Molecular Self-Assembly of Liquid Crystalline Side-Chain Polymers through Intermolecular Hydrogen Bonding. Polymeric Complexes Built from a Polyacrylate and Stilbazoles

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ABSTRACT: A new type of liquid crystalline side-chain polyacrylate has been built through selective intermolecular hydrogen bonding between H-bond donor and acceptor moieties. Polyacrylate P6OBA with a 4-oxybenzoic acid pendant group attached to its side chain through a hexamethylene spacer has been prepared for use as an H-bond donor polymer. A series of *trans*-4-alkoxy-4′-stilbazoles *n*OSz having the linear alkyl chain C_nH_{2n+1} (n = 1–8 and 10) have been used as H-bond acceptors. Self-assembly of the polymer and the stilbazole results in the selective formation of thermotropic side-chain polymeric complexes having well-defined molecular structures. A mesogenic structure that induces a stable mesophase is formed in the polymer side chain through the single hydrogen bond between the benzoic acid pendant group of the polymer and the pyridyl unit of the stilbazole. All polymeric 1:1 complexes exhibit stable and homogeneous smectic A phases. For example, the complex from P6OBA and 2OSz shows a smectic A phase between 89 and 200 °C. The isotropization and melting temperatures show odd–even effects for the terminal alkoxy group. Monomeric 1:1 complexes having the same type of H-bonded mesogen as that of the polymeric complexes have been prepared from 4-(hexyloxy)benzoic acid (6OBA) and the series of stilbazoles. For example, the monomeric 1:1 complex from 6OBA and 2OSz melts at 112 °C and exhibits smectic A and nematic phases. The smectic A–nematic and nematic–isotropic transitions are observed clearly at 128 and 166 °C, respectively. A binary phase diagram of polymeric complex P6OBA–2OSz and monomeric complex 6OBA–2OSz shows complete miscibility over the entire range of composition.

Introduction

Intensive work has been focused on the structure–property relationships of liquid crystalline side-chain polymers[1–6] because they have great potential for various functional materials. For typical mesogenic side-chain polymers, mesogens are attached to polymer backbones through aliphatic flexible spacers. In general, only covalent bonding has been used to build the well-defined molecular structures of the conventional side-chain liquid crystalline polymers.

Our strategy has been to utilize a noncovalent interaction, e.g., hydrogen bonding as a powerful tool to create novel structures of molecular self-assemblies.[7–11] Hydrogen bonding is one of the key interactions for the process of molecular aggregation and recognition in nature. The use of hydrogen bonding for design of molecules may widen the applicability of organic materials. We have found[7–11] that a novel family of liquid crystalline materials is built through intermolecular hydrogen bonding between independent and different components. Well-defined molecular structures with liquid crystalline properties are obtained via a simple self-assembly process between hydrogen bonding donor and acceptor moieties. For example, selective pairing between a substituted benzoic acid and a stilbazole results in the formation of a 1:1 H-bonded complex which functions as a new extended mesogen.[7,8] The mesophase exhibited by the complex shows high thermal stability. In our previous approach toward an H-bonded polymeric complex,[7] a liquid crystalline side-chain polymer was prepared through H-bonding between a polyacrylate having a 4-oxybenzoic acid and a phenyl ester derivative of a stilbazole. The complex exhibited a nematic phase that was highly thermally stable due to the formation of an extended mesogen through hydrogen bonding.

In the present study, side-chain liquid crystalline polymers have been built through selective pairing between a polyacrylate P6OBA having a benzoic acid moiety that operates as an H-bond donor and a series of *trans*-4-alkoxy-4′-stilbazoles *n*OSz which functions as H-bond acceptor (Chart I). Liquid crystalline properties have been examined for the series of polymeric complexes. Monomeric 1:1 H-bonded complexes have also been prepared from 4-(hexyloxy)benzoic acid (6OBA) and the various stilbazoles *n*OSz to understand the polymeric effect of the H-bonded liquid crystals. The phase behavior has been examined for the mixture of polymeric and monomeric complexes.

