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Self-Assembly of Liquid-Crystalline Polyamide Complexes through the Formation of Double Hydrogen Bonds between a 2,6-Bis(amino)pyridine Moiety and Benzoic Acids

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ABSTRACT: Supramolecular liquid-crystalline polymeric complexes derived from polyamides containing 2,6-bis(amino)pyridyl units in their main chains and benzoic acid derivatives have been obtained by the formation of intermolecular double hydrogen bonds. The polymeric complexes behave as single liquid-crystalline polymers and exhibit stable and enantiotropic mesophases. The hydrogen-bonded mesogens laterally connected by flexible spacers form a polymeric structure that is not simply classified as a main-chain or a side-chain type.

Introduction

The use of specific molecular interactions such as hydrogen bonding, charge transfer, and ionic interactions for the design and preparation of self-organized materials such as liquid crystals has attracted much attention[1−8] because a new class of dynamically functional materials are obtained by such approaches. Hydrogen bonding has been used as one of the key means for the preparation of these molecular self-assembled materials.[1−6,9,10] For mesogenic polymers, side-chain,[2,3,6,11,12] main-chain,[13] and network polymers[6c,14,15] have been prepared by the formation of hydrogen bonds between different and independent molecular components (Figure 1A−C). The effects of hydrogen bonding moieties such as hydroxyl and carboxyl groups on mesomorphism have been reported for liquid-crystalline polymers.[16] Hydrogen bonding has been shown to be useful for the development of liquid-crystalline polymer blends because miscibility and structures can be controlled by the interactions between different polymeric components.[17] A variety of low molecular weight complexes have also been obtained by hydrogen bonds between different[18−25] or identical[26] molecules.

Recently, we have shown that 2,6-bis(amino)pyridine moieties can function as a molecular component for mesogenic complexes through the formation of double hydrogen bonds.[27−30] Bis(amino)pyridines are useful components for the design of molecular assemblies.[9a,31,32] Supramolecular mesogenic side-chain polymers have been prepared from a polyacrylate containing a benzoic acid side chain and 2,6-bis(acylamino)pyridines.[27] Self-assembly of 4-(alkoxy)benzoic acids and such pyridine derivatives[28] also leads to the formation of low molecular weight mesogenic complexes. However, these complexes exhibit only monotropic phases with narrow temperature ranges. In a previous paper,[29] we reported that a nylon containing a pyridine ring can form a complex with a 4-(4-(alkoxy)phenyl)benzoic acid by the double hydrogen bonds. The schematic structure of this supramolecular mesogenic polymer is shown in Figure 1D. This is a new structure for liquid-crystalline polymeric

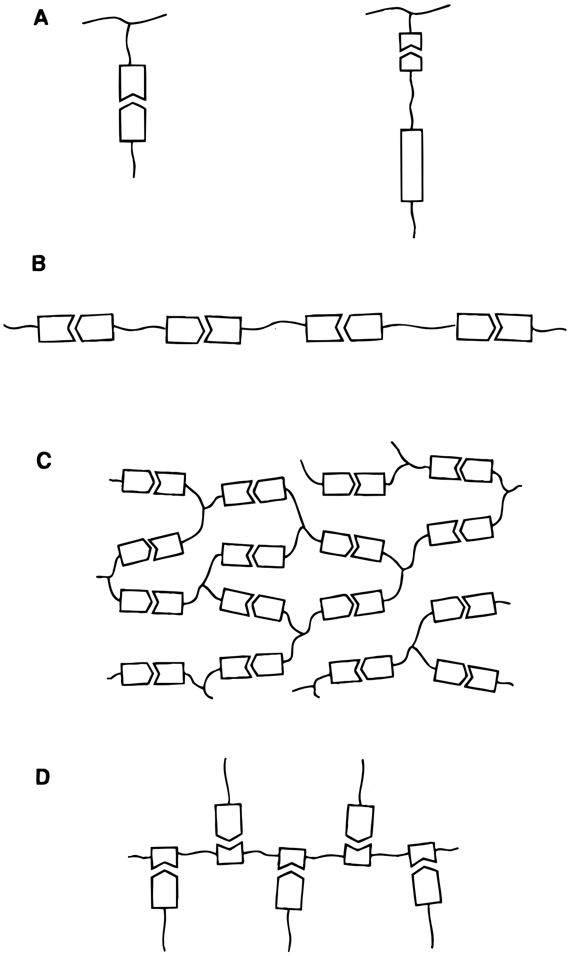

Figure 1. Schematic illustration of supramolecular liquid-crystalline complexes.

