Hydrogen-Bonding-Mediated Generation of Side Chain Liquid Crystalline Polymers from Complementary Nonmesogenic Precursors[†]

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ABSTRACT: Liquid crystalline phases in macromolecular assemblies have been generated by utilizing complementary hydrogen-bonding interaction between functional vinyl polymers and rigid aromatic derivatives. While neither of the individual components is mesogenic, the resulting assemblies exhibited liquid crystalline behavior. Poly((2-dimethylamino)ethyl methacrylate) and poly(2-hydroxyethyl methacrylate) were chosen as the functional polymer backbone bearing proton-accepting and proton-donating groups, respectively. As rigid aromatic units, 4-hydroxybiphenyl, *trans*-4-hydroxystilbene, 4′-methoxy-4-hydroxyazobenzene, and 4-pyridylbenzoate were used. All the polymeric assemblies were obtained as transparent films and they exhibited liquid crystalline properties. Hydrogen-bonding in these assemblies was evident from their FTIR and ^{13}C NMR spectra. The liquid crystalline behavior of these hydrogen-bonded polymeric assemblies was established by DSC, polarizing microscopy, and X-ray diffractometry. Phase diagrams of the mixtures revealed the dependence of the liquid crystalline transitions on the composition of such binary mixtures. Generation of liquid crysalline phases in these hydrogen-bonded polymeric assemblies derived from non-liquid crystalline precursors without the mediation of a flexible spacer is unprecedented. Furthermore, this approach offers a relatively simple route to prepare functional materials with controlled molecular architecture from readily accessible and simpler precursors.

Introduction

Side chain liquid crystalline polymers are opening up exciting vistas as functional and high-performance materials.[1,2] These materials are traditionally prepared by covalently linking a rigid organic molecule to a polymeric backbone via a spacer of 4–6 carbon atoms. Use of secondary interactions to assemble relatively simpler molecules into complex functional macromolecular assemblies having long-range two- and three-dimensional orders has been a novel variation toward designing novel functional materials.[3–5] Generation of liquid crystalline behavior in such molecular assemblies obtained by using hydrogen bonding and other secondary interactions has been reported in the recent literature. Lehn and co-workers[6] demonstrated the generation of mesomorphic molecular assemblies by the complementary hydrogen-bonding-directed polyassociation of nonmesogenic bifunctional heterocyclic chiral and achiral organic compounds such as 2,6-diaminopyridine, tartaric acid (D and L species), and uracil derivatives. Use of chiral hydrogen-bonding components such as tartaric acid derivatives in these systems led to formation of helically wound supramolecular liquid crystalline strands.[6c] Stabilization of mesophases over extended temperature ranges by means of intermolecular hydrogen bonding between mesomorphic aromatic, low molecular weight components such as 4-butoxybenzoic acid and *trans*-4-[(4-ethoxybenzoyl)-oxy]-4′-stilbazole has been reported by Fréchet et al.[7,8] More recently, this group has reported some newer architectures of hydrogen-bonded liquid crystalline assemblies using different 4-alkoxybenzoic acid derivatives as the hydrogen bond donors and bipyridine derivatives as hydrogen acceptors.[9]

In the case of macromolecular liquid crystals, Ringsdorf et al.[10] were among the first to demonstrate the stabilization of discotic-columnar mesophases by introducing electron-rich functional groups such as 2,4,7-trinitrofluorenone and (2,4,7-trinitrofluoren-9-ylidene)-malonodinitrile. The individual functionalized polymers did not possess mesomorphic properties. The charge transfer complexes thus formed were found to be responsible for the generation of the columnar nematic phases as confirmed by a detailed X-ray analysis. Independently, Fréchet and co-workers[11–15] have observed extended mesomorphic phases in the cases of acrylic and siloxane backbone polymers having functional groups capable of hydrogen bonding with a variety of low molecular weight organic mesogens. In these systems, the pendant hydrogen-bonding sites attached to the polymer chain are generally isolated from the amorphous backbone by a spacer of 4–6 methylene units. Some of the typical low molecular weight mesogens used in their study were *trans*-stilbazole ester derivatives. In one case,[13] a mixture of siloxane polymer bearing carbobenzoxy functional groups (hydrogen bond donor) and an optically active acceptor, (*S*)-(−)-*trans*-4-(2-methoxypropyloxy)-4′-stilbazole, produced the hydrogen-bonded smectic chiral complexes exhibiting ferroelectric properties.

These literature reports pertaining to the design of noncovalently bound polymeric liquid crystalline systems converge toward the traditional concept of using a flexible carbon atom spacer between the rigid aromatic core compound and the flexible polymer backbone. This approach also poses some restrictions on the utility of the concept on two counts. First, the procedure involved in the preparation of such materials is as cumbersome as the preparation of the conventional side chain liquid crystalline polymers. Second, only a limited choice of materials is available since it is likely to be restricted to only those materials which can be functionalized via a carbon skeleton spacer. Generating a polymeric liquid crystalline phase from two components, neither of which is liquid crystalline itself, therefore, continues to be a challenging task.

