Use of Intermolecular Hydrogen Bonding between Imidazolyl Moieties and Carboxylic Acids for the Supramolecular Self-Association of Liquid-Crystalline Side-Chain Polymers and Networks

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Received February 23, 1998; Revised Manuscript Received May 6, 1998

ABSTRACT: Liquid-crystalline side-chain polymeric complexes with well-defined structures have been obtained by supramolecular assembly of poly(acrylic acid) and mesogenic compounds containing imidazolyl-terminated alkyl chains. Hydrogen bonds formed between carboxylic acid and *N*-(alkyl)imidazole moieties can function as molecular connectors. The formation of H-bonded liquid-crystalline networks has been achieved by self-assembly of bis-imidazolyl-terminated mesogenic compounds and poly(acrylic acid). These networks exhibit smectic A phases due to the dynamic nature of the noncovalent interaction.

Introduction

Molecular architecture through self-assembly is now one of the central topic of materials science.[1] For liquid-crystalline polymeric materials, the design and preparation of supramolecular structures built through hydrogen bonds between different molecular species have attracted attention[2−19] because such an approach is considered to be important to achieve dynamic functional molecular systems with organized structures. The first example of the supramolecular side-chain polymer contains an H-bonded mesogenic core consisting of a benzoic acid moiety and a stilbazole.[3] Another type of the side-chain polymer connects the mesogenic side chain through H bonds directly to its backbone.[9,10] Hydrogen bonds such as carboxylic acid/pyridine,[3−10,12,14−17] carboxylic acid/aminopyridine,[8] and uracil/2,6-bis(amino)pyridine[13] have been used for the preparation of side-chain, main-chain, and network polymeric structures as well as low molecular weight complexes.[20] Moreover, a variety of mesomorphic or nonmesomorphic polymeric materials involving hydrogen bonds have been reported.[21]

Imidazolyl groups are hydrogen-bonding moieties, which participate in biological processes in nature. These groups have been used for synthetic functional systems.[22] In mesomorphic materials, we described the use of imidazoles for the design of a self-organized system.[23] In this case, imidazole molecules form randomly hydrogen-bonded layers that induce and stabilize a smectic phase. Imidazole derivatives are also considered to be useful as H-bonding components that connect different molecular parts by the formation of stable H bonds. The objective of the present study is to use such an imidazolyl group as an H-bonding connector that leads to well-defined structures of supramolecular polymeric complexes.

We report here the formation of liquid-crystalline side-chain polymers and networks through the hydrogen bonds between imidazolyl moiety and carboxylic acids.

Experimental Section

Materials. Poly(acrylic acid)s (**1a**,**b**) were purchased from Aldrich.

Syntheses of 4-(ω-(Bromo)alkyloxy)-4′-(cyano)-biphenyls. A mixture of 4-cyano-4′-(hydroxy)biphenyl (6.0 g, 31 mmol), 1,6-dibromohexane (14 g, 58 mmol), and potassium carbonate (4.8 g, 35 mmol) in acetone (60 mL) was refluxed with stirring for 16 h. After removal of acetone, the reaction mixture was poured into chloroform and washed with water. The crude product was purified by a silica gel column using chloroform as an eluent. After removal of chloroform and washing with hexane, the white product (6.2 g, 17 mmol) of 4-(6-(bromo)hexyloxy)-4′-(cyano)biphenyl was obtained. Yield: 4-(6-(bromo)hexyloxy)-4′-(cyano)biphenyl, 56%; 4-(10-(bromo)decyloxy)-4′-cyanobiphenyl, 60%. ^{1}H NMR for 4-(6-(bromo)hexyloxy)-4′-(cyano)-biphenyl ($CDCl_3$, ppm): 7.69, 7.64, 7.53, 6.99 (phenyl, 8H), 4.02 (OCH_2, 2H), 3.44 ($BrCH_2$, 2H), 2.0−1.4 (CH_2, 8H).