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materials. A significantly thermally stable mesophase is observed for the complex due to the formation of a triaromatic mesogen and the H-bonding interaction between amide groups.

In the present paper, we report the design and properties of such a new class of the supramolecular liquid-crystalline polymers obtained by self-assembly of 4-(alkoxy)benzoic acids and polyamides containing a 2,6-bis(amino)pyridine moiety.

Experimental Section

Materials. Monomers of polyamides, 2,6-bis(amino)pyridine, and α,*ω*-alkylenedicarboxylic acids were recrystallized from toluene and ethanol, respectively. Lithium chloride was dried with heating in a nitrogen stream for 1 h before use.

Preparation of Polyamides 1a–c. Polyamides **1a**–**c** were prepared from 2,6-bis(amino)pyridines and α,*ω*-alkylenedicarboxylic acids. A typical synthetic procedure given for **1a** is as follows. Suberic acid (0.523 g, 3.00 mmol), lithium chloride (1.00 g, 23.0 mmol), 2,6-bis(amino)pyridine (0.327 g, 3.00 mmol), and $(PhO)_3P$ (0.930 g, 3.00 mmol) were dissolved in DMAc (10 mL) and pyridine (1.5 mL) in a 100 mL flask under a nitrogen atmosphere. The mixture was heated to 100 °C and stirred for 6 h. Then, it was poured into 1 L of cold methanol. The precipitate was filtered and refluxed in methanol to extract low molecular weight products. The product dried in vacuo overnight at 60 °C to give 0.31 g of **1a**. **1a**: yield 41%, $M_n = 2.3 \times 10^3$. **1b**: yield 57%, $M_n = 2.3 \times 10^3$. **1c**: yield 70%, $M_n = 2.9 \times 10^3$.

Preparation of 4-(Alkoxy)benzoic Acid Derivatives. Molecular components, 3-chloro-4-(alkoxy)benzoic acids (**2a**–**d**) and 4-(alkoxy)benzoic acids (**3a**–**d**), were synthesized by etherification of the corresponding alkyl bromide and ethyl 3-chloro-4-(hydroxy)benzoate or ethyl 4-(hydroxy)benzoate, followed by the hydrolysis.

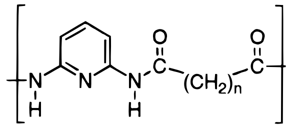
Preparation of Hydrogen-Bonded Complexes. Hydrogen-bonded complexes were prepared by mixing of the components in the molten state under a nitrogen atmosphere. The mixtures, once heated to isotropic homogeneous states, were used for characterization.

Characterization. Thermal properties were examined using a polarizing microscope equipped with a Mettler FP82HT hot stage and a differential scanning calorimeter (Mettler DSC30). The heating and cooling rate of 10 °C/min was used for the DSC measurements. The number average molecular weights of the polyamides were determined by GPC (Tosoh) equipped with a TSK gel GMH_{HR}-N column using 0.01 M LiBr/DMF as an eluent. 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 FP52 hot stage were used for the X-ray measurements.

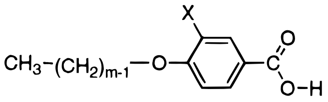
Results and Discussion

The molecular structures of the components in the present study are shown in Chart 1. The thermal properties of polymeric components are given in Table 1. Polyamides **1a**–**c** are nonmesogenic. These polymers exhibit glass transitions in the range of 60–74 °C on heating. Subsequent cold crystallization and melting transitions are observed in the DSC thermograms. Upon cooling at a rate of 10 °C/min, no crystallization behavior is observed. Table 2 shows the transition temperatures of **2a**–**d** and **3a**–**d** on heating.

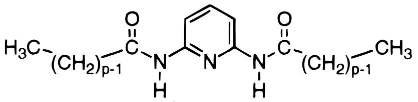
Chart 1



1a : n=6
1b : n=8
1c : n=10



2a : m=6, X=Cl **3a** : m=6, X=H
2b : m=8, X=Cl **3b** : m=8, X=H
2c : m=10, X=Cl **3c** : m=10, X=H
2d : m=12, X=Cl **3d** : m=12, X=H



4a : p=4
4b : p=7

Table 1. Thermal Properties of Polymeric Components 1a–c for Supramolecular Complexes

		transition temp/°C			
		heating[a]			cooling
	$10^{-3}M_n$	T_g	T_c	T_m	T_g
1a	2.3	60	137	222	60
1b	2.3	74		220	72
1c	2.9	70	133	201	70

[a] T_c: cold crystallization temperature.