Experimental Section

Preparation of Poly[4-((6-(acryloyloxy)hexyl)oxy)benzoic acid], P6OBA. 4-((6-(Acryloyloxy)hexyl)oxy)benzoic acid was synthesized using a procedure reported by Portugall et al.[12] Polymerization of the monomer (2.2 g) was carried out in DMF (4.5 mL) with AIBN (1 mol %) at 70 °C for 5 h. After cooling, the polymer solution was poured into methanol. The precipitate was washed with methanol and dried under vacuum at 50 °C. Yield: 85%. [η] = 0.21 (in DMF at 30 °C).

Preparation of *trans*-4-Alkoxy-4′-stilbazoles, *n*OSz. Alkoxystilbazoles were prepared according to the method of Shaw[13] and Chiang.[14] A mixture of 4-alkoxybenzaldehyde (0.12 mol), 4-picoline (0.13 mol), and acetic anhydride (14 mL) was heated at 120 °C for 48 h under a N_2 atmosphere. After cooling, the reaction mixture was poured into cold water. The precipitate was washed with cold water. After drying, the product was purified on a silica gel column using chloroform/methanol 20:1 as eluent followed by recrystallization from acetone. Yield: 10–

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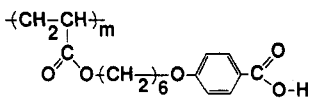
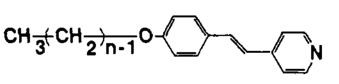
Chart I

H-Bond Donor



P6OBA

H-Bond Acceptor



nOSz

12%. ^{1}H NMR for 3OSz ($CDCl_3$, 27 °C, ppm): δ 8.54, 7.32 (pyridyl), 7.46, 6.91 (phenyl), 7.24, 6.86 (−CH=CH−) 3.94, 1.82, 1.06 (aliphatic). ^{13}C NMR ($CDCl_3$, 27 °C, ppm): δ 150.8, 145.7, 121.3 (pyridyl), 160.4, 129.3, 129.0, 115.5 (phenyl), 133.4, 124.2 (−CH=CH−), 70.3, 23.2, 11.2 (aliphatic).

Preparation of Hydrogen-Bonded Complexes. All complexes examined in the present study were prepared by the evaporation technique[7-11,15] from pyridine solution containing equimolar amounts of H-bond donor and acceptor moieties followed by drying in vacuo at 60 °C. Polymeric binary complexes containing two different stilbazoles were made from pyridine solution containing equimolar amounts of the benzoic acid of P6OBA and the pyridyl unit of the mixtures of 1OSz and 6OSz. Binary mixtures of monomeric and polymeric complexes were prepared from a pyridine solution of equimolar mixtures of an H-bond donor of P6OBA and 6OBA and an H-bond acceptor of 2OSz.

Characterization. DSC measurements were performed on a Mettler DSC 30. The heating and cooling rates of 10 deg/min were used for the measurements of the samples throughout the present study. For the polymeric complexes, samples once heated to 150 °C were used for the measurements and the peak temperatures of the endotherms were taken as the transition temperatures. For monomeric complexes, samples once heated to 20 deg higher than the melting temperatures were used for the measurements and the onset points of the endotherms were taken as the transition temperatures. A polarizing microscope (Olympus BH2) equipped with a Mettler FP82HT hot stage was used for visual observations. NMR spectra were recorded on a JEOL GX-270 spectrometer with TMS as an internal standard. The intrinsic viscosity of the polymer was measured on DMF solution with an Ubbelohde viscometer at 30 °C. FT-IR measurements were conducted on a JASCO FT/IR-200 spectrometer equipped with a Mettler FP84 hot stage.

Results and Discussion

Liquid Crystalline Properties of Monomeric Hydrogen-Bonded Complexes from a Benzoic Acid and a Series of Stilbazoles. In an initial study, the thermal properties of monomeric hydrogen-bonded complexes designed to be incorporated as the mesogenic fragment of the polymeric liquid crystalline complexes in this study have been examined. The monomeric complex was prepared from an equimolar mixture of 4-(hexyloxy)benzoic acid (6OBA) and a *trans*-4-alkoxy-4′-stilbazole *n*OSz. 6OBA which acts as an H-bond donor shows a nematic phase between 106 and 151 °C. A series of *trans*-4-alkoxy-4′-stilbazoles *n*OSz (n = 1–8 and 10; n is the carbon number of the linear alkyl chain of $-C_nH_{2n+1}$) was prepared for the use as H-bond acceptors.