Syntheses of 4-Cyano-4′-(ω-(imidazole-1-yl)alkyloxy)biphenyls (2) and (3). A mixture of imidazole (0.964 g, 14.2 mmol), 4-(6-(bromo)hexyloxy)-4′-cyanobiphenyl (4.03 g, 11.3 mmol), and potassium carbonate (1.96 g, 14.2 mmol) in dry THF (30 mL) was refluxed with stirring for 18 h under a nitrogen atmosphere. After the addition of chloroform, the solution was filtered to remove salts. After the removal of THF and chloroform, the crude product was purified by a silica gel column using chloroform/methanol (30:1) as an eluent. Recrystallization from hexane/ethyl acetate (2:1) gives the white product (2.46 g, 7.13 mmol) of **2**. Yield: **2**, 63%; **3**, 63%. ^{1}H NMR for **2** ($CDCl_3$, ppm): 7.69, 7.63, 7.52, 6.98 (phenyl, 8H) 7.47, 7.06, 6.91 (imidazolyl(Im), 3H), 3.99 (OCH_2, 2H), 3.95 ($ImCH_2$, 2H), 1.9−1.3 (CH_2, 8H).

Synthesis of 4-(6-(Imidazole-1-yl)hexyloxy)-4′-pentyloxybiphenyl (4). 4-(6-(Imidazole-1-yl)hexyloxy)-4′-pentyloxybiphenyl (**4**) was prepared from 4-(6-(bromo)-hexyloxy)-4′-(pentyloxy)biphenyl and imidazole according to the method for the preparation of **2**. Yield: 33%. ^{1}H NMR for **4** ($CDCl_3$, ppm): 7.46 (phenyl, 4H), 6.94, 6.92 (phenyl, 4H), 7.47, 7.06, 6.91 (imidazolyl, 3H), 3.99, 3.97 (OCH_2, 4H), 3.95 ($ImCH_2$, 2H), 1.9−1.3 (CH_2, 14H), 0.94 (CH_3, 3H).

Syntheses of 4-Butyl-4′-(ω-(imidazole-1-yl)alkyloxy)azobenzenes (5) and (6). 4-Butyl-4′-(ω-(imida-

S0024-9297(98)00271-X CCC: $15.00
Published on Web 06/19/1998

zole-1-yl)alkyloxy)azobenzene was prepared from 4-(ω-(bromo)alkyloxy)-4′-(butyl)azobenzene and imidazole according to the method for the preparation of **2**. Yield: **5**, 40%; **6**, 36%. ^{1}H NMR for **5** ($CDCl_3$, ppm): 7.89, 7.79, 7.30, 6.98 (phenyl, 8H), 7.49, 7.07, 6.91 (imidazolyl, 3H), 4.03 (OCH_2, 2H), 3.96 ($ImCH_2$, 2H), 2.68 ($PhCH_2$, 2H), 1.9−1.3 (CH_2, 12H), 0.94 (CH_3, 3H).

Syntheses of 4,4′-Bis(ω-(imidazole-1-yl)alkyloxy)-biphenyls (7) and (8). 4,4′-Bis(ω-(imidazole-1-yl)-alkyloxy)biphenyl was prepared from imidazole and 4,4′-bis(ω-(bromo)alkyloxy)biphenyl. A mixture of imidazole (1.12 g, 16.4 mmol), 4,4′-bis(6-bromohexyloxy)biphenyl (0.703 g, 1.37 mmol), and potassium carbonate (2.26 g, 16.4 mmol) in dry THF (20 mL) was refluxed with stirring for 20 h under a nitrogen atmosphere. After the addition of chloroform/methanol (1:1), the solution was filtered to remove salts. After the evaporation of solvent, the crude product was purified by a silica gel column using chloroform/methanol (4:1) as an eluent followed by recrystallization from hexane/ethyl acetate (1:1) to afford the desired product (0.453 g, 0.932 mmol) of **7**. Yield: **7**, 68%; **8**, 80%. ^{1}H NMR for **7** ($CDCl_3$, ppm): 7.46, 6.93 (phenyl, 8H), 7.47, 7.06, 6.91 (imidazolyl, 6H), 3.97 (OCH_2, 4H), 3.95 ($ImCH_2$, 4H), 1.9−1.3 (CH_2, 16H).