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The present paper describes a new strategy for the preparation of side chain liquid crystalline materials by means of site-specific hydrogen bonding. Utilization of complementary hydrogen bonding between two nonliquid crystalline species, viz., flexible, aliphatic polymers and rigid aromatic phenolic derivatives, for generating a liquid crystalline phases has been demonstrated in this case. A striking feature of this approach is the generation of a liquid crystalline phase without the mediation of any significant flexible carbon atom spacer. The presence of a liquid crystalline phase in these polymeric assemblies has been established by NMR and Fourier transform infrared (FTIR) spectroscopy and thermal analysis. Textures of these mesophases have been confirmed and identified by polarizing optical microscopy and X-ray diffractometry.

Experimental Section

Materials. Unless stated otherwise, all the chemicals were of reagent grade and were obtained from Aldrich or Janssen Chemicals. Whenever required, the reagents were purified either by recrystallization or by distillation prior to use. The solvents were purified following standard purification methods.

Instrumentation and Analyses. Melting points were determined on a Büchi melting point apparatus. FTIR measurements of all the samples were carried out on a Perkin-Elmer 1600 FTIR spectrophotometer having a resolution of 4 cm^{-1}. An average of 64 scans were taken to record the spectra. ^1H and ^{13}C NMR spectra were obtained using a GE 300 spectrometer operating at 300 MHz for ^1H nuclei and 75 MHz for ^{13}C nuclei. The number of scans accumulated to record the spectra was varied depending upon the sample type, sample concentration, and solvent used. Typically, an average of 32 scans and 10 000 scans were taken to record ^1H and ^{13}C spectra, respectively. DSC measurements were made on a Perkin-Elmer DSC-7 instrument. The samples were scanned with a heating rate of 10 °C/min. Polarizing optical microscopic investigations were carried out with a Leitz Laborlux optical microscope equipped with a hot stage. A 40× magnification was used to observe the textures of the annealed samples. X-ray diffraction measurements were carried out on a Philips PW-1840 diffractometer with a 2 kW Ni-filtered Cu Kα X-ray source. The samples were annealed by heating to their isotropization temperatures followed by cooling to room temperature prior to X-ray diffraction studies.

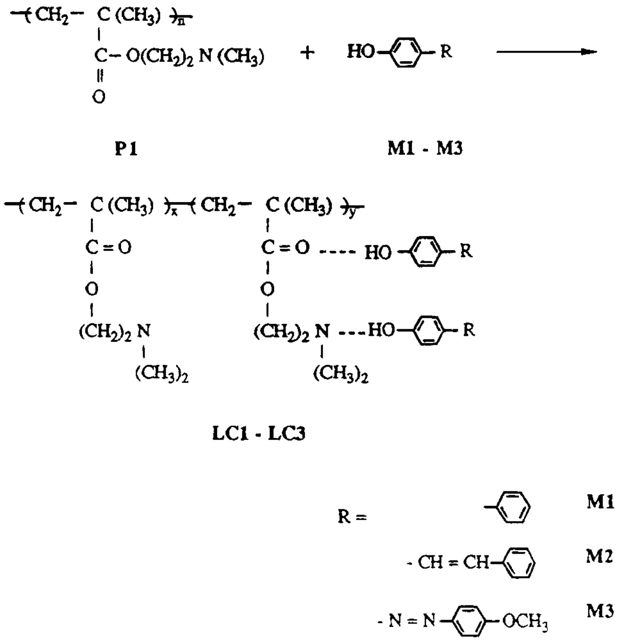
Rigid Aromatic Core Compounds. 4-Hydroxybiphenyl (**M1**) and *trans*-4-hydroxystilbene (**M2**) were obtained from Aldrich and Janssen Chemicals, respectively.

4′-Methoxy-4-hydroxyazobenzene (M3). This compound was prepared by the diazotization reaction between 4-methoxyaniline and phenol following the procedure reported in the literature[16] and was purified by recrystallization from methanol.

4-Pyridylbenzoate. To an aqueous solution of 0.5 mmol of the sodium salt of 4-hydroxypyridine (obtained by reacting equimolar quantities of sodium hydroxide and 4-hydroxypyridine) was added 0.65 mmol of benzoyl chloride slowly at room temperature with vigorous stirring. After addition was complete, the reaction mixture was allowed to stir at room temperature for an additional 4 h. Subsequently, it was extracted with diethyl ether (3 × 50 mL), and the combined organic phase was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was recrystallized from methanol, giving light yellow crystals: yield 65%; mp 106 °C. IR (Nujol): 2975, 1690, 1603, 1585, 997 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 128.0, 130.0, 133.7, 150.0, 173.0.

