Donor/Acceptor Interaction-assisted Mesophase Formation in Liquid Crystals Containing Azobenzenes and Their Polymers

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Azobenzene-based monomers and their polymers containing donor or acceptor groups at terminal positions have been synthesized. The liquid crystalline (LC) mesophase stability of one type of polymer and mixtures of donor or acceptor substituted polymers have been investigated. Mesophase formation and stability of the mixtures were studied using differential scanning calorimetry (DSC) and a hot-stage optical polarizing microscope (HOPM). The mesophase stability of the mixtures was better than those of the individual components. Binary mixture studies of acceptor monomers (**a**) and donor monomers (**d**) show that the pure low molecular weight compounds did not form any molecular aggregates and failed to show LC properties, whereas the mixture of donor substituted azobenzene and acceptor substituted azobenzene exhibits LC property. In the case of polymers, the individual acceptors (**A**) or donors (**D**) exhibit LC property, and their mixture stabilizes the crystallinity of the mesophase. The results of correlation studies of various proportions of mixtures of **a/d** and **A/D** with regard to LC properties and their mesophase stabilities are presented.

Key words: Azobenzene, Mesophase, Donor-Acceptor Interactions, Liquid Crystals, Polymers

Introduction

The research on the functionalization of liquid crystalline polymers (LCPs) and the induction of liquid-crystalline phases by mixing binary components has been intensively investigated in the past decade. The variation of liquid-crystalline phases [1] and the phase formation from non-liquid-crystalline compounds is the result of the combination of different interactions, *i. e.* mesogenic, charge transfer (CT) and hydrogen bonding effects [2]. In particular, tunable columnar phases utilizing C_2 and C_3 symmetric aromatic donor-acceptor complexes have been reported [3, 4]. In addition, the introduction of π-electron acceptors into homomolecular stacks of π-rich mesogens has been recognized as a means of modifying the phase behavior in liquid crystal materials and is important in the development of P-doped materials for one-dimensional charge transport [5 – 7]. It is also known that mesophases with a layered structure (smectic) could be induced in a nematic liquid crystalline phase through steric [8], electronic [9], and hydrogen bonding [10] interactions. The thermal stability of the nematic phase caused by mixing of 4-*n*-butyl-*N*-(4′-methoxybenzylidene)aniline as an electron donor (**d**) and 4-*n*-pentyl-4′-cyanobiphenyl as an electron acceptor (**a**) has also been investigated [11]. For similar mixtures of electron donor and acceptor components, the thermal stability and the induction of smectic phases were reported by Mastunaga and co-workers [12, 13]. From the viewpoint of fundamental research and applications such as photo- and/or electrofunctional materials, the electronic donor-acceptor interaction has attracted much attention [14, 15]. The main objective of this work is to study the structure and mesophase formation behavior of liquid crystalline phases under the influence of donor and acceptor interactions in binary mixtures. We here describe two polymers *viz.*, poly[(4-methoxyphenylazo-4′-phenyloxyhexyl)methacrylate] as donor (**D**) and poly[(4-nitrophenyl-azo-4′-phenyloxyhexyl) methacrylate] as acceptor (**A**) and their corresponding methacrylated monomers (**a** and **d**) as the low molecular weight counterpart.

Experimental Section

Reagents

4-Methoxyaniline, 4-nitroaniline, potassium hydroxide, 2,2′-azo-bis-isobutyrylnitrile (AIBN) and hydroquinone (Merck, Germany), hexane-1,6-diol (Fluka, Switzerland) were used as supplied. Methanol, ethanol, phenol, THF, dichloromethane and other solvents were purified by

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reported procedures [16]. 6-Bromo-1-hexanol [17, 18], 4-hydroxy-4′-nitroazobenzene, and 4-hydroxy-4′-methoxyazobenzene [19] were prepared according to reported procedures.