Table I shows thermal properties of the series of stilbazoles *n*OSz.[16-18] The transition temperatures were taken as the onset temperatures of the endotherms on heating. On heating, smectic phases were clearly observed for the stilbazoles with n = 6–8 and 10. No liquid crystalline behavior is observed for the homologues with n = 1–5 at the heating rate of 10 deg/min. None of the stilbazoles exhibit a mesophase over 88 °C. Bruce et al. reported[16] that stilbazoles (n = 3–12) exhibited smectic E and B phases that were enantiotropic or monotropic.

Table I
Thermal Properties of a Series of *trans*-4-Alkoxy-4′-stilbazoles (*n*OSz)[a,b]

	phase transition behavior[a]							
1OSz	K	134	I					
2OSz	K	149	I					
3OSz	K	110	I					
4OSz	K	90	I					
5OSz	K	84	I					
6OSz	K	68	S	86	I			
7OSz	K	83	S	88	I			
8OSz	K	71	S	74	S	87	I	
10OSz	K	83	S	85	I			

[a] The onset temperatures of the endothermic peaks of DSC thermograms at the heating rate of 10 deg/min were taken as the transition temperatures. Samples cooled to room temperature from isotropic states were used for the measurements. [b] References 16–18.

The evaporation technique from pyridine solution[7-11,15] was used for the formation of the hydrogen-bonded 1:1 complexes of 6OBA and *n*OSz, which will be denoted as complex 6OBA–*n*OSz.

Thermal properties of the series of 6OBA–*n*OSz are given in Table II. All complexes exhibit sharp phase transitions and homogeneous mesophases. The phase transition temperatures of 6OBA–*n*OSz are different from either of the single components of 6OBA and *n*OSz. Figure 1 shows a plot of transition temperatures as a function of the alkyl chain length (n) for the series of 6OBA–*n*OSz. The type of the mesophase is dependent on the alkyl chain length. Nematic phases are seen for complexes with n = 1–5. With longer alkyl chains (n = 6–8 and 10), only smectic phases are observed whereas 6OBA–1OSz shows only a nematic phase. Homeotropic or focal-conic textures that are characteristic of the smectic A phase are observed for the smectic phases that appear below the nematic or the isotropic phase. Schlieren textures observed for the complexes with n = 7, 8, and 10, are attributed to smectic C phases. The enthalpy changes for S_A–N (0.2–1.5 kJ/mol) and S_C–S_A (0.2–0.6 kJ/mol) transitions are typical for these transitions.[19] S_X is an unidentified smectic phase observed for the complexes with n = 6–8 and 10. Mesophase–isotropic transition temperatures (T_i) do not change significantly with varying length of the alkyl chain. Figure 2 illustrates DSC thermogram of 6OBA–3OSz. Endothermic peaks corresponding to melting, smectic A–nematic, and nematic–isotropic transitions, are clearly observed at 102, 130, and 155 °C, respectively. The DSC curve shows that the complex prepared from two different components behaves as a single mesogenic component.

These results confirm the selective formation of the hydrogen-bonded mesogen between the benzoic acid and the stilbazole, as shown in Figure 3. The single hydrogen bond keeps the linear structure of the mesogen that is thermally stable.

The FT-IR spectrum of 6OBA–3OSz which exhibits a smectic phase at 122 °C, is shown in Figure 4. The O—H bands observed at 2500 and 1920 cm^{-1} are indicative of strong hydrogen bonding[20-23] between the carboxylic acid of 6OBA and the pyridyl group of 3OSz. For the benzoic acid dimer which forms weaker H bonds, the O—H band appears at 2900 cm^{-1}. The carbonyl band of 6OBA–3OSz appears at 1697 cm^{-1} whereas the C=O band is observed for the dimer of 6OBA at 1682 cm^{-1}.

