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Thermotropic Liquid-Crystalline Ionic Polymers

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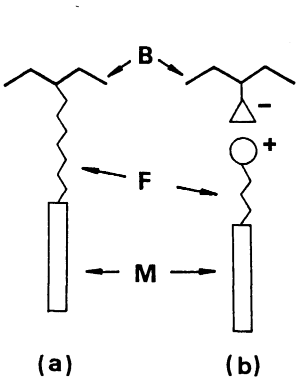
Thermotorpic liquid-crystalline ionic polymers formed between the anionic polymer and the cationic low-mass compound have been prepared, and their thermal properties and orientational structures have been studied. They spontaneously organized homeotropic structures in the smectic phases.

We have described that polymers with ammonium halide moiety and their low-mass model compounds exhibit thermotropic liquid-crystalline phases.1) The experimental results have demonstrated that the ammonium ion moiety is enhanced the thermal stability in the liquid-crystalline phase and effectively functions for the spontaneous formation of the homeotropic structure with high orientational order.

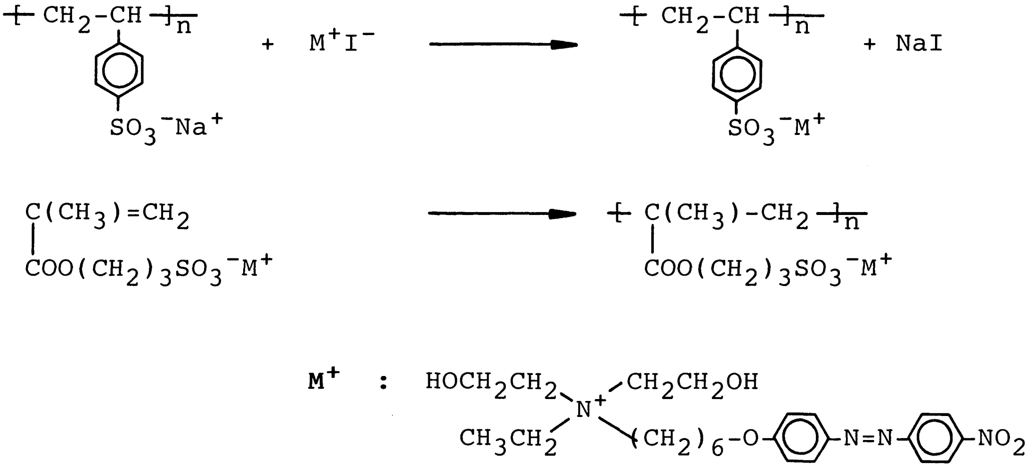
The functional cationic low-mass liquid crystal with ammonium ion group can have various types of mesogenic or nonmesogenic anion-compounds as a counter-ion. Consequently, in this work we have synthesized novel class types of thermotropic liquid-crystalline ionic polymers formed between the anionic polymer and the cationic low-mass liquid crystal with ammonium ion group. This paper reports on the effects of both the ammonium ion group and the structure of anionic polymer for thermal properties and orientational behavior.

The general liquid-crystalline side-chain polymers are usually built with covalent bonds as shown in Fig. 1-a. In liquid-crystalline ionic polymers prepared by us, however, the cationic liquid-crystalline unit is introduced by an ionic bond in the side-chain of anionic polymer backbone as shown in Fig. 1-b.



(a) : general liquid-crystalline side-chain polymer built with covalent bond.
(b) : liquid-crystalline ionic polymer.
B : polymer backbone, F : flexible chain,
M : mesogenic unit, (Δ^-) : anion moiety,
($\bigcirc^+$) : cation moiety.

Fig. 1. Schematic structures in general liquid-crystalline side-chain polymer and liquid-crystalline ionic polymer studied in this work.



Scheme 1.

Scheme 2.

Fig. 2. Synthetic routes of thermotropic liquid-crystalline ionic polymers (pSS and pMS) studied in this work.

Table 1. Transition temperatures of pSS and pMS

Sample	DP	Transition temperatures$^{d)}$ / °C				
pSS	$2^{a)}$	K	56	S	180	I
	$400^{b)}$	G	50	S	215	I
pMS	$2\text{-}6^{a)}$	K	52	S	205	I
	$-^{c)}$	G	65	S	210	I
(M^+I^-		K	40.2	S	170.2	I)$^{e)}$

a)Determined by GPC in THF, calibrated by polystyrene standards.
b)DP of poly(sodium styrenesulfonate) used for ion-exchange reaction.
c)Insoluble in THF because of high DP.
d)K:solid phase, G:glassy phase, S:smectic phase, I:isotropic phase.
e)Phase transition temperatures of low-mass liquid-crystalline compound (M^+I^-) used in this study.

Polystyrene sulfonate type of liquid-crystalline ionic polymer (pSS) was prepared by ion-exchange reaction as shown in Scheme 1 of Fig. 2. Polymethacrylic sulfonate type of liquid-crystalline ionic polymer (pMS) was obtained by radical polymerization in DMF as shown in Scheme 2 of Fig. 2. Thermal and orientational properties of the cationic low-mass liquid crystal (M^+, Fig. 2) used in this preparation has been already reported.[1] The liquid-crystalline complex formed between cationic unit (M^+) and iodide ion (I^-) exhibited the uniaxial smectic phase, and then spontaneously formed the homeotropic alignment.

