

Ionic polymers exhibiting thermotropic liquid crystalline phases

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Two types of novel ionic liquid crystalline polymers were synthesized and their thermal and liquid crystalline properties were examined. The use of Coulombic forces led to the formation of thermotropic smectic phases. The ionic liquid crystal polymer with ammonium ions in the polymer backbone exhibited enantiotropically smectic A phase. The liquid crystalline ion complex polymer displayed enantiotropically smectic A, C, and hexatic smectic phases.

1. INTRODUCTION

The induction or enhancement of liquid crystallinity can be led by noncovalent interactions, for example Coulombic forces, hydrogen bondings, charge transfer. The use of the noncovalent interactions is a new approach in the molecular design of liquid crystalline polymers.[1-6]

In this work, we have synthesized a side chain liquid crystal polymer containing a polyion backbone and a liquid crystalline ion complex polymer. This paper describes the phase transitions and orientational behavior of the ionic liquid crystal polymers.

2. EXPERIMENTAL

2.1. Measurements

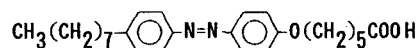
Molecular weights of the polymers were measured with a Toso GPC system (HLC-8020), calibrated with polystyrene standard samples. The thermal and liquid crystalline properties of the polymers were examined with a Mettler TA3000 (DSC20-TC10) system and an Olympus polarizing microscope (BH-2) with a Mettler FP52 hot stage equipped with a Mettler FP5 temperature controller. The orientational structure of the smectic phase was examined by

X-ray diffraction measurement. In the X-ray diffraction measurement, the measuring temperatures were controlled with a Linkam hot stage system.

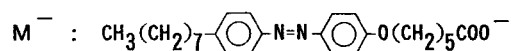
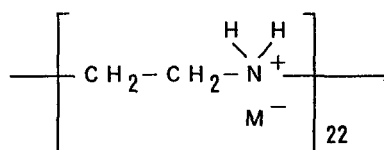
2.2. Synthesis

2.2.1. Synthesis of ion complex polymer

The liquid crystalline ion complex polymer was obtained by the reaction of poly(iminoethylene) and 3-carboxy-1-(4-(4-(octyl)phenylazo)phenoxy)propane(ionizable liquid crystal). In FT-IR measurement, ion complex



Ionizable Liquid Crystal



Ion Complex Polymer

polymer exhibited the ionized carboxyl absorption at 1640 cm^{-1} and 1394 cm^{-1} which replaced the carbonyl absorption at 1711 cm^{-1} in 3-carboxy-1-(4-(4-(octyl)phenylazo)phenoxy)propane. The broad absorption of N-H deformation vibration in poly(iminioethylene) was found at 1600 cm^{-1} and the absorption of N-H stretching vibration at 3300 cm^{-1} in poly(iminoethylene) vanished. These IR data indicate that the poly(iminoethylene) and the mesogenic carboxylic acid formed an ionic complex.

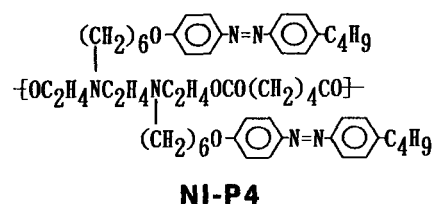
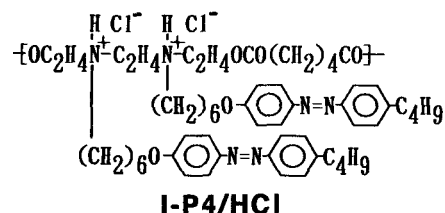
2.2.2. Synthesis of ionic polymers

The ionic liquid crystal polyesters were synthesized by polycondensation of a mesogenic monomer with two hydroxy groups and adipoyl chloride.

