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# Liquid Crystalline Ionic Films Having Homeotropic or Homogeneous Alignment

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The liquid crystalline ionic films (LCIFs), having a perpendicular or a homogeneous alignment, were synthesized by bulk polymerization of an aziridine derivative (AZ6N) in a glass cell. The bulk polymerization process was examined by X-ray diffraction measurement and polarizing microscopy. AZ6N did not show a liquid crystalline phase. However, by the bulk polymerization at the isotropic temperatures, a smectic A domain grew into the isotropic state and finally the smectic A liquid crystalline orientation filled in the glass cell. LCIFs maintained the anisotropic alignment formed in the smectic A state at room temperature.

Key Words: Liquid Crystal Film / Bulk Polymerization / Homeotropic / Homogeneous / X-Ray Diffraction Measurement

# 1. INTRODUCTION

The control of the orientation of anisotropic phase such as liquid crystalline phases is one of the important problems in scientific and technological viewpoints. Liquid crystalline polymers can easily produce anisotropic glasses having a nematic or a smectic alignment. However, the anisotropic glasses usually have a polydomain structure. Several studies were reported on polymer films with anisotropic alignment in relation to bulk polymerization of liquid crystalline monomers such as acrylates, methacrylates, and epoxides.<sup>1-6)</sup> The bulk polymerization of the monomers was performed in a liquid crystal cell with a rubbing treatment to obtain a unidirectional orientation.

In this work, we synthesized a novel aziridine monomer and tried to obtain uniformly aligned smectic films by bulk polymerization of the aziridine monomer in the glass cells. This paper describes the preparation of liquid crystalline ionic films having homogeneous and homeotropic orientational structures.

# 2. EXPERIMENTALS

#### 2-1. MATERIALS

An aziridine monomer (AZ6N) with 4-(4-(nitro)phenylazo)phenoxy unit was synthesized. Liquid crystalline ionic films were obtained by ring-opening polymerization of AZ6N in a liquid crystal cell. In the polymerization, 1,2bis(tosyloxy)ethane was used as an initiator. The polymers synthesized from AZ6N have ionic terminal groups (aziridinium unit).



# 2-2. MEASUREMENTS

The phase transitions were examined with

a Shimadzu differential scanning calorimeter (DSC-50Q), a Mettler thermosystem 3000 and a Nikon polarizing microscope equipped with a Mettler FP900 system (FP90-FP82). The variable X-rav diffraction temperature measurements were performed with a Rigaku X-ray diffractometer RINT2100 system using Ni-filtered Cu-K $\alpha$  radiation. The liquid crystalline samples in the X-ray diffraction measurement were placed on a Linkam hot stage system(TC600PH-HFS91).

## 3. RESULTS AND DISCUSSION

#### 3-1. MONOMER AND LINEAR POLYMER

AZ6N with a nitroazobenzene mesogenic unit did not show a liquid crystalline phase and melted at 58.1 °C (solid-isotropic phase transition point). However, the side chain liquid crystalline polymer (PAZ6N, Mn=8,000) with a linear backbone, which was produced by ring-opening polymerization of AZ6N in a tetrahydrofuran solution, enantiotropically formed a smectic A fluid mesophase with focal conics in the range from 40.0  $^\circ C$ (glass transition point) to 176.0°C. Also, oligomeric materials such as dimer and trimer showed the smectic A phase on heating and cooling The oligomeric materials and processes. PAZ6N have the ionic terminal groups at the end of the skeletal main-chain. The liquid crystal formation and the thermal stability of liquid crystalline orientations are strongly affected by ionic interactions of the ionic terminal groups.<sup>7,8)</sup>

### **3-2. SMECTIC FILMS**

The ring-opening polymerization of AZ6N in the glass cell without orientational treatments was performed at the isotropic temperatures. Batonnets, which clearly show



Figure 1. Optical texture with isotropic and homeotropic (P) domains observed under parallel nicols.



Smectic Mesophase with Layered Structure

Figure 2. Liquid crystal formation by bulk polymerization of AZ6N.

the formation of a smectic liquid crystalline alignment, appeared in the isotropic phase, due to the built of liquid crystalline ionic oligomers by the bulk polymerization. The batonnets easily changed to the dark domains under crossed nicols.

Figure 1 shows the dark domains (P) and the isotropic domains under the parallel nicols at 130°C. The domain P was mainly formed by oligomeric materials made of AZ6N. The orientational structure of the domain P is characterized by a uniaxial interference figure obtained by the conoscopic observation. This indicates the formation of the homeotropic



Figure 3. Rotational angle dependence of transmittance for homogeneouly aligned film: extinction position;  $0^{\circ}$ ,  $90^{\circ}$ ,  $180^{\circ}$  :diagonal position;  $45^{\circ}$ ,  $135^{\circ}$ .



Figure 4. X-Ray diffraction patterns for mixture of isotropic and smectic domains (a) at  $130^{\circ}$ C and smectic film (b) at  $20^{\circ}$ C.

orientational structure. In this the case. corresponds direction director to the perpendicular to the glass plate, because, in the smectic A phase, the azobenzene mesogenic groups are aligned along the layer normal. The homeotropic alignment of the domain Pwas produced by the orientational adsorption of amine groups in the oligomeric materials such as perpendicular alignment agents.<sup>7,8)</sup> The domain  $\boldsymbol{P}$  increased as the bulk polymerization made progress. By the bulk polymerization at 130°C for 50 minutes, the isotropic domain disappeared and the smectic A phase with the homeotropic orientational structure completely filled in the cell (Figure 2).



Figure 5. First order reflections at X-ray smallangle corresponding to smectic layer spacing.

In the case of a glass cell with the rubbing treatment, a homogeneous alignment was easily achieved. The smectic focal conics grew into the isotropic phase. By the advance of the bulk polymerization, the isotropic state completely disappeared and finally changed to the smectic anisotropic state. The smectic sample with the homogeneous orientational structure obviously showed extinction and diagonal positions under crossed nicols, as shown in Figure 3. This indicates that the mesogenic groups are unidirectionally aligned by the rubbing treatment.

The process of the liquid crystal formation by the bulk polymerization was also examined by the X-ray diffraction measurement. The sample comprised of the isotropic and the smectic domains showed the X-ray diffraction pattern consisting of the sharp peaks (first order, second order and third order) at the small-angles and the broad scattering peak in the X-ray wide-angle region, as shown in Figure 4a. The sharp reflections at the X-ray smallangles correspond to the layer spacing of the smectic structure. Figure 5 shows the first order reflections for the various polymerization times. The intensity of the first order reflection increased with polymerization time (Figures 5, 6). The smectic layer spacing decreased as the smectic domain grew into the isotropic phase(Figure 7) and was kept constant



Figure 6. Intensity of first order reflections.



Figure 7. Smectic layer spacings obtained from first order reflection as shown in Figure 6.

when the cell was filled by the smectic A phase. The liquid crystalline ionic film showed a smectic-isotropic phase transition at 170  $^{\circ}$ C. The X-ray diffraction pattern (Figure 4b) of the liquid crystalline ionic film is the same as Figure 4a. This shows that the liquid crystalline ionic film at 20  $^{\circ}$ C has the same alignment as the smectic state at 130  $^{\circ}$ C.

## 4. CONCLUSION

The smectic films with the homeotropic and homogeneous orientational structures were prepared by the bulk polymerization of the aziridine monomer in the glass cell. The homogeneously aligned film was obtained in the glass cell with the rubbing treatment. The bulk polymerization in the cell without orientational treatments gave the smectic film having homeotropic alignment, due to the orientational adsorption of the amine groups.

## 5. REFERENCES

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