Preparation of starting materials

Synthesis of 6-hydroxyhexyloxy-4-phenylazo-4′-nitrobenzene

4-Hydroxy-4′-nitro-azobenzene (0.04 mol, 9.72 g) was dissolved in dry acetone (125 mL), and K_2CO_3 (0.12 mol, 16.57 g) and a catalytic amount (10 %) of KI were added. The mixture was heated to reflux with stirring, 6-bromo-1-hexanol (0.04 mol) was added dropwise to the reaction mixture, and heating was continued at that temperature for 48 h. The reaction mixture was allowed to cool to r. t., filtered, and acetone was removed using a rotary evaporator. The crude product was recrystallized from ethanol; Yield: 65 %. – FTIR (KBr): ν = 3353 (CH_2–OH), 2925, 2887 (C–H str), 1626 (-Ar-NO_2), 1529 (aromatic asym. str), 1272 (Ar-O–CH_2-), and 1253 (C–O–CH_3 str) cm^{-1}. – ^{1}H NMR ($CDCl_3$) δ = 8.37 (d, 2H, Ar-NO_2), 7.94 – 7.99 (m, 4H, Ar-N=N-), 7.03 (d, 2H, Ar-O–CH_2-), 3.59 (t, 2H, Ar-O–CH_2-C), 3.42 (t, 2H, -CH_2–OH). – ^{13}C NMR ($CDCl_3$) δ = 162.9, 156.1, 148.2, 125.6, 123.0, 114.9, 77.4, 63.2.

Synthesis of 6-hydroxyhexyloxy-4-phenylazo-4′-methoxybenzene

6-Hydroxyhexyloxy-4-methoxybenzene was prepared by adopting the procedure described above for 6-hydroxyhexyloxy-4-phenylazo-4′-nitrobenzene: Yield: 55 %. – FTIR (KBr): ν = 3351 (CH_2–OH), 2924, 2888 (C–H str), 1614 (OCH_3), 1523 (aromatic asym. str), 1269 (Ar-O–CH_2-), 1245 (C–O–C), and 844 (C–H out of plane) cm^{-1}. – ^{1}H NMR ($CDCl_3$) δ = 7.84 – 7.89 (m, 4H, Ar-N=N-), 6.97 – 7.01 (m, 4H, aromatic), 4.04 (t, 2H, Ar-O–CH_2), 3.88 (s, 3H, -OCH_3), 3.65 (t, 2H, -CH_2–OH). – ^{13}C NMR ($CDCl_3$) δ = 161.5, 161.2, 147.1, 146.9, 124.3, 114.6, 77.5, 55.5.

Preparation of monomers

*Synthesis of 4′-nitrophenylazo-4-phenyloxyhexyl methacrylate (**a**)*

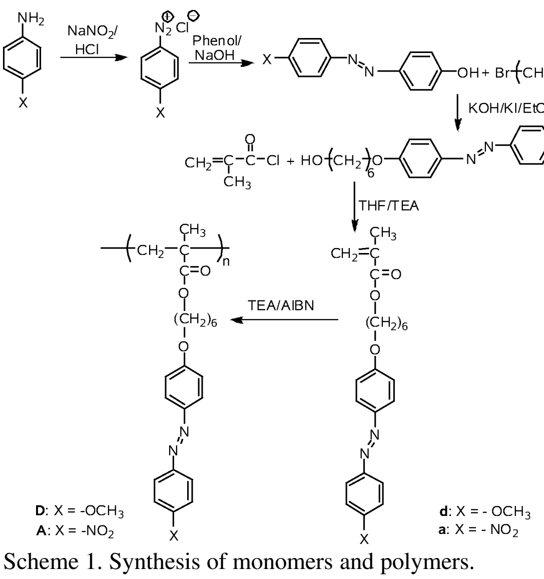
6-Hydroxyhexyloxy-4-phenylazo-4′-nitrobenzene (0.015 mol, 5.16 g), triethylamine (0.015 mol, 2.108 mL), THF (200 mL) and hydroquinone (0.5 mg) were taken in a three-necked flask equipped with stirrer, thermometer and dropping funnel. The mixture was cooled to −5 °C. Methacryloyl chloride (0.015 mol, 1.46 mL) in dry THF (75 mL) was added dropwise with constant stirring at that temperature. The reaction mixture was gradually allowed to attain ambient temperature, and stirring was continued for another 2 h. The amine hydrochloride formed was filtered. The filtrate was thoroughly washed with distilled water, dried over anhydrous sodium sulfate and the solvent evaporated using a rotary evaporator. The crude product was purified by column chromatography over silica gel using a hexane-ethyl acetate mixture; yield: 58 %. – FTIR (KBr): ν = 2925 (methylene chain), 1724 (C=O), 1655 (C=CH_2), 1626 (Ar-NO_2), 1449 (N=N), 1253 (Ar-N=), and 1244 (O–CH_2-). – ^{1}H NMR ($CDCl_3$) δ = 8.37 (d, 2H, Ar-NO_2), 7.94 – 7.99 (m, 4H, Ar-N=N-), 7.03 (d, 2H, Ar-CH_2), 6.10 (t, 1H, =CH_2), 5.55 (t, 1H, =CH_2), 4.16 (t, 2H, Ar-O–CH_2-), 4.04 (t, 2H, CH_2–O-), 1.98 (s, 3H, =C–CH_3). – ^{13}C NMR ($CDCl_3$) δ = 167.6, 162.9, 156.1, 148.2, 146.8, 136.6, 125.6, 114.9.