Characterization. NMR spectra were measured on a JEOL GX-270 spectrometer with TMS as an internal standard. Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 30. Heating and cooling rates were 10 °C/min. Transition temperatures (crystalline−mesomorphic, mesomorphic−isotropic) of polymeric complexes were taken at the maximum point of the peaks. The midpoint of the change in the heat capacity was taken as a glass transition temperature. Optical microscopy observation was performed using an Olympus BH-2 microscope equpped with a Mettler FP82HT hot stage and crossed polarizers. X-ray diffraction patterns were measured with a Rigaku RINT 1500 X-ray diffractometer.

Preparation of Hydrogen-Bonded Complexes. Imidazolyl compounds **2**−**8** and poly(acrylic acid) (**1a**,**b**) were dissolved in methanol, and the solvent was removed by slow evapolation. The blend was then dried at 30−40 °C in vacuo.

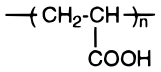
Results and Discussion

Supramolecular Mesogenic Side-Chain Polymers Built by the H Bonds between Imidazoles and Carboxylic Acids. Poly(acrylic acid)s (**1a,b**) were used to form complexes with mono-imidazolyl mesogenic components **2**−**6**. Compounds **2**−**6** are terminated with *N*-imidazolyl moieties (Chart 1). Table 1 gives transition temperatures of poly(acrylic acid)s (**1a**,**b**) and compounds **2**−**6**. Polymers **1a**,**b** are nonmesogenic. Imidazolyl components except monotropic compounds **3** and **5** are nonmesomorphic. In previous papers,[2−7,10,14−16] we have shown that the hydrogen bonds between carboxylic acids and pyridyl moieties result in the formation of a variety of supramolecular liquid-crystalline polymers. We expected imidazolyl moieties also function as H acceptors to form 1:1 complexes with carboxylic acids as shown in Figure 1 because imidazole is a stronger base than pyridine.

Liquid crystallinity has been induced by the complexation of the polymers and the imidazolyl compounds. Thermal properties of the complexes are listed in Table 2. Figure 2shows DSC curves for a 1:1 (molar ratio of carboxylic acid and imidazolyl moieties) complex of **1a** and **2**. The thermal behavior of the complex is different from each of single components **1a** and **2**, and the complex behaves as a single polymer. On heating (Figure 2A), the single glass transition is observed at 10 °C, and a subsequent smectic A phase is seen up to 65 °C. The enthalpy change of the smectic A−isotropic transition is 1.5 kJ/mol. The single component of nonmesogenic poly(acrylic acid) exhibits T_g at 92 °C. These results show that the complex shown in Figure 1 has been obtained by the self-assembly of the two molecular components. The infrared spectra for the complexes support the strong binding of these two components through hydrogen bonds. The O−H stretching bands are observed at 2460 and 2560 cm^{-1}. The splitting of the band suggests the double minimum potential energy of the hydrogen bond.[4,5] For the

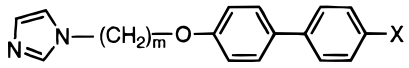
Chart 1

H-Bond Donor Polymer

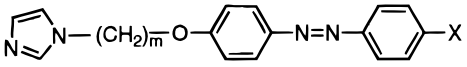


1a: M_n=2x10^3
1b: M_n=4.5x10^5

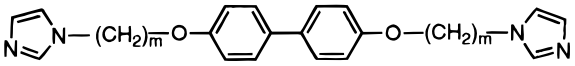
H-Bond Acceptor



2: m=6, X=CN
3: m=10, X=CN
4: m=6, X=O(CH$_2$)$_4$CH$_3$



5: m=6, X=(CH$_2$)$_3$CH$_3$
6: m=10, X=(CH$_2$)$_3$CH$_3$



7: m=6
8: m=10

Table 1. Transition Temperatures of Poly(acrylic acid)s and Imidazolyl-Terminated compounds

compounds	phase behavior[a] heating	phase behavior[a] cooling
1a	G 92 I	I 89 G
1b	G 132 I	I 124 G
2	K 72 I	I 55 K
3	K (43 K)[b] 84 I	I 52 N 47 K
4	K 106 I	I 88 K
5	G −45 S_A (−12 K)[b] 69 I	I 39 N 31 S_A -49 G
6	K 83 I	I 65 K
7	K 91 I	I 68 K
8	K 102 I	I 88 K

[a] Transition temperatures (°C): K, crystalline; G, glassy; S_A, smectic A; N, nematic; I, isotropic. [b] Cold crystallization in parentheses.

