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Structures and Properties of Supramolecular Liquid-Crystalline Side-Chain Polymers Built through Intermolecular Hydrogen Bonds

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ABSTRACT: The design, structure, and properties of supramolecular liquid-crystalline side-chain polymers are described. In particular, we show how several simple H-bonding building blocks can be used for the formation of various liquid-crystalline structures. Poly[4-(6-(acryloyloxy)hexyl- and -undecyloxy)benzoic acid] (P*m*OBA; $m = 6, 11$) have been employed as polymer components. A variety of supramolecular mesogenic "copolymers" based on one polymeric component have been designed and prepared by simple self-assembly. Cooperation of the hydrogen bond and electron donor−acceptor interactions results in the mesophase stabilization for the "copolymeric" supramolecular structures of P*m*OBA with a mixture of *trans*-4-methoxy-4′-stilbazole (1OSz) and *trans*-4-cyano-4′-stilbazole (SzCN) or *trans*-4-nitro-4′-stilbazole ($SzNO_2$). When a bifunctional molecule, 4,4′-bipyridine (BPy), is used as a component for "copolymeric" structures, supramolecular copolymeric networks based on P*m*OBA have been formed by self-assembly. The networks exhibit stable mesomorphic behavior and reversible phase transitions due to the dynamics of the hydrogen bonds.

Introduction

It has recently been recognized that molecular recognition processes between different molecular species through noncovalent interactions are advantageous for the design of functional molecular aggregates such as liquid crystals[1−7] as well as crystalline materials[8] and assemblies in aqueous media.[9] For liquid-crystalline polymers, new types of supramolecular materials have been built through specific intermolecular interactions such as hydrogen bonds,[1−7,10−22] ionic,[23,24] charge-transfer,[25] and ion−dipolar[26] interactions. The use of hydrogen bonds has potential for functional material design because biopolymers such as nucleic acids, polypeptide, and cellulose have hydrogen-bonding groups. The formation and dissociation of hydrogen bonds for these polymers play key roles for biological processes. Supramolecular side-chain mesogenic polymers[1,2,5,6,10−19] as well as network,[20,21] main-chain polymeric,[3,7,22] and low molecular weight complexes[27−32] have been prepared through intermolecular H bonds. Figure 1 shows schematic illustration of conventional (A) as well as supramolecular (B and C) side-chain mesogenic polymers. While conventional liquid-crystalline polymers consist of only covalent bonds (structure A),[33−35] the supramolecular polymeric liquid-crystalline complex may contain an H-bonded mesogenic core (structure B)[1,2,5,6] or an H-bonded linker moiety connecting the mesogenic molecule to the polymer (structure C).[14,16,17] A supramolecular host−guest polymer which is a new variation of structure C has been recently described[14] as well as several other H-bonded structures.[18,19] A great variety of hydrogen bonds have been used to build the supramolecular mesogenic structures. These include systems consisting of carboxylic acid/pyridine,[1,2] carboxylic acid/2,6-diaminopyridine,[6] uracil/2,6-diaminopyridine,[3,7] carboxylic acid/pyridine *N*-oxide,[15] phenol/tertiary amine,[18] and carboxylic acid/tertiary amine.[19] Mesomorphic miscible polymer blends have been prepared through a phenol/pyridine interaction.[36] Nonmesogenic supramolecular blends derived by the interaction between diaminotriazine and maleimide have also been reported.[37] A diol mesogen capable of hydrogen bonding has been used to form side-chain liquid-crystalline polymers.[38]

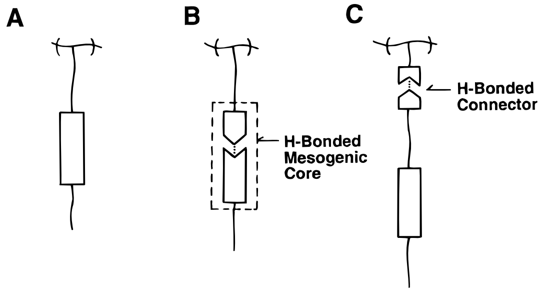

Figure 1. Schematic structures of liquid-crystalline side-chain polymers: (A) conventional type; (B) and (C) supramolecular types.

