

Oriented Liquid Crystalline Films Obtained by Thermal Polymerization of Amphiphilic Acrylate

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The preparation of oriented liquid crystalline films was performed by thermal polymerization of an amphiphilic acrylate monomer (AA), consisting of an azobenzene unit and a polyethyleneimine chain, in sandwich cells. AA showed no mesophase. The oligomers and polymers obtained by polymerization of AA exhibited a smectic A phase with a focal conic fan texture. In the region of the smectic A mesomorphic temperatures, a homeotropic structure was spontaneously formed by adsorption of the ionic terminal moiety of AA unit. The oriented polymer film with a homeotropic alignment was obtained by the thermal polymerization of AA for 15h at 60°C in the cell without alignment treatment. The formation of the homeotropic structure was clearly characterized by a uniaxial conoscopic figure. The polymerization of AA in the cell with rubbing treatment led to the preparation of a homogeneously oriented polymer film, clearly exhibiting extinction and diagonal positions under the crossed nicols.

Key words: Liquid Crystal, Amphiphilic, Oriented Film, Smectic A, X-Ray

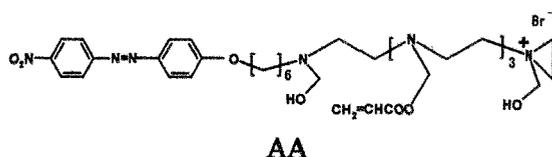
1. INTRODUCTION

Amphiphiles can self-assemble into various order structures in solutions and liquid crystalline phases [1]. This nature is of high importance in the field of supramolecular chemistry. The amphiphilic molecules have hydrophilic and hydrophobic parts and can form smectic layer structures with hydrophilic and hydrophobic sublayers. The amphiphilic molecules with aromatic-mesogenic moieties (AMAs) in the hydrophobic unit form liquid crystalline phases by interactions between the aromatic-mesogenic units as well as anisotropy formed by segregation of the hydrophilic and hydrophobic parts [2]. In the

systems such as AMAs, the sublayer that hydrophilic units aggregate can be considered as a reaction field and the hydrophobic units act in forming the liquid crystalline glass [3]. When vinyl groups are introduced into a hydrophilic moiety of the amphiphilic molecule such as AMAs, the vinyl groups locating in the hydrophilic sublayers can polymerize efficiently because they exist near here. In this work, a new amphiphilic monomer, having acrylate groups in a hydrophilic chain, was synthesized. This paper describes the preparation of liquid crystalline polymer systems by thermal polymerization of the amphiphilic monomer.

2. EXPERIMENTALS

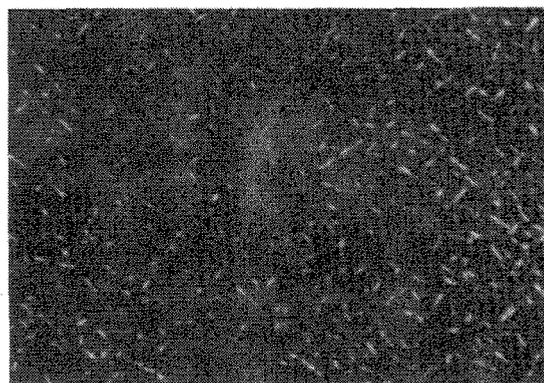
A low-molecular-weight amphiphilic mesogen (Az6N) with a nitroazobenzene rigid-rod group was obtained by ring-opening polymerization of aziridine-1-ethanol using 6-bromo-1-[4-(4-nitrophenylazo)phenoxy]-hexane as the polymerization initiator. An amphiphilic monomer (AA) that three acrylate units were linkage to one Az6N molecule on the average was synthesized by the reaction of acryloyl chloride and Az6N. The thermal polymerizations were performed in sandwich glass cells.



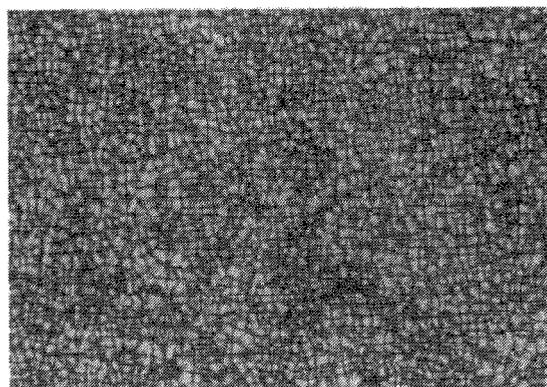
The phase transitions were estimated by polarizing microscopy (Olympus polarizing microscope equipped with a Mettler hot stage FP82) and DSC (Mettler DSC-20 and Shimadzu DSC-50Q). The X-ray diffractions were measured with a Rigaku Rint 2100 X-ray diffractometer with Ni-filtered Cu-K α radiation at various temperatures; the samples were inserted into a Linkam hot stage HFS91.

