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Synthesis and characterization of thermotropic liquid crystalline polyphosphates containing photoreactive moieties

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New dual mesogens, with α -methylstilbene and *p*-substituted azobenzene as main chain and side chain, respectively, and containing liquid crystalline polyphosphates, were synthesized. The pendant azobenzene units were unsubstituted or substituted with F, Cl, and Br atoms. All the polymers were synthesized by solution polycondensation using 4,4'-bis(10-hydroxydecyloxy)- α -methylstilbene and 4-substituted phenylazo-4'-phenyloxydecylphosphorodichloridates. A model polymer was synthesized from bis(10-hydroxydecyloxy-4,4'-diphenylpropane) and phenylazo-4'-phenyloxydecylphosphorodichloridate for comparison. The polymers were characterized by FTIR spectroscopy, ¹H and ³¹P NMR, and intrinsic viscosity. Microstructure and mesomorphic properties were determined by hot stage polarizing optical microscopy, differential scanning calorimetry and variable temperature X-ray diffraction. In addition, the polymers were examined for thermal properties by thermogravimetry, electrochemical behaviour by cyclic voltammetry and photo-physical properties by UV spectroscopy. The electrochemical studies reveal that the azobenzene moiety was reduced at 0.95 in the anodic scan. UV irradiation studies indicated that the time taken for completion of photoisomerization depends on the size and dipole moment of the terminal substituents.

1. Introduction

Stilbene-based compounds/polymers offer attractive properties and possess novel features for technological innovation, with potential use in electroluminescence [1], therapeutic agents [2], optical brighteners and laser dyes [3]. Many applications are proposed for main chain and side chain liquid crystalline polymers, such as optical data storage [4] and information displays [5]; the importance of combined main chain/side chain LC polymers has also been reviewed [6]. Beck and Ringsdorf characterized some of the chemical structures of main chain and side chain mesogens containing azobenzene and azoxybenzene, and observed that they may influence the molecular packing and order of the mesophase [7–9]. Kricheldorf et al. propose phosphorous-containing main chain liquid crystal polymers (MC-LCPs) as fire retardant polymers with higher char yield [10].

4,4'-Dihydroxy- α -methylstilbene (DHAMS) is an interesting mesogenic core, easily prepared and reacted with diacid chlorides to give MC-LCPs [11–13]. Bicerano [14] predicted the characteristic ratio and persistence length for ordinary DHAMS-containing

polycarbonate, which was found to be much stiffer than a random coil polymer and also much more flexible than LCPs. Cox *et al.* [15, 16] synthesized series of planar and non-planar stilbene derivatives and indicated that non-planar *trans*-stilbene derivatives exhibit lower melting points than their planar counterparts. The lower melting point and improved solubility of α methylstilbene derivatives increases the cross-section of the mesogen [17–21].

Azo groups are sensitive to light and heat, which is a basic condition for the use of these polymers in communication technologies [22]; moreover, the behaviour of azo groups towards different kinds of signal may be adjusted by choice of substituents [23, 24]. Azobenzene-based side chain liquid crystal polymer (SC-LCPs) are extensively studied because of their great potential as novel technological materials in, for example, optical switching elements [25], digital and holographic optical components, and for reversibility in optical data storage [26, 27].

Phosphorous-containing liquid crystalline polymers possess high polarity in comparison with that of nonphosphorous systems; this plays a substantial role in properties such as flame retardancy, glass transition, solubility, dielectric constant and stability [28]. Polymers with dual mesogenic main chain and side chain,

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and possessing phosphorous in the backbone, are hitherto unreported in the literature. This paper deals with the synthesis, characterization, electrochemical and photo-physical studies of combined main chain/ side chain liquid crystalline polyphosphate esters. The esters are derived from 4,4'-dihydroxy- α -methylstilbene in the main chain and variously substituted azobenzene phosphate units in the side chain, enabling us to investigate the influence of the substituents on side chain orientation, and the thermotropic properties of LC behaviour. A model polymer was also synthesized from bis(10-hydroxydecyloxy-4,4'-diphenylpropane) in the main chain and phenylazo-4'-phenyloxydecylphosphorodichloridate in the side chain, for comparative photo-physical studies.

