Twin Liquid Crystals and Segmented Thermotropic Polyesters Containing Azobenzene—Effect of Spacer Length on LC Properties

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ABSTRACT: We report systematic studies on a homologous series of twin liquid crystalline (LC) molecules based on phenyl and naphthyl azobenzene (**PnP** and **NpnNp**) as well as segmented copolyesters based on them. The twin series had the structure azobenzene–oligooxyethylene–azobenzene, where the ethyleneoxy length was varied from 2 to 6 units. The LC properties of the twin series depended on the chemical structure of the azo-chromophore and also the length of the central oligooxyethylene segment. The **PnP** series exhibited smectic LC properties for n > three oligooxyethylene units. Conversely, **NpnNp** series exhibited spherulitic phases only for the shortest member –**Np2Np**. One non-LC short spacer twin (**P2P**) and one LC long spacer twin (**P6P**) were incorporated as part of a main chain polyester com-

INTRODUCTION Azobenzene as a chromophore has been studied widely for its most important property of photoisomerization due to which it finds application in a variety of areas like optical data storage, molecular switches, display devices, nonlinear optical devices, photomechanical systems, and so forth.¹⁻⁶ Liquid crystalline (LC) azobenzenes (side chain or main chain) have generated lot of interest because of their large photoinduced anisotropy and photochemical phase transitions.⁷⁻⁹ In general, main chain polymers are mostly condensation polymers which can be synthesized by melt condensation or by the solution route. Solution polymerization has been the method of choice for most of the reported main chain azobenzene polymers mainly due to its low degradation temperatures which precluded a melt condensation route.¹⁰⁻¹⁶ However, the molecular weights reported using the solution polymerization are generally very low corresponding to less than 10 unit incorporation on an average.^{13-14,17} The melt condensation route has the advantage that it is devoid of solvent and also helps to build the molecular weight. However, it is only applicable to monomers having low melting temperatures (<150 °C).

In this article, we report our design of twin azobenzene systems which could directly be used as AA type monomer in a posed of fully aliphatic segments of sebacate and di or tetraethylene glycol (DEG/TEG) units by melt polycondensation. Non-LC **P2P** formed LC polymers even at low (5 mol %) incorporation in DEG-based copolymers, whereas the LC-**P6P** could do so only at 30 mol % incorporation. The LC properties of the twin molecules as well as copolymers were studied using differential scanning calorimetry, polarized light microscopy (PLM) along with variable temperature wide angle X-ray diffraction. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 2770–2785, 2012

KEYWORDS: azobenzene; azo polymers; main chain copolyester; liquid crystalline polymers (LCP); melt polycondensation; polycondensation; twin liquid crystal

melt polycondensation route. These twin azobenzene units were designed having the structure azobenzene-spacer-azobenzene, where the spacer was oligooxyethylene of varying length and two types of azobenzene chromophores—one based on simple phenol (**PnP**) and the other on naphthol (**NpnNp**) were used. The terminal azobenzene moieties were functionalized with -C(0)OMe units so that transesterification could be done with diols to form polyesters.

Twin molecules having the structure mesogen-spacer-mesogen or spacer-mesogen-spacer have long been considered as ideal representatives for "segmented main chain liquid crystal polymers" [-(flexible segment-rigid cores)_{*n*}-].^{18–20} Although started out as model systems to understand the behavior of main chain liquid crystalline polymers, it was soon evident that these twin liquid crystals were interesting systems on their own. A vast majority of the studies comparing homologous twin systems and the related main chain polymers dealt with polymethylene chains as the flexible units. The reason for this being the interesting "odd–even" oscillation observed in the isotropization temperatures and entropies as a function of the even or odd parity of the number of atoms in the methylene spacer length.^{18,21} Conversely, the poly(oxyethylene) units preferred a "gauche" conformation and the twins with

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poly(oxyethylene) central spacer generally did not show oddeven oscillation of the isotropic-LC transition entropy.^{22,23} In the design of our azobenzene twin molecules, the choice of oligooxyethylene as the central spacer was very important, as it served two purposes, first, it reduced the melting transition of the resulting twin molecules so that melt polycondensation route could be adopted, and second, it improved their solubility considerably. Another important aspect was that the polar oligooxyethylene spacer units are usually incompatible with the rigid rod-like azobenzene mesogen resulting in segregation into separate domains leading to mesophase formation. Not many reports are available for azo-based twin systems, where the central spacer segment is based on oligooxyethylene $-(CH_2CH_2O)_n$.^{24,25}

Copolymerization is a versatile means to fine-tune the mesophase stability and sometimes the nature of the mesophase as well. Segmented chain copolymers can be synthesized starting from two premesogenic comonomers or one mesogenic and one nonmesogenic monomer. The twin azobenzene molecules were incorporated in varying mole ratios in a main chain polyester based on dimethyl sebacate (DMS) and DEG/TEG. This choice of the polyester scaffold for introducing the azobenzene moieties were also interesting as DEG and sebacate formed a semicrystalline polyester, whereas TEG and sebacate resulted in a completely amorphous polymer. The questions that we addressed in this systematic study were the following (1) the effect of spacer length on the liquid crystalline properties of the two twin series, (2) the effect of the chromophore - phenylazo versus naphthylazo on the liquid crystalline characteristics of twin molecules having the same spacer length, and (3) the effect of copolymerization of mesogenic and nonmesogenic twin molecules with nonmesogenic comonomers. The mesophase behavior of the twin molecules and copolyesters were investigated by differential scanning calorimetry (DSC), polarizing light microscopy (PLM) in combination variable temperature wide angle X-ray diffraction studies (VT-WXRD).

EXPERIMENTAL

Materials

Diethylene glycol (DEG), tri, tetraethylene glycol (TEG), hexaethylene glycol, DMS, titaniumtetrabutoxide (Ti(Obu)₄), ptoulene sulfonyl chloride, and α -naphthol were purchased from Aldrich Company and were used as such. P-amino benzoic acid, phenol, sodium nitrite, potassium carbonate, and potassium iodide were purchased from Merck Chemicals. Dimethyl formamide (DMF), tetrahydrofuran (THF), and methanol were purchased locally and were purified using standard procedures.

