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Supramolecular Liquid-Crystalline Polyamides. Polymeric Complexes Formed through Hydrogen Bonding between Benzoic Acid Derivatives and a 2,6-Diaminopyridine Moiety in the Polymer Backbone

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Abstract : Supramolecular liquid-crystalline polyamide complexes were obtained by the formation of double hydrogen bonding between a 2,6-bis(acylamino)pyridyl moiety in the backbone of a polyamide and 4-alkyloxybenzoic acid derivatives. These polymeric complexes behaved as single components of liquid-crystalline polymers and exhibited stable and enantiotropic mesophases when benzoic acid derivatives had substituents such as methoxy, methyl, chloro, and nitro groups at 3-position. Supramolecular copolymeric structures were also formed by complexing the polyamide with two kinds of 4-alkyloxybenzoic acids.

1. Introduction

Aromatic polyamides such as poly(1,4-benzamide) and poly(1,4-phenyleneterephthalamide) have been known to be high-strength and high-modulus fibers obtained from lyotropic liquid-crystalline phases[1,2]. Thermotropic mesomorphic behavior was observed for a number of aromatic polyamides[3,4]. Recently, supramolecular thermotropic liquid-crystalline polyamides were obtained by the self-assembly of polymers and small molecules through hydrogen bonding, which is a non-covalent interaction[5,6]. A wide variety of well-defined mesogenic polymeric structures such as side-chain[7], main-chain[8], and network[9] polymers as well as low-molecular-weight complexes[10] have also been prepared by the formation of hydrogen-bonded complexes. For supramolecular polyamides, we have reported that aromatic nylons containing a 2,6-diaminopyridine moiety in their backbones are able to form mesogenic complexes with a 4-(4-alkyloxyphenyl)benzoic acid and 3-substituted 4-alkyloxybenzoic acids through the double hydrogen bonds[5,6]. Although the mesogen of

the polymeric complexes consists of only two benzene rings, they show stable mesophases up to high temperatures around 200 °C [6]. This high thermal stability can be attributed to the network formation of the interaction between the amide groups in the polyamide backbone[5,11].

In this paper, we report the preparation and mesomorphic properties of supramolecular polyamides formed by the complexation of 3-substituted 4-alkyloxybenzoic acids with the polymer containing a 2,6-diaminopyridine moiety. Copolymeric supramolecular polyamides have been obtained by using a mixture of the benzoic acids with different substituents for complexation.

2. Experimental

2.1 Syntheses of Benzoic Acid Derivatives and a Polyamide

The syntheses of benzoic acid derivatives used in the paper were reported in a previous paper[6] except for **Me-8OBA**. **Me-8OBA** was synthesized from *o*-cresol by etherification with octyl bromide and regioselective bromination of aromatic ring[12] followed by the

Grignard reaction with CO₂. Polyamide **P8APy** containing a 2,6-diaminopyridine moiety was prepared as previously reported[6]. The inherent viscosity of **P8APy** was 0.21 dL/g in DMF at 30 °C.

Chart I Molecular structures of the components in this study.

Thermal properties: **MeO-8OBA**: K 109 I, **Me-8OBA**: K 114 I; I 98 N 90 K, **H-8OBA**: K 100 Sc 107 N 148 I, **Cl-8OBA**: K 98 I; I 95 N 88 K, **NO₂-8OBA**: K 114 I. (K: crystalline; N: nematic; Sc: smectic C; I: isotropic)

2.2 Preparation of Hydrogen-Bonded Complexes

Hydrogen-bonded complexes were prepared by mixing of the components in molten state under a nitrogen atmosphere. Copolymeric complexes containing two different benzoic acids were prepared from a polyamide and two dissimilar benzoic acids maintaining the exact 1:1 stoichiometry between the 2,6-diaminopyridine moieties in the polyamide and the carboxylic groups in the benzoic acids. The mixtures once heated to isotropic homogeneous states were used for the experiments.

2.3 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 rate of 10 °C/min was used for the DSC measurements. For polymeric complexes, samples heated once to molten states were used for the measurements.

3. Results and Discussion

H-8OBA has enantiotropic liquid crystallinity and other benzoic acids show monotropic or no mesophases. None of the benzoic acids show mesophases over 150 °C. Polyamide **P8APy** is nonmesogenic and semi-crystalline. The DSC thermogram of **P8APy** on heating is shown in Figure 1A. **P8APy** exhibits glass

Fig. 1 DSC curves of polyamide **P8APy** (A) and polymeric complex **P8APy/MeO-8OBA** (B) on heating.