2. Experimental

2.1. Materials and methods

Dichloromethane, chloroform, methanol, phenol and substituted anilines (SD fine, India) were purified in the usual manner [29]; phosphorus oxychloride (SRL, India) was distilled before use. 1,10-Decanediol chloroacetone (Merck, Germany) and (Fluka, Switzerland) were used as received; 10-bromodecanol was prepared by a procedure reported elsewhere [30]. 4,4'-dihydroxy- α -methylstilbene was synthesized by the condensation of chloroacetone with phenol in the presence of concentrated sulphuric acid and recrystallized from ethanol/water in equal proportions. 4-Substituted-4'-azobenzenes were prepared by adopting a procedure similar to that reported elsewhere [31].

2.2. Synthesis of monomers 2.2.1. 4,4'-Bis(10-hydroxydecyloxy)-α-methylstilbene

4,4'-Dihydroxy-α-methylstilbene was dissolved in dry DMF (15 ml), followed by anhydrous potassium carbonate (0.05 mol) and 5 wt% of potassium iodide. The mixture was heated to 90°C with constant stirring, 10-bromodecanol (0.011 mol) was added dropwise to the reaction mixture and the reaction continued for 2 days. The reaction mixture was then cooled to room temperature and poured into ice-cold dilute hydrochloric acid solution. The precipitated product was filtered, washed with water until neutral and then dried *in vacuo*. Yield: 50%, m.p. 182°C (lit. 182–183°C). IR (KBr)(cm⁻¹): 1260(C–O–C asymmetric stretch), 1471 (CH₂), 1680 (*trans*-C–C), 3445 (phenolic OH). 1 H NMR (DMSO-d₆-TMS, δ): 1.24 (s, α -CH₃), 4.9 (S, trans-ethylene) 7.09 (m, aromatic ortho to CH) 6.95 (d, aromatic ortho to CH₃) 6.73 (d, 2H aromatic meta to CH) 6.68 (d, 2H, aromatic meta to C-CH3).

2.2.2. 4-(10-Hydroxydecyloxy)-4'-substituted (X)

azobenzene (X=H, F, Cl, Br)

4-(10-Hydroxydecyloxy)azobenzene was prepared using a similar procedure to that adopted for the synthesis of 4,4'-bis(10-hydroxydecyloxy)- α -methylstilbene. All other substituted azobenzenes were prepared in a similar manner. Yield: 85–90%. ¹H NMR (CDCl₃, δ): 7.3 (m, 5H, aromatic benzene) 6.8 (d, *ortho* to azo) 6.6 (d *meta* to azo) 3.5 (t, hetroatom O–CH₂) 1.3 (t, aromatic ether CH₂) 1.2 (m, CH₂).

2.2.3. 4-Substituted (X) phenylazo-4'phenyloxydecylphosphordichloridates

4-(10-Hydroxydecyloxy)azobenzene (0.02 mol) was dissolved in dry chloroform (25 ml), and freshly distilled phosphorus oxychloride (0.04 mol) was added. The reaction mixture was slowly heated to 50° C with constant stirring over 1 h and then raised to reflux conditions. The reaction was continued until HCl evolution ceased. Excess phosphorus oxychloride was distilled off under reduced pressure and the residue connected to high vacuum for several hours. The reddish brown solid thus obtained was used immediately for the polymerization reaction without further purification [24].

2.3. Polymerization

2.3.1. Poly{4,4'-bis(10-hydroxydecyloxy)-αmethylstilbene[4-(10-hydroxydecyloxy)-4'-(X)azobenzene]phosphate}s

Polymers I-IV (see the scheme) were prepared by solution polycondensation at room temperature using triethylamine (TEA) as acid scavenger. The typical methodology for preparation of polymer I is as follows. 4,4'-Bis(10-hydroxydecyloxy)-α-methylstilbene (0.05 mol) was dissolved in dry chloroform (20 ml); dry TEA (0.1 mol) was added under inert atmosphere and the mixture stirred at room temperature. To this phenylazo-4-phenyloxydecylphosreaction mixture, phorodichloridate (0.05 mol) dissolved in chloroform was added dropwise over a period of 30 min. During the addition, the solution became homogeneous, and the reaction continued for 24 h. The solution was then concentrated and poured into excess methanol, giving a yellow precipitate which was filtered and dried in a vacuum oven at 50°C. Polymers II-IV were prepared in a similar manner. Yield: 75–80%. IR (KBr)(cm⁻¹): 1262 (Ar-O-C), 1244 (P-O), 1588 (C-C), 763 (P-O), 1500 (-N=N), 3441(P–OH), 2924 (CH₂). ¹H NMR (CDCl₃, δ): 1.66 (s, =CH, α-CH₃), 6.7 (s, *trans*-ethylene) 7.4 (d, aromatic ortho to = CH) 7.2 (d, aromatic ortho to $-CH_3$) 6.9–7.0(d, aromatic ortho to O–CH₂) 4.0 (m, aromatic O-CH₂) 1.29,1.55(m, O-CH₂) 6.5 (d, azo