Table 2. Thermal Properties of Benzoic Acid Derivatives 2 and 3

	transition temp[a]/°C						
2a	K	121	I				
2b	K	98	I				
2c	K	101	I				
2d	K	105	I				
3a	K	108	N	154	I		
3b	K	100	S_C	108	N	148	I
3c	K	98	S_C	126	N	143	I
3d	K	94	S_C	132	N	138	I

[a] K, crystalline; S_C, smectic C; N, nematic; I, isotropic.

The 1:1 complexes of the polyamides and the benzoic acids were prepared by direct mixing in molten states. The complexes from **1a**–**c** and **2a**–**d** behave as single polymeric components and exhibit liquid crystallinity. Figure 2 shows the DSC curves of a 1:1 complex **1c**/**2c**. On heating, the glass transition followed by the exothermic crystallization peak is seen at 33 °C. The melting peak is observed at 101 °C (Figure 2A). The enthalpy change of the transition is 27.8 kJ/mol. Microscope observation shows that a mesophase is formed after melting of **1c**/**2c**, while single component **1c** is nonmesogenic and **2c** is nonmesomorphic above 100 °C. The X-ray diffraction pattern of **1c**/**2c** in the mesophase consists of one sharp peak due to the layer spacing at 26.8 Å and one diffused halo at 4.6 Å (Figure 3). In the DSC curve on further heating, a broader peak due to the mesomorphic–isotropic transition appears at 177 °C. The enthalpy change of isotropization is 15.9

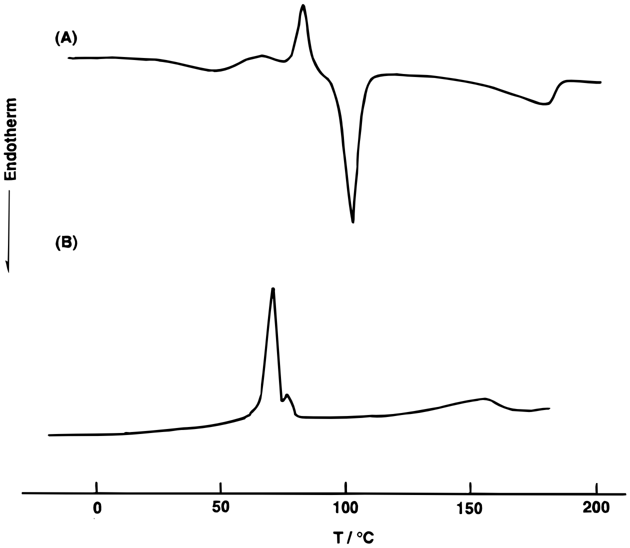


Figure 2. DSC thermograms of supramolecular complex **1c**/**2c** on (A) heating scan and (B) cooling scan.

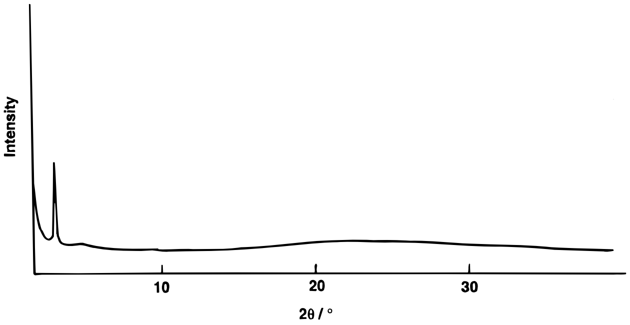


Figure 3. X-ray diffraction pattern of the complex (an unoriented sample) formed from **1c** and **2c** at 120 °C.

Table 3. Thermal Properties of Supramolecular Complexes 1/2

	transition temp[a]/°C				
1a/2a	K	113	M	218	I
1a/2b	K	92	M	221	I
1a/2c	K	93	M	211	I
1b/2a	K	113	M	177	I
1b/2b	K	94	M	177	I
1b/2c	K	98	M	186	I
1c/2a	K	113	M	176	I
1c/2b	K	96	M	174	I
1c/2c	K	101	M	177	I
1c/2d	K	101	M	182	I

[a] Determined by DSC measurement on heating. M: mesophase.