We have previously reported H-bonded polymeric complexes consisting of poly[4-(6-(acryloyloxy)hexyloxy)benzoic acid] (P6OBA) and *trans*-4-alkoxy-4′-stilbazole (*n*OSz).[10] All of these complexes are obtained by self-assembly processes and display stable liquid-crystalline behavior. The advantage of these supramolecular polymers is the simplicity of the formation of various copolymeric structures. Copolymers of any desired composition can be prepared from one polymer sample by simple mixing.

In this report, we show how the combination of several molecular building blocks shown in Chart 1 can be used to construct a variety of new liquid-crystalline

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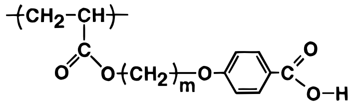
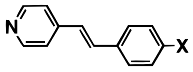
Chart 1

H-Bond Donor Polymer



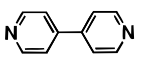
P6OBA : m=6
P11OBA : m=11

H-Bond Acceptor



SzCN : X=-CN
SzNO$_2$: X=-NO$_2$
1OSz : X=-OCH$_3$
6OSz : X=-O(CH$_2$)$_5$CH$_3$

H-Bond Bifunctional Acceptor



BPy

homopolymeric and copolymeric structures through self-assembly involving intermolecular hydrogen bonds. The structures and properties of complexes such as supramolecular "copolymers" with electron donor/acceptor interactions and networks are reported.

Experimental Section

Preparation of Poly[4-(6-(acryloyloxy)hexyloxy)benzoic acid] (P6OBA) and Poly[4-(11-(acryloyloxy)undecyloxy)benzoic acid] (P11OBA). The synthesis of P6OBA ($[\eta] = 0.21$ in DMF at 30 °C) is reported in a previous paper.[10] P11OBA was prepared by the same method for P6OBA. Yield of P11OBA: 91%. $[\eta] = 0.23$ (in DMF at 30 °C).

Preparation of *trans*-4-Substituted-4′-Stilbazoles. Stilbazole derivatives, *trans*-4-methoxy-4′-stilbazole (1OSz),[10,39] *trans*-4-cyano-4′-stilbazole (SzCN), and *trans*-4-nitro-4′-stilbazole (SzNO$_2$) were synthesized by condensation reactions involving 4-picoline and 4-substituted benzaldehydes. 1OSz: yield 14%; mp 134 °C. ^{1}H NMR of 1OSz (CDCl$_3$, 27 °C) δ 8.54, 7.33 (pyridyl), 7.48, 6.92 (phenyl), 7.26, 6.87 (−CH=CH−), 3.82 (methyl). ^{13}C NMR (CDCl$_3$, 27 °C) δ 150.0, 144.9, 120.6 (pyridyl), 160.2, 128.9, 128.3, 114.2 (phenyl), 132.6, 123.7 (−CH=CH−), 55.3 (methyl). SzCN: yield 43%; mp 139 °C. ^{1}H NMR of SzCN (CDCl$_3$, 27 °C) δ 8.63, 7.40 (pyridyl), 7.69, 7.64 (phenyl), 7.30, 7.13 (−CH=CH−). ^{13}C NMR (CDCl$_3$, 27 °C) δ 150.2, 143.4, 121.0 (pyridyl), 140.4, 132.5, 127.3, 111.7 (phenyl), 131.0, 129.5 (−CH=CH−), 118.6 (−C≡N). SzNO$_2$: yield 37%; mp 164 °C. ^{1}H NMR of SzNO$_2$ (CDCl$_3$, 27 °C) δ 8.64, 7.32 (pyridyl), 8.26, 7.69 (phenyl), 7.35, 7.18 (−CH=CH−). ^{13}C NMR (CDCl$_3$, 27 °C) δ 150.4, 143.3, 121.0 (pyridyl), 147.4, 142.4, 127.4, 124.1 (phenyl), 130.6, 130.4 (−CH=CH−).