Measurements

¹H and ¹³C NMR spectra were recorded on a Bruker-AVENS 200 MHz spectrometer. Chemical shifts are reported in ppm at 25 °C using CDCl₃ or CDCl₃/TFA as solvent containing small amount of tetramethylsilane (TMS) as internal standard. The purity of the compounds was determined by elemental analysis as well as high resolution mass spectrometry (HRMS)/matrix-assisted laser desorption/Ionization-time of

flight (MALDI-TOF) in combination with size-exclusion chromatography (SEC). Elemental analysis was done by Thermofinnigan flash EA 1112 series CHNS analyzer. The HRMS mass spectral analysis was done using a Autoconcept mass spectrometry instruments (MSI) UK in EI mode. The MALDI-TOF analysis was done on Voyager-De-STR MALDI-TOF (Applied Biosystems, Framingham, MA) equipped with 337-nm pulsed nitrogen laser used for desorption and ionization. One micromolar solution of sample was premixed with 2,5 dihydroxy benzoic acid matrix in CHCl₃ and mixed well before spotting on 96-well stainless steel MALDI plate by dried droplet method for MALDI analysis. For small molecules, SEC was performed using polystyrene standards for the calibration in CHCl₃ as eluent. The flow rate of CHCl₃ was maintained as 1 μ L/min throughout the experiments and the sample solutions at concentrations 3-4 mg/mL were filtered and injected for recording the chromatograms at 30 °C. The molecular weights of the polymers were determined by gel permeation chromatography (GPC), which was performed using a Viscotek VE 1122 pump, Viscotek VE 3580 RI detector and Viscotek VE 3210 UV/vis detector in THF using polystyrene as standards. Infrared spectra were recorded using Bruker FT-IR (ATR mode) spectrophotometer in the range of 4000-600 cm⁻¹. UV-Vis spectra were recorded using a Perkin Elmer Lambda-35 UV-Vis spectrometer. The thermal stability of all the model compounds and azo copolyesters were analyzed using Perkin-Elmer: STA 6000 thermogravimetric analyzer (TGA) under nitrogen atmosphere from 40 to 800 °C at 10 °C/min. DSC was performed using a TA Q10 model. About 2-3 mg of the samples had taken in aluminium pan, well-sealed and scanned at 10 °C/min. The instrument was calibrated with indium standards before measurements. The phase behaviours of the molecules were analyzed using LIECA DM2500P polarized optical microscope equipped with Linkam TMS 94 heating and cooling stage connected to a Linkam TMS 600 temperature programmer. The transition from isotropic to liquid crystalline phase was monitored by the evolution of characteristic textures. WXRD were recorded by a Philips analytical diffractometer using Cu K α emission and the spectra were recorded in the range of (2 θ) 3–50° and analyzed using X'pert software. Powder X-ray diffraction of all the samples were carried out in a PANalytical X'pert Pro dual goniometer diffractometer. An X'celerator solid-state detector was used in wide-angle experiments. The radiation used was Cu K α (1.54 Å) with a Ni filter and the data collection was carried out using a flat holder in Bragg-Brentano geometry. Care was taken to avoid sample displacement effects. Variable temperature in situ XRD experiments were carried out in an Anton-Paar XRK900 reactor.

Synthesis of Azo Dye

The hydroxy azobenzoic acid and the corresponding ester were synthesized as described in our earlier report.¹⁴

Synthesis of Azo Model Compounds Synthesis of 4-(4'-Methoxy-phenylazo)-Benzoic acid methyl ester (P0)

4-(4'-hydroxy-phenylazo)-benzoic acid (1 g, 4 mmol), 0.5 mL sulfuric acid, and 20 mL dry methanol were refluxed



overnight. The reaction mixture was then poured into cold water, neutralized with base and the precipitate was filtered, washed with water and dried. The crude product was purified by column chromatography using hexane-ethyl acetate (v/v 95/5) mixture. Yield = 0.9 g (86%). mp: 169 °C. ¹H NMR (200 MHz CDCl₃): δ (ppm): 8.18 (2H, d, Ar), 7.92 (4H, m, Ar), 7.02 (2H, d, Ar), 3.94 (3H, s, $-C(0)OCH_3$), 3.90 (3H, s, OCH_3). ¹³C NMR (CDCl₃) δ ppm: 52.10, 55.57, 114.37, 122.34, 125.16, 130.55, 131.30, 147.19, 155.49, 162.76, 166.57. FTIR (KBr) (cm⁻¹): 3004, 2949, 2842, 1718, 1602, 1583, 1499, 1434, 1313, 1281, 1282, 1153, 1106, 1024, 959, 866, 840, 776, 698, 556. HRMS m: 270.29. HRMS m+1: 271.15. ELEM. ANAL calculated for C₁₅H₁₄N₂O₃: C, 66.66; H, 5.22; N, 10.36. Found: C, 66.32; H, 5.18; N, 9.97.

Synthesis of 4-(4'-Methoxy-naphthalen-1-ylazo)-Benzoic acid methyl ester (Np0)

A similar procedure as above was adopted using 4-(4'-hydroxy-naphthalen-1-ylazo)-benzoic acid. The crude product was purified by column chromatography using hexane-ethyl acetate (v/v 95/5) mixture. Yield = 1 g (90%). mp: 141 °C. ¹H NMR (200 MHz CDCl₃): δ (ppm): 8.99 (1H, d, Ar), 8.34 (1H, d, Ar), 8.23 (2H, m, Ar), 8.00 (3H, m, Ar), 7.72 (1H, d, Ar), 7.62 (1H, d, Ar), 6.93 (1H, d, Ar), 4.11 (3H, s, -C(0)OCH₃), 3.97 (3H, s, OCH₃) ¹³C NMR (CDCl₃) δ ppm: 52.28, 55.93, 103.78, 113.74, 122.17, 122.58, 123.02, 125.54, 125.88, 127.87, 130.61, 131.18, 132.88, 141.57, 155.59, 159.34, 166.65. FTIR (KBr) (cm⁻¹): 3053, 2953, 2843, 1717, 1602, 1579, 1468, 1433, 1392, 1247, 1192, 1095, 1014, 955, 922, 870, 815, 758. HRMS m: 320.12. ELEM. ANAL calculated for C₁₉H₁₆N₂O₃: C, 71.24; H, 5.03; N, 8.74. Found: C, 71.45; H, 5.16; N, 8.35.