Synthesis of *N,N'*-bis(2-hydroxyethyl)-*N,N'*-bis(1-(4-(4-(butyl)phenylazo)phenoxy)hexane)ethylenediamine. A mesogenic monomer with two hydroxy groups was obtained by the reaction of 6-bromo-1-(4-(4-(butyl)phenylazo)phenoxy)hexane and *N,N'*-bis(2-hydroxyethyl)ethylenediamine in the presence of potassium carbonate. 6-Bromo-1-(4-(4-(butyl)phenylazo)phenoxy)hexane and *N,N'*-bis(2-hydroxyethyl)ethylenediamine were dissolved in ethanol, and to the solution, potassium carbonate was added. The mixture was reacted at 80°C for 100h. After the reaction, the mixture was filtered off, and the filtrate was evaporated. The mesogenic monomer [N,N'-bis(2-hydroxyethyl)-N,N'-bis(1-(4-(4-(butyl)phenylazo)phenoxy)hexane)ethylenediamine] was dissolved in chloroform, and to the chloroform solution, hexane was added. The precipitated mesogenic monomer was isolated and dried. $^1\text{H NMR}$ (CDCl_3): $\delta = 0.94$ (t 6H), 1.6(m 24H), 2.6(m 16H), 3.6(s 4H), 4.0(t 4H), 6.9(d 4H), 7.3(d 4H), 7.8(d 4H), 7.87(d 4H). The mesogenic monomer showed following phase transitions; Crystal 32.0°C Smectic C 54.0°C Nematic 59.0°C Isotropic.

Synthesis of ionic and nonionic polyesters. The ionic polymer was prepared by the reaction of adipoyl chloride and the

mesogenic monomer in the tetrahydrofuran (THF) solution. Hydrogen chloride prepared in this polymerization process was neutralized with the amine units in the mesogenic monomer. After the polymerization, the THF solution incorporating the ionic polymer was condensed and added to excess methanol.



The precipitated ionic polymer was filtered off and dried. A nonionic polymer was obtained by the reaction of the ionic polymer and triethylamine. The ionic polymer was dissolved into a THF solvent, and to the THF solution, triethylamine was added. Triethylammonium chloride precipitated and then filtered off. The THF solution containing the nonionic polymer was added to excess methanol. The precipitated nonionic polymer was filtered off and dried.

3. RESULTS AND DISCUSSION

3.1. Phase transitions of ion complex polymer

This liquid crystalline ion complex polymer showed enantiotropically smectic A, C, and X (hexatic smectic) phases (Table 1), encompassing both an arrangement due to the anisotropic counterions and fluid anisotropy arising from ionic aggregation. The liquid crystalline ion complex polymer exhibited schlieren and schlieren mosaic textures in the smectic C and smectic X phases, respectively.

A perpendicular structure, which is characterized by a uniaxial conoscopic figure, spontaneously formed in the smectic A phase. The ionizable liquid crystal that shows enantiotropic smectic C and monotropic hexatic smectic phases could not maintain a liquid crystalline arrangement at room temperature because of crystallization (Table 2). However, the liquid crystalline structure of the liquid crystalline ion complex polymer was unaltered at

Table 1. Phase transitions of liquid crystalline ion complex polymer

Phase transition temp. ^a /°C	
heating	G 25.2 SmX 70.6 SmC 146.5 SmA 180.2 I
cooling	G 15.5 SmX 68.8 SmC 126.1 SmA 177.9 I

a) G; glassy; SmX; hexatic smectic; SmC; smectic C; SmA; smectic A; I; isotropic.

Table 2. Phase transitions of ionizable liquid crystal

Phase transition temp. ^a /°C	
heating	K 140.5 SmC 141.5 I
cooling	K 132.4 SmX 140.4 SmC 141.2 I

a) K; solid; SmC; smectic C; SmA; smectic A; Sm1; smectic F or I; I; isotropic.

temperatures below the glass transition temperature, due to the polymer nature and the ionic aggregation. A temperature (T_i) of the liquid crystalline ion complex polymer at which an isotropic phase forms was higher than T_i of the ionizable liquid crystal. Furthermore, in the liquid crystalline ion complex polymer, the enantiotropic smectic A phase was induced in a temperature range above T_i of the ionizable liquid crystal and the smectic X phase was also stabilized on a heating process. These differences indicate that the ion complexation through Coulombic forces leads to the induction and enhancement of liquid crystallinity.

In the smectic A and C phases, two Bragg reflections corresponding to the smectic layer spacing are on the small angles and broad scattering peak is on the wide-angle region. The X-ray diffraction pattern in the smectic X phase consisted of two small-angle and one wide-angle Bragg reflections. The single sharp peak at the wide-angle results from the organization of a hexatic packing in the smectic X phase. The layer spacing of the smectic A phase is 5.52 nm, while an extended distance of the side-group is 2.75-2.9 nm. A possible packing model proposed for the smectic A phase is a bilayer structure (Fig. 1). The smectic layer spacings of the smectic C and X phases were 5.32 nm and 5.6 nm, respectively. In the smectic C phase, a possible packing model is a tilted bilayer structure, and the smectic X phase has a bilayer structure with a hexatic packing.