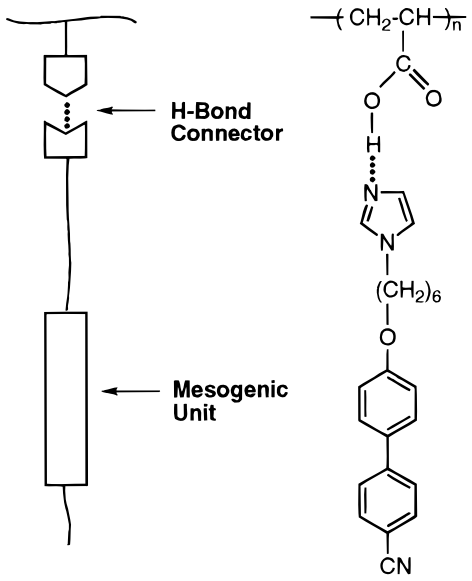


Figure 1. Molecular structure of the hydrogen-bonded side-chain polymer built by the H bond between imidazole and carboxylic acid moieties.

Table 2. Transition Temperatures of H−Bonded Side-Chain Liquid-Crystalline Polymeric Complexes

complexes[a]	phase behavior[b] heating									cooling				
1a/2				G	10	S_A	65	I	I	65	S_A	6	G	
1b/2				G	19	S_A	102	I	I	100	S_A	16	G	
1a/3		G	−3	S_A	(59	K)[c]	83	I	I	64	S_A	−7	G	
1b/3				G	6	S_A	106	I	I	103	S_A	2	G	
1a/4				K	103	S_A	118	I	I	107	S_A	87	K	
1b/4		K	77	K	107	S_A	127	I	I	118	S_A	69	K	
1a/5				G	−19	S_A	82	I	I	75	S_A	−24	G	
1b/5				G	−18	S_A	98	I	I	90	S_A	−20	G	
1a/6						K	81	I	I	75	S_A	43	K	
1b/6	G	−15	S_A	(56	K)[c]	79	S_A	95	I	I	93	S_A	−12	G

[a] All complexes are made from equimolar amounts of imidazolyl and carboxylic acid moieties. [b] Transition temperatures (°C): K, crystalline; G, glassy; S_A, smectic A; I, isotropic. [c] Cold crystallization in parentheses.

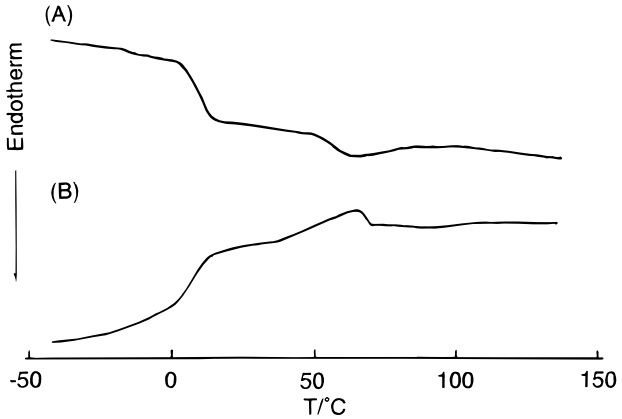


Figure 2. DSC thermograms of the polymeric complex of **1a** and **2**.

complexes based on the polymer **1b** with higher molecular weight, the smectic A phases are observed in wider and higher temperature ranges. The highest mesomorphic−isotropic transition temperature has been achieved for the complex of **1b** and **4**. Crystallization behavior is observed for the complexes derived from **4**. Azobenzene-containing complexes containing **5** or **6** also show smectic A phases. The results of X-ray diffraction