Preparation of Hydrogen-Bonded Complexes. All hydrogen-bonded complexes examined in the present study were prepared by the evaporation method described in the previous paper.[2,10,11] Copolymeric complexes containing two different stilbazoles were prepared from a polyacrylate and two dissimilar stilbazoles maintaining the exact 1:1 stoichiometry between the carboxylic acid unit of the polyacrylate and the pyridine unit of the stilbazoles.

Characterization. DSC measurements were performed on a Mettler DSC 30. Heating and cooling rates were 10 °C/min in all cases. For polymeric complexes, samples heated once to 150 °C and cooled to 0 °C were used for all measurements. First-order transitions (crystalline−liquid crystalline, liquid crystalline−isotropic) were taken at the maximum point of the endothermic peaks. Glass transition temperatures (T_g) were read at the midpoint of the change in the heat capacity. For monomeric complexes, once molten, samples were used for measurements and the onset points of the endotherms were taken as the transition temperatures. NMR spectra were recorded on a JEOL GX-270 spectrometer with TMS as the internal standard. The intrinsic viscosity of the polymers was measured on DMF solutions with an Ubbelohde viscometer at 30 °C. X-ray diffraction measurements were carried out by a Rigaku X-ray Rad 2B system using Ni-filtered Cu Kα radiation. Samples placed on a Mettler FP 52 hot stage were used for the X-ray measurements.

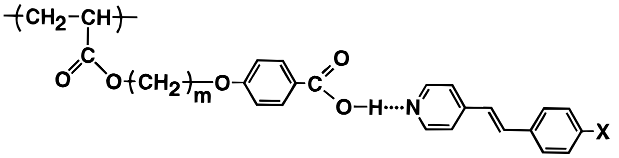


Figure 2. Structure of supramolecular liquid-crystalline side-chain polyacrylates built by hydrogen bonding.

Table 1. Thermal Properties of H-Bonded Side-Chain LC Polymeric Complexes

1:1 H-bonded complex	phase transition behavior[a]								
P6OBA−SzCN					G	38	S$_A$	200 (16.2)	I
P11OBA−SzCN			G	35	S$_1$	58 (8.6)	S$_A$	209 (17.5)	I
P6OBA−SzNO$_2$	G	55	S$_1$	95 (10.9)	S$_2$	153 (9.1)	S$_A$	209 (8.8)	I
P11OBA−SzNO$_2$	G	40	S$_1$	92 (15.4)	S$_2$	168 (2.4)	S$_A$	212 (12.3)	I
P6OBA−1OSz			G	38	S$_1$	74 (9.2)	S$_A$	194 (9.5)	I
P11OBA−1OSz			G	38	S$_1$	63 (6.6)	S$_A$	190 (15.6)	I
P6OBA−6OSz	G	38	S$_1$	64 (1.6)	S$_B$	124 (4.9)	S$_A$	192 (20.2)	I
P11OBA−6OSz	G	46	S$_1$	69 (3.6)	S$_B$	121 (3.4)	S$_A$	199 (19.6)	I

[a] Transition temperatures (°C) and enthalpies of transition (J/g, in parentheses). G: glassy; S: smectic; I: isotropic.

Results and Discussion

Supramolecular Mesogenic Homopolymer. The self-assembly processes of H-bond donors and monofunctional H-bond acceptors shown in Chart 1 were used to obtain supramolecular "homopolymeric" complexes given in Figure 2. The polyacrylates of P6OBA and P11OBA with hexamethylene ($m = 6$) and undecamethylene ($m = 11$) spacers, respectively, were employed as H-bonding donor polymers (Chart 1). The stilbazoles of SzCN and SzNO$_2$ with polar groups were complexed with the polymers. The liquid-crystalline behavior of a series of homopolymeric complexes of P6OBA and *trans*-4-alkoxy-4′-stilbazole (*n*OSz) reported in a previous paper[10] was also examined by X-ray measurements. The thermal properties of the polymeric complexes are listed in Table 1. These complexes exhibit stable mesomorphic behavior. In particular, the complexes containing strong polar cyano and nitro groups display isotropization temperatures in excess of 200 °C, which is higher than those of complexes with alkoxy groups. The stronger dipolar interactions by cyano and nitro groups may stabilize the mesophases for this H-bonded system. The widest temperature range of the smectic A phase is seen for P6OBA−SzCN. The highest T_i is achieved for P11OBA−SzNO$_2$, which exhibits ordered smectic and smectic A phases. Slight increases in isotropization temperatures are observed for these polymer complexes when the hexamethylene spacer is replaced by the undecamethylene spacer, except for P*m*OBA−1OSz. Alkoxy and cyano end groups in the para position of the mesogenic core have been widely used for conventional liquid-crystalline side-chain polyacrylates.[33−35] The

