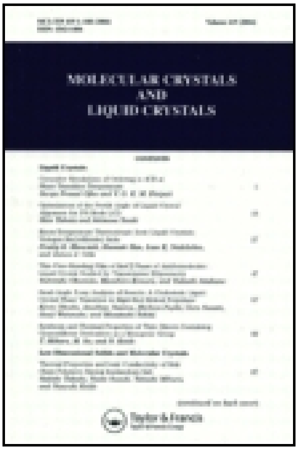

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Phase Transitions of Ionic Liquid-Crystalline Polymethacrylate Having a Piperidinium Skeleton

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Phase Transitions of Ionic Liquid-Crystalline Polymethacrylate having a Piperidinium Skeleton

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An ionic liquid-crystalline polymethacrylate [P-Pi/MeI] having a piperidinium skeleton in a mesogenic side-chain was synthesized. Its nonionic family [P-Pi] was also prepared, and phase transitions of P-Pi/MeI and P-Pi were compared.

Both P-Pi/MeI and P-Pi exhibit enantiotropically smectic phases. Ionic P-Pi/MeI shows enhanced thermal stability in comparison with nonionic P-Pi. A temperature of P-Pi/MeI, at which an isotropic phase forms, is higher than that of P-Pi. P-Pi/MeI also shows a higher glass transition temperature when compared to P-Pi.

Also, nonionic and ionic low molecular weight model compounds were prepared, and their thermal properties were compared.

Keywords: ionic liquid-crystalline polymer, piperidinium skeleton, phase transition

INTRODUCTION

Recently, the effects of ammonium ions in ionic thermotropic liquid-crystalline side-chain polymers were studied.[1–4] The ammonium ions acted in producing a smectic phase and enhanced the thermal stability in the smectic phase. We are convinced that the introduction of the ammonium ion into nonionic liquid-crystalline polymers leads to the formation of smectic phases having enhanced thermal stability.

We have synthesized an ionic thermotropic liquid-crystalline polymethacrylate [P-Pi/MeI] with an ammonium ion in a spacer unit and its nonionic family [P-Pi]. This paper describes phase transitions of ionic P-Pi/MeI and nonionic P-Pi. We also report thermal properties of the low molecular weight model compounds corresponding to the mesogenic side chains of P-Pi/MeI and P-Pi.

CHEMICAL STRUCTURES AND PREPARATIONS

Chemical structures of low molecular weight model compounds and liquid-crystalline polymethacrylates are shown in Figure 1.

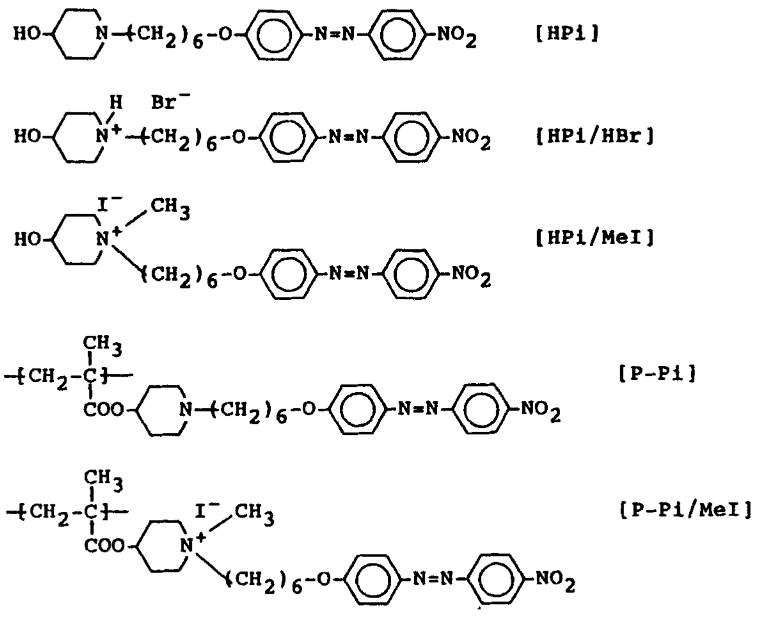

FIGURE 1 Chemical structures of model compounds and polymethacrylates.