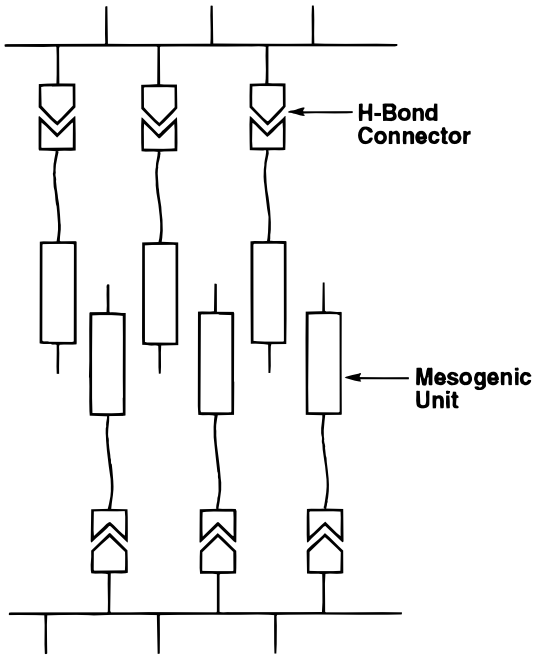


Figure 3. Schematic illustration of the liquid-crystalline side-chain polymer formed by self-assembly of **1a** and **2**.

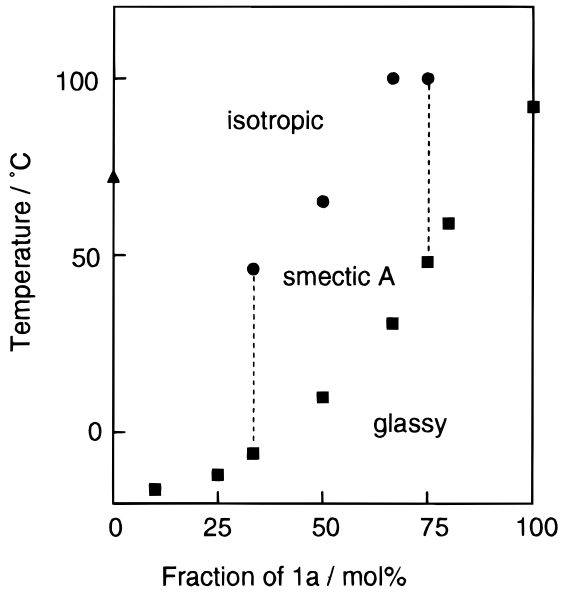


Figure 4. Phase diagram for the binary mixture of polyacrylate **1a** and imidazolyl monofunctional compound **2** on heating: (▲) crystalline-isotropic transition; (■) glass transition; (●) smectic A-isotropic transition.

measurements for the polymeric complex also support the existence of smectic A phases. The X-ray pattern of complex **1a**/**2** obtained at 27 °C consists of one sharp inner peak at 45 Å and a broad halo at 4.3 Å. The length of the side chain of the complex obtained by molecular modeling is 25 Å, which indicates that the cyanobiphenyl moiety is interdigitated in the smectic A phase, as shown in Figure 3.

The phase diagram for the binary mixture of polyacrylate **1a** and imidazolyl compound **2** on heating is shown in Figure 4. These compounds are miscible over the whole range of composition. Focal conic and homeotropic textures characteristic of a smectic A phase are observed for the mixtures containing between 33 and 75 mol % of **1a**. For the mixtures containing less than 33% of **1a**, cold crystallization is seen after the

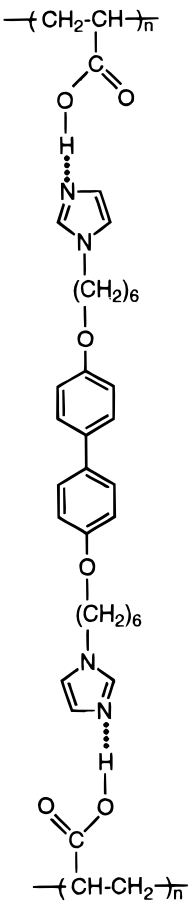


Figure 5. Molecular structure of the hydrogen-bonded network derived from **1a** and **7**.

glass transition and no stable liquid-crystalline phases are observed on heating.

