

Liquid Crystalline Ionomers Exhibiting Thermotropic Mesophases

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Abstract

Liquid Crystalline ionomers were synthesized by copolymerization of nonionic-mesogenic and ionic-nonmesogenic monomers. The liquid crystalline ionomers showed a thermotropic smectic A phase. The phase transition temperatures of the liquid crystalline ionomers increased with content of the ionic mesogenic component, due to the aggregation of ionic units. The ionic interactions can lead to enhancement of the thermal stability and the liquid crystal formation.

Key words : Liquid Crystalline Ionic Polymer, Ionomer, Thermal Property, Smectic A, Ionic Interaction

1. Introduction

Various types of liquid crystalline polymers have been synthesized from theoretical and applied viewpoints. However, few thermotropic liquid crystalline polymers having ionic units have been reported.¹⁾ We described that ammonium ion moieties in thermotropic liquid crystalline polymers enhance the thermal stability and the ability of liquid crystal formation. It was reported by several research groups that the use of ionic interactions is useful to the formation of thermotropic liquid crystalline phases.^{2,3)} We synthesized new thermotropic liquid crystalline copolymers, which are species of ionomers, by radical polymerization of nonionic liquid crystalline and ionic nonmesomorphic methacrylate monomers. This paper describes thermal and liquid crystalline properties of the thermotropic ionomers consisting of aromatic-mesogenic and

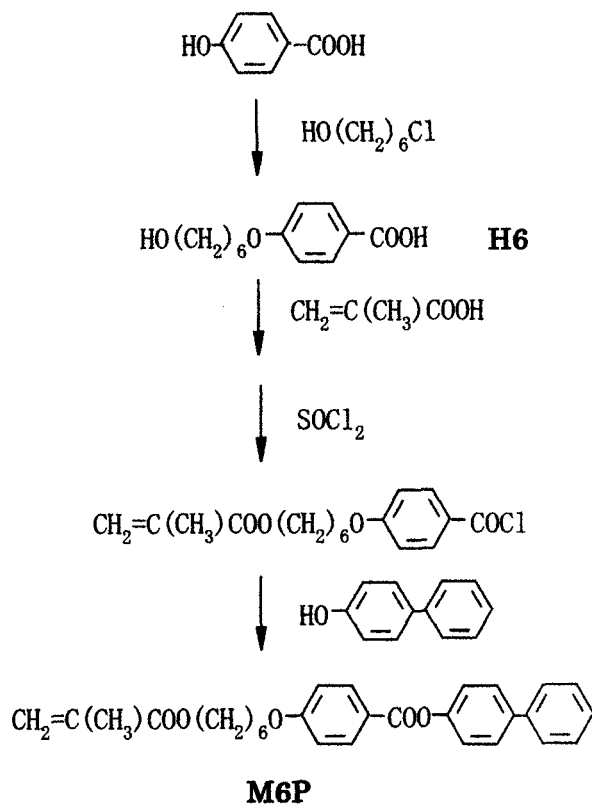
ionic-nonmesomorphic components.

2. Experimentals

2-1. Materials

Mesogenic monomers

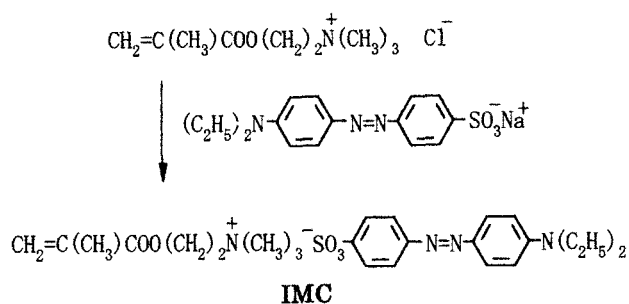
Potassium hydroxide (10 g) was dissolved in ethanol (500 ml), and to the solution 6-chlorohexanol (0.1 mol) and 4-hydroxybenzoic acid (0.1 mol) were added. The mixture was refluxed for 24 h. After the reaction, ethanol was evaporated, and the crude was dissolved in water (70 ml). To the solution, hydrochloric acid (12 N, 30 ml) was added, and the precipitate was filtered off. The precipitate was washed with cooled water and purified by recrystallization from ethanol. The product (H6) was dried under reduced pressure.



Scheme 1. Synthesis of nonionic mesogenic monomer.

H6 (5.0 g), methacrylic acid (70 ml), 4-toluenesulfonic acid (3.0 g), and hydroquinone (2.0 g) were dissolved in chloroform (70 ml). The solution was refluxed for 24h. After the reaction, chloroform (500 ml) was added, and the chloroform solution was washed with distilled water to remove excess methacrylic acid. The crude was obtained by evaporating chloroform from the solution. The crude was purified by recrystallization from 2-propanol. The product (M6) was dried under reduced pressure. M6 (5.0 g) dissolved in thionyl chloride (20 ml) with a small amount of *N,N*-dimethylformamide. The solution was stirred for 2 h. From the solution, excess thionyl chloride was removed under reduced pressure. The product (M6Cl) was dissolved in tetrahydrofuran (THF). The THF

solution of M6Cl was added dropwise to a THF solution of 4-phenylphenol and triethylamine, and the mixture was stirred for 12 h. After the removal of THF, the crude was dissolved in chloroform (400 ml). The chloroform solution was washed with distilled water, and the crude was obtained by evaporating chloroform. Recrystallization from ethanol gave the product (M6P). $^1\text{H NMR}$ (CDCl_3): 1.4-1.8 (m, 8H), 1.95 (m, 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), 7.8-8.15 (m, 6H), 8.39 (d, 2H).