Scheme. Synthesis of polymers I-V.

aromatic *ortho* to O–CH₂) 7.8 (d, azo aromatic *meta* to O–CH₂) 7.9(d, azo aromatic *meta* to X) (see figure 1). ³¹P NMR: -13.4δ , and -19.8δ .

2.3.2. Poly{bis[4,4'-diphenylpropaneoxydecyl (azobenzeneoxydecyloxy)phosphate]}(V)

This polymer was synthesized in a similar manner to that used for polymers I–IV. Yield: 60%. FTIR (cm⁻¹): 2980(isopropyl), 1262(Ar–O–C), 763(P–O), 1244(P=O), 1500(–N=N), 2924(CH₂).

2.4. Characterization

The intrinsic viscosity of the polymers was measured using a suspended level Ubbelohde viscometer in dichloromethane (0.5 g dl) at $30 \pm 2^{\circ}$ C. High resolution ¹H and ³¹P NMR spectra were recorded on a Brucker spectrometer (300 MHz). ³¹P NMR spectra were recorded using triphenylphosphine as external standard in a dual (³¹P/¹H) probe. ¹H NMR spectra of the main chain monomer were recorded using dimethylsulphoxide (Aldrich) containing TMS (0.03%) as a solvent, while the polymer spectra were recorded using deutrated chloroform. FTIR spectra were recorded on a Nicolet FTIR Impact 440 spectrophotometer using potassium bromide pellets.

DSC and TGA thermograms were recorded on Perkin-Elmer TGA-7 and DSC-7 systems, respectively, under nitrogen. The heating rate for both DSC and TGA was 10°C min⁻¹ with a nitrogen flow of 50 ml min⁻¹. Polarizing microscopy studies were performed with a Euromax polarizing microscope attached to a Linkam HFS 91 heating stage and a TP-93 temperature programmer. Samples were placed between two thin glass cover slips and processed with heating



Figure 1. ¹H NMR spectrum of polymer I.

and cooling rates of 2° C min⁻¹. Photographs were taken with a Nikon FM10 camera and printed on Konica 400 film.

Powder X-ray diffractograms were obtained with a Seifert powder diffractometer using an ISO Debyeflex 3000 generator equipped with a Guinier camera using Cu K_{α} radiation of wavelength 1.5406 Å. Variable temperature X-ray diffractograms were recorded in air with a scan resolution of 0.001°, using resistive heating with a Pt-Rh thermocouple. The samples were introduced into 1-mm Lindemann glass tubes.

Electrochemical studies were performed using an EG & G model cyclic voltammeter; the working electrode was glassy carbon, with Ag/AgCl as the reference electrode and supported with platinum as an ancillary electrode with 0.1 M tetrabutylammonium percholarate/dichloromethane solution and ferrocene as internal standard. Photoisomerization studies of the polymers were carried out using 350–420 nm UV irradiation from a low pressure mercury lamp. The polymer were dissolved in dichloromethane in a 1-cm quartz cuvette; it was irradiated for 1 min and the UV absorption of the solution was then immediately measured on a Shimadzu UV–1610 spectrophotometer. The

measurement was repeated until reduction in absorbance was complete.

3. Results and discussion

3.1. Synthesis

The main chain-containing stilbene monomer 4,4'bis(10-hydroxydecyloxy)- α -methylstilbene was synthesized under Williamson's ether conditions using α -methylstilbene and 10-bromodecanol in the presence of DMF, with a catalytic amount of potassium iodide. In a similar manner, 4-substituted-4'-hydroxy (X) azobenzenes (X=H, F, Cl, Br) were prepared and alkylated. The alkylated side chain azobenzene derivatives were reacted with an excess of phosphorus oxychloride to give the corresponding phosphorodichloridates, with were used for polymerization reactions without further purification. The polymers were prepared by solution polycondensation at ambient temperature in good yield.