Table II
Thermal Properties of Monomeric H-Bonded Complexes 6OBA–nOSz from 4-(Hexyloxy)benzoic Acid (6OBA) and *trans*-4-Alkoxy-4′-stilbazoles (nOSz)

1:1 H-bonded complex	phase transition behavior[a]												
6OBA–1OSz					K	91 (25.5)	N	158 (2.5)	I				
6OBA–2OSz			K	86 (8.0)	K	112 (52.1)	S_A	128 (0.2)	N	166 (5.5)	I		
6OBA–3OSz					K	102 (22.3)	S_A	130 (0.3)	N	155 (3.1)	I		
6OBA–4OSz					K	103 (20.4)	S_A	142 (1.5)	N	156 (7.3)	I		
6OBA–5OSz					K	105 (19.9)	S_A	146 (1.5)	N	151 (8.7)	I		
6OBA–6OSz	K	70 (5.4)	K	94 (7.6)	K	103 (9.5)	S_X	112 (2.5)	S_A	156 (11.7)	I		
6OBA–7OSz	K	78 (12.9)	K	84 (9.7)	K	102 (9.3)	S_X	117 (3.6)	S_C	122 (0.6)	S_A	157 (14.7)	I
6OBA–8OSz			K	60 (17.4)	K	91 (8.1)	S_X	122 (4.2)	S_C	127 (0.3)	S_A	159 (14.3)	I
6OBA–10OSz					K	60 (29.0)	S_X	124 (4.0)	S_C	141 (0.2)	S_A	159 (15.3)	I

[a] Transition temperatures (°C) and enthalpies of transitions (kJ/mol, in parentheses). Key: K, crystalline; S, smectic; N, nematic; I, isotropic. S_X is an unidentified smectic phase.

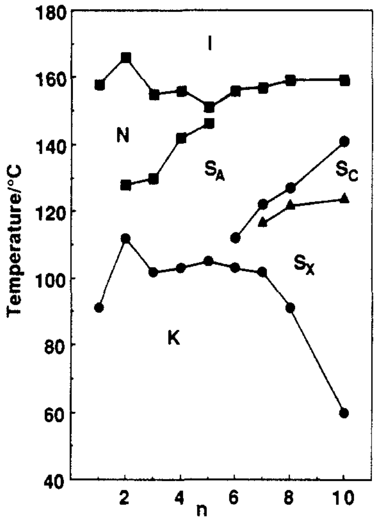


Figure 1. Plot of transition temperatures against the carbon number (*n*) in the alkyl chain for the series of 1:1 hydrogen-bonded complex 6OBA–*n*OSz.

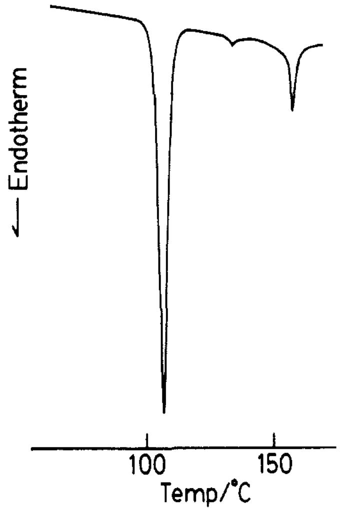


Figure 2. DSC thermogram of the 1:1 hydrogen-bonded complex 6OBA–3OSz on heating.

The type of the H-bonding interaction based on pyridine depends on the acidity of A–H as shown.[20–24]

$$\mathrm{A{-}H + Py \rightleftharpoons \underset{I}{A{-}H\cdots Py} \rightleftharpoons}$$
$$\mathrm{\underset{III}{(A\cdots H\cdots Py)} \rightleftharpoons \underset{II}{A^{-}\cdots H^{+}Py} \rightleftharpoons A^{-} + H^{+}Py}$$

Benzoic acids (pK_a ~ 4) form a type I strong hydrogen bond with pyridine.[20–23] For a complex of phenol (pK_a = 10) and pyridine, the O–H stretching band appears at 3010 cm^{-1}, which indicates a type I weak hydrogen bond.[22] In contrast, trifluoroacetic acid (pK_a = 0.23), a much stronger acid than benzoic acid, forms a quasi-type III complex that shows partial ionic character.[22,24] The O–H band observed[22] at 1630 cm^{-1} is at a lower frequency than those observed for the type I hydrogen bond.