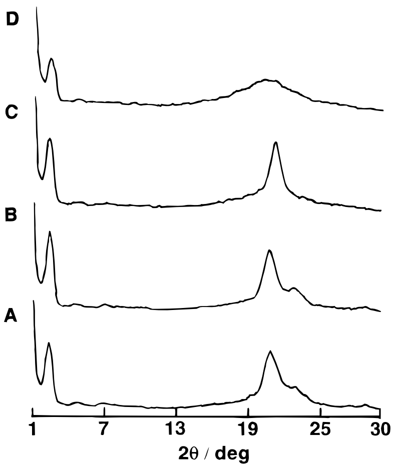


Figure 3. X-ray diffraction patterns of liquid-crystalline polyacrylate P6OBA−6OSz: (A) 30 °C; (B) 50 °C; (C) 80 °C; (D) 140 °C.

isotropization temperatures of cyano-containing polymers are generally higher than those of the corresponding methoxy-containing polymers.[33−35] The self-assembled polymeric complexes prepared in this study show a similar tendency. The nitro group is not often used for the end group of the conventional side-chain mesogenic polymers because it may inhibit polymerization. However, since the nitro group is a useful functionality for active molecules designed for use in nonlinear optics,[33,40] it is usually introduced in conventional systems by the chemical modification of polymers based on the polystyrene backbones[40,41] or of polymers obtained by polycondensations.[42,43] In contrast, in the hydrogen-bonded system, the nitro group is easily incorporated into the polyacrylate side chain by a simple self-assembly process.

Infrared spectra have been obtained for P6OBA−SzCN to compare the state of the hydrogen bond. It was expected the hydrogen bond of P*m*OBA−SzCN and P*m*OBA−SzNO$_2$ would be weaker than that of P*m*OBA−*n*OSz because the cyano group decreases the basicity of the stilbazole. The O−H stretching band of P6OBA−SzCN is observed at 2486 cm^{-1}, which is 13 cm^{-1} higher than that for P6OBA−1OSz. This shift suggests that the hydrogen bond becomes weaker by the replacement with the cyano group. However, despite this weaker strength of the hydrogen bond resulting from the decrease of the basicity of the pyridyl moiety by the electron-withdrawing group, the mesophase remains stable. Cooperation of the H-bonding and the dipolar interactions in the self-assembled structures may stabilize the mesophase. It is expected that mesophase stability can be correlated to the sum of the synergistic effects of H-bonding and associative dipolar interactions in the self-assembled structures.

In our earlier report on several polymeric complexes P6OBA−*n*OSz with alkoxy end groups, we had reported that crystalline phase region still remained to some extent at temperatures that exceeded the glass transition temperature (T_g).[10] However, a more detailed analysis by X-ray diffraction has now shown that ordered smectic phases are formed above T_g for the complexes from P6OBA and *n*OSz and that no crystalline phase exists above T_g. X-ray diffraction patterns of P6OBA-6OSz for each phase obtained on heating are shown in Figure 3. The length of the fully stretched conformation of the side chain of the complex is estimated to be 37.0 Å. One sharp inner reflection at 37.4 Å and three peaks at 4.28, 3.90, and 3.11 Å are seen at 30 °C (Figure 3A). A similar pattern is observed at 50 °C above the glass transition temperature, which suggests that no crystalline phase exists and an ordered smectic phase (S$_1$) like a smectic E phase exists between 35 and 64 °C (Figure 3B). Two sharp reflections at 38.4 and 4.2 Å are observed at 100 °C. One sharp inner peak at 38.7 Å and one diffused halo at 4.4 Å are observed at 140 °C (Figure 3D). This phase is a smectic A phase because of the results of the miscibility test and these X-ray patterns.[10] The phase between 64 and 124 °C (Figure 3C) is assigned to be a smectic B phase because the two sharp reflections exist and the layer spacing is almost the same as that of the smectic A phase.