The intrinsic viscosity of the polymers was measured in dichloromethane solution at 30°C, with results shown in table 1. These results show that the polymers have moderately high molecular masses. The infrared spectra of all the polymers show absorptions around

Table 1. Intrinsic viscosity, UV and TGA data for polymers I-IV.

Polymer	Pendant group	$\eta_{\rm int}/{\rm dl}{\rm g}^{-1}$	λ _{max} /nm	Stages of de	composition ten	M	C1 11	
				Ι	II	III	loss at 600°C/%	600°C/%
Ι	Unsubstituted	0.35	350	260	360	440	70	30
II	Fluoro	0.41	349	290	400	460	78	22
III	Chloro	0.46	354	300	400	460	75	25
IV	Bromo	0.50	353	320	410	490	72	28

919 and 2924 cm⁻¹, corresponding to P–O–C aliphatic stretching and aliphatic CH₂ stretching, respectively [32]. The absorption band around 1520 cm⁻¹ represents the *trans*-exocyclic double bond [33]. All the polymers showed absorptions around 1070, 1150 and 1244 cm⁻¹, due to P=O stretching [34]. The ³¹P NMR spectra of the polymer show two signals: the resonance signal crossponding to -13.4δ is due to the P atom in the main chain; the signal at -19.8δ is the P atom at the chain ends, confirming the incorporation of phosphorus in the polymer backbone.

3.2. Thermal and LC phase characterization

The TGA thermograms of the polymers are shown in figure 2. These indicated that all the polymers are stable up to 260°C. Three-stage decomposition was observed for all the polymers loss data are shown in table 1. The first stage decomposition of all the polymers takes place in the range 260–300°C, with a sharp differential curve. This may be ascribed to the evolution of nitrogen gas from the azo group present in the side chain [35]. Subsequent decompositions take places between 400 and 460°C. The second decomposition may be attributed to the cleavage of phosphate esters in combination with aliphatic spacers. The final stage cleavage may be due to breaking of the ether linkage in the aromatic backbone [36]. The decomposition of the polymers was



Figure 2. TGA thermograms of polymers I-IV.

almost complete at 600°C, the unsubstituted polymer showing the highest char yield of all. Substitution on the pendant phenyl ring affects the char yield in the following order: F < Cl < Br. The high percentage of char yield for these polymers may be attributed to the formation of phosphoric acid as final product [24].

Hot stage polarizing optical microscopy (POM) photographs of polymers I, II, III and IV are shown in figure 3. The main chain monomer and the polymers exhibited enantiotropic monomorphic liquid crystalline behaviour during the cooling cycle. The main chain monomer, unsubstituted polymer (I) and fluoro, chloro and bromo substituted polymers (II, III and IV) showed mosaic and leaf-like textures indicating the presence of smectic phases [37, 38]. Possible smectic phases that may be assigned for these mosaic textured polymers are SmA, SmB, SmF, CrE, and CrG or CrH [39, 40]. The π -electron density and additional central double bonds, coupled with the increase in polarizibility that leads to an increase in the length of the terminal alkyl chains in the monomers, promote the occurrence of the smectic phases for polymers I-IV [41]. It is interesting to note that the $T_{\rm m}$ of the polymers (table 2) was found to be considerably lower than for the main chain monomer. This may be ascribed to the incorporation of phosphorous, and to the lateral azobenzene substituent perturbing the mesogen packing efficiency [42]. The model polymer V exhibited the nematic LC phase.

DSC thermograms of the polymers are shown in figure 4; phase transition temperatures observed from DSC measurements are summarized in table 2. The T_g of polymers I and IV was fairly low, in the range 60–63°C. This may be ascribed to the incorporation of the phosphorous group and disturbance of the molecular close packing by the lateral substitution of the pendant group. The T_m and T_i values are attributed to the highly polar nature of the phosphorous atom with a high bond angle which would greatly reduce these transition temperatures [36]. The flexible polymethylene spacer that separates the mesogens along the main and side chains, thereby provides chemical periodicity to the polymer backbone. The flexibility in



Figure 3. POM photographs for polymers I–IV during first cooling: (a) I at 150°C, (b) II at 140°C, (c) III at 145°C, (d) IV at 150° C.

the chains and the segmental motion favoured high order in liquid crystalline structures.