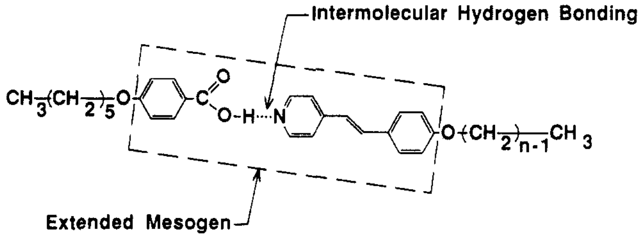


Figure 3. Structure of the hydrogen-bonded mesogen formed by the selective intermolecular hydrogen bonding between 6OBA and *n*OSz.

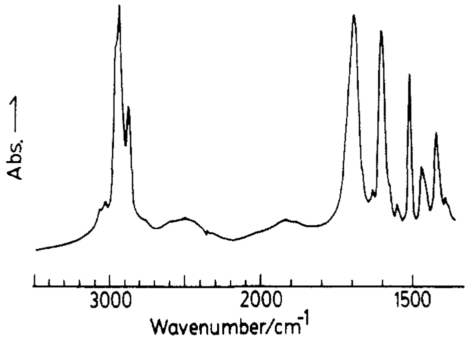


Figure 4. IR spectrum of hydrogen-bonded complex of 6OBA and 3OSz at 122 °C.

Liquid Crystalline Properties of Side-Chain Polymeric Complexes from a Polyacrylate Having a Benzoic Acid Moiety and a Series of Stilbazoles. Polyacrylate P6OBA containing a benzoic acid moiety was prepared by radical polymerization of the corresponding monomer.[25] The benzoic acid unit functions as a hydrogen-bond donor. The polymeric complexes were prepared by the same method used for the monomeric complex. An equimolar amount of the benzoic acid group of the acrylate polymer and the stilbazole was used for the formation of each 1:1 complex.

Thermal properties of the series of polymeric complexes P6OBA–*n*OSz are given in Table III. A plot of the transition temperatures as a function of the carbon number (*n*) of the stilbazole unit is shown in Figure 5. Significant effects attributable to hydrogen bonding are observed on the thermal behavior of the complexes. All of the complexes prepared from P6OBA and *n*OSz exhibit stable mesophases and clear phase transitions. The isotropization temperature does not decrease significantly as the

Table III
Thermal Properties of Polymeric H-Bonded Complexes P6OBA–*n*OSz from Polyacrylate P6OBA and Stilbazoles *n*OSz

1:1 H-bonded complex	phase transition behavior[a]								
P6OBA–1OSz			g	38	K_1	74 (4.7)	S_A	194 (4.7)	I
P6OBA–2OSz			g	51	K_1	89 (7.9)	S_A	200 (5.7)	I
P6OBA–3OSz	g	39	K_1	85 (5.1)	K_2	97 (2.3)	S_A	192 (6.8)	I
P6OBA–4OSz	g	40	K_1	84 (6.7)	K_2	111 (2.1)	S_A	200 (10.5)	I
P6OBA–5OSz	g	34	K_1	79 (4.0)	K_2	114 (2.1)	S_A	192 (8.2)	I
P6OBA–6OSz	g	35	K_1	64 (0.9)	K_2	124 (2.8)	S_A	197 (11.6)	I
P6OBA–7OSz	g	34	K_1	71 (1.7)	K_2	126 (3.8)	S_A	191 (13.8)	I
P6OBA–8OSz	g	35	K_1	68 (1.3)	K_2	133 (3.3)	S_A	190 (12.1)	I
P6OBA–10OSz	g	35	K_1	68 (1.2)	K_2	135 (4.6)	S_A	181 (13.4)	I

[a] Transition temperatures (°C) and enthalpies of transitions (kJ/mol, in parentheses). Key: g, glassy; K, crystalline; S, smectic; I, isotropic.