α,ω-Bis(4-Diethyleneoxyphenyl-4'-azophenyl)Methylbenzoate (P4P)

4- (4-Hydroxy-phenyl-1-ylazo)benzoic acid methyl ester (0.3 g, 1.17 mmol), TEG ditosylate (0.4 g,0.97 mmol), anhydrous potassium carbonate (0.29 g, 0.58 mmol), a catalytic amount of KI were dissolved in 10 mL of dry DMF. The mixture was stirred at 80 °C for 48 h under nitrogen. The resulting solution was cooled to room temperature, poured into water. The product was filtered, washed with water and dried. The crude product was purified by column chromatography using $CHCl_3$ -methanol (v/v 96/4) mixture. Yield = 0.265 g (34%). mp:140 °C. ¹H NMR (200 MHz CDCl₃): δ (ppm): 8.17 (4H, d, Ar), 7.89 (8H, m, Ar), 7.01 (4H, d, Ar), 4.20 (4H, t, -OCH₂-CH₂O), 3.94 (6H, s, -C(0)OCH₃), 3.90 (4H, m, -OCH₂-CH₂O-CH₂-), 3.76 (4H, m, -OCH₂-CH₂O-CH₂-). $^{13}\mathrm{C}$ NMR (CDCl_3) δ ppm: 52.27, 67.74, 69.57, 70.67, 70.86, 114.86, 122.34, 125.12, 130.55, 131.14, 147.00, 155.26, 161.82, 166.60. FTIR (KBr) (cm⁻¹): 3017, 2932, 2866, 1721, 1602, 1499, 1437, 1407, 1285, 1257, 1191, 1145, 1108, 1060, 957, 867, 840, 774, 697, 553. ELEM. ANAL calculated for C₃₆H₃₈N₄O₉: C, 64.47; H, 5.71; N, 8.35; Found C, 64.61; H, 5.82; N, 8.82. MALDI-TOF m+1: 693

A similar procedure was adopted for the synthesis of the naphthylazo twin molecules as well. Synthetic and characterization details are given in Supporting Information.

Synthesis of Polymers: Melt Polycondensation *SDP2P-5%*

DMS (0.412 g, 1.788 mmol (*x* mol)), **P2P** (0.0548 g, 0.094 mmol (1–*x* mol)), DEG (0.200 g, 1.884 mmol) were taken in a test tube-shaped polymerization apparatus and melted by placing in oil bath at 100 °C with constant stirring to melt the solid. Once a homogenous mixture was formed, the reaction mixture was cooled to room temperature and 1 mol % of titaniumtetrabutoxide (Ti(Obu)₄) was added as a catalyst. The polycondensation apparatus was made oxygen and moisture free by nitrogen purge. The polymerization tube was immersed in the oil bath at 150 °C and the polymerization was carried out with slow nitrogen purge for 4 h. The resultant viscous mass was further condensed by applying high vaccum (0.01 mm of Hg) at 150 °C for 2 h. The polymer was dissolved in THF, filtered to remove catalyst and precipitated in cold methanol to obtain the azo copolyester.

Yield = 0.350 g (48 %). ¹H NMR (200 MHz CDCl₃): δ (ppm): 8.17 (4H, d, Ar), 7.90 (8H, m, Ar), 7.04 (4H, d, Ar), 4.50 (4H, s, Ar—C(0)—OCH₂—CH₂O), 4.23–3.67 (22H, oligooxyethylene region), 2.31 (4H, t, Alph-C(0) OCH₂—CH₂), 1.59 (4H, m, —C(0)0—CH₂—CH₂—R—CH₂—CCH₂—C(0)0—), 1.28 (8H, m, —C(0)0—CH₂—CH₂—(CH₂)₄—CH₂—CC(0)0—).

SDNpnNp-x

DMS, naphthyl twin azobenzene (**NpnNp**), and DEG were taken as monomers, adopting the same polymerization procedure.

STPnP-x

DMS, phenyl twinazobenzene (**PnP**), and TEG were taken as monomers, adopting the same polymerization procedure.

RESULTS

The synthesis of the twin azobenzenes along with P0 and Np0—model compounds without ethylene glycol units is given in Scheme 1. The detailed procedure for the synthesis of the diazo dyes and their ester has already been reported earlier.¹⁴ The twin series having the structure—azo dye-(oligooxyethylene spacer)_n-azodye were synthesized by coupling the ditosylate of different oligooxyethylene with the azo dye esters. P0 and Np0 were synthesized by refluxing the azodye in the presence of acid in methanol as solvent. Normally introduction of ether linkage at phenolic position requires the reaction of alkyl halide in the presence of base. However, in these push-pull azo systems carrying out of esterification for longer time resulted in the esterification of carboxyl group as well as introduction of ether linkage at the phenolic position. This was confirmed by the appearance of two -OCH₃ peaks of ester and ether linkage in the ¹H NMR spectra. The structures of all the azo dye molecules are shown in Scheme 1. The structural characterization of the azo twin series were done by ¹H NMR and ¹³C NMR spectroscopy (Supporting Information). The purity of all molecules were confirmed by SEC (Supporting Information), high-resolution mass spectroscopy or matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) (Supporting Information) and along with elemental analysis. The SEC analysis showed

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SCHEME 1 Synthesis of phenyl and naphthyl twin azobenzenes.

single peak for all molecules confirming their purity. In the HRMS or MALDI-TOF analysis, molecular ions m, or m+1 radicals were obtained. Scheme 2 shows the incorporation of the twin azobenzenes into a main chain polyester backbone by melt polycondensation. The most widely used reactions for the preparation of polyesters are direct esterification of diacid/diacid chloride with diol or transesterification of diester with diol which are usually performed at high temperature in the melt. Generally, the degradation temperature of the azobenzene chromophore is lower than the melting temperature; thereby making it impossible to carry out melt polycondensation. Conversely, solution polymerization generally result in very low molecular weight oligomers, as the poor solubility leads to its precipitation from the polymerization medium before build-up of high molecular weight occurs.¹⁶ These difficulties were overcome in the polymerization reported here by designing the azobenzene dimethyl ester as a twin molecule with oligooxyethylene units which not only lowered the melting temperatures but also improved the solubility and the miscibility in the molten reaction medium. DMS and DEG/TEG were used as the AA and BB monomers, respectively, into which varying amounts of the different azo twin dimethyl esters were introduced as the A'A' monomer. Two homopolyesters of DMS with DEG named as (SD-homo) and with TEG named as (ST-homo) were synthesized. For

the copolymers, the total mole equivalents of AA (DMS) and A'A' (dimethylester of azotwin) were kept equal to that of the BB (diol), that is, sum of AA and A'A ': BB = 1:1. Scheme 3 shows the general structure of the random azo copolymers. The incorporation of the azo molecule into the aliphatic polyester backbone was determined from the proton NMR spectra. Table 1 gives the list of different copolymer compositions that were carried out with the actual incorporation of the azo content determined from ¹H NMR analysis given in brackets. The polymers based on sebacate/DEG were named as SDPnP-x% and SDNpnNp-x%, respectively, where the *n* represented the number of central ethylene glycol units in the azo twin segment and x represented the mol % incorporated. Similarly, the polymers based on sebacate/ TEG were named as STPnP-x%. Two sets of twin molecules were chosen to be incorporated into polyester; P2P (the smallest spacer twin which was not liquid crystalline) and P6P (the largest spacer twin which was liquid crystalline). For the copolymers, the highest azo solid content that could be taken in the feed was \sim 30 mol % for the higher spacer twin. For the shorter spacer twins, the poor solubility/miscibility of the azo molecule in the other molten components limited the feed to \sim 15 mol %. Thus, in the P2P polymer series, 5 and 15 mol % incorporation of P2P could be achieved with both DEG and TEG. Although a 30 mol % P2P in the