Phase transition temperatures of pSS and pMS are listed in Table 1. pSS and pMS exhibited enantiotropic smectic phases, regardless of molecular weights. A fan shaped texture was observed in the smectic phase of pMS, and in the smectic phase of pSS fan and schlieren textures were found. The schlieren texture in pSS indicates the existence of a tilt smectic phase.

Isotropization temperatures raise with increasing DP in both pSS and pMS. This data corresponds to the result reported for general liquid-crystalline comb-like polymers.[2,3]

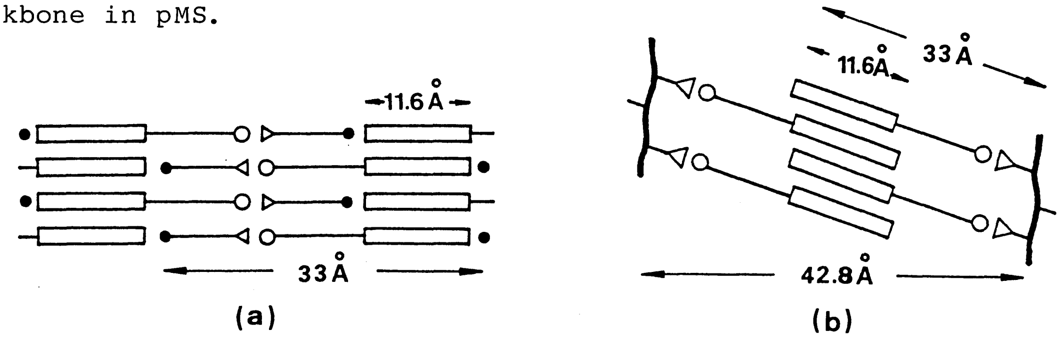
pMS spontaneously formed homeotropic alignment in smectic phases. The homeotropic structure of pMS remained unaltered on cooling in the solid phase. The observation of the conoscopic figure is available to determine an orientational condition.[4] The orientational state in pMS was confirmed by the observation of a conoscopic figure with a clear isogyre. The conoscopic figure was the same as that observed in the low-mass liquid crystal M^+I^-. It indicates that the smectic phase in pMS has an optically uniaxial property.[1]

pSS with low DP of 2 was also homeotropically aligned, however, pSS with high DP of 400 unclearly exhibited the formation of homeotropic structure. This indicates that the anionic polystyrene backbone impedes the spontaneous formation of homeotropic structure in the cationic liquid-crystalline unit M^+ because of the rigidness of polystyrene.

X-Ray diffractions for annealed samples of pMS and pSS were measured at RT. The scattering peak located at 2.67° indicates the existence of the smectic layer, and the smectic layer spacing (33.0 Å) calculated from this value is equal to the mesogenic side-chain length (33-34.5 Å). This demonstrates that pMS has a single layer structure in the smectic phase. In general smectic polymethacrylates and polyesters having mesogen with polar terminal group are well-known to exhibit the partial bilayer. Therefore, in the case of pMS in our study, p-nitroazobenzene mesogenic groups (11.6 Å) also overlap with each other. Further, the ammonium salt moiety in the side-chain also aggregates with each other, and plays a major role for formation of the smectic layer structure. A possible arrangement model in the smectic phase of pMS studied in this work is a monolayer-like structure, and is schematically illustrated in Fig. 3(a).

pSS exhibited a scattering peak in the X-ray small angle region, which is indicative of a periodic layer structure. The mesogenic side-chain length (L) is 33 Å, and the smectic layer spacing (42.8 Å) is less than twice L. This fact and the schlieren texture observed in the smectic phase of pSS indicate that pSS forms a tilt-partial bilayer structure which p-nitroazobenzene mesogens overlap with each other in the smectic phase. A schematic illustration of a packing model is a tilt-partial bilayer structure as a smectic C, and is shown in Fig. 3(b).

Though pSS and pMS have the same cationic liquid-crystalline unit, as shown in Fig. 3(a) and 3(b), pMS and pSS exhibit the monolayer-like and the tilt-partial bilayer structures, respectively. This difference in the layer structures of pSS and pMS is dependent on the orientational property of anionic polymer main-chain because the rigidness of the styrene type of backbone in pSS is larger than that of the alkylmethacrylate type of backbone in pMS.



(a) (b)

Fig. 3. Possible packing models in pMS (a) and pSS (b) : (△) ; anion moiety : (○) ; cation moiety : (●) ; polymer backbone in pMS.

References
1)S. Ujiie and K. Iimura, Chem. Lett., 1990, 995.
2)S. G. Kostromin, R. V. Talroze, V. P. Shibaev, and N. A. Plate, Makromol. Chem., Rapid Commun., 3, 803 (1982).
3)H. Stevens, G. Rehage, and H. Finkelmann, Macromolecules, 17, 851 (1984).
4)F. Hessel and H. Finkelmann, Polym. Bull., 15, 349 (1986).

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