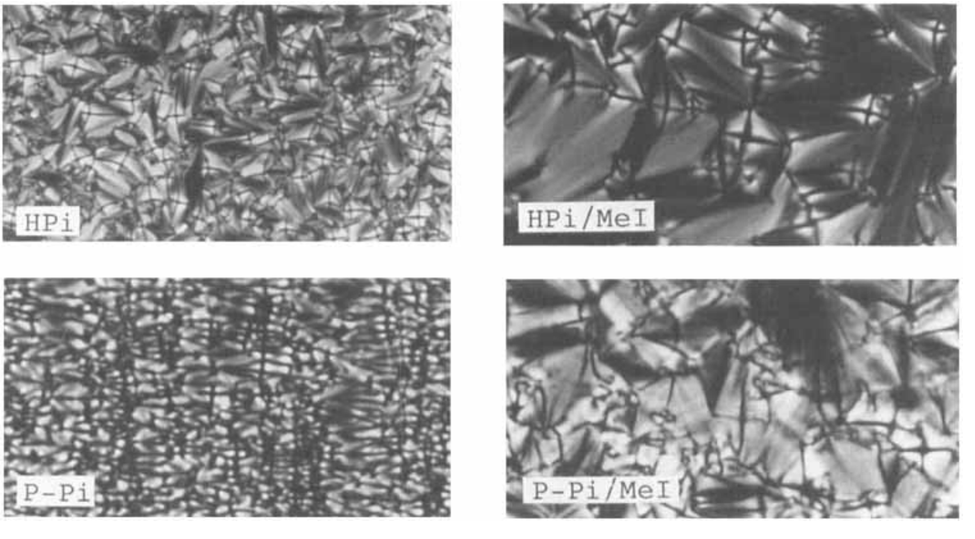

FIGURE 2 Smectic textures. See Color Plate XIII.

4-Hydroxy-1-(6-(4-(4-nitrophenylazo)phenoxy)hexyl)piperidine [HPi] and 4-hydroxy-1-(6-(4-(4-nitrophenylazo)phenoxy)hexyl)piperidinium bromide [HPi/HBr] were prepared by the reaction of 4-hydroxypiperidine with 6-bromo-1-(4-(4-nitrophenylazo)phenoxy)hexane. 4-Hydroxy-1-methyl-1-(6-(4-(4-nitrophenylazo)phenoxy)hexyl)piperidinium iodide [HPi/MeI] was prepared by the reaction of HPi with iodomethane.