*Synthesis of 4′-methoxyphenylazo-4-phenyloxyhexyl methacrylate (**d**)*

The monomer **d** was prepared by adopting the procedure described above for **a**. Yield: 52 %. – FTIR (KBr): ν = 2925 (methylene chain), 1724 (–C=O), 1655 (-C=CH_2), 1449 (N=N), 1253 (-Ar-N=), 1244 (Ph-O–CH_2-). – ^{1}H NMR ($CDCl_3$) δ = 7.85 – 7.89 (m, 4H, Ar-N=N-), 6.96 – 7.01 (m, 4H, Ar), 6.09 (s, 1H, =CH_2), 5.54 (s, 1H, =CH_2), 3.87 s, 3H, -OCH_3), 1.93 (s, 3H, = C–CH_3). – ^{13}C NMR ($CDCl_3$) δ = 167.6, 161.5, 147.0, 146.9, 136.59, 125.1, 124.3, 114.6, 68.3, 55.5.

Polymerization

The monomers **a** and **d** were polymerized by free radical polymerization using AIBN as initiator. A representative procedure for the polymerization of **a** is as follows: Monomer **a** and AIBN (5 wt.-%) were dissolved in dry THF, and a gentle stream of nitrogen was passed through the solution. The



Scheme 1. Synthesis of monomers and polymers.

solution was kept in an oil bath at 55 °C for 24 h. Then the solution was cooled and poured into excess methanol to precipitate the polymer. The crude polymer thus obtained was reprecipitated twice using chloroform and methanol to yield polymer **A**. Polymer **D** was prepared by adopting procedure similar to that used for **A** (Scheme 1).

Measurements

The viscosity of the polymers was measured with an Ubbelohde viscosimeter at 30 ± 1 °C using $CHCl_3$ as solvent. The infrared spectra were obtained with a Bruker IFS 66V FT spectrophotometer using KBr pellets. High-resolution ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard. The DSC measurements were performed on a Mettler Toledo STAR^e system and used to scan all synthesized polymers in unsealed aluminum pans as reference. The scans were carried out at a heating rate of 5 °C/min. The liquid crystalline texture of all the polymer mixtures was studied by using a Euromax polarizing microscope equipped with a Linkem HFS91 heating stage and a TP-93 temperature programmer. The samples were made by placing small quantities of the material between two thin glass cover slips, and the anisotropic behavior was observed by heating and/or cooling at a rate of 5 °C/min. The photographs were taken with a Nikon FM10 camera and exposed on a Konica film.

Results and Discussion

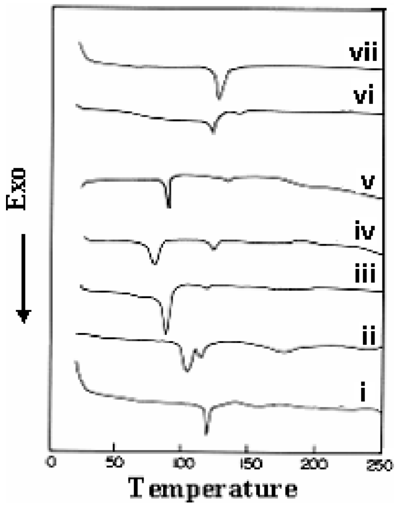


Fig. 1. DSC traces of samples with various proportions of monomers **a** in **d**. i: 0 : 100; ii: 0 : 100; iii: 40 : 60; iv: 50 : 50; v: 60 : 40; vi: 80 : 20; vii: 100 : 0.

Table 1. Transition temperatures (°C) of various compositions of monomers **a** in **d**.

