolymers *3*

%-mol *1* in comonomer feed	%-mol *2* in comonomer feed	Isotropization temperature, °C
30	70	34.67
40	60	35.04
50	50	67.62
90	10	37.57

amines *1* and *2* may not be found, and predicting the type of copolymers that may be formed becomes complicated. The randomness of incorporation of these amines would also explain the lack of any significant trend in the observed transition temperatures for the copolymers.

4.3 Properties of DIF-based Polymers

Polymers (crosslinked and uncrosslinked) obtained from *6* and *2* exhibited the characteristic FTIR bands as shown in Figure 5. The spectra for the polymers showed the disappearance of the epoxide band absorption at 912 cm^{-1} and the appearance of the –CN absorption band at 2222 cm^{-1}. A broad peak near 3500 cm^{-1} indicated the presence of the –OH groups. A more intense absorption at this region was observed for the thermoset.

FTIR was used to monitor the structural changes that accompany the crosslinking reaction of the mixture. A sample of the mixture containing *6*, *2*, and *7* was dissolved in chloroform and was casted directly on the KBr plate. The solvent was allowed to dry and the sample was covered with another KBr plate. This was scanned prior to heating. The spectrum obtained was subtracted from each of the resulting spectra taken after the curing process (done by heating the cell for 15-30 minutes at different temperatures). Figure 6 shows the subtraction results of the spectra for the polymer cured at different temperatures. Epoxy ring absorption at 912 cm^{-1} decreases with an increase in the curing temperature. At a cure temperature starting at 150°C, a very intense peal at 1349 cm^{-1} started to appear. This corresponds to the C-N stretch exhibited by secondary and tertiary amine. Also, a decrease in the absorption band due to the –CN at 2225 cm^{-1} was observed at higher temperature. This might indicate that at high temperatures, the cyano group has participated in the crosslinking process.