Table 4. Layer Spacings of Complexes 1c/2a–c Obtained from X-ray Diffraction Patterns and Lengths of the Mesogens by Molecular Modeling

	layer spacing from X-ray pattern/Å	length of the mesogen estimated by molecular modeling[a]/Å
1c/2a	25.7	20
1c/2b	26.6	23
1c/2c	28.6	25

[a] The length of the H-bonded mesogen from the pyridyl ring to the methyl group of the alkoxy group.

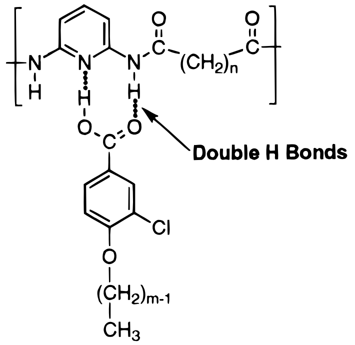


Figure 4. Molecular structure of supramolecular polyamides formed through double hydrogen bonds.

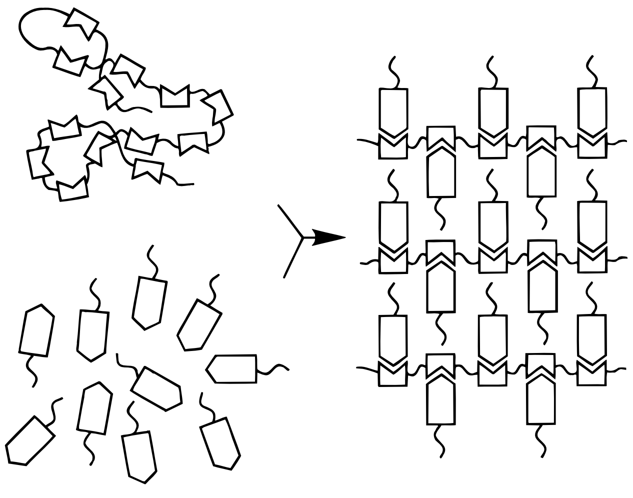


Figure 5. Schematic illustration of molecular self-assembly of a nylon containing a heterocyclic ring and benzoic acids and a proposed liquid-crystalline structure of the supramolecular polyamides based on X-ray measurements.

kJ/mol. These transitions are not seen for each of the single components. Upon cooling (Figure 2B), two exothermic peaks, which correspond to isotropic–mesomorphic and mesomorphic–crystal transitions, are seen at 156 and 71 °C. Table 3 presents the thermal properties of the 1:1 complexes of **1**/**2**. All of these complexes exhibit enantiotropic mesophases. In contrast, only monotropic mesophases have been observed for low molecular weight and side chain polymeric complexes containing such doubly hydrogen-bonded mesogens.[27,28] The highest melting temperatures are achieved for complexes **1a**–**c**/**2a** containing the (hexyloxy)benzoic acid, which has the shortest alkyl chain in this series. When the length of the alkylene spacer of the polyamide moiety increases, the isotropization temperatures show an increasing trend. Complex **1a**/**2b** exhibits the lowest melting and the highest isotropization temperatures. This mesomorphic temperature range is 129 °C.

Table 4 shows the layer spacings obtained by the X-ray diffraction patterns of complexes **1c**/**2a**–**c** in liquid-crystalline states and the estimated lengths of the mesogenic part from the end of the pyridyl unit to the methyl moiety of the alkoxyl group. The layer spacings increase as the alkoxy chain lengths (*m*) of **2** increase. A proposed complex structure of the supramolecular polyamide is shown in Figure 4. Schematic illustration of this molecular association resulting in the ordered structure is shown in Figure 5. The polyamides recognize and bind the benzoic acid components to their backbones and self-assemble into layered structures.