Stoichiometric % of mixture		Transition temperature	
a	**d**	Cr-Smc	Smc-Iso
0	100	118	–
20	80	101	121
40	60	84	123
50	50	78	125
60	40	95	130
80	20	120	134
100	0	138	–

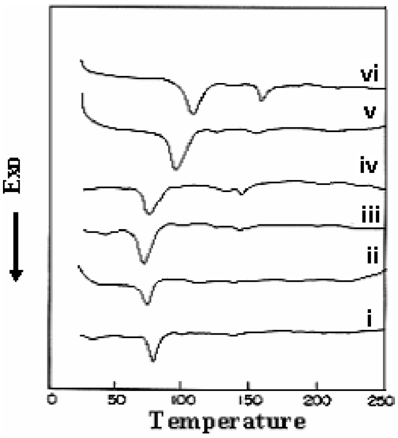


Fig. 2. DSC traces of samples with various proportions of polymer **A** in **D**. i: 0 : 100; ii: 20 : 80; iii: 40 : 60; iv: 60 : 40; v: 80 : 20; vi: 100 : 0.

The structure of the synthesized monomers (**a** and **d**) and polymers (**A** and **D**) was confirmed by various spectral techniques. Seven different stoichiometric mixtures (%) of **a** in **d** (0 : 100, 20 : 80, 40 : 60, 50 : 50, 60 : 40, 80 : 20, 100 : 0) were prepared in THF solution and subsequent evaporation of the solvent. DSC and HOPM were used to evaluate the liquid crystalline phases formed by the mixtures. In the DSC traces, no liquid crystalline behavior was observed either in pure **a** or **d**, but their stoichiometric mixtures displayed liquid crystalline properties (see Fig. 1). The mesophase stability observed with respect to the percentage of **a** and **d** is shown in Fig. 1. Of the seven mixtures, the 50 : 50 mixture displayed significantly enhanced mesophase stability over a wide temperature range (Table 1). The mesophase stability of other mixtures was significantly reduced when compared to the 50 : 50 mixture, with the effect on the melting point being more dramatic than on the clearing points as illustrated in Fig. 4. The melting point of the mixture decreased smoothly with increased percentage of another component up to the 1 : 1 ratio, then the melting point increased