Synthesis of AzoCopolymer series

SCHEME 2 Synthesis of random azo copolymers from Phenyl and Naphthyl twin azobenzenes.

feed was attempted, the polymerization could not be practically carried out due to the large solid content of **P2P** which was immiscible in the other two components, namely 100 mol % DEG/TEG and 70 mol % DMS. In the **P6P** polymer series, 5 and 30 mol % incorporated polymers were synthesized using both DEG and TEG. The proton NMR signals of the copolymers were identified by comparison with the NMR spectra of the corresponding twin molecule with the homopolymer. The formation of the polymer was confirmed by the appearance of the new peak at 4.5 ppm (indicated by circle in Fig. 1) corresponding to the new aromatic ester linkage. The integrated area of the aromatic protons of azobenzene



SCHEME 3 Structure of random azo copolymers.

Turin	Polymer (% Azo Incorporation	лла	мл а		
Iwin		<i>W</i> _n	<i>W</i> _w	PDI	LC
DEG series					
P2P	SDP2P-5 (4.5)	8300	13,000	1.57	\checkmark
	SDP2P-15 (14)	14,400	26,200	1.80	\checkmark
P6P	SDP6P-5 (5.4)	13,800	19,000	1.37	Х
	SDP6P-30 (25)	4000	5030	1.24	\checkmark
Np2Np	SDNp2Np-5 (5)	46,800	67,800	1.44	Х
Np6Np	SDNp6Np-5 (5)	16,300	25,900	1.59	Х
	SDNp6Np-30 (30)	7400	13,800	1.86	Х
TEG series					
P2P	STP2P-5 (5)	25,300	38,000	1.50	Х
	STP2P-15 (17)	12,700	22,720	1.78	\checkmark
P6P	STP6P-5 (6)	13,660	19,540	1.43	Х
	STP6P-30 (31)	18,900	32,900	1.73	Х
Homopolymers					
	DMS/DEG	8700	12400	1.42	Х
	DMS/TEG	18000	28400	1.57	Х

TABLE 1 Molecular Weight of the Random Azo Copolymers

Molecular weights as determined by gel permeation chromatography in THF at 30 °C using polystyrene standards for calibration.

was compared with the $-(O-C(O) - CH_2)$ protons of the sebacate to determine the mol incorporation of the azobenzene into the polymer backbone. Figure 1 shows the representative proton NMR spectra of the twin molecule **P6P** and its copolymer with sebacate and DEG-**SDP6P-5**%. All the random copolymers thus developed have good solubility in common organic solvents. The molecular weight and polydispersity of the polymers were determined by GPC and the



FIGURE 1 ¹H NMR of phenyl twin azobenzene P6P, homopolymer SD-homo, and random azo copolymer SDP6P5.

Compound	λ_{max} Abs (ϵ , M ⁻¹ , cm ⁻¹)	Photoisomerization (%)
P0	253, 355, 445	92
P2P	253, 355, 447	80
P3P	253, 355, 447	91
P4P	253, 355, 447	90
P6P	253, 356, 447	90
Np0	280, 415	42
Np2Np	280, 415	42
Np4Np	280, 415	47
Np6Np	280, 415	52

TABLE 2 Absorption and Photoisomerization Data of thePhenyl and Naphthyl-based Twin Azobenzenes Series in THF

values are given in Table 1. In general, it was observed that the molecular weight of the DEG-based copolymers were lower as compared to that of the TEG copolymers. In the DEG copolymer series, higher (30 mol %) incorporation of azo dye resulted in a drastic reduction of the molecular weight. The TEG-based copolymers had reasonably high molecular weights in the range of M_n 12,700–25,300. This is quite remarkable considering the fact that earlier reports on homopolymer of the single chromophore 4,4'-azodibenzoyl chloride with TEG resulted in polymers with very low molecular weight ($M_n \sim 2300$) corresponding to only five repeat units.¹⁶

Photophysical Properties

The absorption spectra of the twin molecules and polymers were recorded in THF and the peak absorption values are given in Table 2. The absorption spectra of azobenzenes consist of three major bands. The lowest energy transition occurs at ~430–440 nm and is assigned to the n- π^* transition. The second transition occurs in the UV region around 320 nm and is assigned to the π - π ^{*} transition for trans azobenzene (for cis azobenzene the π - π^* band occurs around 280 nm). The peak maximum of this band is sensitive to the polarity and also to the presence of substituents. The third energy transition around 230-240 nm is considered to arise from the π - π ^{*} transition in the phenyl rings. In push-pull substituted aromatic azobenzene systems, there is an overall red shift of the π - π * transitions.²⁶ Thus, the simple phenolbased azobenzene molecules, for example, P0 with the ester group at one end and methoxy group at the other end had the n- π^* transition at ~445 nm, the π - π^* transition at 355 nm and the aromatic phenyl π - π * transition at \sim 253 nm. Conversely, in the more conjugated naphthol-based azobenzene series the n- π^* band was almost wholly overlain by the bathochromically shifted π - π * band, which appeared at 411 nm. The aromatic phenyl π - π * transitions was observed at \sim 279 nm. Figure 2 compares the absorption spectra of **PO** and NpO in THF. The twin molecules as well as copolymers had the absorption spectra similar to that of the respective model compounds. The twin azobenzenes were irradiated with a 50-W short arc mercury vapor lamp with an output wavelength in the range 280-450 nm in combination with



FIGURE 2 Normalized UV absorption spectrum of P0 and Np0 in THF.

either a 360 nm (for Phenylazo series) or a 450 nm (for the naphthylazo series) Oriel bandpass filter. The samples in THF (1 \times 10⁻⁶ M) had kept in the dark for overnight was irradiated and the absorption was recorded at every 5–10 s interval to trace the trans to cis photoisomerization. The change in absorption spectra of **P0** and **Np0** as



FIGURE 3 Photoisomerization studies of model compounds (a) P0 and (b) Np0 in THF.