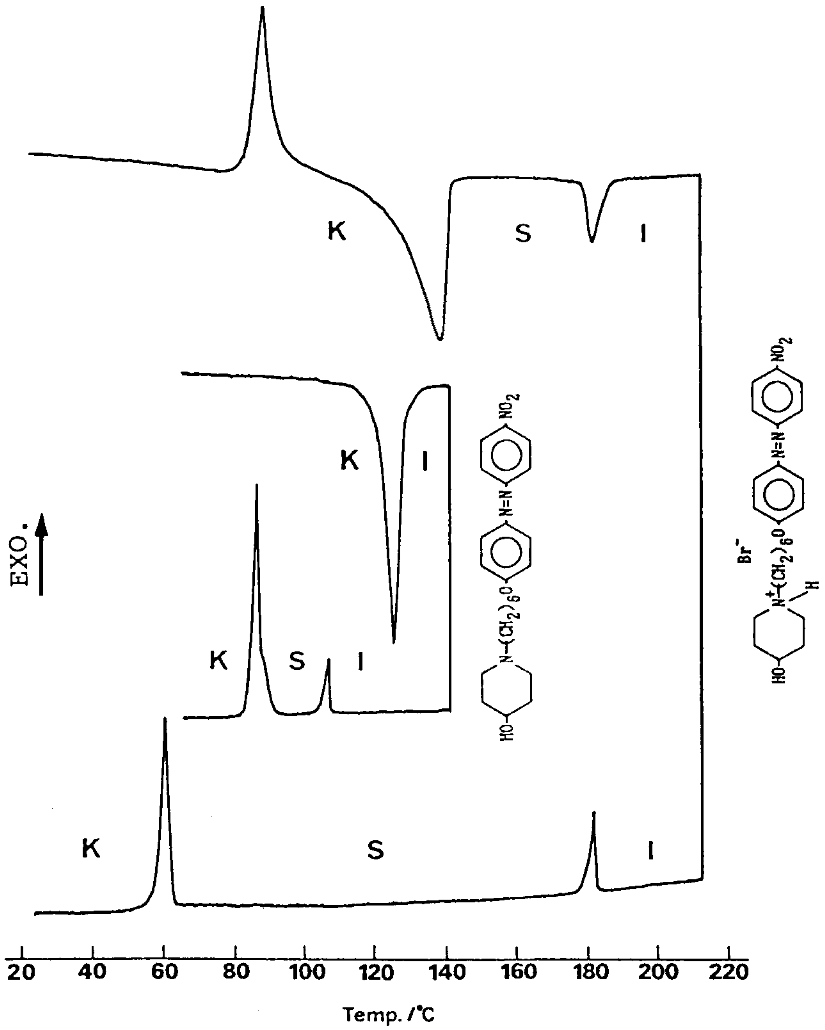

FIGURE 3 DSC curves of nonionic HPi and ionic HPi/HBr.

The nonionic liquid-crystalline polymethacrylate [P-Pi] was obtained by radical polymerization of a mesogenic monomer prepared by the reaction of HPi with methacryloyl chloride. The ionic liquid-crystalline polymethacrylate [P-Pi/MeI] was prepared by the reaction of P-Pi with iodomethane.

MEASUREMENTS

The phase transitions were measured with an Olympus polarizing microscope BH-2 equipped with a Mettler FP52 hot stage apparatus with a Mettler FP5 temperature controller. The thermal properties were determined with a Mettler TA3000 system (TC 10, DSC 20) at a scanning rate of 2°C/min.

TABLE I

Phase transition temperatures of model compounds

Sample	Phase transition temperatures[a] / °C											
	heating						cooling					
HPi	K			124.9	I		I	106.4	S	86.2	K	
HPi/HBr	K	137.8	S	182.0	I		I	182.0	S	60.1	K	
HPi/MeI	G	27.5	S	189.6	I		I	189.2	S	25.3	G	

a) K; solid: G; glassy: S; smectic: I; isotropic.

Molecular weight of the polymers was determined by a Toso GPC (HLC-802UR), calibrated with standard polystyrenes.

RESULTS AND DISCUSSION
PHASE TRANSITIONS OF MODEL COMPOUNDS

The DSC curves of nonionic HPi are shown in Figure 3. HPi formed a monotropically smectic phase with a fan texture (see Figure 2). However, ionic HPi/HBr, which is the ionic form of HPi, exhibited an enantiotropically smectic phase with a fan texture, as shown in Figure 3. In ionic HPi/MeI, also, an enantiotropically smectic phase formed, and a fan texture was observed as shown in Figure 2. Furthermore, the temperatures (T_i) of ionic HPi/HBr and HPi/MeI, at which the isotropic phases form, were much higher than T_i of nonionic HPi (see Table I and Figure 3).

The ammonium salts in the ionic model compounds aggregate by Coulomb's force, which is absent in nonionic HPi, and act in producing and stabilizing the smectic phase. Consequently, the ionic model compounds form the enantiotropically smectic phases with enhanced thermal stability. This demonstrates that the introduction of an ammonium ion into a nonionic liquid crystal leads to the formation of the smectic phase with enhanced thermal stability.