Copolymeric complexes have been made from a mixture of benzoic acids with different alkoxy chains. The transition temperatures of polyamide **1c** and mixtures of **2a** and **2c** are given in Figure 6. The decrease of the melting points is observed, while the isotropization

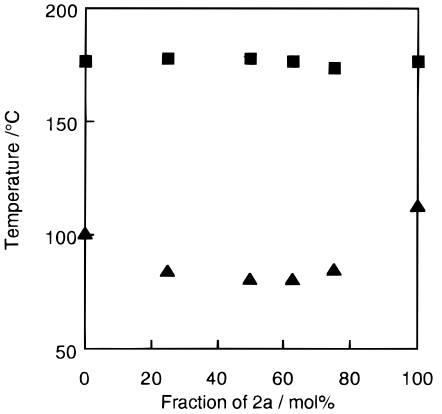


Figure 6. Phase diagram of the transition temperatures of copolymeric complexes **1c**/(**2a** and **2c**): (▲) crystalline−mesomorphic; (■) mesomorphic−isotropic.

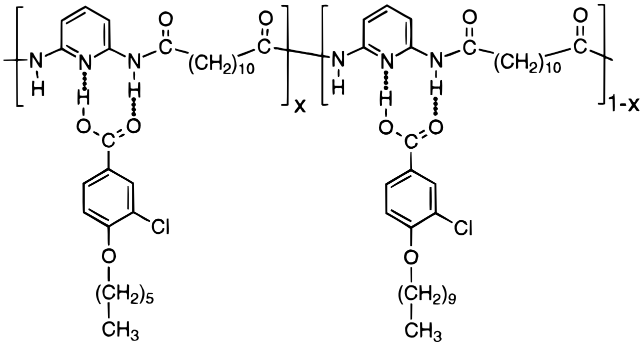


Figure 7. Proposed molecular structure of the supramolecular copolymeric complex.

temperatures are almost constant. This behavior is normal for liquid-crystalline copolymers, which supports the formation of supramolecular polymeric structures shown in Figure 7.

It should be noted that no stable behavior as polymer complexes is observed when simple 4-(alkoxy)benzoic acids with no chloro substituent are attempted to complex with the polyamides. For the mixtures of the polyamides and the simple alkoxybenzoic acids, transition peaks due to each of the single components are seen in the DSC thermograms, which suggests the phase separation of these two components. Visual observation on a polarizing microscope also supports the existence of the phase separation. In contrast, stable mesogenic complexes are obtained for the 4-(alkoxy)benzoic acids with a chloro substituent in the 3-position. The chloro substituent of the benzoic acids for supramolecular polyamides is needed for the stable complex formation, which contributes to the induction of enantiotropic phases. In contrast, for low molecular weight complexes (Figure 8), monotropic smectic B phases are observed for **4**/**3**,[28] while complexes with a chloro substituent exhibit no mesomorphism, as given in Table 5. Self-association energies of the polyamides are expected to be stronger than those of low molecular weight amide compounds. Therefore, a substituent electronic effect on the acidity of the benzoic acid and the dipole−dipole interaction between the chloro substituents might be important for the stabilization of the self-assembled structures of the polyamides and the low molecular weight molecules.

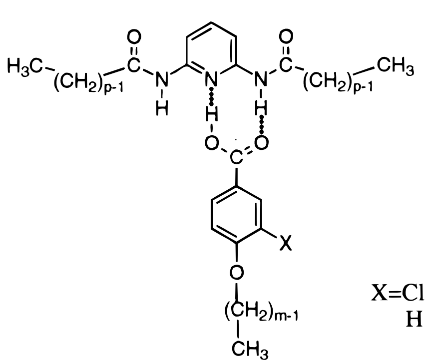


Figure 8. Molecular structure of the low molecular weight complex between 2,6-bis(acylamino)pyridine (**4**) and benzoic acid derivatives.

Table 5. Thermal Properties of Doubly Hydrogen-Bonded Complexes of Low Molecular Weight Molecules

	transition temp[a]/°C				
4a/**2c**[b]	I	67	K		
4a/**2d**[b]	I	64	K		
4b/**2c**[b]	I	58	K		
4b/**2d**[b]	I	67	K		
4a/**3c**[c]	I	83	$\mathrm{S_B}$	71	K
4a/**3d**[c]	I	86	$\mathrm{S_B}$	67	K
4b/**3c**[c]	I	78	$\mathrm{S_B}$	68	K
4b/**3d**[c]	I	78	$\mathrm{S_B}$	69	K

[a] K, crystalline; $\mathrm{S_B}$, smectic B; I, isotropic. [b] Nonmesomorphic compounds. [c] Monotropic compounds. Reference 28.

The present results demonstrate a novel design for liquid-crystalline polymeric systems. The mesophases have been induced by molecular recognition processes on the polymer backbones, which results in the formation of a new mesogenic structure.

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