In order to confirm the identity of the smectic mesophase, variable temperature X-ray diffraction (XRD) measurements were carried out, Variable temperature at room temperature, 50, 100, 140 and 175°C, and after cooling again to room temperature, for the polymer IV, as shown in figure 5. The XRD pattern of the polymer shows a low angle peak at $2\theta = 3.9^{\circ}$, corresponding to a layer thickness of 21.23 Å at 100°C, and 22.1 Å at 140°C. The diffraction pattern indicates that the mesogenic rigid rods are arranged in layers, and the polymer therefore exhibits a smectic LC phase [39, 43]. A resolved halo peak was also found in the region of $2\theta = 20^{\circ}$, 21° , 22° and 23° with *d*-spacings of 4.0, 3.9, 3.8 and 3.4 Å, respectively, at 140°C. On increasing the temperature above isotropization, the peak diminishes and the original crystallinity is regained on cooling, confirming the presence of an enantiotropic liquid crystalline phase.

3.3. Electrochemical behaviour of the polymers

The redox properties of polymer III were characterized by cyclic voltammetry in a conventional solid electrode in dichloromethane. The cyclic voltammogram of polymer III is shown in figure 6. The data represent an irreversible electron processes in the anodic scan. Two irreversible multi-electron process are visible at E=0.95 and 1.55 mV versus ferrocenium/ ferrocene as an internal standard. The first process is attributed to the N=N moiety. The resultant linear sigma plot of the peak current versus scan rate confirmed that this process is influenced by surface adsorption. This result may be attributed to irreversible oxidation of the azobenzene moiety of the mesogenic group [44].

3.4. Photo-physical properties

It is noteworthy that the reported polymers contain dual chromophores, namely, the stilbene and azobenzene moieties; the double bonds of these

		DSC				POM			
Polymer	Pendant group	$\overline{T_{g}}$	$T_{\rm m}$	T_{i}^{a}	ΔT	$T_{\rm m}$	$T_{\rm i}$	ΔT	Type of mesophase
Ι	Unsubstituted	60	150	173	23	150	170	20	Smectic
II	Fluoro		130	148	18	135	150	15	Smectic
III	Chloro		138	158	20	140	157	17	Smectic
IV	Bromo	62	140	161	21	142	160	18	Smectic

Table 2. DSC and POM data for polymers I-IV: temperatures in °C.

 ${}^{a}T_{i}$ observed only during the first heating cycle.



Figure 4. DSC thermograms of polymers I-IV.

molecules favour the *trans-cis*-isomerization resulting in the loss of planar geometry of the *trans*-isomer in both the ground and excited states. The stilbene chromophore is photoisomerised to the *trans*-form and does not return to the *cis*-form, because of a cooperative motion effect [45]. On the other hand, in the azobenzene moiety, isomerization takes place to the *cis*-form which then returns to its *trans*-form. By exposing the polymers to light of the appropriate wavelength, the *trans-cis* conformational changes can



Figure 5. Vairable temperature XRD for polymer IV at different temperatures: (a) r.t., (b) 50°C, (c) 100°C, (d) 140°C, (e) 175°C, (f) after cooling to r.t.



Figure 6. Cyclic voltammogram of polymer III.

be observed. The photoisomerization studies were performed in dichloromethane solution (0.0002 M); representative absorption spectra of polymer II are shown in figure 7. The absorbance and time intervals of each irradiation for all the polymers are depicted in the figure 8. A sharp absorption peak was observed in the region of 240 nm, which represents the stilbene chromophore in the *trans*-form. With continuous irradiation of light, the absorbance gradually increases. The λ_{max} at 354 nm before irradiation due to the π - π * transition of *trans*-azobenzene, on continuous irradiation with different intervals of time, shows a decrease in absorbance.

An increasing trend of the cis-isomer was also



Figure 7. Absorption spectra of polymer II at different intervals of time.



Figure 8. Photoisomerization of polymers I–V in concentration of 2×10^{-4} molar.

observed at λ_{max} 438 nm due to the n- π^* transition of the azobenzene moiety. This may be due to the size and dipolar moment of the pendant substituents. After completion of irradiation with visible light (>350 nm), the absorbance was restored owing to cis-trans photochemical back-isomerization. Indeed, this effect may be caused only by the presence of the azobenzene moiety [46]. In the model polymer V, the azobenzene moiety shows a regular decrease in absorbance on irradiation for different intervals of time, and isomerization of the cis- and trans-forms observed in the wavelength region 426 and 386 nm, clearly indicates an effect only of the azobenzene chromophore (figure 9). It is interesting to note that the completion of trans-cisisomerization took place in a shorter time for the dual chromophoric mesogen-containing polymers than for



Figure 9. Absorption spectra of model polymer V at different intervals of time.

the model polymer containing only the azobenzene moiety. This may be attributed to the synergistic effect of α -methylstilbene and azobenzene chromophores present in the polymer backbone along with the pendant substituent effect of the side chain. The switching time needed for complete *trans-cis*-isomerization is in the following order: IV > III > II > I > V.