Scheme 2. Synthesis of ion complex type of monomer.

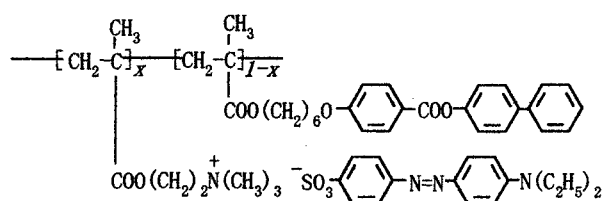
Ionic monomer

An ionic methacrylate monomer was obtained by an ion-exchange reaction between sodium 4-(4-(*N,N*-diethylamino)phenylazo)benzenesulfonate (EO, ionic azobenzene) and 2-(methacryloyloxy)ethyltrimethylammonium chloride (MEAC). A solution of EO (0.05 mol) and MEAC (0.1 mol) in ethanol (100 ml) was refluxed for 12h. The mixture was filtered off, and the filtrate was condensed at 80°C under reduced pressure. After cooling to room temperature, the product (IMC) was precipitated and collected by filtration. $^1\text{H NMR}$ (CDCl_3): 1.2 (t, 6H), 1.92 (m, 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).

Polymerization

Polymers were prepared by radical polymerization. The monomers and AIBN were dissolved in DMF. The DMF solution was reacted at 60°C under nitrogen atmosphere. After 24h, the DMF solution was poured to methanol, and the precipitate was filtered off and washed with acetone. The product was dried under reduced pressure.



Scheme 3. Structure of liquid crystalline ionic copolymer [P(M6P-IMC- x)].

2-2. Measurements

Phase transitions were estimated by polarizing microscopy (an Olympus polarizing microscope with a Mettler hot stage FP82) and DSC (a Mettler DSC10 and a Shimadzu DSC-50Q). The X-ray diffraction patterns were measured with a Rigaku Rint 2100 diffractometer at various temperatures, using Ni filtered Cu-K α radiation. The measuring temperature was controlled with a Linkam hot stage.

3. Results and Discussion

Monomers

Mesogenic M6P exhibited a nematic phase with a schlieren texture on a first heating process. However, on a second heating process, a smectic A phase as well as the nematic phase

was formed with a fan texture, due to the polymerization. Ionic IMC showed no liquid crystalline phase.

Table 1. Phase transition temperatures of liquid crystalline ionomers

Sample	x	Transition temp. ¹⁾ /°C		
		T _g	T _{A-N}	T _{N-I}
PM6P	0	53.7	110.2	128.2
P(M6P-IMC-0.1)	0.1	81.0	150.2	171.2
P(M6P-IMC-0.3)	0.3	89.5	178.5	212.3
P(M6P-IMC-0.5)	0.5	98.9	D	

1) T_g; glass transition point; T_{A-N}; smectic A-nematic phase transition point; T_{N-I}; nematic-isotropic phase transition point; D; thermal decomposition.

Polymers

A homopolymer (PM6P: Mn=13,000) obtained by polymerization of nonionic M6P showed nematic and smectic A phases on heating and cooling. By cooling the isotropic liquid, droplets appeared, and a schlieren texture formed. Batonnets formed in the nematic phase at a nematic-smectic phase transition point. In the smectic A phase, PM6P showed a focal conic fan texture. An ionic polymer (PIMC) made from IMC exhibited no mesophase.

Ionic copolymers (ionomers) prepared by copolymerization of nonionic M6P and ionic IMC showed liquid crystalline phases. The ionomer [P(M6P-IMC- x)], having the IMC content (x) of 0.1 (Mn=10,000) or 0.3 (Mn=11,000), exhibited nematic and smectic A phases. P(M6P-IMC-0.5, Mn=9,000) showed a smectic A phase without a nematic phase. The mesomorphic temperature range became broader with increasing IMC

contents. Glass transition and isotropization temperatures increased with IMC contents. The increase in the ionic IMC content enhanced thermal stability of the liquid crystalline phase.



Figure 1. Structure of smectic A phase for ionic P(M6P-IMC- x): full rectangle, nonionic mesogenic core; open rectangle, ionic azobenzene; full square, ammonium ion.

The layer spacing of the smectic A phase of nonionic PM6P without the IMC component is 2.96 nm, corresponding to a mesogenic side-chain length of 2.7 nm. Ionic P(M6P-IMC-0.1) with the IMC component showed the smectic layer spacing of 3.15 nm. A possible packing model of nonionic PM6P is a single layer structure, in which the mesogenic side-groups overlap each other. In the case of ionic P(M6P-IMC-0.1), it is expected that the ionic azobenzene components are incorporated within the smectic single layer as shown in Figure 1.

4. Conclusions

The thermotropic liquid crystalline ionic copolymers (ionomers) were synthesized. The ionomers formed a smectic A phase and showed the focal conic fan texture and the perpendicular structure. The ionic components so enhanced thermal stability of the smectic A phase. The introduction of the ionic species into liquid crystalline systems leads to the formation of

thermotropic smectic systems and the improved thermal stability of the liquid crystalline systems.

5. References

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