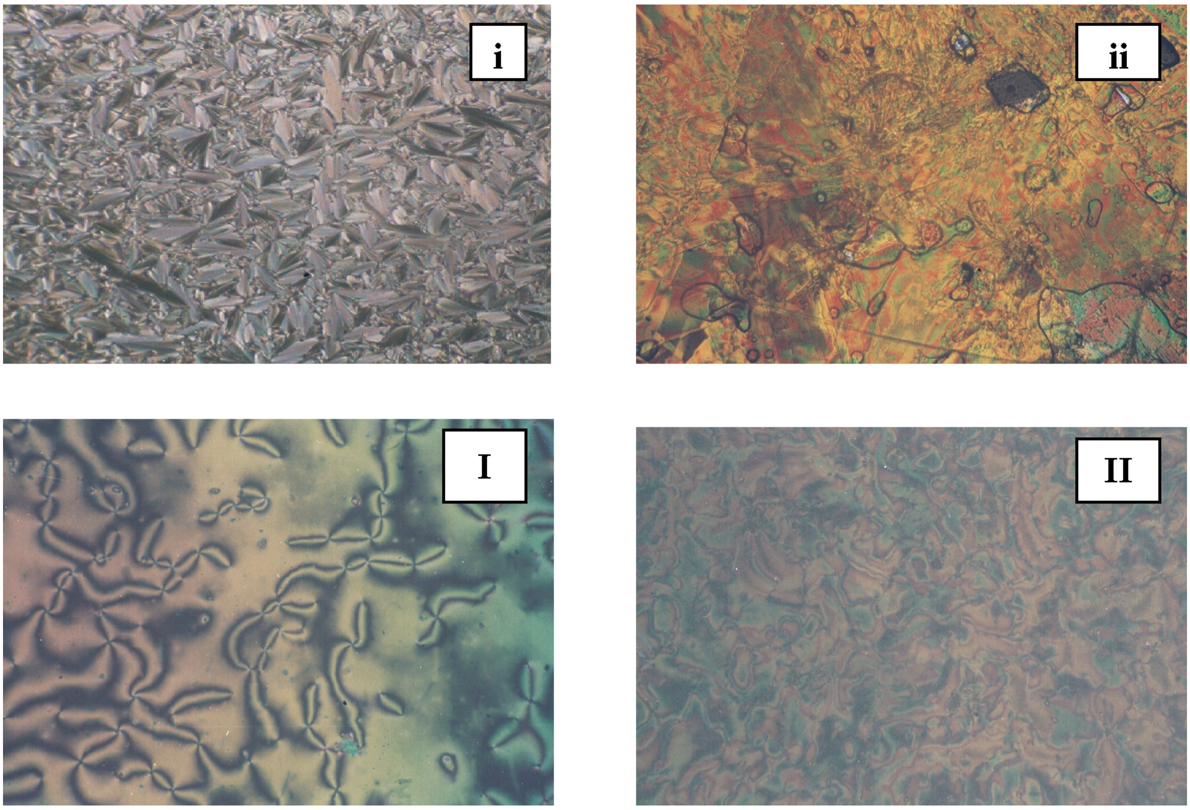


Fig. 3. Representative HOPM photographs of mixtures of monomers and polymers. Above: i: monomer **a** in **d** (50 : 50) exhibiting smectic phases; ii: monomer **a** in **d** (80 : 20) exhibiting nematic phases. Below: polymer **A** in **D** (40 : 60) exhibiting nematic (**I**) and smetic (**II**) phases.

smoothly. These data reveal that the methoxy group present in **a** and the nitro group present in **d** do not have any interaction with nearby molecules, the samples undergoing only one melting transition. Whereas for mixtures the acceptor-donor charge transfer complexation operating between the methoxy-substituted benzene ring and the nitro-substituted benzene ring leads to the formation of mesomorphic aggregates; thus, two endothermic peaks for melting (large enthalpy) and isotropic transition (small enthalpy) are observed.

The bulk optical characteristics of the components **a** and **d** and their mixtures were observed by melting small amounts of the sample between glass cover slips, then cooling slowly (5 °C/min) under a polarizing microscope. Again, the pure forms of either **a** or **d** do not show any liquid crystalline properties, rather they undergo simple melting. Fig. 3 shows the optical texture of the 50 : 50 and 80 : 20 mixtures of **a** in **d**. On cooling from the isotropic phase, the mixtures display a fo-

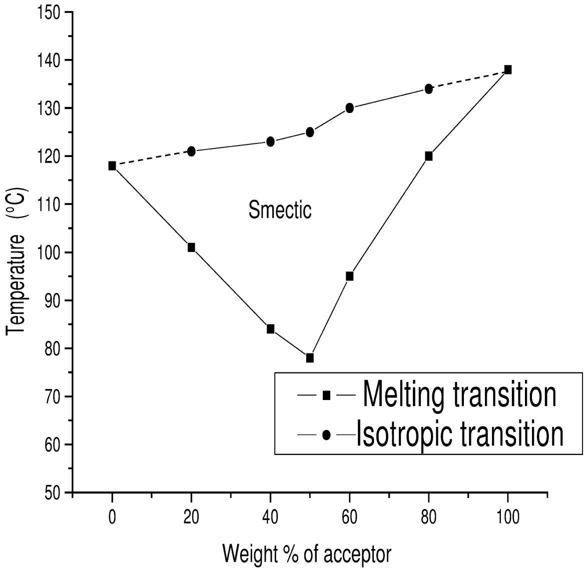


Fig. 4. Binary phase diagrams of the mixtures of monomers **a** and **d**.

Table 2. Transition temperatures (°C) of various compositions of polymer **A** in **D**.

Weight-% of mixture of polymer		Transition temperature		
A	**D**	Cr-N	Smc-N	N-Iso
0	100	76	95	137
20	80	71	111	135
40	60	65	122	130
60	40	69	128	140
80	20	87	120	148
100	0	92	113	153

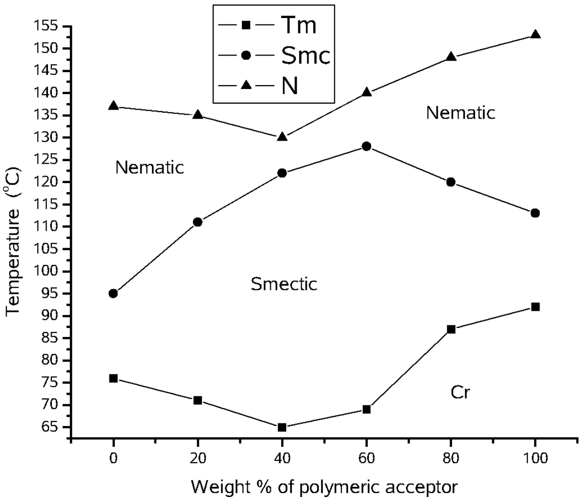


Fig. 5. Binary phase diagrams of the mixtures of polymers **A** and **D**.

cal conic fan structure (Fig. 4) attributed to the smectic A phase.