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ABLE 3 Thermal Data of Twin Azobenzene	s (PnP, NpnNp)	, and Random Azo	Copolymers	(SDPnP-x%,	STPnP-x%)
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Sample	T _m ª (C-LC) (°C)	∆ <i>H</i> m ^ª (C-LC) (J/g)	T _{cl} ª (C/LC-I) (°C)	∆H _{cl} ª (C/LC-I) (J/g)	7 _c ^b (I/Lc-LC/C) (°C)	∆H _c ^b (I/LC-LC/C) (J/g)	7 _с ь (LC/C-C) (°C)	∆ <i>H</i> c ^b (LC/C-C) (J/g)	7 _D e (°C)
P0	-	-	169	129.2	163	-114.8	149	-6.49	241
P2P	-	-	215	114.5	205	-115.9			304
P3P	-	-	173	84.1	*1781	-4.8	158.13	-54.9	315
					172	-10.8			
					69.5				
P4P	-	-	140	47.2	132	-6.9	118	-32.9	304
P6P	-	-	119	95.4	106	-14.4	87	-55	339
Np0	128	25.4	141	54.3	106	-	101	-93.7	267
Np2Np	-	-	190	78.0	123	-	113	-63.0	331
Np4Np	19 ^c	-	139 ^d	87.34	-	-	-	_	325
Np6Np	-6 ^c	-	34	6.97			-	-	331
SDP2P5	34	44.6	66.5	3.9	*25	-	-5.2	46.6	385
SDP2P15	24	14.5	90	8.4	75		-13.6	-13.3	360
					47	-9.3			
SDP6P30	45	0.5							
	64	1.7	117	0.48	90	-	64	-13.5	335
	79.5	7.8							
STP2P15	8	0.7	99	8.7	*80	_	25	-11	364

 $^{\rm a}$ During second heating cycle with 10 $^{\circ}\text{C/min}.$

 $^{\rm b}$ During second cooling cycle with 10 $^{\circ}\text{C/min}.$

^c Glass Transition (T_{g}) during second heating cycle.

^d During first heating cycle.

representative samples of the PnP and NpnNp series on UV irradiation is shown in Figure 3 and the inset in the figure shows the % conversion as a function of photoirradiation time. Table 2 shows the % trans to cis conversion at the photostationary state for both series. The phenylazo series reached the photostationary state with more than 80% conversion within 15 s of irradiation. The phenylazo twin series exhibited increasing extent of trans to cis photoisomerization with increase in the central oligooxyethylene spacer length. The longer members like the P4P and P6P had the highest extents of isomerization of 90% (Supporting Information, Fig. S11) similar to the isolated chromophore **P0** (92%). Conversely, the maximum extent of trans to cis photoisomerization exhibited by the NpnNp twin series was $\sim 40\%$ in the photostationary state (\sim 30 s). No noticeable trend of % conversion with spacer length was apparent in this series. The reversibility of the photoisomerization was confirmed by following the back conversion to the trans state on keeping in the dark for overnight. Molecules of both series attained the original trans absorption spectra fully on keeping in the dark. The reduced isomerization efficiency of the naphthyl azo twins in comparison with the phenyl azo series is due to its bulky nature which hindered the motion. The photoisomerization in the copolyesters were similar to those observed for the corresponding twin molecules. One would have expected the covalent linkage of azobenzene group to the polymer main chain backbone would result in fewer

^e $T_{\rm D}$ -10 % weight loss under N₂ atmosphere in TGA. $T_{\rm m}$ -melting temperature. $T_{\rm cl}$ -Clearing temperature. $T_{\rm c}$ -cooling cycleNote- "*" transitions observed in PLM.

degrees of freedom and hence to a lower extent of photoisomerization compared to the twin molecule. However, no such difference in extent of photoisomerization was observed indicating that the polymer backbone provided enough flexibility for the alignment of azo groups in the main chain.^{27,28}

Thermal Mesophase Characteristics of Twin Molecules

The thermal stability of the azotwins were determined by TGA under nitrogen atmosphere (Supporting Information, Figures S12 and S13). No weight loss was observed until they were heated up to 200 °C. Table 3 compares the 10 wt % decomposition temperature of the single azochromophore (P0 and Np0) with that of the respective twin series. The twin molecules had much higher decomposition temperatures compared with the single chromophore. The connection of two mesogens to form a dimeric or twin structure is known to afford better thermal as well as mesogenic stability to the latter compared to the single molecule. The thermotropic liquid crystalline tendency of the azo twin series were studied using DSC analysis coupled with PLM and temperature dependent wide angle X ray diffraction (WXRD) studies. In the phenylazo twin series, monotropic mesophases were exhibited by members having spacer length greater than 2. Thus, P3P, P4P, and P6P exhibited smectic A (S_A) phases on cooling, with P3P additionally exhibiting nematic phase as well. Figure 4 shows the second heating and cooling scans in the DSC thermogram of the phenyl twin



FIGURE 4 DSC thermograms of (a) Phenyl twin azobenzenes P3P, P4P and P6P and (b) Naphthyl twin azobenzenes Np0 and Np2Np.

azochromophores P3P, P4P, P6P. The enthalpy values and phase transition temperature are given in Table 3. The melting (heating cycle) and isotropic to LC transition (cooling cycle) were decreased with increase in spacer length. Model compound **P0** was not liquid crystalline and exhibited a sharp melting at 168 °C in the heating cycle. In the cooling cycle, two transitions were observed at 163 °C and 149 °C, which corresponded to the isotropic to crystal and crystal to crystal transitions, which were confirmed by the PLM. The twin molecule **P2P** also did not exhibit a mesophase during the heating or cooling cycle and had a melting transition at 215 °C. Conversely, P3P was monotropic and exhibited multiple transitions in the cooling cycle, which were confirmed to be liquid crystalline phases based on observation under the PLM. There was only one melting transition in the second heating cycle at 173 °C with an enthalpy of 84 J/g. Although cooling, sharp transitions were observed at 172, 166, 158, and at 155 °C. Although DSC did not show any transition above 172 °C (while cooling), typical nematic textures were observed at 178 °C in the PLM as shown in Figure 5a on cooling from the isotropic melt. This nematic threads remained only for 2–3 $^\circ$ C, which was too weak to be detected by DSC and then batonnets started appearing at 173 °C, which coalesced into the typical focal conic textures of smectic A (S_A) (Fig. 5 b,c). The focal conic textures remained until 169 °C then suddenly the texture was changed into multicolored grainy features, which is corresponded to the second transition observed in DSC with peak maxima at 166 °C (Fig. 5d). Beyond this temperature, DSC showed transitions at 158 and 155 $^\circ\text{C}$ associated with huge enthalpy change of 54.9 J/g (compared to the smaller values of 10.8 and 4.8 J/g of the LC transitions); but under the PLM, sharp changes were not discernible. This transition at 158 °C was confirmed to be crystallization based on the large enthalpy change as well as from the variable temperature WXRD measurements, which showed the appearance of multiple sharp peaks corresponding to crystallization around