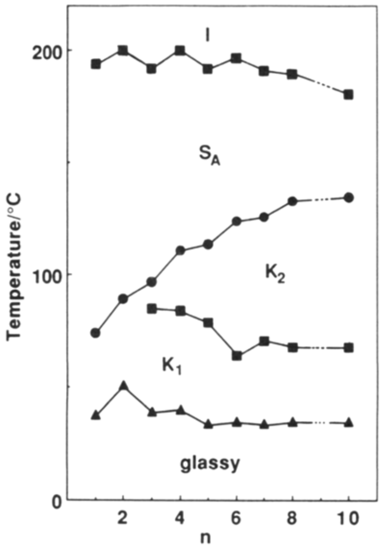


Figure 5. Plot of transition temperatures against the carbon number (*n*) in the alkyl chain for the series of 1:1 hydrogen-bonded polymeric complex P6OBA–*n*OSz.

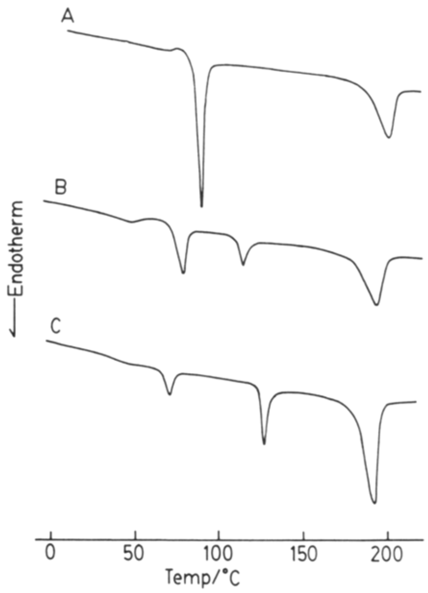


Figure 6. DSC thermograms of the polymeric hydrogen-bonded complexes on heating: (A) P6OBA–2OSz; (B) P6OBA–5OSz; (C) P6OBA–7OSz.

Figure 7. Photomicrograph of a focal conic texture of polymeric complex P6OBA–1OSz at 185 °C on cooling.

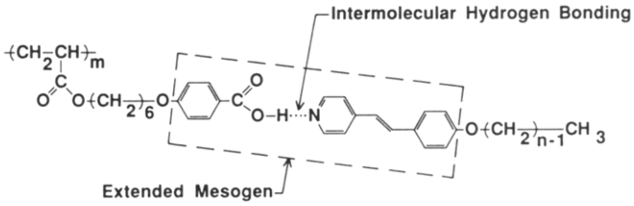


Figure 8. Structure of the side-chain liquid crystalline polymer formed by the selective intermolecular hydrogen bonding between P6OBA and *n*OSz.

chain length increases. For example, P6OBA–2OSz exhibits two endothermic peaks of crystal–smectic A and smectic A–isotropic transitions at 89 and 200 °C, respectively, as shown in Figure 6A. The glass transition behavior is seen at 51 °C. These transitions are not observed for the individual H-bond donor and acceptor components. Three endothermic peaks corresponding to crystal–crystal, crystal–smectic A, and smectic A–isotropic transitions are observed for P6OBA–5OSz (Figure 6B) and P6OBA–7OSz (Figure 6C). The same DSC curves are obtained upon repeated heating and cooling runs. The enthalpy change of isotropization of P6OBA–7OSz is 2.4 times larger than that of P6OBA–2OSz. All of the polymeric complexes show only smectic A phases that are stable and homogeneous while the type of mesophase of the monomeric complex is affected by the alkyl chain length of *n*OSz. Figure 7 shows a focal-conic texture of the smectic phase for P6OBA–1OSz at 185 °C. At this temperature, each H-bond donor and acceptor shows an isotropic phase. The clearing temperature (T_i) of the complex based on the polymeric H-bond donor is higher than that of the corresponding monomeric complex. For example, T_i of P6OBA–2OSz is 200 °C, which is 34 deg higher than that of 6OBA–2OSz.