Mesogenic H-Bonded Networks Derived from Bis-Imidazolyl Compounds and Poly(acrylic acid)s. We previously reported two types of mesogenic networks, which are novel molecular structures for mesomorphic materials.[7,14−16] The first type involves a hydrogen-bonded mesogen derived from 4,4′-bipyridine and a benzoic acid moiety in the side chain of polyacrylates.[7,14] The second type is networks obtained by the complexation of multifunctional low-molecular-weight compounds.[15−17] These networks exhibit stable liquid-crystalline behavior and thermally reversible phase transitions.

To obtain a new network structure from bifunctional mesogenic moieties by noncovalent cross-links between two polymer chains shown in Figure 5, bis-imidazolyl compounds **7** and **8** have been complexed with poly(acrylic acid)s **1a**,**b**. Thermal properties of the complexes are given in Table 3. These complexes exhibit smectic A phases. For example, complex **1a**/**7** exhibits a smectic A phase form 20 to 62 °C on heating, while each of the components is nonmesomorphic. The enthalpy change of the smectic A−isotropic transition per one mesogenic component is 1.4 kJ/mol. Homeotropic and oily textures are observed for the mesophase of complex **1a**/**7**. One sharp inner peak at 35 Å and a broad halo at 4.4 Å are observed in the X-ray diffraction pattern of **1a**/**7**. The length of the H-bonded complex between the two backbones of poly(acrylic acid) and bifunctional compound **7** with fully extended conformation is estimated to be 39 Å by molecular modeling. This

Table 3. Transition Temperatures of H−Bonded Liquid-Crystalline Polymeric Networks

complexes[a]	phase behavior[b]													
	heating							cooling						
1a/**7**			G	20	S_A	62	I	I	57	S_A	17	G		
1b/**7**			G	38	S_A	101	I	I	93	S_A	36	G		
1a/**8**	K	82	K	96	S_A	111	I	I	98	S_A	70	K		
1b/**8**	K	62	K	85	S_A	121	I	I	115	S_A	62	K	53	K

[a] All complexes are made from equimolar amounts of imidazolyl and carboxylic acid moieties. [b] Transition temperatures (°C): K, crystalline; G, glassy; S_A, smectic A; I, isotropic.

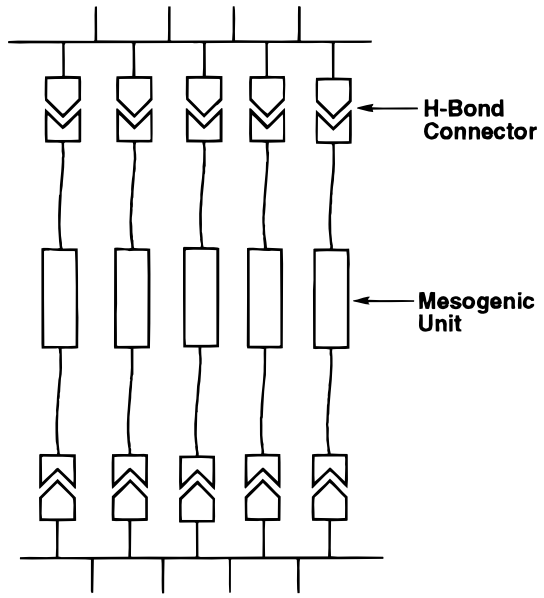


Figure 6. Schematic illustration of the liquid-crystalline network structure formed by self-assembly of **1a** and **7**.

suggests that a nearly stretched conformation of **7** forms the hydrogen-bonded network structure illustrated in Figure 6. Although covalently cross-linked networks with high density do not show mesomorphism, liquid crystallinity has been induced for the hydrogen-bonded networks. The dynamic nature of hydrogen bonds, which causes fast exchange of the molecular pair of complexes, may contribute to the mesomorphism of the networks. Thermally reversible phase transitions due to the dissociation and association of H bonds are observed between smectic and isotropic phases.

The present results reported here show that the imidazole moieties can be used as connecting parts with H-bonding donors for the formation of functional self-organized materials.

Acknowledgment. Financial support of Grant-in-Aid for Scientific Research on Priority Areas, "New Polymers and Their Nano-Organized Systems" (No. 277/08246101) from Ministry of Education, Science, Sports, and Culture is gratefully acknowledged. The authors thank Mr. Hideshi Hattori of Dai Nippon Printing Co., Ltd., for the X-ray measurements.

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MA980271I