this temperature (Fig. 6, plot f). The overall LC window exhibited by P3P was thus \sim 20 °C (from 178 to 158 °C). Figure 6 shows the VT-WXRD data as a plot of intensity versus 2 θ recorded from 2 θ = 3–35° at various temperature intervals, whereas cooling from the isotropic phase. The plot "a" at 185 °C corresponded to the isotropic phase, plot "b" at 178 °C in Figure 6 showed a broad peak around $2\theta = 20^{\circ}$, which could be assigned to the lateral distance between mesogens of about 4 Å, characteristic of the nematic phase.²⁹ Plot "c" at 172 °C corresponded to the S_A phase and plot "d" corresponded to the colored grainy LC phase as observed under the PLM. Although WXRD did not show any characteristic features of smectic phase until 164 °C, room temperature WXRD recorded for the low angle region of $2\theta = 0.5-10^{\circ}$ (Supporting Information, Fig. S22) clearly showed the existence of a peak at low angle corresponding to molecular length of 33.5 Å around $2\theta = 2.8^{\circ}$.

P4P exhibited monotropic behavior with two transitions observed only during the cooling cycle. Figure 7a,b shows the focal conic fan-shaped textures typical of smectic A phases observed at 125 °C on cooling from the isotropic melt. The LC window was around 14 °C. P6P also exhibited similar behavior as P4P with a monotropic transition corresponding to broken fan-like smectic texture and an LC window of 20 °C. The variable temperature WXRD plot of P4P and P6P are given in the Supporting Information. A surprising feature observed in the variable temperature WXRD plot of the three molecules P3P, P4P, and P6P were the appearance of sharp crystalline-like d spacings during the mesophase in the 2θ region from 20 to 25° , which corresponded to the packing of oligooxyethylene units. Similar observation has been reported for azoxy-based liquid crystalline polyesters, where this has been attributed to the retention of order of the solid in the mesophase also.¹⁷ In a highly ordered smectic mesophase, the layered order of the solid state would be maintained. P4P and P6P also exhibited peaks at



FIGURE 5 Polarized Light microscope images of Phenyl twin azobenzene **P3P** (a) at 178 °C (schlieren texture), (b) at 172 °C (Batonnets), (c) at 170 °C (focal conic texture- S_A), and (d) at 166 °C (unidentified S_X phase).

multiple intervals indicating layered structure in the LC phase. For instance, in the LC phase at 125 °C, P4P showed two reflections at $2\theta=4.53^\circ$ and 9.31° which corresponded to the *d*-spacing values of 19.74 and 9.50 Å, respectively, (Supporting Information, Fig. S18). Similarly, P6P also showed peaks at $2\theta = 6.02^{\circ}$ and 12.05° which corresponded to d-spacing values of 14.80 and 7.36 Å, respectively (Supporting Information Fig. S19). In all these molecules, existence of the low angle peak corresponding to molecular length gave support for the smectic LC Phase (Supporting Information, Fig. S22).³⁰ Supporting Information, Figure S22 compares the low angle X-ray measurements for the PnP series at room temperature, which clearly indicated a shift in the peak position to lower angle with an increase in the oligooxyethylene segment indicating longer periodicity for the higher spacer members. Noteworthy was the observation of the sharp peak around $2\theta \sim 25^{\circ}$ corresponding to a d spacing of \sim 3.5 Å in these **PnP** twin molecules, which in aromatic molecules is usually attributed to the π -stacking interaction.^{31,32} This feature was a clearly distinguishing one, while comparing the packing in the NpnNp twin series (described below).

Compared with the phenylazo twin series, the naphthylazo twin series had lower clearing temperatures. This is expected as a lateral substitution on the core is known to cause fall in clearing temperature.³³ In the naphthylazo twin series, multiple transitions were observed in the DSC thermogram of **Np0** and **Np2Np**. Figure 4b shows the second heating and cooling scans in the DSC thermogram of **Np0** and **Np2Np** of the naphthyl series and their enthalpy values



FIGURE 6 Variable temperature wide angle X-ray diffraction of Phenyl twin azobenzene **P3P**.



FIGURE 7 Polarized Light microscope images of phenyl and Naphthyl twin azobenzenes (a) **P4P**-136 °C (focal conic texture- S_A , 40X magnification) (b) **P4P**-128 °C (focal conic texture- S_A) (c) **P6P**-109.7 °C (fan like texture- S_A) (d) **P6P**-104.8 °C (focal conic texture- S_A , 40X magnification) (e) **Np0**- 30 °C (Spherulitic texture) (f) **Np2Np**- 30 °C (Spherulitic texture).

and phase transitions are given in Table 3. Model compound **Np0** exhibited two transitions both in the heating (126 and 141 °C) and cooling cycle (106 and 101 °C) and observation under the PLM indicated spherulitic textures as shown in Figure 7e. The spherulitic phase remained frozen until room temperature and the texture was stable even after a month. The twin molecule **Np2Np** also exhibited sperulitic texture at 123 °C on cooling, (Fig. 7f), which remained stable until room temperature. The Supporting Information shows the variable temperature WXRD data of **Np0** and **Np2Np** taken

at various intervals during cooling from the isotropic melt. Compared with the **PnP** series, **Np0** and **Np2Np** were crystalline and had several sharp reflections both in the low angle and wide angle region. However, the oligooxyethylene segment packing that was observed in **PnP** series $\sim 2\theta = 20-25^{\circ}$ as well as the π stacking interaction observed $\sim 2\theta = 25^{\circ}$ were not observable in **Np2Np**. **Np4Np** and **Np6Np**, Conversely, exhibited glass transition $T_{\rm g}$ during heating and cooling (Supporting Information, Fig. S15). **Np4Np** also exhibited a melting transition at 139 °C during the first



FIGURE 8 DSC thermograms of P2P, SD-homo, SDP2P-5 and SDP2P-15.

heating cycle. Subsequent cooling and heating cycles showed only a $T_{\rm g} \sim 19$ °C. In the case of **Np6Np**, a melting transition was observed in the first heating cycle following which it showed a $T_{\rm g} \sim -6$ °C in the cooling cycle. In the second heating cycle, in addition to $T_{\rm g}$ a large cold crystallization exotherm and a sharp small endotherm were observed at 26 °C and 36 °C, respectively, which could be attributed to the crystallization of the oligooxyethylene component. The lower glass transition temperature for **Np6Np** implied increased plasticization due to increased flexibility of the hexaethylene glycol spacer compared with TEG. From the above observation, it was clearly evident that in **Np4Np** and **Np6Np** the thermal properties were determined mostly by the spacer than by the aromatic units.

