CHEMISTRY LETTERS, pp. 1969-1972, 1991.

Thermal Properties and Ferroelectric Like Behavior of Liquid-Crystalline Ionic Polyethylenimine Derivative

Seiji UJIIE* and Kazuyoshi IIMURA
Department of Chemistry, Faculty of Science,
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

Liquid-crystalline ionic polyethylenimine derivatives have been synthesized, and their thermal properties and dielectric behavior have been studied. They exhibited thermotropic smectic phases. The ferroelectric like behavior was confirmed by dielectric measurement and observation of the hysteresis loop with the Sawyer-Tower circuit.

In the previous papers, we described on the thermal properties and orientational behavior of liquid-crystalline polymers (LCIPs) with an ammonium ion group.[1-3] LCIPs exhibited the enantiotropically smectic phases. Ammonium ion groups in LCIP enhanced thermal stability of the smectic phase, and were effective to spontaneously form the homeotropic alignment. In the smectic layer of LCIP, ammonium ion groups independently aggregated to form the sublayer. We think that the aggregation of ammonium ion groups in LCIP is useful to form the smectic layer structure, and the ammonium ion group is regarded as one of smectogens. Recently we have synthesized liquid-crystalline polyethylenimine derivatives with ionic skeletal main chain (LCPEI-n-CH_3), and have investigated on the effect of ammonium ion moiety for the liquid-crystal formation. In the present study, we report on thermal properties and ferroelectric like behavior of LCPEI-n-CH_3.

Structures of LCPEI-n-CH_3 are shown in Fig. 1. LCPEI-n-CH_3 was prepared by additional reaction of polyethylenimine with 4-(6-bromohexyloxy)phenylazo-4'-methylbenzene.[1] Identification of the resultant compounds was performed by ^1H NMR measurement. The introduction ratios of the mesogenic side-chain in LCPEI-n-CH_3 were 70 - 80%. Phase transition temperatures determined by orthoscopic observation and DSC measurement are shown in Fig. 2. In general, it is reported that the phase transition temperatures of liquid-crystalline polymers depend on the degree of polymerization.[5-7] In LCPEI-n-CH_3, however, glass transition and isotropization temperatures are independent of the degree of polymerization (n). LCPEI-n-CH_3 exhibited the glass transition temperature (T_g) even in n of 3, and in the n range of 3 to 1300 they showed similar T_gs and isotropization temperatures. The aggregation of ammonium ion moieties is considered to play a major role for formation and stabilization of the smectic layer.[1] In the case of LCPEI-n-CH_3, the ammonium ion moiety in the structure functions as a smectogen, and the organization of the ammonium ion moiety intensely affects the phase transition temperatures more than that of the methylazobenzene mesogen and the polymer effect. Consequently, the phase transition temperatures are independent of n.

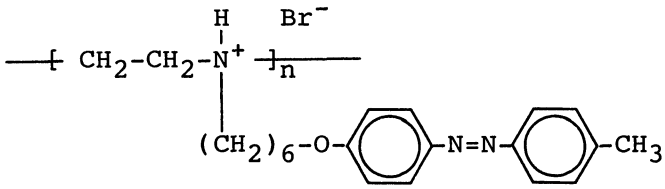

Fig. 1. Structures of LCPEI-n-CH_3: n=3, 4, 5, 6, and 1300.[4]

The smectic layer structures of LCPEI-6-CH_3 and LCPEI-1300-CH_3 were studied by X-ray diffraction measurement of melt drawn fibres. The aligned samples of LCPEI-6-CH_3 and LCPEI-1300-CH_3 exhibited the sharp Bragg reflections at small angles on the equator. The wide angle crescents were located on the meridian perpendicular to the position of the Bragg spots. In addition the smectic layer spacings (4.9 nm) of LCPEI-6-CH_3 and LCPEI-1300-CH_3 were equal to twice the mesogenic side-chain length including the counter-anion (2.4 - 2.5 nm). In this case, LCPEI-6-CH_3 and LCPEI-1300-CH_3 form smectic A-like bilayer structures. A possible model of the smectic layer structure is shown in Fig. 3. In the smectic phases, ammonium halide moieties aggregate to form a sub-layer, and mesogenic side groups organize a bilayer arrangement.

Dielectric behavior of the liquid-crystalline polymers gives an important information for their orientational behavior.[8-10] Dielectric constant of LCPEI-6-CH_3 as a function of temperature is shown in Fig. 4. The dielectric constant became maximum at the temperature near the isotropization temperature (T_i) determined by DSC measurement. In addition, a ferroelectric like hysteresis loop was observed by the Sawyer-Tower method. Figure 5 shows the hysteresis loop observed under the electric field of 15 MV/m/60 Hz in the smectic phase of LCPEI-6-CH_3. In the isotropic phase, the hysteresis loop was not found. The

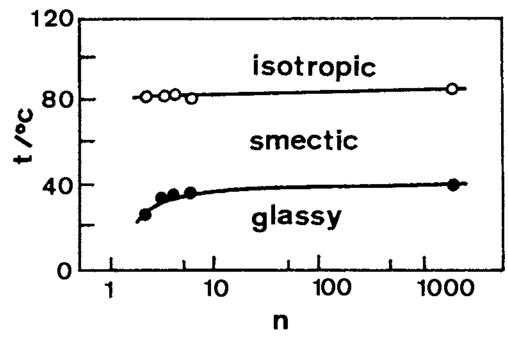

Fig. 2. Phase transition temperatures of LCPEI-n-CH_3: (●) ; glass transition temperature, (○) ; isotropization temperature.