Polymer Synthesis. In this study poly(2-(dimethylamino)ethyl methacrylate) (**P1**) and poly(2-hydroxyethyl methacrylate) (**P2**) were used as the proton-accepting and proton-donating flexible polymer components, respectively. Both polymers were synthesized by free-radical polymerization. The inhibitor and stabilizer-free monomers were used for the polymer synthesis. The solution polymerization of these monomers was carried out in 1,4-dioxane at 78 °C using 2,2′-azobis(isobutyronitrile) as the free-radical initiator. The viscous polymer solution thus formed was diluted with fresh 1,4-dioxane to a concentration of about 1% (w/v) and filtered through a 0.4 μm Teflon filter into another single-necked flask. The solution was freeze-dried to a constant weight. The white flakes of polymer thus obtained were stored (sealed) under an argon atmosphere till used.

Scheme 1



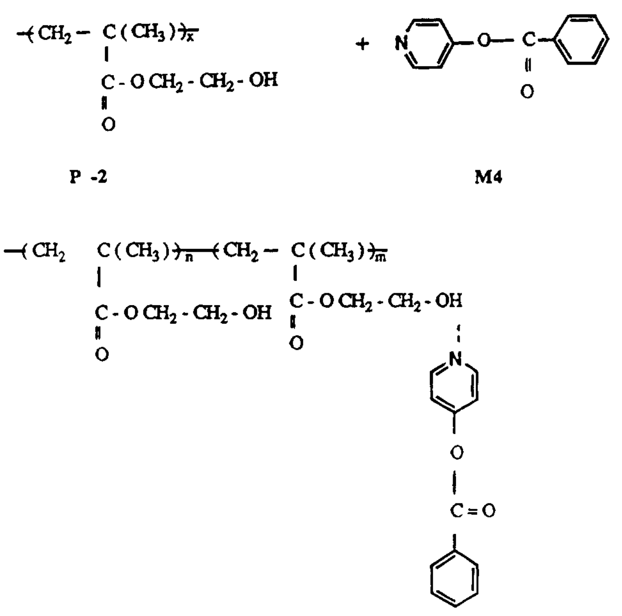
Preparation of Hydrogen-Bonded Macromolecular Assemblies. The hydrogen-bonded polymeric complexes (**LC1**–**LC4**) were prepared by mixing methanolic solutions of the rigid core organic compounds and polymers in appropriate molar proportions. Complete removal of methanol was ensured, initially by slow evaporation followed by vacuum drying for 2 weeks at 45 °C.

Results and Discussion

Preparation and Spectroscopic Investigation of Hydrogen-Bonded Macromolecular Assemblies. Formation of these macromolecular assemblies was promoted by the site-specific hydrogen bonding between the complementary hydrogen-bonding functional groups of the polymers and rigid aromatic compounds. This process of hydrogen-bonding-directed molecular recognition leading to the generation of the functional assemblies is illustrated in Schemes 1 and 2 using polymers **P1** and **P2**, respectively. The compositions of the various assemblies thus prepared are summarized in Table 1.

In the case of polymer **P1**, its side chain ester substituent possesses two potential proton-accepting sites, *viz.*, the ester carbonyl and the tertiary amino group. On the other hand, polymer **P2** possesses the primary hydroxyl group as the sole proton-donating site. In general, literature reports on the preparation of side chain liquid crystalline polymers involves a spacer arm of 4–6 methylene carbons between the polymer chain and the rigid armatic cores. This holds good for both covalent and hydrogen-bonded systems. On the other hand, the polymer systems utilized in our study consist of no significant spacer (**P1**) or a very short two-carbon spacer (**P2**). To elucidate the hydrogen-bonding patterns in the functional assemblies based on these polymers, infrared spectroscopy and ^{13}C NMR spectroscopy were employed. In the case of polymer **P1**-based

Scheme 2



LC4

Table 1. Summary of the Mesomorphic Properties of the Hydrogen-Bonded Liquid Crystalline Polymers and Their Precursors[a]

		transition temp (K)		
entry	sample	T_1	T_2	*d*-spacing[b] (Å)
1	**P1**	313 (T_g)		
2	**P2**	353 (T_g)		
3	**M1**	438 (T_m)		
4	**M2**	463 (T_m)		
5	**M3**	473 (T_m)		
6	**M4**	379 (T_m)		
7	**P1/M1 (LC1)**	401 (LC)	439 (I)	4.9
8	**P1/M2 (LC2)**	399 (LC)	428 (I)	5.2
9	**P1/M3 (LC3)**	421 (LC)	442 (I)	4.7
10	**P2/M4 (LC4)**	313 (LC)	325 (I)	5.1