The behavior of the polymeric complexes is attributed to the formation of a hydrogen-bonded structure of side-chain liquid crystalline polymers through selective intermolecular hydrogen bonding between H-bond donor polymer and H-bond acceptor stilbazole, as shown in Figure 8. It is noteworthy that the molecular structure built through intermolecular hydrogen bonding behaves as one component of liquid crystalline polymer and shows

Table IV
Thermal Properties of Binary Mixtures of Polymeric Hydrogen-Bonded Complexes of P6OBA-(1OSz/6OSz)

mole ratio of complex P6OBA-(1OSz/6OSz)	phase behavior[a]			
P6OBA:1OSz:6OSz	T_g	K_1-K_2	K_2-S_A	S_A-I
100:100:0	38		74 (4.7)	194 (4.7)
100:90:10	40		80 (3.8)	197 (3.3)
100:75:25	40	72 (2.5)	82 (2.5)	190 (6.3)
100:60:40	40	74 (2.1)	91 (2.5)	195 (7.5)
100:50:50	39	71 (1.7)	96 (2.1)	195 (7.5)
100:40:60	40	70 (2.1)	100 (2.5)	193 (9.2)
100:25:75	39	69 (1.7)	108 (2.5)	196 (10.0)
100:10:90	34	65 (1.3)	117 (2.9)	195 (11.7)
100:0:100	35	64 (0.8)	124 (2.9)	197 (11.7)

[a] Transition temperatures (°C) and enthalpies of transitions (kJ/mol, in parentheses).

high thermal stability. The O-H bands observed at 2500 and 1910 cm^{-1} in the FT-IR spectra confirm the formation of the hydrogen-bonded mesogen.

No nematic phases are observed for polymeric complexes, while the corresponding monomeric complexes with n = 1-5 show nematic phases. These polymeric effects were also observed for conventional side-chain liquid crystalline polymers.[4,5]

It should be noted that the isotropization and melting temperatures show odd-even effects as a function of n, as can be seen in Figure 5. This observation cannot be attributed to an effect of the degree of polymerization because the polymeric complexes are based on the same sample of the H-bond donor polymer. For conventional side-chain mesogenic polymers, no systematic work[26] has been reported on the effect of varying the length of the alkyl terminal unit of the mesogen from n = 1 to 10.

The enthalpy change of the isotropization increases as the alkyl chain becomes longer whereas the isotropization temperature shows no significant difference. This result shows that the degree of molecular order in the mesomorphic state becomes higher with an increase in the length of the terminal alkyl group.

Polymeric complexes with copolymer structures, which will be denoted as P6OBA-(1OSz/6OSz), have been prepared from an equimolar amount of the benzoic acid of P6OBA and mixtures of 1OSz and 6OSz. Table IV and Figure 9 show phase behavior of the complexes. The complexes exhibit clear phase transitions and homogeneous mesophases over the entire range of the composition of the stilbazoles. The same type of focal-conic texture observed for each of the complexes of P6OBA-1OSz and P6OBA-6OSz is seen for P6OBA-(1OSz/6OSz). The smectic temperature range becomes narrower and the melting transition temperature becomes higher as the content of 6OSz increases. The glass transition temperature does not change as the ratio of 6OSz is varied. The enthalpy change of S_A-I shows an increasing trend as the ratio of 6OSz increases.

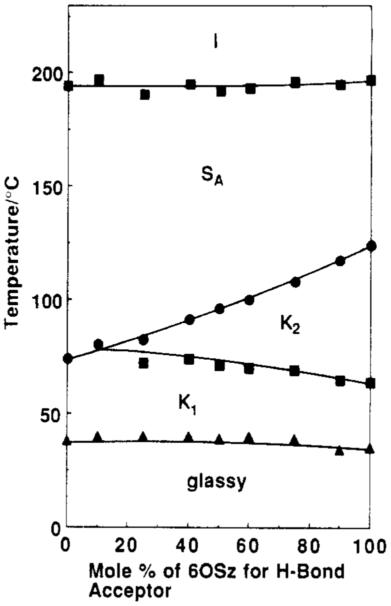


Figure 9. Binary phase diagram of polymeric complexes of P6OBA-(1OSz/6OSz).