PHASE TRANSITIONS OF IONIC AND NONIONIC LIQUID-CRYSTALLINE POLYMETHACRYLATES

Nonionic P-Pi and ionic P-Pi/MeI showed glassy-smectic and smectic-isotropic transitions. Phase transition temperatures of nonionic P-Pi and ionic P-Pi/MeI are shown in Figure 4. In ionic P-Pi/MeI with a molecular weight above 6900, the smectic-isotropic phase transition temperature (T_i) was not measured because of the thermal decomposition.

In enantiotropically smectic phases of P-Pi and P-Pi/MeI, the fan textures were observed, as shown in Figure 3, and the phase transition temperatures increased with increasing molecular weight. In the molecular weights above 6900, ionic P-

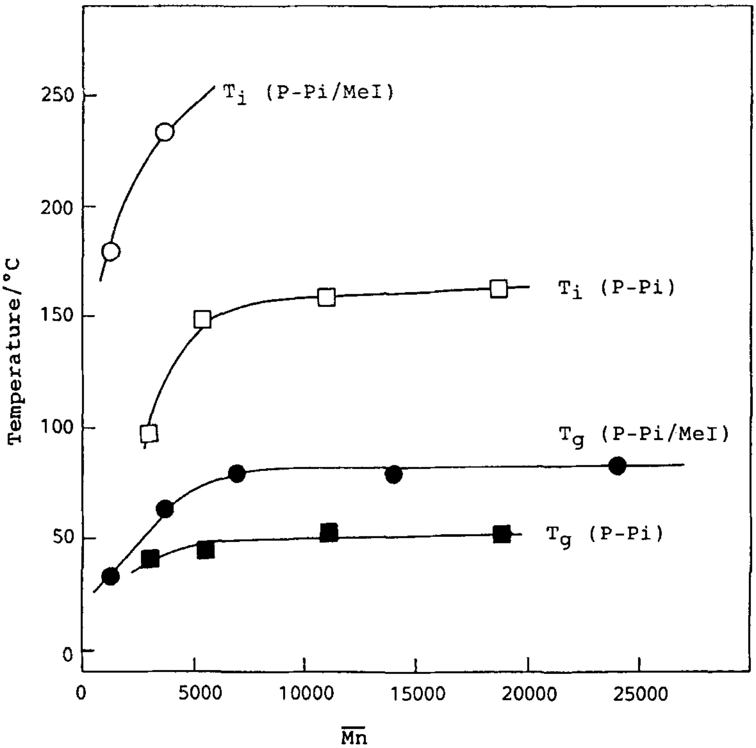

FIGURE 4 Phase transitions of nonionic P-Pi and ionic P-Pi/MeI: T_g; glass transition temperature: T_i; smectic-isotropic phase transition temperature.

Pi/MeI exhibited 30°C higher glass transition temperature (T_g) when compared to nonionic P-Pi. Furthermore, T_i of P-Pi/MeI was much higher than T_i of P-Pi.

These correspond to the results obtained for the model compounds (HPi/MeI and HPi). Nonionic P-Pi and HPi form the smectic phase by interactions between the mesogenic groups. In ionic P-Pi/MeI and HPi/MeI, however, the smectic phase forms by the aggregation of ammonium salts in addition to the interactions between the mesogenic groups. The aggregation of ammonium salts in P-Pi/MeI and HPi/MeI acts effectively, forming the smectic phase and enhances the thermal stability of the smectic phase.

References

1. S. Ujiie and K. Iimura, *Macromolecules*, **25**, 3174 (1992).
2. S. Ujiie and K. Iimura, *Mol. Cryst. Liq. Cryst. Letters*, **8**(5), 111 (1992).
3. S. Ujiie, Y. Tanaka and K. Iimura, *Mol. Cryst. Liq. Cryst.*, in press.
4. S. Ujiie and K. Iimura, *Chem. Lett.*, 995 (1990).