Similarly, the corresponding monomers were polymerized and the polymers mixed in various proportions (%) (100 : 0, 80 : 20: 60 : 40, 40 : 60, 20 : 80, 0 : 100) of **A** in **D** in THF solution and subsequently evaporating the solvent. Their liquid crystalline properties were analyzed by using DSC and a polarization microscopy. Polymer **A** and **D** exhibit enantiotropic mesomorphism in their pure form as shown in Fig. 2. The mixtures of **A** and **D** display differences in smectic mesophase stability. When the content of acceptor (**A**) in the donor (**D**) mixture is increased, the smectic mesophase stability increases and shows a maximum for 1 : 1 mixtures (Table 2). On further increase, the mesophase stability decreases. Formation of the mesophase in the pure form of either **a** or **b** is due to support rendered by the methacrylic backbone. Increase in mesophase stability in binary mixtures is largely due to donor/acceptor complex formation in the melt. This is further confirmed by observing the phase diagram generated from DSC thermograms of binary mixtures of **A** in **D** shown in Fig. 5. This phase diagram suggests that for the 1 : 1 mixtures of structurally complementary electron donor and electron acceptor mixtures the behavior to alter and/or create a mesophase is different from that of the individual components.

Conclusion

Two types of monomers and polymers containing electron releasing and electron acceptor substituents were synthesized and characterized. Studies of binary mixtures of monomers reveal that a mesophase is formed only in the binary mixture of donor and acceptor substituted species. Mesophase stability largely depends on the composition of the mixtures of donor and acceptor substituted components of the rigid segments. However, the polymers exhibit mesophasic nature even in pure form due to backbone support, and the stability of the mesophase largely resides on the donor-acceptor interactions.

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[1] F. D. Saeva, G. A. Reynolds, L. Kaszczuk, *J. Am. Chem. Soc.* **1982**, *104*, 3524.

[2] H. Bengs, M. Ebert, O. Karthaus, B. Kohne, K. Praefeke, H. Ringsdorf, J. H. Wendorff, R. Wustefeld, *Adv. Mater.* **1990**, *2*, 141.

[3] J. J. Reczek, K. R. Villazor, V. Lynch, T. M. Swager, B. L. Iverson, *J. Am. Chem. Soc.* **2006**, *128*, 7995.

[4] L. Y. Park, D. G. Hamilton, E. A. McGehee, K. A. McMenimen, *J. Am. Chem. Soc.* **2003**, *125*, 10586.

[5] H. Ringsdorf, R. Wustefeld, E. Zerta, Z. M. Ebert, J. H. Wendorff, *Angew. Chem. Int. Ed.* **1989**, *28*, 914.

[6] D. Goldmann, D. Janietz, D. Schmidt, J. H. Wendorff, *Angew. Chem. Int. Ed.* **2000**, *39*, 1851.

[7] M. Weck, A. E. Eunn, K. Matsumoto, G. W. Coates, W. B. Lobkovky, R. H. Grubbs, *Angew. Chem. Int. Ed.* **1999**, *38*, 2741.

[8] B. Ziemnicha, A. de Vries, I. W. Doane, S. L. Arora, *Mol. Cryst. Liq. Cryst.* **1986**, *132*, 289.

[9] S. Diele, G. Pelz, W. Weissflog, D. Demus, *Mol. Cryst. Liq.Cryst.* **1998**, *3*, 1947.

[10] L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071.

[11] J. W. Park, C. S. Bank, M. M. Labes, *J. Am. Chem. Soc.* **1975**, *97*, 4378.

[12] K. Araya, Y. Matsunaga, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 989.

[13] K. Araya, Y. Matusunaga, *Mol. Cryst. Liq. Cryst.* **1981**, *67*, 153.

[14] N. Koide, S. Ogura, Y. Aoyama, *Mol. Cryst. Liq. Cryst.* **1991**, *198*, 323.

[15] W. T. Ford, M. Bautista, M. Zhao, R. J. Reeves, R. Powell, *Mol. Cryst. Liq. Cryst.* **1991**, *198*, 351.

[16] D. D. Perrin, W. L. F. Armarigo, *Purification of Laboratory Chemicals*, Pergamon Press, New York, **1998**.

[17] S. Kumaresan, P. Kannan, *J. Appl. Polym. Sci.* **2004**, *91*, 455.

[18] E. Vedejs, M. J. Arnost, J. P. Hagen, *J. Org. Chem.* **1979**, *44*, 3230.

[19] K. Rameshbabu, P. Kannan, R. Velu, P. Ramamurthy, *Liq. Cryst.* **2005**, *32*, 823.