[a] The liquid crystalline polymer contains 25 mol % of the rigid compound with respect to repeating monomer units. [b] Based on the X-ray scattering data; T_g = glass transition, T_m = melting point, LC = liquid crystalline melting temperature, and I = isotropic.

systems, shifting of the infrared stretching vibration bands of the ester carbonyl (1737 cm^{-1}) and tertiary amino C−N (1068 cm^{-1}) bonds of the pure polymer to 1724 and 1053 cm^{-1}, respectively, upon mixing with the proton-donating molecules attests to the formation of hydrogen bonding at both sites. These features of the IR spectra using **M1** as the rigid core are presented in Figure 1. Similarly, shifting of hydroxyl stretching vibration bands of the free phenolic derivatives (**M1**, **M2**, and **M3**) from *ca.* 3600 to *ca.* 3400 cm^{-1} upon complexation with polymer further supports the formation of strong intermolecular hydrogen bonding between the two components. In the case of macromolecular assembly **LC4** based on **P2** and **M4**, formation of such hydrogen bonding can be visualized from their ^{13}C NMR spectra. The aromatic and carbonyl carbon regions of **M4** and its complex with **P2** are shown in Figure 2. As can be seen from these spectra, the α-carbon atom of the pyridine ring (C=N) is shifted downfield from 150 to 153 ppm upon complexation with proton-donating polymer **P2**. This suggests that the site-specific hydrogen bonding has taken place at the basic nitrogen atom of 4-pyridylbenzoate. Moreover, formation of transparent films from these polymeric complexes also supports complete miscibility of the aliphatic polymers and the aromatic rigid compounds over a broad concentration range.

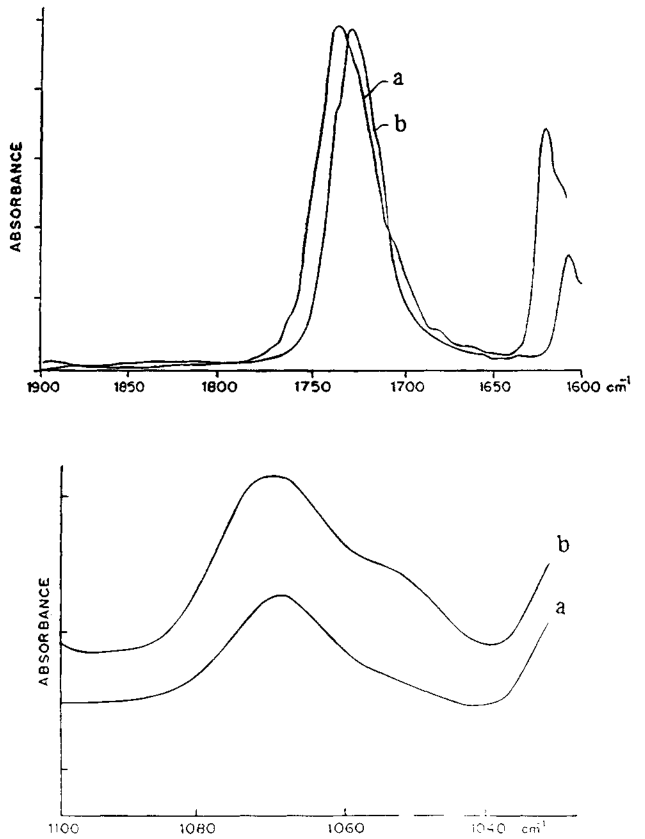


Figure 1. FTIR spectra of the carbonyl (top) and C−N bond (bottom) stretching of (a) polymer **P1** and (b) macromolecular assembly **LC1**.

Thermal, Microscopic, and X-ray Analysis of the Macromolecular Assemblies. Thermal transitions associated with these hydrogen-bonded macromolecular complexes and their individual constituents were investigated to study their mesomorphic behavior. DSC thermograms of the macromolecular assembly **LC3** and its associated components **P1** and **M3** are shown in Figure 3. The thermogram of **LC3** reveals the appearance of mesophases as the sample is heated from the glassy to the isotropic region. The aliphatic acrylic polymers and the rigid aromatic derivatives do not have any propensity to form liquid crystalline phases on their own. This is evident from the absence of any such mesomorphic transitions in their thermograms. A similar type of thermal behavior was observed with other assemblies. The absence of the thermal transitions due to the individual polymers (**P1** and **P2**) and the rigid aromatic compounds supports the occurrence of strong hydrogen bonding between the two components in the macromolecular assemblies. Thus, it appears that the macromolecular complexes possess entirely different characteristics compared to their constituent components. The thermal transitions of these macromolecular complexes lie between the glass transition temperatures of the respective polymers and the melting points of the rigid aromatic compounds. Hence, these transitions conceivably arise from the mesophases, thus attributing to the generation of liquid crystalline properties in these macromolecular complexes. Although, in some cases the liquid crystalline transitions were not observed during the cooling cycle, the mesomorphic transitions were observed during the second heating of

