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Thermotropic Liquid-Crystalline Copolymers Containing Ionic Group

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Thermotropic liquid-crystalline copolymers containing an ionic group have been synthesized, and the effects of the ionic component for their liquid-crystalline properties have been studied.

Various types of liquid-crystalline polymers have been prepared from theoretical and applied viewpoints. However, few thermotropic liquid-crystalline polymers having an ionic unit have been reported. We described that ammonium ion moieties in the liquid-crystalline polymer enhance the thermal stability in the smectic phase.[1] In this work we have synthesized novel thermotropic liquid-crystalline copolymers by copolymerization of a liquid-crystalline comonomer with a non-liquid-crystalline ionic comonomer. And the relationship between the thermotropic liquid-crystalline properties and the ionic comonomer component has been studied.

The synthetic route of thermotropic liquid-crystalline copolymers containing ionic group is shown in Fig. 1. The liquid-crystalline methacrylic comonomers with biphenyl moiety (MCB) or 4-nitroazobenzene moiety (MCNAB) were prepared by the methods described in the literatures.[2,3] The non-liquid-crstalline ionic methacrylic comonomer (IMC) was obtained by ion-exchange reaction between sodium 4-(4-diethylaminophenylazo)benzene sulfonate (EO) and methacryloyloxy-2-ethyltrimethylammonium chloride (MEAC). Identification of comonomers was performed by ^{1}H-NMR measurement.[4] MCB exhibited a nematic phase, and MCNAB formed nematic and smectic phases. However, IMC has no liquid-crystalline phase. The liquid-crystalline copolymers (P[MCB-(IMC)n] and P[MCNAB-(IMC)n]) containing ionic groups were synthesized by radical polymerization in N,N-dimethylformamide (DMF). The polymers except P[MCB-(IMC)0] prepared from MCB were precipitated from the DMF solution during radical polymerization reaction. The precipitated polymer was filtered off, and was washed with acetone. P[MCB-(IMC)0] was reprecipitated by adding methanol to the DMF solution, and the precipitate was filtered off, and was washed with methanol.

