CHEMISTRY LETTERS, pp. 995-998, 1990.

Ammonium Halide Type Thermotropic Liquid-Crystalline Polyethylenimines and Those Low-Mass Model Compounds

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Thermotropic liquid-crystalline polyethylenimines with an ammonium halide moiety and those low-mass model compounds exhibited enantiotropically smectic phases. They were homeotropically aligned with the formation of an ammonium bilayer. The homeotropic structure of the liquid-crystalline polyethylenimine remained unaltered below Tg on cooling.

Molecular interactions and the shape of a molecule are generally known to affect significantly on the orientational properties of the liquid-crystalline state. We synthesized thermotropic liquid-crystalline polyethylenimines with an ammonium halide moiety and those low-mass model compounds, and studied on their thermal and orientational properties. Particularly, the spontaneous formation of an uniform orientation and the thermal stability of the liquid-crystalline state were investigated.

Liquid-crystalline model compounds (LCMCs) were synthesized by a modification of the literature method.[1,2] Structures of LCMCs are shown in Fig. 1. Phase transition temperatures of LCMCs are listed in Table 1.

M1 has the structure displaced from the tertiary ammonium halide moiety of A1 to the tertiary amine, and exhibited an enantiotropically smectic phase. However, the smectic temperature range (58.6 °C) of M1 was narrower than that of A1 by 91.5 °C. The isotropization temperature (119.8

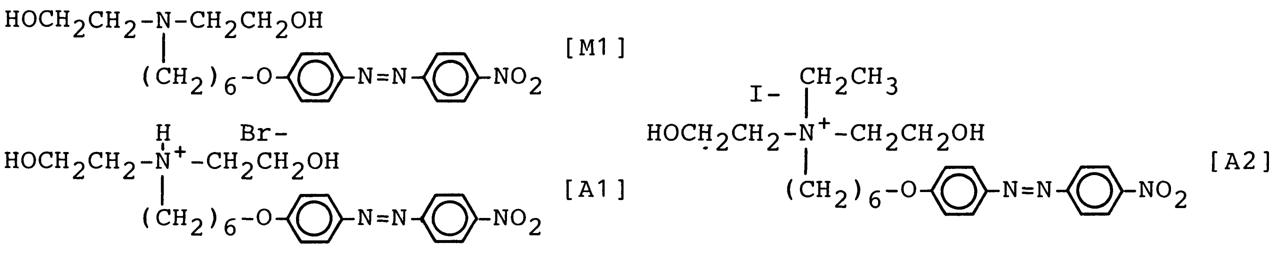


Fig. 1. Structures of liquid-crystalline low-mass model compounds (M1,A1 , and A2).

Table 1. Phase transition temperatures of LCMCs

Sample	Phase transition temperatures[a)] / °C					$SR^{b)}$ / °C
M1	K	61.2	S	119.8	I	58.6
A1	K	56.9	S	207.0	I	150.1
A2	K	40.5	S	170.2	I	129.7

a) K;solid state: S;smectic phase; I;isotropic phase.
b) SR;smectic temperature range.

°C) of M1 was also lower than that of A1 by 87.2 °C. From these results the thermal stability of the smectic phase of A1 is higher than that of the smectic phase of M1 because ammonium halides moieties have an ionic bond and play a major role for the formation of the smectic layer structure.[3)]

A2 with the quaternary ammonium halide moiety also exhibited a smectic phase similar to A1. The isotropization temperature of A2 was lower than that of A1 by 36.8 °C because a steric hinderance is taken place by ethyl group in the quaternary ammonium halide moiety.

In genaral, it is known that alkylammonium halides are used to obtain the homeotropic orientation of the liquid crystalline phase.[4)] In the case of A1 and A2, the homeotropic orientation is formed by the effect of the ammonium halide moiety. The homeotropic orientation of A2 remained unaltered in the solid state on cooling. This was confirmed by observing an isogyre characteristic of an optical-uniaxial phase as shown in Fig. 2. The homeotropically aligned sample for A2 exhibited two scattering peakes ($2\Theta=2.54°$, $5.12°$) relating to the smectic layer spacing (d) in the X-ray small angle region. The d calculated from the first order diffraction angle is 34.8 Å, and while, the molecular length of A2 is 24.5 Å. The smectic phase of A2 is the optical-uniaxial phase such as smectic A phase. From these experimental facts, in both smectic and solid phases the neighboring mesogenic groups (11.4 Å) overlap with each other, and the ammonium halide moieties form ionic and hydrogen bonds. Therefore, a schematic illustration of the orientational structure as shown in Fig. 3 is proposed for A2.

