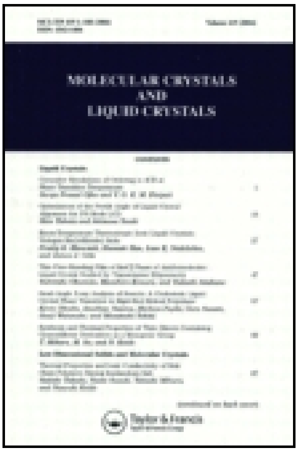

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Thermal Behavior of Ionic Liquid-Crystalline Side-Chain Polymer

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Thermal Behavior of Ionic Liquid-Crystalline Side-Chain Polymer

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Both nonionic liquid-crystalline side-chain polymer [P(A—CH_3)] and ionic family [P(A—CH_3/CH_3I)] of P(A—CH_3) were prepared. Nonionic P(A—CH_3), having an alkylamine spacer, exhibited solid-smectic and smectic-isotropic phase transitions. Ionic P(A—CH_3/CH_3I), having an alkylammonium spacer, showed glassy-smectic and smectic-isotropic phase transitions. Ionic P(A—CH_3/CH_3I) exhibited the enhanced thermal stability by the aggregation of ammonium ions formed by Coulomb's force in comparison with nonionic P(A—CH_3). The enhanced thermal stability in ionic families was also concluded from experimental results obtained for nonionic and ionic low molecular weight liquid-crystalline compounds corresponding to mesogenic side groups of P(A—CH_3) and P(A—CH_3/CH_3I).

INTRODUCTION

We have been interested in the synthesis and in the mesomorphic behavior of ionic thermotropic liquid-crystalline polymers. Recently, we reported the effect of ammonium ions on ionic thermotropic liquid-crystalline polymers with ionic polymer backbones.[1,2] Ammonium ions in the ionic polymer backbone acted, forming the smectic phase and enhanced the thermal stability of the smectic phase. In this paper, we report the thermal properties of ionic thermotropic liquid-crystalline side-chain polymers with an ammonium ion in a spacer unit.

RESULTS AND DISCUSSION

A nonionic low molecular weight liquid-crystalline compound (A—CH_3) was prepared by the reaction of 6-bromo-1-((4-((4-nitrophenyl)azo)phenyl)oxy)hexane with N-methylethanol amine. An ionic low molecular weight liquid-crystalline compound (A—CH_3/CH_3Br) was obtained by the reaction of A—CH_3 with methyl bromide. The structures of A—CH_3 and A—CH_3/CH_3Br are shown in Figure 1. A nonionic liquid-crystalline side-chain polymer [P(A—CH_3)] was obtained by radical polymerization of methacrylic monomer prepared from A—CH_3 with methacryloyl chloride. Ionic P(A—CH_3/CH_3I) was prepared by the reaction of P(A—CH_3)

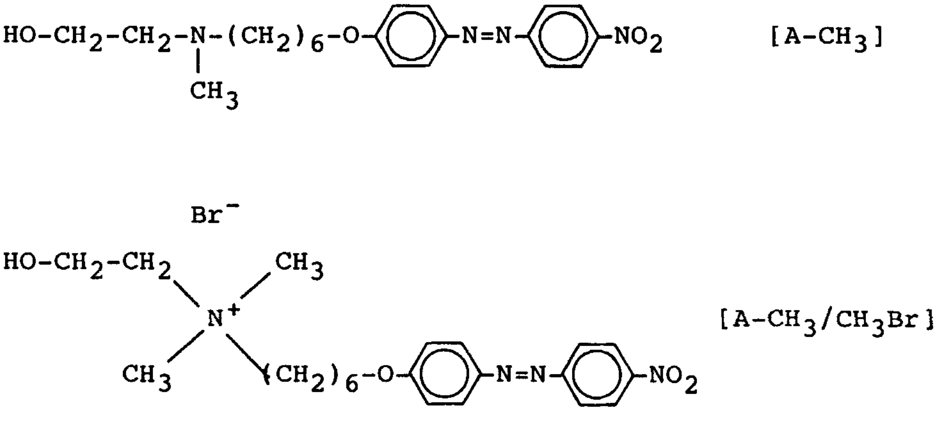


FIGURE 1 Structures of nonionic and ionic low molecular weight liquid-crystalline compounds.

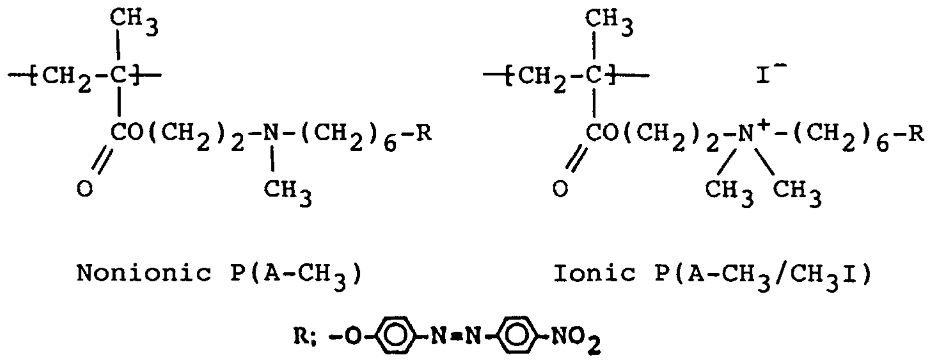


FIGURE 2 Structures of nonionic and ionic liquid-crystalline polymers.