4. Conclusion

A series of new combined-type liquid crystalline polyphosphate esters, containing α -methylstilbene and substituted azobenzenes, respectively, as main and side chain mesogens attached to the phosphorous through decamethylene spacers, were prepared and characterized. TGA indicates that the polymers are thermally stable up to 260°C, and that three decomposition stages in the range 260-490°C occur. In these polymers, the melting transition appeared in the range 138-150°C, and are attributed to transitions caused by segmental motion of the main and side chain moieties. Polymers I-IV exhibited smectic phases, while the model polymer V showed α nematic phase. Variable temperature XRD analysis confirmed the presence of smectic phases in polymers I-IV. Electrochemical studies revealed irreversible peaks at a highly anodic current in different scan cycles. By plotting the square root of scan rate versus peak current a linear curve was obtained passing through the origin. The regression sigma plot was also calculated, giving a value of nearly 0.1, indicating that the system was an adsorption-controlled potential process. UV studies confirmed photoisomerization of the polymers, and the cooperative motion effect was also induced. The time taken for completion of cistransformation was also investigated among the synthesized polymers. In the case of the model polymer, a regular decrease in the absorbance with time of irradiation confirms the change in isomerization due to the azobenzene moiety.

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References

- [1] BURROUGHES, J. H., BRADELY, D. D. C., BROWN, A. R., MARKS, R. N., MACKAY, K., FRIEND, R. H., BURNS, P. L., and HOLMES, A. B., 1990, *Nature*, 347, 4539.
- [2] KABALAKA, G. W., WU, Z., and JU, Y., 2001, *Tetrahedron Lett.*, 42, 4759.
- [3] MEIER, H., 1992, Angew. Chem., 31, 1399.
- [4] ATTARD, G. S., 1991, in *High Value Polymers*, edited by A. H. Faweett, Special Publ.No. 87 (Cambridge: Royal Society of Chemistry).

- [5] RUAN, J., GE, J. J., ZHANG, A., SHI, J., WAN, S. Y., HARRIS, F. W., and CHENG, S. Z. D., 2002, *Macro*molecules, **35**, 736.
- [6] ZENTAL, R., 1998, in *Hand Book of Liquid Crystals*, vol. 3, edited by D. Demus, J. Goodby, G. W., Gray, H. J. Weiss, V. Vill (New York: Wiley-VCH), p. 52.
- [7] BECK, B., and RINGSDORF, H., 1985, Makromol. Chem. Rapid. Commun., 6, 291.
- [8] BECK, B., and RINGSDORF, H., 1986, Makromol. Chem. Rapid. Commun., 7, 389.
- [9] BECK, B., and RINGSDORF, H., 1989, Makromol. Chem. Rapid. Commun., 190, 2511.
- [10] KRICHELDORF, H. R., KOZIEL, H., and WITEK, E., 1988, Makromol. Chem. Rapid. Commun., 9, 217.
- [11] ROVIELLO, A., and SIRIGU, A., 1980, *Makromol. Chem.*, 181, 1799.
- [12] ZAHER, S. H., and BHUSAN, B., 1953, Nature, 171, 746.
- [13] PERCEC, V., CHAIN, S. H., and DIMITRIS, T., 1988, *J. polym. Sci. A*, **26**, 2047.
- [14] BICERANO, J., 1998, Comp. theor. polym. Sci., 8, 9.
- [15] COX, R. J., YOUNG, W. R., and AVIRAM, A., 1972, J. Am. chem. Soc., 94, 3976.
- [16] Cox, R. J., 1972, Mol. Cryst. liq. Cryst., 19, 111.
- [17] ROVIELLO, A., and SRIGU, A., 1982, *Makromol. Chem.*, 183, 409.
- [18] ROVIELLO, A., and SRIGU, A., 1982, Makromol. Chem., 183, 895.
- [19] PERCEC, V., ASAMI, K., and TOMAZOS, D., 1991, Mol. Cryst. liq. Cryst., 205, 67.
- [20] PERCEC, V., SHAFFER, T. D., and NAVA, H., 1984, J. polym. Sci. polym. Lett., 2, 627.
- [21] LIN, C. K., KUO, J. F., and CHEN, C. Y., 2001, Euro. polym. J., 37, 303.
- [22] NUYKEN, O., SCHERER, C., BAINDL, A., BRENNER, A. R., DAHN, U., GARTNER, R., KAISER-ROHRICH, S., KOLLEFRATH, R., and MATUSCHE, P., 1997, Prog. polym. Sci., 22, 93.
- [23] KUMARESAN, S., and KANNAN, P., 2004, J. appl. polym. Sci., 91, 455.
- [24] KUMARESAN, S., and KANNAN, P., 2003, J. polym. Sci. A., 41, 3188.
- [25] TSUTSUMI, O., KITSUNAI, T., KANAZAW, A., SHIONO, T., and IKEDA, T., 1998, *Macromolecules*, **31**, 355.
- [26] XIE, S., NATANSOHN, A., and ROCHON, P., 1993, Chem. Mater., 5, 403.