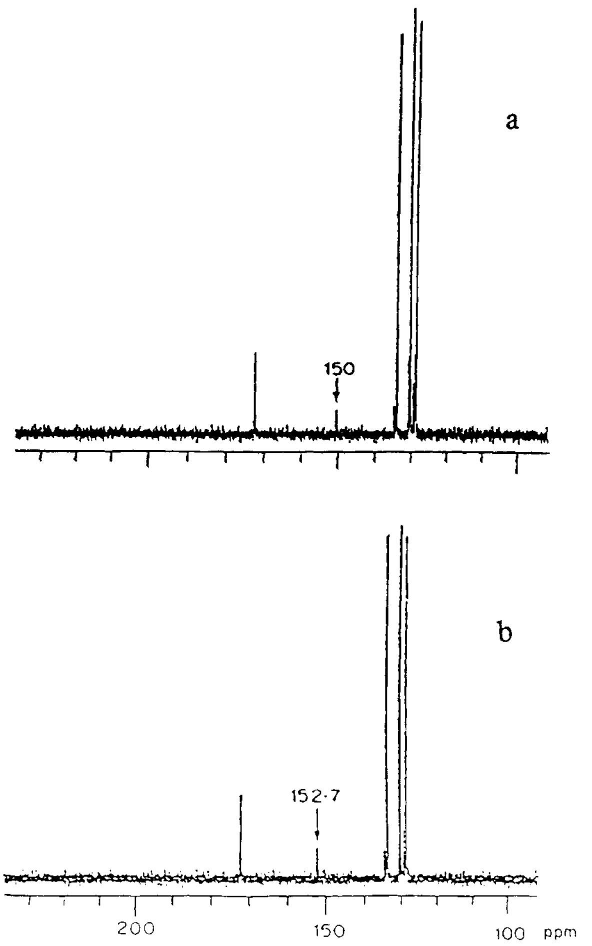


Figure 2. ^{13}C NMR spectra of (a) **M4** and (b) its complex **LC4**.

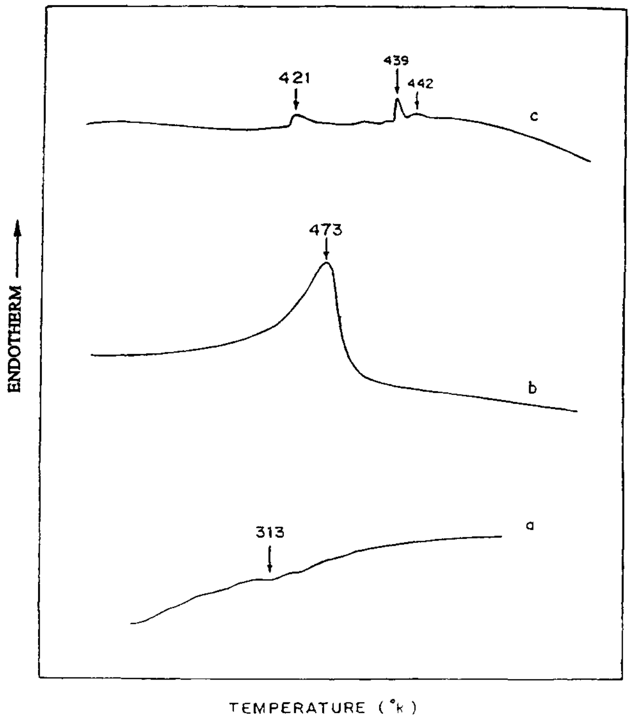


Figure 3. DSC thermograms of (a) polymer **P1**, (b) rigid aromatic compound **M3**, and (c) their complex **LC3**.

the samples. Furthermore, the presence of the liquid crystalline phases in the annealed samples, as observed by polarizing microscopy and X-ray diffractometry (*vide infra*) at room temperature, suggests that the mesophases are frozen in the annealed matrices. These observations lend support to the reversibility of these mesomorphic transitions.

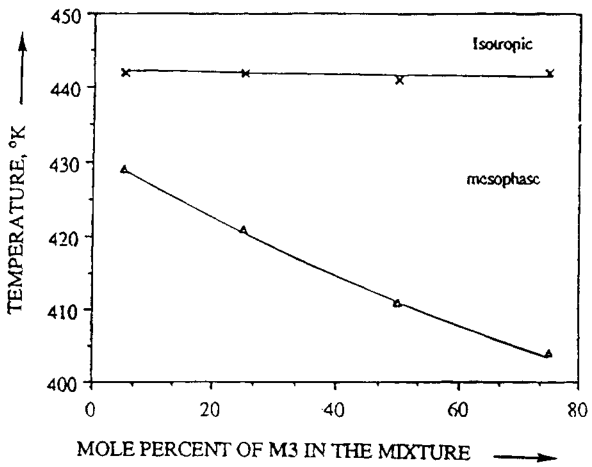


Figure 4. Binary phase diagram of the complexes formed between polymer **P1** and the rigid aromatic compound **M3**.