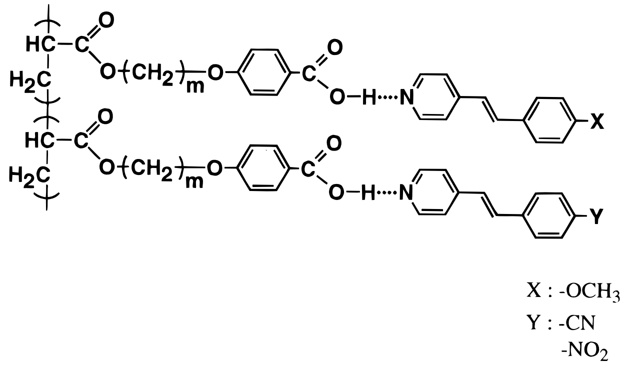


Figure 4. Structure of supramolecular liquid-crystalline “copolymers”.

For P6OBA−1OSz, a layer spacing of the smectic A phase at 160 °C is 37.1 Å, which is larger than those of P6OBA−SzCN and P6OBA−SzNO$_2$. The layer spacings measured by X-ray diffraction of the smectic A phase for P6OBA−SzCN and P6OBA−SzNO$_2$ are 33.7 and 31.8 Å at 165 °C, respectively. These results indicate that the overlapping of the hydrogen-bonded mesogenic cores in the smectic layer for the complexes containing cyano and nitro groups is larger than that of the methoxy-containing complex. In contrast, for conventional side-chain polymers containing methoxy and nitro end groups, overlapping of the aromatic mesogens for the methoxy-containing polymer is larger than is observed for the nitro-containing polymer.[41] This difference may be caused by the difference of the electronic state between the hydrogen-bonded and covalently-bonded cores.

Supramolecular “Copolymeric” Structure. To obtain random “copolymers”, the polyacrylate with the pendant carboxylic acid can be simply complexed with a mixture of two or more different H-bond acceptors. In this study, stilbazoles containing electron donor and acceptor end groups have been used as components (Figure 4). Table 2 gives thermal properties of copolymeric complexes with $x = 0.5$. Figure 5 shows the phase diagrams of liquid-crystalline copolymers of P6OBA and a mixture of SzCN and 1OSz, which will be denoted as P6OBA−(SzCN/1OSz). Higher T_i and T_m values are observed for the copolymeric complexes than for the corresponding homopolymeric complexes as a result of the additional electron donor−acceptor interactions between H-bonded side-chain mesogens. DSC thermograms of homopolymeric and copolymeric ($x = 0.5$) complexes of P6OBA or P11OBA with SzCN and 1OSz as H-bond acceptors are shown in Figure 6. The T_i of P6OBA−(SzCN/1OSz) is higher than those of P6OBA−SzCN and P6OBA−1OSz by 11 and 17 °C, respectively. For copolymeric complexes ($x = 0.5$), the melting transition peak becomes sharper when compared to the homopolymeric P6OBA−1OSz, while P6OBA−SzCN shows no crystallization behavior. Furthermore, the

Table 2. Thermal Properties of Supramolecular Side-Chain Liquid-Crystalline Copolymeric Complexes

H-bonded complex	phase transition behavior[a]								
P6OBA−(1OSz/SzCN) ($x = 0.5$)	G	40	S_1	84 (10.6)	S_A	211 (16.5)	I
P11OBA−(1OSz/SzCN) ($x = 0.5$)	G	42	S_1	75 (10.5)	S_A	209 (19.8)	I
P6OBA−(1OSz/SzNO$_2$) ($x = 0.5$)	G	34	S_1	83 (8.8)	S_A	213 (15.5)	I
P11OBA−(1OSz/SzNO$_2$) ($x = 0.5$)	G	41	S_1	75 (12.5)	S_A	214 (20.6)	I

[a] Transition temperatures (°C) and enthalpies of transition (J/g, in parentheses). G: glassy; S: smectic; I: isotropic.