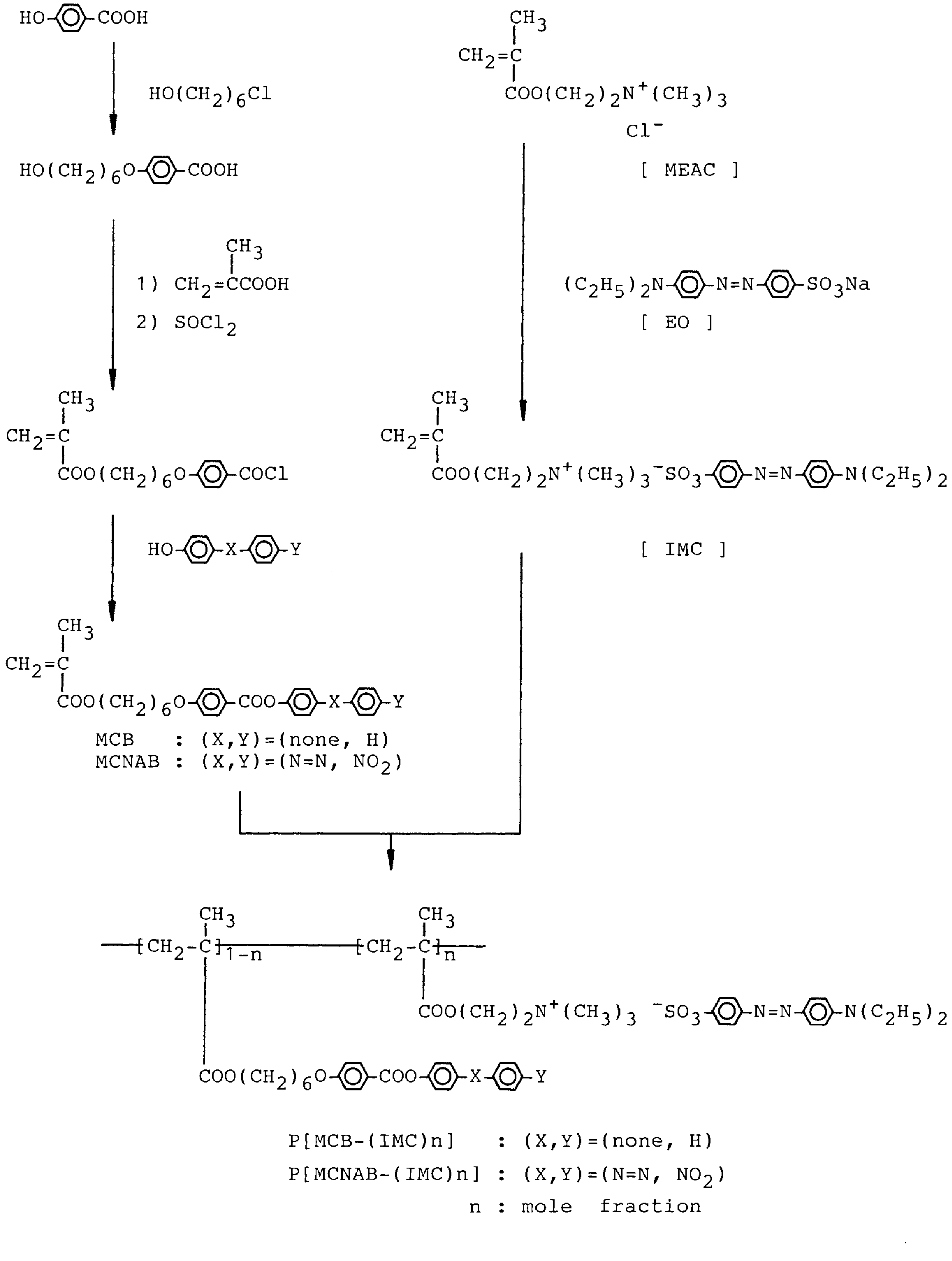

Fig. 1. Synthetic route of liquid-crystalline copolymers containing ionic group.

Table 1. Phase transition temperatures of liquid-crystalline copolymers containing ionic group

Sample	n[a]	Phase transition temperatures[b] / °C							LC range
P[MCB-(IMC)n]	0	G	53.7	S	110.2	N	128.2	I	74.5
	0.1	G	81.0	S	150.2	N	171.2	I	90.2
	0.3	G	89.5	S	178.5	N	212.3	I	122.8
	0.5	G	98.9	M	240	D			-
P[MCNAB-(IMC)n]	0	G	45.0	S			300.0	I	255.0
	0.3	G	75.0	S			-[c]	I	-
	0.5	G	100.0	S			-[c]	I	-

a)Mole fraction of non-liquid-crystalline ionic methacrylic comonomer.
b)G:glass state, S:smectic phase, N:nematic phase, I:isotropic phase, M:unidentified mesophase, D:thermal decomposition.
c)Isotropization temepratures were not determined because of thermal decomposition.

P[(IMC)1] prepared from IMC exhibited no mesophase. Both P[MCB-(IMC)n] and P[MCNAB-(IMC)n] exhibited enantiotropic liquid-crystalline phases. Nematic and smectic phases in P[MCB-(IMC)n] exhibited schlieren and fan-like textures, respectively. In the smectic phase of P[MCNAB-(IMC)n], fan-like and sanded textures were observed.