The X-ray data of A1 indicates that the orientational structure in the smectic phase of A1 is the same as that of A2 as shown in Fig. 3.

In the solid state of A1, however, the destruction of the homeotropic bilayer structure was indicated by the conoscopic observation and the X-ray measurement. The isogyre observed in the smectic phase of A1 (Fig. 2) disappeared in the conoscopic figure. And intensity of the scattering peak locating at the first order diffraction angle ($2\Theta= 2.42°$) became extremely small with the passage of time.

The structure of the liquid-crystalline polyethylenimine (LCPEI) with ammonium halide moieties is shown in Fig. 4. LCPEIs were prepared by

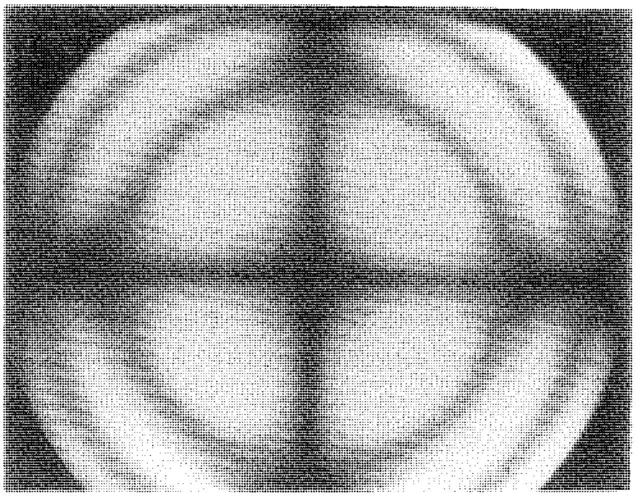


Fig. 2. Conoscopic figure of homeotropic alignment for A2: Crossed polarizers: Objective ×40.

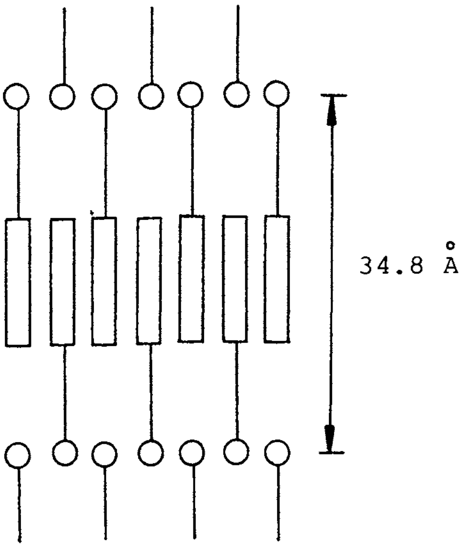
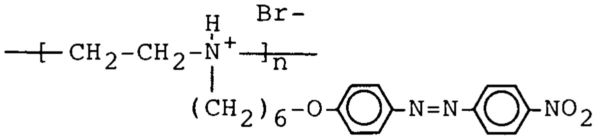


Fig. 3. Schematic orientational structure of A2: ○ ;ammonium halide moiety: ——— ;flexible spacer: ▭ ;mesogenic group.

substitution reaction of polyethylenimine with bromoalkyl mesogenic compounds in a similar manner to the preparation of LCMCs. Phase transition temperatures of LCPEIs are listed in Table 2. LCPEI exhibited an enantiotropically smectic phase. Isotropization temperatures of the polymers are well-known to be dependent on the degree of polymerization (DP).[5,6] However, isotropization temperatures of LCPEIs studied in this work are independent of DP, as listed in Table 2, and are constant at 210 °C which is the same temperature as that of the low-mass model compound A1 with the ammonium halide moiety. Ammonium halide moieties of LCPEI intensively affect the formation of the smectic layer structure in analogy with the case of A1. So the thermal stability of the smectic phase is enhanced by the ionic bonds formed by ammonium halide moieties.



$$-\!\!\left[CH_2-CH_2-\underset{(CH_2)_6-O-C_6H_4-N=N-C_6H_4-NO_2}{\overset{H\ \ Br^-}{N^+}}\right]_n-$$

Fig. 4. Structure of liquid-crystalline polyethylenimine with ammonium halide moiety.