Table 1 Thermal Properties of Polymeric Complexes of **P8APy/X-8OBA**

Polymer complex P8APy/X-8OBA	Phase behavior (°C) ^{a)}				
P8APy/MeO-8OBA	K	108 (37.6)	M	187 (18.5)	I
P8APy/Me-8OBA	K	98 (27.2)	M	185 (25.5)	I
P8APy/H-8OBA	Phase separation				
P8APy/Cl-8OBA ^{b)}	K	94 (18.3)	M	177 (24.0)	I
P8APy/NO₂-8OBA	K	87 (17.3)	M	183 (20.2)	I

^{a)}K: crystalline, M: mesophase, I: isotropic. Enthalpy changes of the endothermic peaks are in parentheses (J/g).

^{b)}Ref. 6.

transition behavior at 74 °C followed by the melting at 220 °C on heating. The enthalpy change of the melting is 37.0 J/g. As was observed for the chloro substituent of the benzoic acids at the 3-position[6], the complexes of **P8APy** and 4-alkoxybenzoic acid derivatives (**MeO-8OBA**, **Me-8OBA**, and **NO₂-8OBA**) with methoxy, methyl, and nitro substituents at the 3-position show stable liquid-crystalline behavior until about 200 °C as single components as shown in Figure 2. Table 1 lists thermal properties of these supramolecular polyamides containing benzoic acid moieties with polar and non-polar groups. Figure 1B presents the DSC curve for complex **P8APy/MeO-8OBA**, which shows the highest isotropization and melting temperatures.

Fig. 2 Chemical structure of homopolymeric complexes **P8APy/X-8OBA**.

The glass transition followed by the peak due to cold crystallization is seen at 70 °C. The mesomorphic temperature range of the complexes are about 80-100 °C. These complexes would form smectic layered structures as was observed for **P10APy/Cl-mOBA**[6].

Random copolymeric complexes shown in Figure 3 have been prepared by the complexation of **P8APy** with a mixture of two different benzoic acid derivatives. Two benzoic acids containing electron-donating and electron-withdrawing substituents have been used as components, which were expected to stabilize the mesophase of the polymeric complexes by the interaction of electron-donating and electron-withdrawing groups[13,14]. Figure 4 shows DSC curves

Fig. 3 Chemical structure of copolymeric complex of **P8APy** with **MeO-8OBA** and **NO₂-8OBA**.

Fig. 4 DSC curves of copolymeric complex of an equimolar amount of **P8APy** and a mixture of **MeO-8OBA/NO₂-8OBA** ($x = 0.5$), which will be denoted as **P8APy/(MeO-8OBA/NO₂-8OBA)** ($x = 0.5$).

of the copolymeric complex of **P8APy** and **MeO-8OBA** and **NO₂-8OBA** ($x = 0.5$ in Figure 3). On heating, the melting peak is seen at 91 °C with the enthalpy change of 18.1 J/g followed by the isotropization peak at 190 °C. The complex shows birefringence and fluidity in the temperature range between the two peaks of the DSC (Figure 5). Phase separation cannot be seen under a microscopic observation. These results show that this polymeric mixture consisting of three components behaves as a simple liquid-crystalline polymer. The enthalpy change on the isotropization of **P8APy/(MeO-8OBA/NO₂-8OBA)** ($x = 0.5$) is 23.2 J/g, which is larger than each of **P8APy/MeO-8OBA** and **P8APy/NO₂-8OBA**, as listed in Table 1. This result suggests

Fig. 5 Polarized photomicrograph of P8APy/(MeO-8OBA/NO₂-8OBA) ($x = 0.5$) at 140 °C.

the stabilization on the liquid-crystalline phases by the interaction of electron-donating and electron-withdrawing groups of the copolymeric complex.

The phase diagram of liquid-crystalline copolymers of P8APy with a mixture of MeO-8OBA and NO₂-8OBA is shown in Figure 6. The continuous change of the melting temperatures and slight positive deviation of isotropic temperatures can be seen over the whole range of composition, which indicates the formation of stable copolymeric complexes. However, the stabilization effect on the liquid-crystalline phases via the interaction of electron-donating and withdrawing benzoic acids for the polyamide copolymers is not so noticeable as was reported in different systems[13,14].

The self-assembly of the supramolecular structure is schematically illustrated in Figure 7. In the polymeric

Fig. 6 Phase diagram of copolymeric complexes P8APy/(MeO-8OBA/NO₂-8OBA) for the mole fraction of MeO-8OBA.

Fig. 7 Schematic illustration of the formation of supramolecular polyamides PnAPy/(X-mOBA/Y-mOBA).

system, the substituents of 4-alkoxybenzoic acids would fill the vacant space in the supramolecular polyamides and have effect on the stabilization of the anisotropic supramolecular structures.

Supramolecular polymers consisting of a variety of molecular parts through non-covalent interactions would be versatile for new design of fiber materials which have high performance and dynamic functions [7,15].

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