- [27] RAMESH, C. AHUJA., JURGEN, MAACK., and TACHIBANA, H., 1989, J. Phys. Chem., 99, 9221.
- [28] ANNAKUTTY, K. S., and KISHORE, K., 1989, J. Sci. ind. Res., 48, 479.
- [29] PERRIN, D. D., and ARMAREGO, W. L. F., 1988, *Purification of Laboratory Chemicals*', 3rd Edn (New York: Pergamon Press).
- [30] JAGLOWSKI, A. J., SINGLER, R. E., and ATKINS, E. D. T., 1995 *Macromolecules*, 28, 1668.
- [31] FURNISS, B. S., HANNAFORD, A. J., SMITH, P. W. G., and TATCHELL, A. R., 1994, *Vogel's Textbook* of *Practical Organic Chemistry*; 5th Edn (London: ELBS).
- [32] KISHORE, K., KANNAN, P., and IYANAR, K., 1991, J. polym. Sci. A, 29, 1039.
- [33] TANAKA, C., SASAKI, M., and SHIMADA, T., 2000, US Patent 6 066 757.
- [34] IYANAR, K., PREMA, K., and KISHORE, K., 1988, Chem. Eng. Data., 330, 220.
- [35] LEE-JIN, J. H., JO, B. W., KIM, J. S., ZIN, W. C., and KANG, Y. S., 1999, Acta. Polym., 50, 399.
- [36] SENTHIL, S., and KANNAN, P., 2002, *Liq. Cryst.*, **29**, 1297.
- [37] KELLER, H., and HATZ, R., 1980, in *Handbook of Liquid Crystals* (Weinheim: Verlag Chemie), pp. 1–29.
- [38] GRAY, G. W., and GOODBY, J. W. G., 1984, *Smectic Liquid Crystals–Textures and Structures* (Glasgow and London: Leonard Hill).
- [39] DEMUS, D., DIELE, S., GRANDE, S., and SACKMANN, H., 1983, in *Advances in Liquid Crystals*, edited by G. H. Brown (New York: Academic Press), pp. 1–85.
- [40] WAN, C. H., KUO, J. F., and CHEN, C. Y., 2000, *Liq. Cryst.*, 27, 523.
- [41] GRAY, G. W., and WINSOR, P.A., 1974, *Liquid Crystals and Plastic Crystals* (New York: Ellis Harwood).
- [42] ROZES, L. N., CAMPISTRON, I., THOMAS, M., RYEX, D., and KAJZAR, F., 1998, *Macromol. Chem. Phys.*, **11**, 199.
- [43] TASAKA, T., PETROV, V. F., OKAMOTO, H., MORITA, Y., SUETAKE, K., and TAKENAKA, S., 2002, *Liq. Cryst.*, 29, 1311.
- [44] YU, C., HARRISON, W. T. A., IMRIE, C. T., and RIDER, K. S., 2002, J. mater Chem., 12, 578.
- [45] HIKMET, R. A., ZWERVER, B. H., and LUB, J., 1994, *Macromolecules*, 27, 6722.
- [46] ICHIMURA, K., 2000, Chem. Rev., 100, 1847.