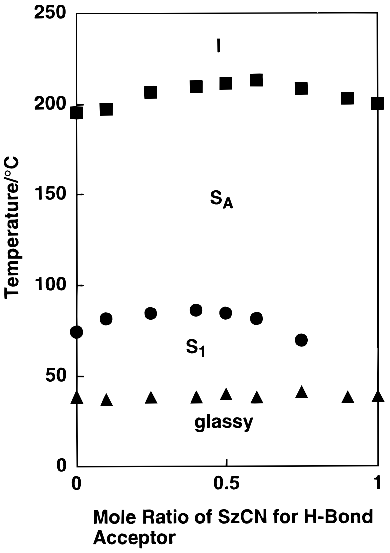


Figure 5. Phase diagram of the supramolecular "copolymeric" complexes derived from P6OBA and a mixture of 1OSz and SzCN.

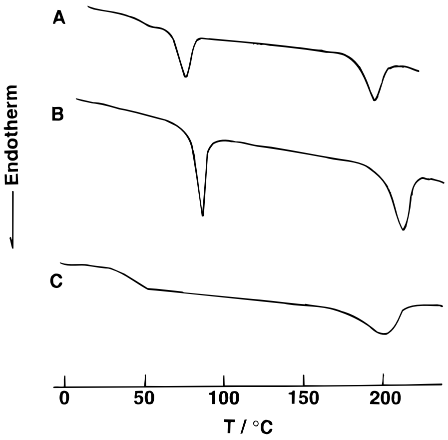


Figure 6. DSC thermograms of hydrogen-bonded liquid-crystalline polyacrylates: (A) "homopolymeric" complex P6OBA−1OSz; (B) "copolymeric" complex of P6OBA and the 1:1 mixture of 1OSz and SzCN; (C) "homopolymeric" complex P6OBA−SzCN.

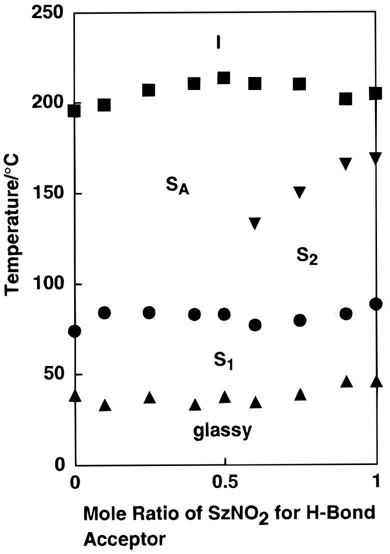


Figure 7. Phase diagram of the supramolecular "copolymeric" complexes derived from P6OBA and a mixture of 1OSz and SzNO$_2$.

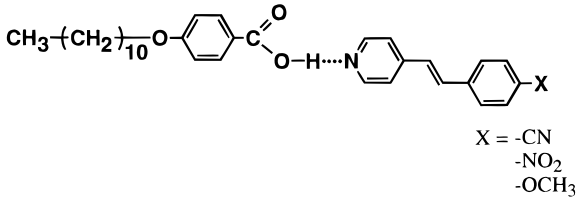


Figure 8. Structure of low molecular weight H-bonded complexes.

enthalpy changes of isotropization are larger than those of homopolymeric complexes P*m*OBA−SzCN and P*m*OBA−1OSz. The phase diagram of liquid-crystalline copolymers of P6OBA and a mixture of SzNO$_2$ and 1OSz shown in Figure 7 also exhibits stabilization and a wider temperature range of the smectic A phases. For conventional polymers (Figure 1, structure A), the mesophase stabilization due to electron donor−acceptor interaction is also observed.[35,41,44,45] In the present case, synergistic cooperation of the hydrogen bond and electron donor−acceptor interactions leading to the mesophase stabilization is seen for the "copolymeric" supramolecular assemblies. No mesophase stabilization is observed for "copolymeric" polyacrylate P6OBA−(1OSz/6OSz) containing only electron donor end groups.[10] X-ray measurements performed with the complex of P6OBA−(SzNO$_2$/1OSz) ($x = 0.5$) show a layer spacing of 33.2 Å at 160 °C.