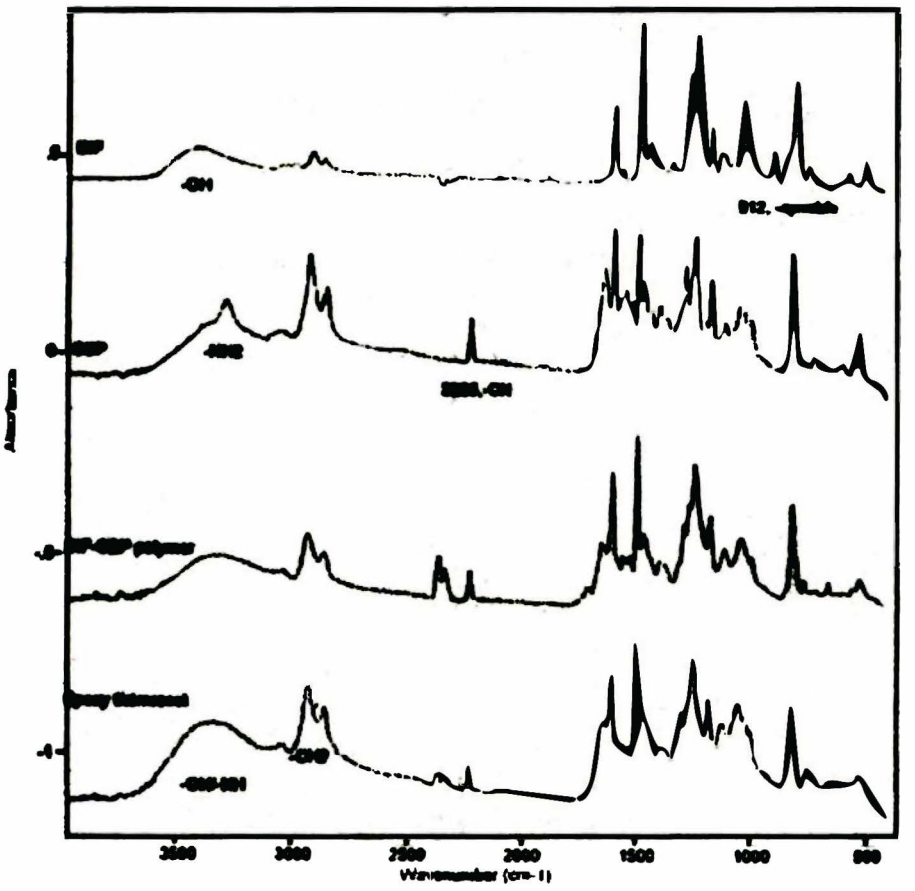

Figure 5. FTIR spectra of DIF (6), CBP (2), DIF-CBP (polymer from 6 and 2), and thermoset (from 6, 2, and 7)

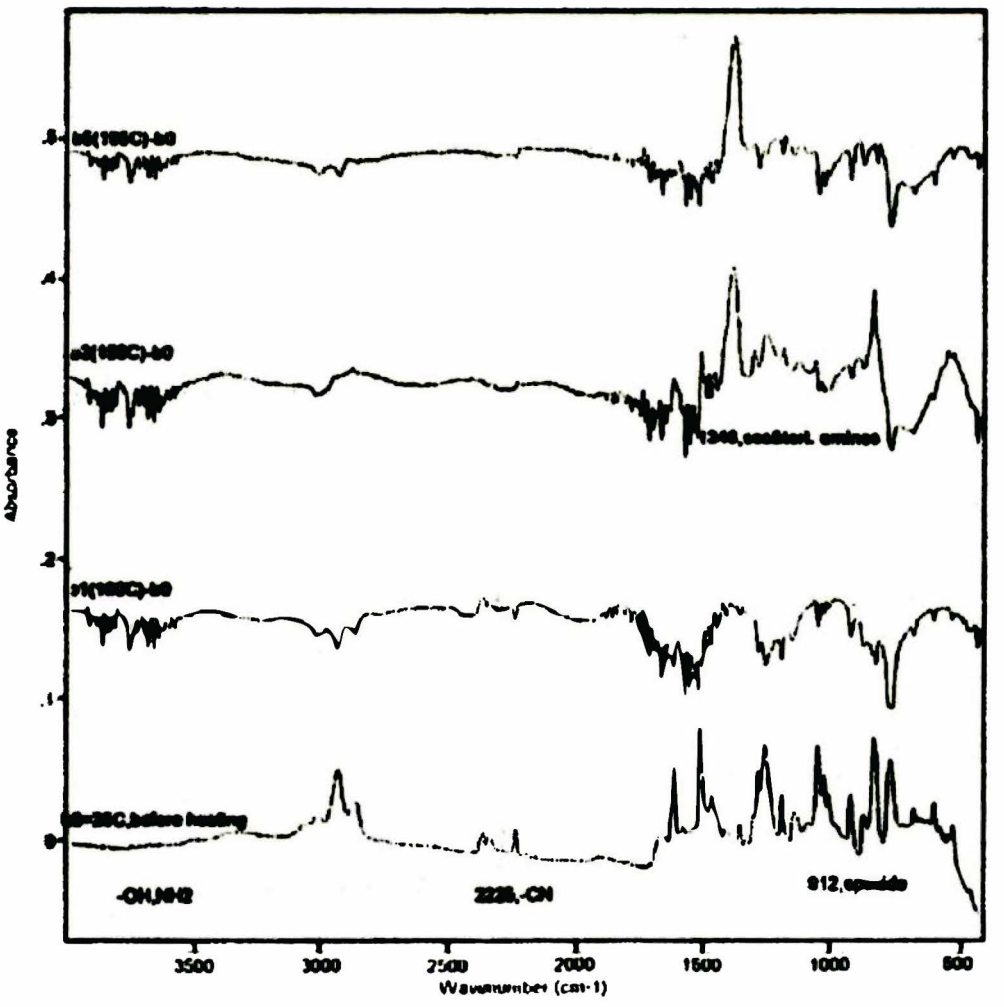

Figure 6. Subtraction spectra of cured DIF-based polymer

5. ACKNOWLEDGMENT

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