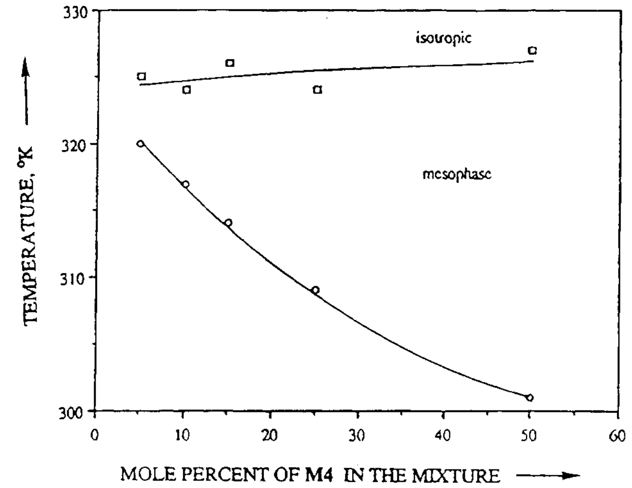


Figure 5. Binary phase diagram of the complexes formed between polymer **P2** and the rigid aromatic compound **M4**.

To ascertain the compositional effects on the mesomorphic properties of these macromolecular assemblies, a number of such complexes based on **P1** and **M3** were prepared by varying the concentration of the latter in the binary mixture. The results on the thermal properties of these mixtures are illustrated by the phase diagram in Figure 4. These composition-dependent thermal data of the polymeric liquid crystalline assemblies suggest that the mesophase is stable over a wider temperature range at higher concentration of the rigid core molecules in the mixture. A similar type of behavior was exhibited by the system based on **P2** and **M4**, too (see Figure 5). These observations may be attributed to the higher degree of cooperative intermolecular interactions and to the paired mesogen effect[17] at the higher concentration of hydrogen-bonded species. Such composition-dependent enhancement in the thermal transition temperatures due to the enhanced degree of intermolecular hydrogen-bonded interactions has been reported in the case of miscible polymer blends, also.[18]

To further confirm the mesomorphic nature of these assemblies and to identify their textures, hot stage polarizing microscopy was employed. For the microscopic study, all the samples were annealed from their isotropization temperatures prior to analysis. The

