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Supramolecular Liquid−Crystalline Side-Chain Polymers Built through a Molecular Recognition Process by Double Hydrogen Bonds

Takashi Kato,*,† Masahisa Nakano,† Tomonori Moteki,† Toshiyuki Uryu,† and Seiji Ujiie‡

Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan, and Department of Material Science, Shimane University, Matsue, Shimane 690, Japan

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A wide variety of structures of liquid−crystalline polymers have been prepared using a synthetic approach to build mesogenic molecular structures.[1,2] In this case, only covalent bonds are generally used to achieve the desired molecular structure. Recently, molecular architectures through self-assembly processes by specific molecular interactions such as hydrogen-bonding,[3−6] ionic,[7,8] ionic−dipolar,[9] and charge transfer[10] interactions have been recognized to be a new strategy for building the molecular structures of liquid−crystalline polymers. Hydrogen bond is one of the most important means of interaction for these processes due to its stability and directionality. Side-chain,[11−18] main-chain,[19,20] and network[5] polymers with liquid−crystalline properties have been built by supramolecular self-assembly through the formation of hydrogen bonds between different and independent components.

The molecular recognition process by the single hydrogen bond between carboxylic acids and pyridines has been used for the formation of mesogenic side-chain polymeric complexes.[3−5,11−15] This concept has been extended to obtain mesogenic H-bonded main-chain polymers from complementary components of diacids and bipyridines.[19] Polymeric complexes through triple hydrogen bonds between uracil and bis(acylamino)pyridines have also been reported to show liquid−crystalline behavior.[6,20] The hydrogen-bonding interaction between carboxylic acid and pyridine *N*-oxide also contributes to the formation of side-chain mesogenic polymers.[17]

It is known that doubly hydrogen-bonded molecular complexes are formed between 2-(acylamino)pyridines and carboxylic acids.[21−23] The behavior of the complexes in solution and crystalline states is well established. However, no mesomorphic complexes have been reported. Our intention has been to use this double hydrogen-bonding pattern for the design and preparation of mesogenic polymers to obtain versatile functional self-organized materials.

In this communication, we report a new approach involving a liquid−crystalline poly(acrylate) with a doubly hydrogen-bonded side-chain mesogen, which is a novel type of supramolecular polymers.

Poly(acrylate) **1** having a benzoic acid moiety through the undecamethylene spacer was used as a hydrogen-bonding side-chain polymer.[24] This type of polymer has been demonstrated to form hydrogen-bonded mesogens with stilbazoles in their side chains.[3−5,11−14] A glass transition at 67 °C and an endothermic transition at 184 °C on heating are observed for polymer **1**. Nonmesogenic 2,6-bis(acylamino)pyridines **2a** (m = 4) and **2b** (m = 7) were selected for the use of H-bonding components that recognize the side chain of the polymer **1**.[24] Compounds **2a**,**b** melt to isotropic liquids at 121 and 108 °C, respectively. The formation of the supramolecular structure from these hydrogen-bonding components has been designed as shown in Figure 1. The polymeric complexes were prepared by evaporation from pyridine solution containing equimolar amounts of carboxylic acid and 2-aminopyridyl moieties. This method was successfully used for the preparation of the hydrogen-bonded complexes of carboxylic acid and pyridine moieties.[3−5]

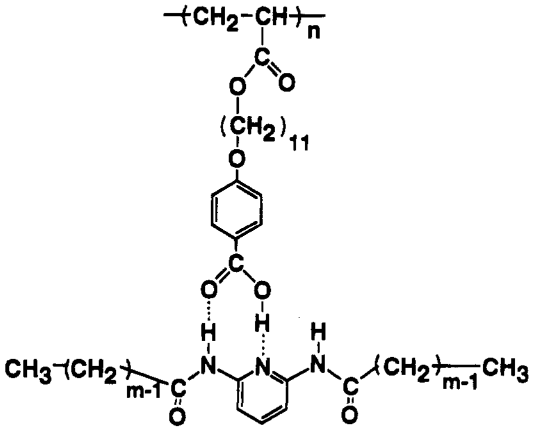

Figure 1. Proposed structure of the supramolecular side-chain polymer formed by molecular recognition through double hydrogen bonds.

Chart 1

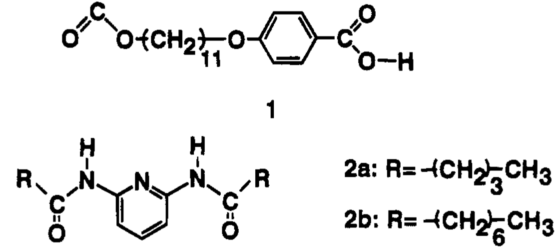

Figure 2A shows the DSC thermograms of the 1:1 hydrogen-bonded complex of **1** and **2a**.[25] On heating, only one endothermic peak due to the transition of crystal−isotropic liquid is observed at 111 °C. The enthalpy change of the transition is 39.9 J/g. Upon cooling, two exothermic transitions are seen at 98 and 80 °C. The enthalpies of these transitions are 6.5 and 33.1 J/g, respectively. These transitions are not observed for each of the single components of **1** and **2a**. Polarizing microscopy observation has shown that a mesophase is formed between the two exotherms.[26] The complex of **1** and **2b** also exhibits a monotropic mesophase from 97 to 83 °C. Unfortunately, X-ray diffraction patterns of the monotropic mesophase of these "homopolymeric" complexes could not be obtained because of crystallization during the measurement.[27]

One advantage of the hydrogen-bonded liquid−crystalline polymers is the simplicity of the preparation of "copolymers".[3] Copolymers of any desired compositions can be prepared by simple mixing and self-assembly of the desired H-bonding components.[3] Supramolecular side-chain copolymers were prepared from equimolar amounts of the benzoic acid of **1** and the 2-aminopyridyl moiety of the mixture of **2a**,**b**. A wider

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† The University of Tokyo.
‡ Shimane University.