Thermal Mesophase Characteristics of Azobenzene Copolymers

Linear aliphatic polyesters are generally crystalline and have low melting points (less than 100 $^{\circ}$ C) with the melting points increasing with the number of methylene groups between the ester groups. When the diols are polyethylene glycols, the melting transition as well as the percentage crystallinity of the polymer decreases and for higher glycols, the polymers become amorphous. When aromatic units in the form of aromatic dicarboxylic acids are introduced into the polyester backbone, they not only increase the melting transition but also induce thermotropic liquid crystallinity to the polymer. In addition, π bond stabilization in the form of azo linkages have been shown to contribute to the rigidity of the ring, which also stabilizes the mesophase formation.³¹ For instance, the literature reports the mesophase characteristics of a series of low-molecular weight polyesters formed by 4,4'-azodibenzoyl chloride with DEG, triethylene glycol, and TEG.^{17,34} The DEG-based azo copolymers exhibited mesophase, whereas the tri and TEG-based azo copolymers were not liquid crystalline.

The homopolymers of DMS with DEG and TEG - SD-homo and ST-homo were characterized for their thermal stability and crystallinity using TGA and DSC measurements. The homo as well as copolyesters were thermally stable till 300 °C (Supporting Information, Fig. S14). SD-homo was semicrystalline and exhibited cold crystallization and double melting peaks while heating, whereas sharp crystallization was observed at 8 °C while cooling (Fig. 8). Such double melting transitions have been observed for the crystallization of other polymers also where it has been shown that it is an after effect of annealing during the DSC scan which results in crystallites with different degrees of perfection.³⁵ The lower endotherm transition (at 34 °C) is due to the melting of initial crystallites produced during the crystallization process, whereas the higher temperature endotherm (47 °C) corresponds to crystal reorganization during melting (melting of more perfect crystals). Figure 9a shows the spherulitic crystals of SD-Homo observed under PLM after annealing the sample at 25 °C for 1 h. Conversely, increasing the chain length from DEG to TEG resulted in a completely amorphous homopolymer-ST-homo. The DEG-based copolymers incorporating varying mol % of the twin molecules P2P (short non-LC twin) and P6P (long LC twin) were analyzed for their thermal characteristics. Figure 8 compares the second heating and cooling cycles of twin molecule P2P and homopolymer SD-homo along with the respective copolymers SDP2P-5 and SDP2P-15. P2P was not liquid crystalline and had a melting transition at 215 °C, which crystallized at 205 °C in the cooling cycle. The 5 mol % incorporation of P2P (SDP2P-5) exhibited a sharp melting transition at 34 °C (enthalpy of 44.6 J/g) with another broad weak transition around 65 °C (3.9 J/g). While cooling, a broad exotherm was observed (30 to -13 °C) with a sharp peak centered at -5°C. Annealing the sample at 25 °C and observation under PLM showed the typical thread-like pattern of the nematic phase as shown in Figure 9b. An isothermal crystallization experiment was carried out by annealing the sample at 25 $^{\circ}$ C for 30 min, followed by rapid cooling to -5 $^{\circ}$ C. The sample was then heated at a rate of 10 °C/min, which is also plotted (in red) along with the second heating cycle in Figure 8. It showed two endothermic transitions at 33 and 45 °C, respectively, similar to that of the SD-Homo. The isothermal annealing in the nematic phase followed by rapid cooling allowed for the reorganization of the crystals which





FIGURE 9 Polarized light microscope images of homopolymer and random azo copolymer (a) SD-homo- 30 °C (Spherulitic crystalline phase) (b) SDP2P5-30 °C (Nematic texture) (c) SDP2P15- 77 °C (Nematic texture) (d) SDP2P15- 45 °C (Smectic phase) (e) SDP6P30-91 °C (Nematic droplets) (f) STP2P15- 30 °C (Nematic droplets).

was observed as the double melting in the following heating cycle.³⁵ On increasing the incorporation of **P2P** from 5 to 15 mol %, biphasic nature was evident in the DSC transitions with coexistence of two distinct phases. The first one corresponded to the crystalline regions of the sebacate and DEG polymer and the second corresponded to the liquid crystalline phase of the aromatic unit. In the first heating cycle, transition corresponding to the melting of the reorganized crystallites at 45 °C was visible along with two more transitions at lower temperatures 22 and 7 °C; and a higher one corresponding to the nematic to isotropic transition of the

aromatic units at 92 °C. In the second heating cycle, three endothermic transitions were observed at 10 °C, 24 °C enthalpy (14.5 J/g) and 90 °C enthalpy (8.4 J/g). On cooling, a grainy texture (Fig. 9c) was observed under PLM around 100 °C, which produced typical nematic threads on further cooling. Correspondingly, in DSC a weak transition enthalpy (0.44 J/g) was observed around 92 °C. Variable temperature WXRD of **SDP2P-15** is given in Figure 10. The XRD pattern of the polymer was broad and had lesser number of peaks compared to that of the twin molecule indicating the lower crystallinity. Plots "a" and "b" at 140 and 100 °C,



FIGURE 10 Variable temperature wide angle X-ray diffraction of random azo copolymer SDP2P15.

respectively, corresponded to isotropic phase, whereas plots "c" and "d" recorded at 88 and 85 °C, respectively, corresponded to the nematic phase. DSC showed a broad transition having a large enthalpy of 9.3 J/g with a peak centered at 47 °C. Observation under PLM showed a change in texture around this temperature indicating formation of a more ordered smectic phase (Fig. 9d).^{36,37} This was further confirmed by the appearance of more reflections in the wide angle region of the variable temperature WXRD recorded at this temperature (Fig. 10, plot "e"). This ordered phase was retained until room temperature of 25 °C as observed under PLM as well as WXRD. Higher incorporation of P2P in the DEG copolymer series was not possible due to practical reasons; however, the longer spacer twin molecule P6P could be incorporated up to 30 mol %. SDP6P-5 did not exhibit a LC phase but only a melting and crystallization in the heating and cooling cycles, respectively. Supporting Information, Figure S16 compares the second heating and cooling cycles of P6P, SD-Homo along with that of SDP6P-5 and SDP6P-30 copolymers. Here also, at higher incorporation biphasic regions were distinguishable in the DSC thermogram, corresponding to the crystalline sebacate/DEG domains and liquid crystalline azoaromatic domains. Thus, multiple transitions were observed in the heating cycle of SDP6P-30 and while cooling, nematic droplets were observed at around 90 °C under the PLM (Fig. 9e).