Effect of Dipolar Groups on Low Molecular Weight Complexes. Low molecular weight complexes (Figure 8) with structures related to the polymers examined in this study have been prepared to compare the effect of dipolar interactions with that observed for polymeric complexes. The three stilbazoles, SzNO$_2$, SzCN, and 1OSz, were complexed with 4-(undecyloxy)benzoic acid (11OBA). The transition temperatures of the resulting supramolecular complexes and their mixtures are given in Table 3. It is seen that the isotropization temperature of the equimolar mixture of 11OBA−(1OSz/SzCN) and 11OBA−(1OSz/SzNO$_2$) is higher than that of the averages of those of the individual homocomplexes. However, the isotropization temperatures do not exceed those of *homo*complexes, while for the polymeric complexes the T_i values of the copolymers are higher than those of either of the homopolymers. These results suggest that the side-chain polymeric structure enhances electron donor−

Table 3. Thermal Properties of H-Bonded Monomeric Complexes

H-bonded complex	phase transition behavior[a]						
11OBA−1OSz	K	83 (106.3)	S_A	148 (−)[b]	N	150 (5.8)	I
11OBA−SzCN			K	98 (60.0)	S_A	163 (19.0)	I
11OBA−SzNO$_2$	K	86 (16.6)	S_1	142 (13.4)	S_A	166 (10.0)	I
11OBA−(1OSz/SzCN) ($x = 0.5$)			K	80 (43.0)	S_A	163 (21.9)	I
11OBA−(1OSz/SzNO$_2$) ($x = 0.5$)			K	74 (67.6)	S_A	164 (22.6)	I

[a] Transition temperatures (°C) and enthalpies of transition (J/g, in parentheses). G: glassy; S: smectic; I: isotropic. [b] The S_A−N transition is overlapped with isotropization peak.

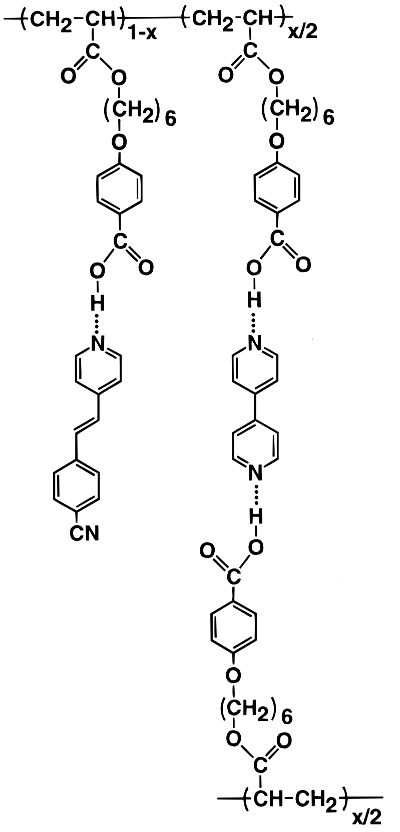


Figure 9. Structure of supramolecular cross-linked polymers obtained from P6OBA and a mixture of SzCN and BPy.

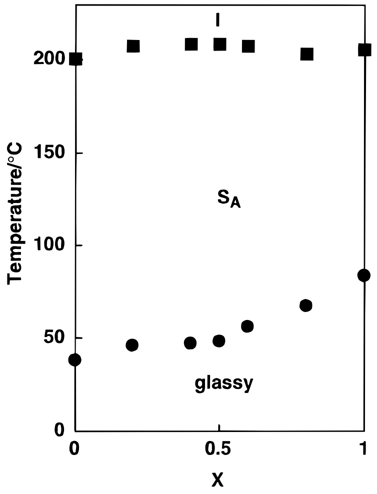


Figure 10. Phase diagram of the supramolecular polymeric complexes derived from P6OBA and a mixture of SzCN and BPy.