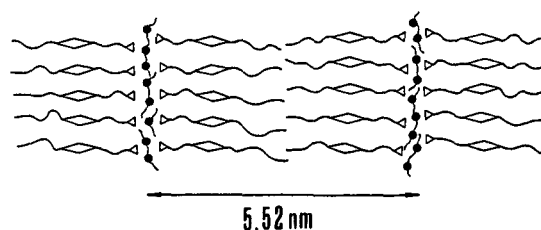


Fig. 1. Possible packing model of liquid crystalline ion complex polymer: ●; ammonium ion; △; anionic unit in the mesogenic group.

3.2. Phase transitions of ionic and nonionic liquid crystalline polyesters

Fig. 1 shows DSC curves of an ionic liquid crystal polyester with a tetramethylene spacer in a polymer backbone (I-P4/HCl, $M_n=9,000$) and its nonionic family (NI-P4, $M_n=8,400$). I-P4/HCl formed a smectic C phase with a broken fan texture and obviously displayed the glassy-smectic C and smectic C-isotropic phase transitions. However, NI-P4 did not produce any smectic phase and exhibited sharp peaks at the solid-nematic and nematic-isotropic phase transition points in the DSC measurement. In the nematic phase of NI-P4, a threaded texture formed.

I-P4/HCl exhibited 130°C higher meso-

phase-isotropic phase transition temperatures (T_i) than NI-P4. This difference is due to aggregation of the ions through Coulombic forces in I-P4/HCl.

I-P4/HCl spontaneously formed a pretilted homeotropic structure, due to the ammonium ions acting surface treatment agents.[3] On cooling the isotropic liquid of I-P4/HCl, the broken fan texture with a black region formed. By annealing the state, the broken fan texture vanished and was replaced to the black region. This black region was characterized by a biaxial conoscopic figure.

The orientational structure of the smectic phase of the ionic polymer was studied by X-ray measurement. The powder sample of I-P4/HCl exhibited sharp peaks at small angles,

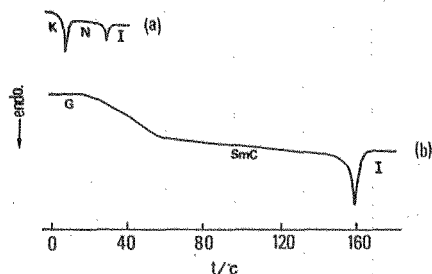


Fig. 2. DSC curves of NI-P4 (a) and I-P4/HCl (b).

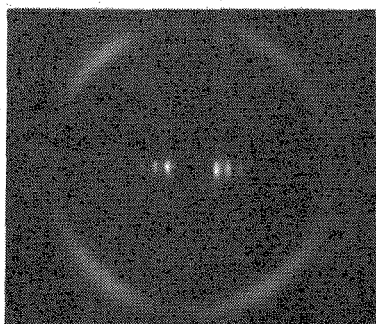


Fig. 3. X-ray diffraction pattern of oriented sample of I-P4/HCl.

corresponding to the smectic layer spacing, and a broad wide-angle peak that shows an unordered smectic phase such as a smectic A or C phase. In the oriented fibre of I-P4/HCl, which was obtained by drawing fibre at the smectic C temperature, the sharp Bragg spots at small angles were on the equator, and

the wide-angle reflections consisted of four diffuse crescents, which show a tilted smectic phase (Fig. 2).[7] Then, the fibre axis is along

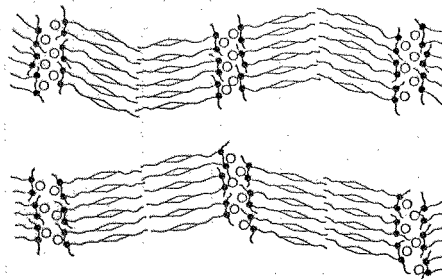


Fig. 4. Possible packing models of I-P4/HCl.

to the meridian. The mesogenic side groups were aligned for the direction perpendicular to the fibre axis. The wide-angle diffuse crescents are due to the disordered orientation in the tilted smectic layer of I-P4/HCl. The tilt angle in the smectic C phase determined from the splitting between the wide-angle crescents was 30° . The smectic layer distance (d) was 4.8nm, while the length (L) of the extended mesogenic side group was 2.4nm. In this case, considering the tilt angle, the relationship between d and L is $2L < d / \cos 30^\circ$. As a consequence, the d spacing is 0.7nm longer than twice the mesogenic side group. This indicates the presence of the ionic sublayer in the smectic C phase (Fig. 4).[2]

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