Three copolymers of the naphthylazo twin series were synthesized – **SDNp2Np-5**, **SDNp6Np-5**, and **SDNp6Np-30** and were analyzed for their thermal characteristics. They did not exhibit any thermotropic liquid crystalline behavior. Compared with the phenylazo twin series, only the lowest member of the napththylazo twin molecule—**Np2Np** exhibited LC behavior; with the higher members already having lost the flexible/rigid balance required for mesophase formation. The introduction of more flexible segments via copolymerization would be counter intuitive in inducing mesophase abilities in the **NpnNp** copolymer series. A series of copolymers were developed using TEG as the BB monomer instead of DEG. Because the naphthylazo copolymers did not exhibit any LC tendencies with DEG, the probability of mesophase formation with a more flexible TEG could be ruled out. Therefore, only P2P and P6P were incorporated into copolyesters with DMS and TEG. 5 and 15 mol % incorporated P2P, namely, STP2P-5 and STP2P-15 were analyzed for their thermal properties. The DEG-based copolymers were all obtained as solid powders, whereas STP2P-5 was a viscous liquid. The DSC thermogram of the ST-homo with that of its 5 and 15 mol % azo copolymers STP2P-5 and STP2P-15 have given in Supporting Information Figure S17. The ST homopolymer did not show any transition in the heating or cooling cycles. STP2P-5 exhibited a cold crystallization followed by melting at 6 °C in the first heating cycle but in the following cycles no transitions were observed. After 15 mol % incorporation of P2P, new transitions were observed in the DSC thermogram of STP2P-15. Two transitions were observed at 8 and 99 °C while heating but only one transition was observed at around 25 °C while cooling. Annealing the sample at 80 °C resulted in the formation of nematic droplets (Fig. 9f) under the PLM. The copolymers STP6P-5 and STP6P-30 did not exhibit any mesophases when observed under PLM and their DSC also was devoid of any transitions.

DISCUSSION AND CONCLUSION

Two series of twin azobenzene molecules were synthesized and studied for the effect of varying central oligooxyethylene spacer segment on the liquid crystalline characteristics. These twin azobenzene moieties were also introduced as part of main chain copolyester composed of sebacate and DEG or TEG.

The following observations and conclusions were drawn based on the experimental analysis.

- (a) Main chain azobenzene-based polymers are normally synthesized by the solution polymerization method, as the melt condensation route would result in degradation of azo chromophores. The strategy of incorporating the azobenzene chromophore as a part of a twin molecule having the structure azobenzene-oligooxyethylene-azobenzene could circumvent this problem by reducing the melting temperature of the twin molecule and also improving their solubility as well as miscibility in the molten reaction medium. Thus, main chain azobenzene copolymers incorporating upto 30 mol % azo twin chromophores with reasonably high molecular weights in the range $M_n \sim 12,700$ to 25,300 could be achieved.
- (b) The linking of a polar oligooxyethylene unit with a nonpolar rigid aromatic azo chromophore is expected to result in stable mesophases due to the mutual non solubility.³⁸ The twin series based on phenylazo (**PnP**) and naphthylazo (**NpnNp**) had a combination of nonpolar (N) azobenzene units with polar (P) oligooxyethylene units linked as triphilic N-P-N system leading to incompatibility. If the incompatibility between the flexible



oligooxyethylene units and the rigid azobenzene units results in segregation into separate domains, then, a smectic phase is preferred as in the twins P3P, P4P, and P6P. However, this flexibility is lost in the shorter twin molecule **P2P** which in spite of having a *N-P-N* triphilic character did not exhibit any LC phase. Considering the naphthylazo twin series, even though they also formed triphilic N-P-N systems, the naphthyl ring on the azobenzene expanded the breadth of the rigid aromatic core making the chromophore lose out on the axial to equatorial ratio and only the lowest spacer Np2Np exhibited spherulitic phase. The NpnNp twin series of molecules had lower melting transitions than the **PnP** series of the same spacer length and also had better solubility. The increased solubility also implied lesser microphase separation. The higher (n = 4 and 6) members were so flexible that they exhibited only a glass transition in their DSC thermograms.

(c) The short (n = 2) and long (n = 6) spacer twins in both **PnP** and **NpnNp** series were incorporated in varying mole ratios into an aliphatic copolyester composed of sebacate and DEG as well as TEG. At higher incorporation of the **PnP** units, biphasic regions were observed in the DSC thermograms of both DEG and TEG copolymers and they exhibited liquid crystalline phases. Conversely, **Np2Np** and **Np6Np** failed to induce mesogenicity even on 30 mol % incorporation in DEG copolymers.

The analysis of the LC behavior of the two series of twin molecules and their main chain copolyesters thus showed that they were dependent on the length of the oligooxyethylene linkers as well as the nature of the azo chromophore (phenylazo vs. naphthylazo). Incorporation of "rigid azoaromatic twin" units into a nonmesogenic polymer helped to induce mesogenicity in the copolymer. Although the twin molecules exhibited smectic LC phases, their incorporation in the copolymer at low incorporation resulted mostly in nematic LC phase. The randomness of the sequence along the copolymer chain would impose restrictions on the translational mobility of the monomeric units of the polymer, thereby making it unfavorable for the formation of the layered smectic phases. Another noteworthy point is that the rigid azoaromatic twin units cannot be considered as the "mesogen" as that would imply that the liquid crystalline properties of the polymer was related only to the presence of these aromatic units. The studies presented here clearly showed that two polymers (DEG and TEG copolymers) containing the same "mesogen" unit behaved differently; one was mesogenic, whereas the other was not. The observation of mesogenicity is a complex phenomenon, especially in a random copolymer and both the "rigid" and the "flexible" spacer would be expected to have almost equal contribution in deciding the final outcome.

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