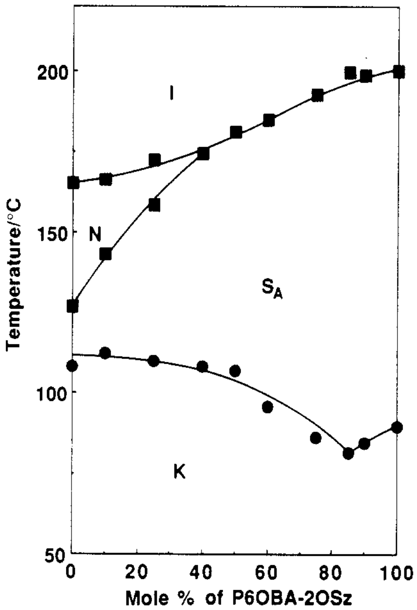


Figure 10. Binary phase diagram of polymeric complex P6OBA-2OSz and monomeric complex 6OBA-2OSz.

The phase behavior (Figure 10) of binary mixtures of polymeric and monomeric complexes has been examined for the mixture of P6OBA-2OSz and 6OBA-2OSz. The polymeric complex P6OBA-2OSz shows a smectic A phase from 89 to 200 °C. The monomeric complex 6OBA-2OSz exhibits a smectic A (112-128 °C) and a nematic (128-166 °C) phase. These two complexes are miscible over the entire range of composition. Homogeneous smectic A phases are observed on microscopic observation of the mixtures. Nematic phases are seen for the mixtures having more than 25 mol % of the monomeric complex. For binary mixtures of conventional side-chain liquid crystalline polymers and low molecular weight liquid crystalline compounds, phase separation and immiscibility are often observed.[27-29] This mixture of H-bonded complexes has therefore some potential as a new type of functional liquid crystalline blend.

Conclusion

A new type of side-chain liquid crystalline polymer is built through selective intermolecular hydrogen bonding. The polymeric complex exhibits a more thermally stable mesophase than the corresponding monomeric complex due to the formation of side-chain mesogenic polymer structure. Self-assembly of the polymeric complex through the hydrogen bonding is shown schematically in Figure 11. Recognition between the H-bond donor polymer and the acceptor molecule through hydrogen bonding results in the formation of a liquid crystalline polymeric self-assembly. This is a new type of molecular recognition in molecular aggregates. The self-assembled complex has well-defined structure and exhibits a stable mesophase. The results obtained in the present study present a new possibility of molecular design of functional organic polymeric materials through intermolecular interactions.

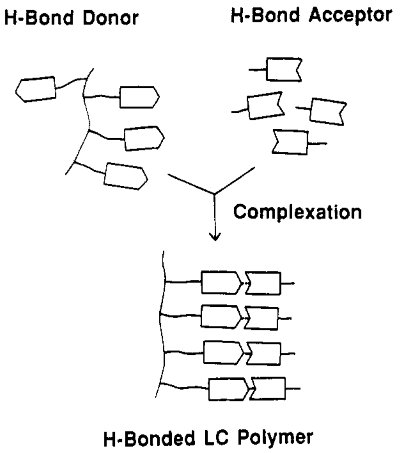


Figure 11. Schematic illustration of self-assembly of the side-chain liquid crystalline polymer through selective recognition between H-bond donor and acceptor moieties.

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References and Notes

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(17) In Table I, the onset temperatures of the endotherms of phase transitions at the heating rate of 10 deg/min were taken as transition temperatures. The peak temperatures of the endotherms agree well with transition temperatures reported in ref 16.
(18) Bruce et al. reported[16] that 5OSz showed smectic E and B phases from 85.2 to 86.8 °C on heating. They used various heating rates for the measurements. However, at the condition of the heating rate of 10 deg/min, no stable liquid crystalline phase could be observed clearly.
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(25) In a previous paper,[7] we reported P6OBA exhibited a mesophase-like texture between 140 and 155 °C. As for the sample of P6OBA prepared for the present study, the polymer shows isotropization at 178 °C. This behavior is due to the difference of molecular weights. The study of thermal behavior of P6OBA itself and related polymers is now in progress, and the results will be reported elsewhere.
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