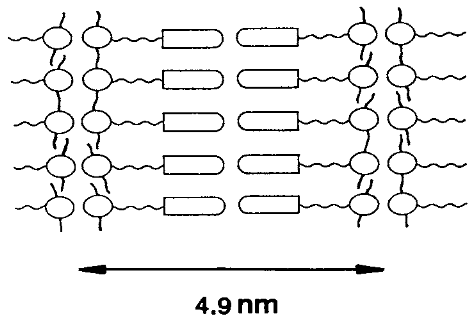

Fig. 3. Possible model of smectic layer structure proposed for LCPEI-6-CH_3 and LCPEI-1300-CH_3: (▭) ; mesogenic group, (◯) ; ammonium halide moiety.

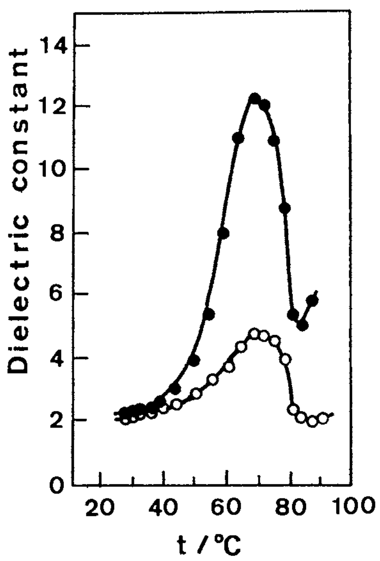

Fig. 4. Temperature dependence of dielectric constant of LCPEI-6-CH_3: (●) ; 20 Hz, (○) ; 100 Hz.

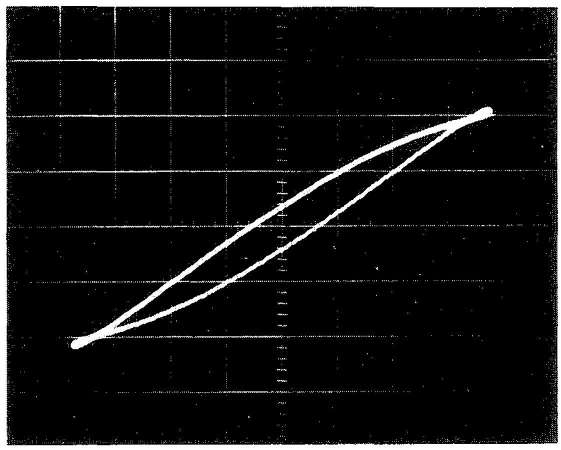

Fig. 5. Hysteresis loop observed in smectic phase (54.5 °C) of LCPEI-6-CH_3: Horizontal ; 15 MV/m/div, Vertical ; 0.022 mC/m^2/div.

existence of the hysteresis loop indicates a possibility of ferroelectricity in LCPEI-6-CH_3. When LCPEI-6-CH_3 exhibits a ferroelectric like property, the presence of the maximum dielectric constant is explained by the Curie-Weiss' law, and the temperature of the dielectric constant peak is related to the Curie point. In general, a ferroelectricity in the liquid crystals and the liquid-crystalline polymers is well-known to generate in the chiral tilted smectic phase.[11,12] However, LCPEI-6-CH_3 is an achiral compound, and exhibits the smectic A-like phase. In the case of LCPEI-6-CH_3, we think that the ferroelectric like property is related to the aggregation of ammonium ionic moieties. This consideration explains that the orientational behavior of ammonium halide moieties dominates the liquid-crystalline and dielectric properties of LCPEI-n-CH_3. So the ferroelectric like smectic state changes into the isotropic phase, and the hysteresis loop disappears in the isotropic phase when the aggregation of ammonium ion moieties becomes disorder. Detailed study is in progress.

References

1) S. Ujiie and K. Iimura, Chem. Lett., 1990, 995.
2) S. Ujiie and K. Iimura, Chem. Lett., 1991, 411.
3) S. Ujiie, Y. Tanaka, and K. Iimura, Chem. Lett., 1991, 1037.
4) n=3 : diethylenetriamine (Tokyo Kasei : TCI), n=4 : triethylenetetramine (TCI), n=5 : tetraethylenepentamine (TCI), n=6 : pentaethylenehexamine (TCI), n=1300 : polyethylenimine (Aldrich) containing equal amounts of primary, secondary and tertiary amine groups with molecular weight of 50000 to 60000.
5) H. Stevens, G. Rehage, and H. Finkelmann, Macromolecules, 17, 851 (1984).
6) S. G. Kostromin, R. V. Talroze, V. P. Shibaev, and N. A. Plate, Makromol. Chem., Rapid Commun., 3, 803 (1982).
7) S. Ujiie and K. Iimura, Chem. Lett., 1990, 1031.
8) R. Zentel, G. R. Strobl, and H. Ringsdorf, Macromolrcules 18, 960 (1985).
9) H. Kresse, S. Kostromin, and V. P. Shibaev, Makromol. Chem., Rapid Commun., 2, 369 (1981).
10) G. S. Attard, G. Williams, G. W. Gray, D. Lacey, and P. A. Gemmel, Polymer, 27, 185 (1986).
11) R. B. Meyer, L. Lebert, L. Strzelecki, and P. Keller, J. Phys. (France), 36, 69 (1975).
12) V. P. Shibaev, M. V. Kozlovsky, L. A. Beresnev, L. M. Blinov, and N. A. Plate, Polym. Bull., 12, 299 (1984).

(Received June 29, 1991)