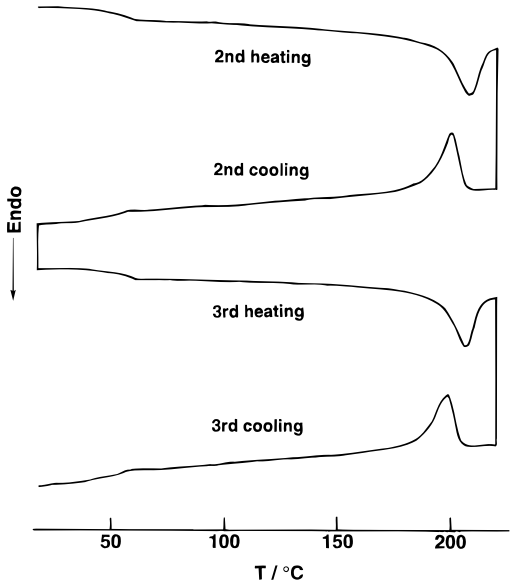


Figure 11. DSC thermograms of liquid-crystalline polymeric networks of P6OBA−(SzCN/BPy) ($x = 0.6$) on repeated heating and cooling run.

acceptor interaction which contributes to mesophase stabilization in the self-assembling H-bonded system.[47,48]

Supramolecular Liquid-Crystalline Networks. It has been shown that a wide temperature range of a smectic A phase is observed for P6OBA−SzCN. In order to self-assemble a supramolecular H-bonded network, a bifunctional H-bonding acceptor 4,4′-bipyridine (BPy) that leads to cross-linked structures was added to the P6OBA−SzCN system, keeping the 1:1 stoichiometry of the donor and acceptor, as shown in Figure 9. Figure 10 shows the phase diagram of the complexes of P6OBA and a mixture of SzCN and BPy. It is seen that these networks show smectic A phases over a wide range of temperature. For example, the cross-linked complex of P6OBA−(SzCN/BPy) ($x = 0.6$) exhibits a smectic A phase from 56 to 206 °C. The enthalpy change at isotropization of the complex is 15.5 J/g, while those of side-chain polymer P6OBA−SzCN and fully cross-linked polymer P6OBA−BPy are 16.2 and 24.9 J/g, respectively. It is noteworthy that the smectic A phase is observed near room temperature for the networks. We have reported that P6OBA−(6OSz/BPy) exhibits smectic B and A phases.[20] For this cyano-containing complex, no smectic B phase is observed and the smectic A phase is extended to a lower temperature range. Reversible phase transitions are observed for H-bonded networks of P6OBA−BPy and P6OBA−(6OSz/BPy), which are fully and partially cross-linked complexes, respectively. Figure 11 shows the DSC thermograms of the H-bonded complex P6OBA−(SzCN/BPy) ($x = 0.6$) on repeated heating and cooling scans. Reversible phase transitions are seen in these thermograms. Partial dissociation of the hydrogen bonds may occur in the isotropic phases.[20,27c,d] In these complexes, the dynamic nature of the hydrogen bonds is important for the induction of the mesomorphic phases.

Anisotropic networks that have either high or low covalent cross-linking density have attracted attention because of potential for applications in electronics and optics.[49−51] The self-assembled mesogenic networks prepared in this study may be interesting for applications as they show unique properties which are different from those of conventional covalently-bonded polymer networks[49−51] because the formation and the dissociation of these hydrogen bonds can occur in response to changes in their environment or as a result of external stimuli.[49]

Conclusion

For the supramolecular mesogenic materials reported here, a variety of structures with controlled liquid crystallinity can be simply obtained by self-assembly processes from only one polymer sample and several molecular components. This versatility would be useful for the design of functional molecular systems.

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