TABLE I

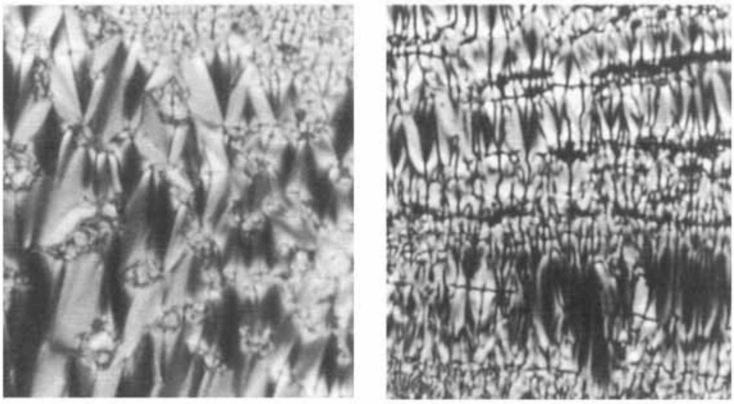
Phase transition temperatures of nonionic A—CH_3 and ionic A—CH_3/CH_3Br

Sample	Phase transition temp.[a] / °C	SR[b] / °C
A-CH_3	K 57.5 SmA 88.0 I	30.5
A-CH_3/CH_3Br	K 108.1 SmA 198.4 I	90.3

[a] K : solid phase, SmA : smectic A phase, I : isotropic phase; [b] SR : smectic temperature range.

with methyl iodide. Phase transitions were characterized with a Mettler TC10A-DSC20 system and an Olympus polarizing microscope BHSP.

A—CH_3 and A—CH_3/CH_3Br exhibited enantiotropically smectic A phases with fan textures. In homeotropically aligned samples of A—CH_3 and A—CH_3/CH_3Br, optically uniaxial conoscopic figures, which are characteristic of the smectic A



(A) P(A-CH_3) (B) P(A-CH_3/CH_3I)

FIGURE 3 Fan textures observed for P(A—CH_3) and P(A—CH_3/CH_3I). See Color Plate XI.

TABLE II

Phase transition temperatures of nonionic and ionic liquid-crystalline side-chain polymers

Sample	$\overline{Mn}$	Phase transition temp.[a] / °C				
P(A-CH_3)	3500	K	46.5	SmA	75.5	I
	18000	K	52.5	SmA	136.2	I
P(A-CH_3/CH_3I)	4500	G	69.5	SmA	228.0	I
	23000	G	72.4	SmA	250	D

[a] K : solid phase, G : glassy state, SmA : smectic A phase, I : isotropic phase, D : thermal decomposition.

phase, were observed. A—CH_3/CH_3Br exhibited 110.4°C higher smectic-isotropic phase transition temperature in comparison with A—CH_3 (see Table I). The enhanced thermal stability of A—CH_3/CH_3Br is caused by an aggregation of ammonium ions formed by Coulomb's force which is absent from nonionic A—CH_3.[1,2]

P(A—CH_3/CH_3I) formed an enantiotropically smectic phase with a fan texture (see Figure 3). A conoscopic figure of an oriented sample of P(A—CH_3/CH_3I) was characterized as optically uniaxial. P(A—CH_3) also showed an optically uniaxial smectic phase with a fan texture (see Figure 3). P(A—CH_3) and P(A—CH_3/CH_3I) exhibited amorphous halos in the wide-angle X-ray region. This indicates the absence of a long range orientational order in the smectic layer. From the above, we identified that enantiotropically smectic phases of P(A—CH_3) and P(A—CH_3/CH_3I) have the smectic A orientational order.

Phase transition temperatures of P(A—CH_3) and P(A—CH_3/CH_3I) are listed in

Table II. Phase transition temperatures of P(A—CH_3) and P(A—CH_3/CH_3I) increased with increasing molecular weight. The isotropization temperature (T_i) of P(A—CH_3/CH_3I) with a molecular weight ($\overline{Mn}$) of 4500 was higher by 91.8°C than T_i of P(A—CH_3) with $\overline{Mn}$ of 18000 because ammonium ions in P(A—CH_3/CH_3I) aggregate by Coulomb's force in the same manner as A—CH_3/CH_3Br.

P(A—CH_3/CH_3I) showed a glassy-smectic phase transition and maintained smectic orientations at temperatures below the glass transition. In P(A—CH_3), however, the glass transition temperature was not measured, and P(A—CH_3) crystallized at a solid-smectic phase transition. The glass transition in P(A—CH_3/CH_3I) is due to the restriction of thermal motions in polymer backbones by the aggregation of ammonium ions.

This study demonstrates that interactions formed between ammonium ions act effectively to enhance the thermal stability of liquid-crystalline phases.

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References

1. S. Ujiie and K. Iimura, *Mol. Cryst. Liq. Cryst. Letters*, **8(5)**, 111 (1992).
2. S. Ujiie and K. Iimura, *Macromolecules*, **25**, 3174 (1992).