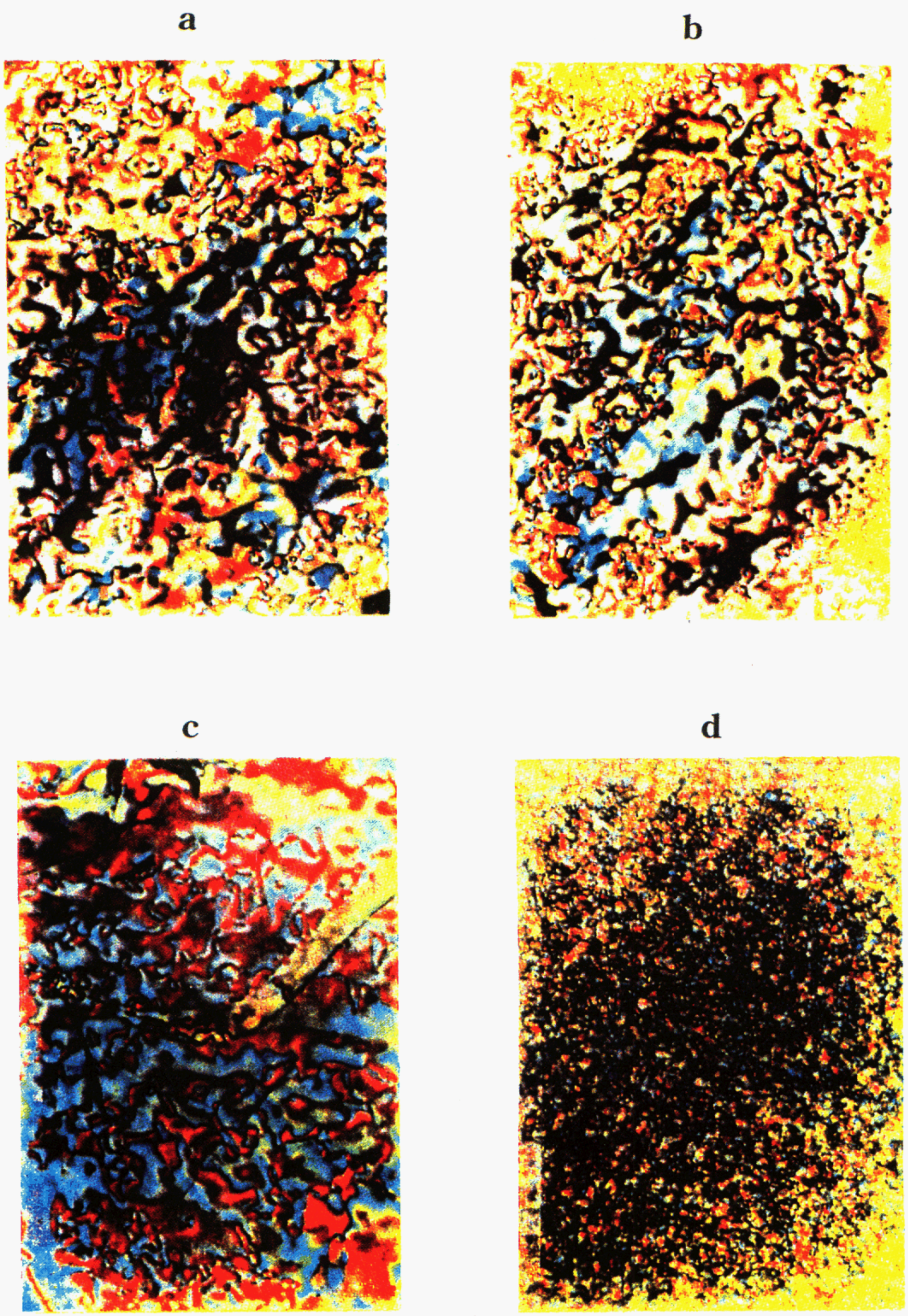


Figure 6. Polarized photomicrographs of the annealed hydrogen-bonded polymeric complexes: (a) **LC1**; (b) **LC2**; (c) **LC3**; (d) **LC4**.

photomicrographs of the various liquid crystalline assemblies are shown in Figure 6. The liquid crystalline nature of all these polymeric assemblies is clearly evident from their birefringent patterns. The threadlike textures in most of the cases suggest the presence of nematic phases. Although polarizing microscopy provides evidence to support the existence of liquid crystalline phases, a detailed X-ray analysis would enable such phases to be confirmed and identified more precisely.

Several reports on the analysis of textures of liquid crystalline materials using polarizing microscopy exist in the literature.[19] However, X-ray diffractometry has been found to be a more reliable technique for ascertaining the morphology of a liquid crystalline polymer.[20] A texture is normally correlated with the degree of order. For instance, the smectic phase is associated with long-range order (two- or three-dimensional order) and hence is usually characterized by a crystalline-like d-spacing pattern (d > 20 Å) in its X-ray diffraction pattern. On the other hand, such higher level ordering seldom occurs in nematic liquid crystals. In the majority of the cases of nematic side chain liquid crystalline polymers, X-ray analysis is usually restricted to recording the absence of small-angle reflections. Therefore, it has been concluded that most of the nematic side chain liquid crystalline polymers are characterized with a one-dimensional type of ordering (cf. smectic liquid crystalline polymers).[20] However, in the oriented samples of nematic liquid crystals, the X-ray diffraction patterns are characterized with lower values of *d*-spacings. Generally, the values of *d*-spacings in the case of nematic phases are of the order of 4–5 Å.[21] X-ray diffraction studies of glassy polymers are usually carried out on annealed samples.[13] Since the mesophase(s) of these liquid crystalline assemblies are likely to be frozen in the glassy polymer matrix, X-ray diffraction measurements on all the samples were performed in their annealed state. X-ray diffraction patterns of all the liquid crystalline assemblies in this study (**LC1**–**LC4**) showed the presence of only one crystalline peak corresponding to a *d* value of *ca.* 4.7 Å. The X-ray diffraction data thus obtained are summarized in Table 1. It can be concluded from this study that all the polymeric assemblies appear to possess nematic phases.

This X-ray diffraction result in the context of our thermal analysis data appears to be somewhat confusing. We observe multiple thermal transitions in the DSC thermograms of **LC2** and **LC3**, and by the usual convention the lower temperature transitions are ascribed to a more organized phase (smectic phase) and the higher temperature transitions to the lesser organized phases such as nematic phases. At this stage, since very little is known about the exact structure of these phases, we can only propose that there may be more than one type of mesomorphic phase present in these systems. Furthermore, melting transitions due to breaking of hydrogen bonds will also appear to be similar to any of those we observe in these cases. However, the enthalpy (peak area) associated with such transitions is generally higher than that of any of the liquid crystalline melting transitions. Therefore, it is harder to propose the existence of any higher order phases (*viz.*, smectic) in these hydrogen-bonded polymeric liquid crystalline assemblies. Nevertheless, we have relied on not only the thermal analysis data but a combination of polarizing microscopy and X-ray diffraction results to establish the presence of liquid crystalline phases in these polymeric assemblies.