As listed in Table 1, the glass transition temperatures (T_gs) in P[MCB-(IMC)n] and P[MCNAB-(IMC)n] increase with increasing mole fraction of IMC, regardless of the structure of liquid-crystalline component with 4-nitroazobenzenebenzoate or biphenylbenzoate mesogenic groups. The isotropization temperatures (T_is) in P[MCB-(IMC)n] raised with increasing mole fraction of IMC. In P[MCNAB-(IMC)n], however, T_i was not determined because of the thermal decomposition. In P[MCB-(IMC)n], the liquid-crystalline temperature range (T_i-T_g) also became broad with increasing mole fraction of IMC. In general, the increase in a fraction of a non-liquid-crystalline component in liquid-crystalline copolymer is known to restrict the mesophase formation of a liquid-crystalline copolymer.[5,6] However, the non-liquid-crystalline IMC used in our work enhanced the thermal stability of the liquid-crystalline phase. This corresponds to the experimental result reported in our previous study.[1]

The smectic layer spacing of P[MCB-(IMC)0] without IMC component is 2.96 nm, and the mesogenic side-chain length is 2.7 nm. In this case, a possible packing model of P[MCB-(IMC)0] is a smectic A like single layer structure in which the mesogenic side groups overlap with each other. The smectic layer spacing of P[MCB-(IMC)0.1] with IMC component was determined to be 3.15 nm. One of the possible packing models proposed for the smectic layer structure of P[MCB-(IMC)0.1] is schematically illustrated as shown in Fig. 2. IMC component is incorporated into the smectic A like single layer. No scattering peaks in the small angle X-ray scattering region were found for P[MCB-(IMC)0.3] and P[MCB-(IMC)0.5].

The layer spacing (d) of P[MCNAB-(IMC)0] without IMC component was determined to be 3.63 nm by X-ray diffraction measurement. The d is less than twice the mesogenic side-chain length (L=2.9 nm), and is in excess of L. P[MCNAB-(IMC)0] forms a partial bilayer structure because in the smectic layer the mesogenic units having the strongly polar nitro group overlap with each other. A similar smectic layer structure was reported on the liquid-crystalline side-chain polymers with cyanobiphenyl mesogenic group.$^{7-9)}$ The smectic layer spacings of P[MCNAB-(IMC)n] with IMC component were 3.6 nm - 3.77 nm. In this case, all P[MCNAB-(IMC)n] form a smectic partial bilayer similar to that of P[MCNAB-(IMC)0] without IMC component. And IMC component in P[MCNAB-(IMC)n] is incorporated into the smectic layer such as the case of P[MCB-(IMC)0.1].

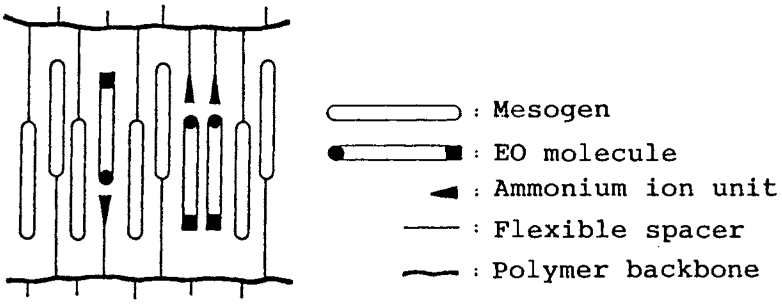

Fig. 2. Schematic illustration of possible packing model for smectic layer structure of P[MCB-(IMC)0.1].

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4) ^{1}H NMR ($CDCl_3$) : MCNAB ; 1.2-1.9 (m 8H), 1.95 (s 3H), 4.06 (t 2H), 4.17 (t 2H), 5.55 (s 1H), 6.11 (s 1H), 6.99 (d 2H), 7.42 (d 2H), 7.9-8.1 (m 6H), 8.39 (d 2H) : MCB ; 1.4-1.9 (m 8H), 1.95 (s 3H), 4.05 (t 2H), 4.17 (t 2H), 5.55 (s 1H), 6.11 (s 1H), 7.0 (d 2H), 7.1-7.8 (m 9H), 8.15 (d 2H) : IMC ; 1.20 (t 6H), 1.92 (s 3H), 2.8-4.0 (m 13H), 4.2-5.0 (m 4H), 5.65 (s 1H), 6.12 (s 1H), 6.75 (d 2H), 7.5-8.2 (m 6H).
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