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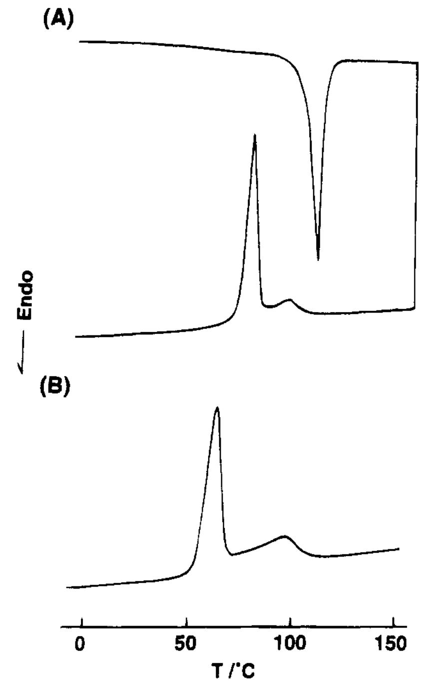

Figure 2. DSC thermograms of the polymeric hydrogen-bonded complexes: (A) polymeric complex of **1** and **2a** on heating and cooling and (B) copolymeric complex of **1** and a mixture of **2a**,**b** (molar ratio, **1**:**2a**:**2b** = 1:0.8:0.2) on cooling.

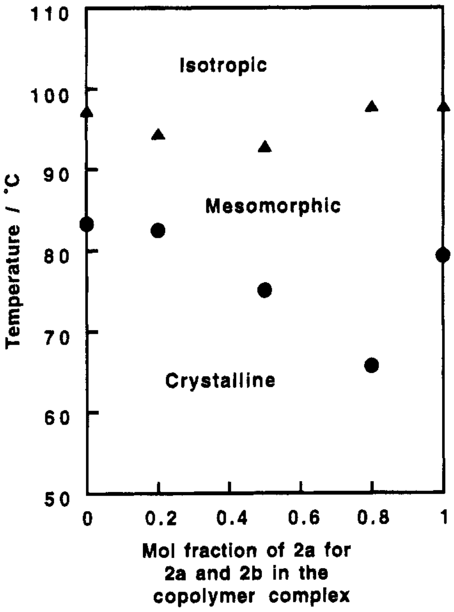

Figure 3. Phase diagram of copolymeric complexes of **1** and a mixture of **2a**,**b** on cooling.

mesomorphic temperature range has been achieved for "copolymer" structure. Figure 2B exhibits a DSC thermogram on cooling of the copolymer containing **1** and a mixture of **2a**,**b** (molar ratio, **1**:**2a**:**2b** = 1:0.8:0.2). For the copolymer, the crystallization peak shifts to the lower temperature, whereas the temperature of isotropic–mesophase transition shows no shift. Figure 3 shows a phase diagram of the copolymer complex of **1** and mixtures of **2a**,**b** on cooling. The transition temperatures are plotted against x, which is the molar fraction of **2a** for all bis(acylamino)pyridines of **2a**,**b** in the copolymer structure. The behavior of the transition temperature curves also suggests that the phase between the two exothermic peaks is a mesophase. These results show that the poly(acrylate) and the bis(acylamino)pyridines form the polymeric complex as shown in Figure 1, and it behaves as a single polymeric component.

X-ray diffraction patterns have been obtained for the "copolymer" with $x = 0.8$ (molar ratio, **1**:**2a**:**2b** = 1:0.8:0.2; Figure 2B), which has the widest temperature range of the monotropic phase from 98 to 66 °C.[27,28] A sharp inner peak at 20.2 Å and a diffused halo at 4.4 Å are only observed at 85 °C. This also shows that the complex forms a mesomorphic phase, which is not a crystalline phase. The mesogenic molecular structure reported here is unique because the two alkyl chains do not lie on the long axis of the aromatic core and the side chain moiety has no simple rod shape. The type of the mesophase and the pattern of the molecular packing are now under investigation.[29]

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(24) Polymer **1** was prepared by the polymerization of 4-[(11-acryloylundecyl)oxy]benzoic acid in DMF with AIBN (1 mol %). [η]: 0.23 dL/g. Bis(acylamino)pyridines **2a**,**b** were prepared from 2,6-diaminopyridine and the corresponding acyl chloride.

(25) Thermal properties were examined using a polarizing microscope equipped with a Mettler FP82HT hot stage and by differential scanning calorimetry (Mettler DSC30). DSC measurements were performed at heating and cooling rates of 10 °C/min. The peak temperature was taken as the transition temperature.

(26) The complex shows a fluid melt state with birefringence, though no clear texture was observed.

(27) X-ray diffraction measurements were carried out by a Rigaku X-ray Rad 2B system using Ni-filtered Cu $K\alpha$ radiation. Samples placed on a Mettler FP52 hot stage were used for the X-ray measurement.

(28) For copolymers, crystallization did not occur during the X-ray measurement. The rate of crystallization might become slower because of the random structure of the copolymer.

(29) The length of the fully stretched conformation of the long axis of the side chain is estimated to be about 31 Å by molecular modeling.

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