These results on liquid crystalline behavior can be explained on the basis of the formation of polymeric supramolecular assemblies by selective molecular recognition between the polymer and the rigid core aromatic compound. The resulting supramolecules (**LC1**–**LC4**) may be considered as copolymers consisting of hydrogen-bonded and nonbonded monomers. The structure of the resulting copolymer appears to be similar to that of the conventional side chain liquid crystalline polymer where the polymer backbone acts as the flexible carrier attached to rigid core molecules via hydrogen bonding. Our systems may appear to be akin to the urazole-modified polybutadiene systems discovered by Stadler and co-workers.[22] Such urazole-modified polybutadiene-based systems have also been described as supramolecules possessing long-range orientational orders as evident from their thermal and X-ray diffraction data.

With regard to the mechanism of the generation of mesophases in these hydrogen-bonded macromolecular assemblies, the orientation of the rigid molecules to the liquid crystalline state is possibly achieved by breaking and re-forming hydrogen bonds during the annealing process. At this stage, however, no definite mechanism can be offered to explain these results. Nevertheless, these initial results on the generation of liquid crystalline polymers from nonliquid crystalline precursors without the mediation of a flexible spacer are unprecedented and interesting *per se*.

Conclusions

We have developed a methodology to use intermolecular hydrogen bonding for generating liquid crystalline phases in polymeric systems from nonmesogenic precursors. The idea of using intermolecular hydrogen bonding to generate long-range orientation in polymers, as demonstrated in this study, is exciting not only because of its intrinsic fundamental merit but also because of the fact that the novel materials generated through such strategies will have a wide spectrum of applications such as in information storage, molecular switches, and display devices. This new approach offers a relatively simple method to prepare novel functional materials with controlled molecular architecture from readily accessible and simpler precursors. The methodology also offers the potential to tune the properties of these materials by introducing different functional groups for specific applications.

References and Notes

(1) McArle, C. *Side Chain Liquid Crystal Polymers*; Blackie: Glasgow, 1989.
(2) Ringsdorf, H.; Wusterfeld, R. *Philos. Trans. R. Soc. London A* **1990**, *330*, 95.
(3) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *29*, 1304.
(4) Lindsey, J. S. *New J. Chem.* **1990**, *15*, 153.
(5) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312.
(6) (a) Brienne, M.-J.; Gabard, J.; Lehn, J.-M.; Stibor, I. *J. Chem. Soc., Chem. Commun.* **1989**, 1868. (b) Fouquey, C.; Lehn, J.-M.; Levelut, A.-M. *Adv. Mater.* **1990**, *5*, 254. (c) Gulik-Krzywicki, T.; Fouquey, C.; Lehn, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 163.
(7) Kato, T.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1989**, *111*, 8533.
(8) (a) Kato, T.; Wilson, P. G.; Fujishima, A.; Fréchet, J. M. J. *Chem. Lett.* **1990**, 2003. (b) Kato, T.; Adachi, H.; Fujishima, A.; Fréchet, J. M. J. *Chem. Lett.* **1992**, 2659.
(9) Kato, T.; Fréchet, J. M. J.; Wilson, P. G.; Saito, T.; Uryu, T.; Fujishima, A.; Jin, C.; Kaneuchi, F. *Chem. Mater.* **1993**, *5*, 1094.
(10) Ringsdorf, H.; Wusterfeld, R.; Zerta, E.; Ebert, M.; Wendorf, J. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 914.
(11) Kato, T.; Fréchet, J. M. J. *Macromolecules* **1989**, *22*, 3819.
(12) Kumar, U.; Kato, T.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6630.
(13) Kumar, U.; Fréchet, J. M. J.; Kato, T.; Ujiie, S.; Timura, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1531.
(14) Kato, T.; Kihara, H.; Uryu, T.; Fujishima, A.; Fréchet, J. M. J. *Macromolecules* **1992**, *25*, 6836.
(15) Kumar, U.; Fréchet, J. M. J. *Adv. Mater.* **1992**, *4*, 664.
(16) Kapitza, H.; Zentel, R. *Makromol. Chem.* **1988**, *189*, 1793.
(17) Kuschel, F.; Madicke, A.; Diele, S.; Utschick, H.; Ringsdorf, H. *Polym. Bull.* **1990**, *23*, 373.
(18) De Meftahi, M. V.; Fréchet, J. M. J. *Polymer* **1988**, *29*, 477.
(19) Demus, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: Weinheim, 1978.
(20) Shibaev, V. P.; Plate, N. *Adv. Polym. Sci.* **1984**, *60/61*, 173.
(21) Ober, C. K.; Jin, J.; Lenz, R. W. *Adv. Polym. Sci.* **1984**, *59*, 135.
(22) De Lucca Freitas, L.; Stadler, R. *Macromolecules* **1987**, *20*, 2478.

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