Table 2. Phase transition temperatures of LCPEIs

DP	Phase transition temperatures[a)]/ °C				
6	g	48	S	210	I
1300	g	55	S	210	I

a)g;glass state: S;smectic phase: I;isotropic phase.

LCPEIs also exhibited the homeotropic structure, and it was kept in the solid state on cooling. In this case, the orientational order in the homeotropic structure is lower than that of A1 or A2 because the isogyre as shown in Fig. 5 is unclear in comparison with that shown in Fig. 2. The smectic layer spacing of LCPEI is 29.6 Å ($2\Theta=2.98^\circ$) which is less than twice of the mesogenic side-chain length (21 Å). When mesogenic groups (11.4 Å) overlap with each other, a possible model of the smectic layer structure is a tilted phase such as the smectic C state as shown in Fig. 6. On the other hand, the isogyre as shown in Fig. 5 may indicate a possibility of the smectic A like optical-uniaxial phase as illustrated in Fig. 6. Detailed study on the orientational structure of LCPEI is in progress.

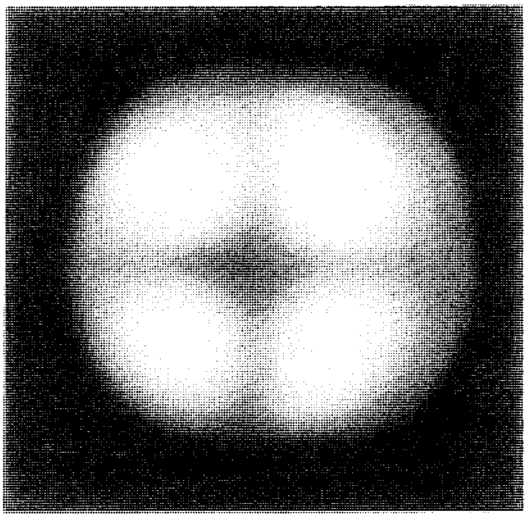


Fig. 5. Conoscopic figure of homeotropic alignment of LCPEI: Crossed polarizers: Objective ×100.

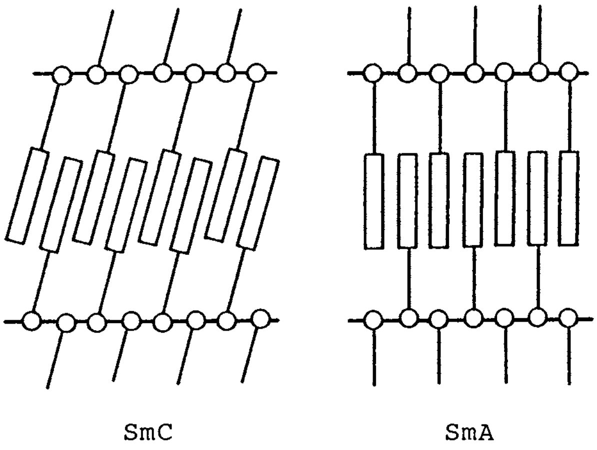


Fig. 6. Schematic orientational structures proposed for LCPEI:SmC; smectic C layer structure: SmA; smectic A layer structure: ○ ; ammonium moiety: —— ;flexible spacer: ▭ ;mesogenic group.

References

1) L. -F. Tietze and T. Eicher, "Reaktionen und Synthesen im organisch-chemischen Praktikum," Georg Thieme Verlag Stuttgart, New York (1981).

2) Y. Okahata, H. Ihara, M. Shimomura, S. Tawaki, and T. Kunitake, Chem. Lett., 1980, 1169.

3) T. Kunitake, Y. Okahata, M. Shimomura, S. Yasunami, and K. Takarabe, J. Am. Chem. Soc., 103, 5401 (1981).

4) J. E. Proust, L. Ter-Minassian-Sarage, and E. Guyron, Solid State Commun., 11, 1227 (1972).

5) S. G. Kostromin, R. V. Talroze, V. P. Shibaev, and N. A. Plate, Makromol. Chem., Rapid Commun., 3, 803 (1982).

6) H. Stevens, G. Rehage, and H. Finkelmann, Macromolecules, 17, 851 (1984).

(Received March 27, 1990)