3. RESULTS AND DISCUSSION

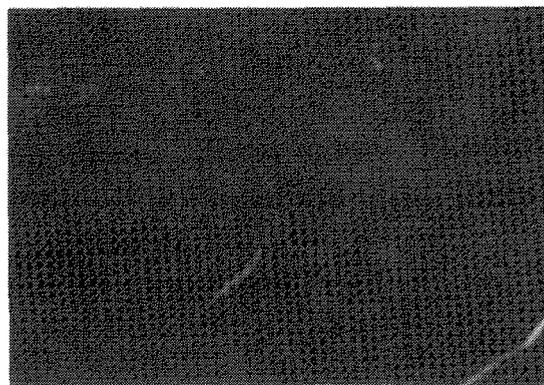
An amphiphilic acrylate monomer (AA) showed a liquid phase at room temperature. AA was inserted into a sandwich cell without the surface treatment. The cell was put in a hot stage at 60°C. The polymerization of AA immediately began at 60°C and a lot of anisotropic domains clearly appeared in an isotropic phase (Figure 1a). The anisotropic region increased and a smectic A phase filled in the cell by the polymerization of AA (Figure 1b). A focal conic fan texture was observed in the smectic A phase.



a



b



c

Figure 1. Optical textures at 60°C: a; after 30min, Iso+SmA; b; after 12h, focal conics of SmA; c; after 15h, homeotropic structure formed in SmA.

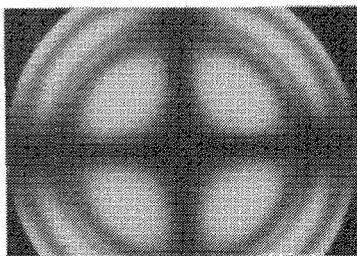
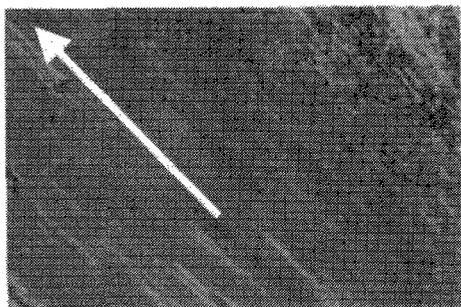
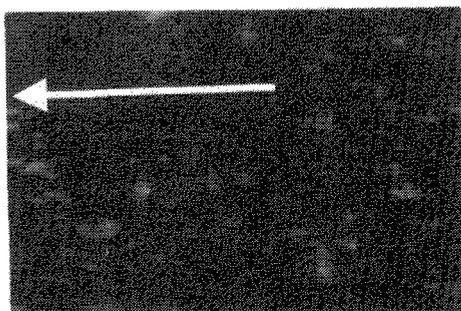


Figure 2. Uniaxial conoscopic figure of homeotropic structure (Figure 1c) obtained by thermal polymerization of AA.



a



b

Figure 3. Diagonal (a: 45°) and extinction (b: 0°) positions observed in homogeneous structure obtained by thermal structure in rubbing cell.

After 15h (Figure 1c), the homeotropic structure was formed spontaneously and a uniaxial conoscopic figure was observed (Figure 2). The formation of the homeotropic structure is due to the physical adsorption of ionic terminal groups [2].

By the polymerization of AA in the rubbing cell, a homogeneously oriented

polymer was prepared. As shown in Figures 3 and 4, diagonal (Figure 3a) and extinction (Figure 3b) positions were appeared every 45° by the rotation of oriented film under the crossed nicols.

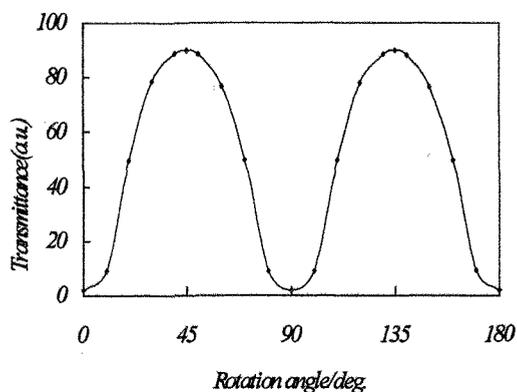


Figure 4. Relationship between transmittance and rotational angle: 0, 90, and 180° ; extinction positions: 45 and 135° ; diagonal positions.

The X-ray diffraction measurement showed the formation of a smectic layer structure by the polymerization for 1h as shown in Figure 5. After 12h, the liquid crystalline sample obtained by polymerization of AA in the cell without the surface treatment exhibited first, second, and third order inner reflections (Figure 5).

The smectic samples with the homeotropic and homogeneous structures obtained from AA in the cell showed the X-ray diffraction pattern consisting of sharp reflections, corresponding to the smectic layer spacing, at small-angles and the wide-angle halo.

The oriented polymer film reversibly showed a smectic A-isotropic phase transition point at 160°C (by polarizing microscopy). The smectic layer spacing of the oriented polymer film was 56 \AA . While, the extended molecular length of AA is 38 \AA . In this case, a possible packing model is illustrated in Figure 6.

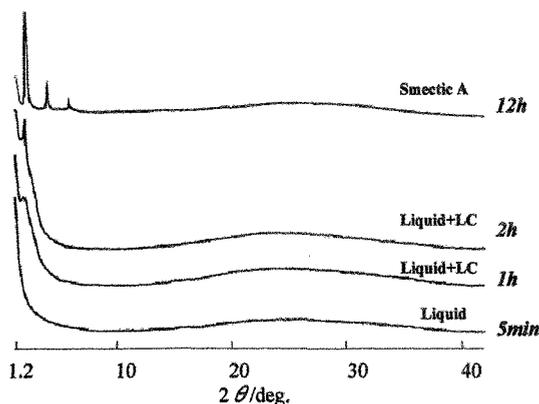


Figure 5. Relationship between X-Ray diffraction patterns and reaction times on polymerization process of AA at 60°C.

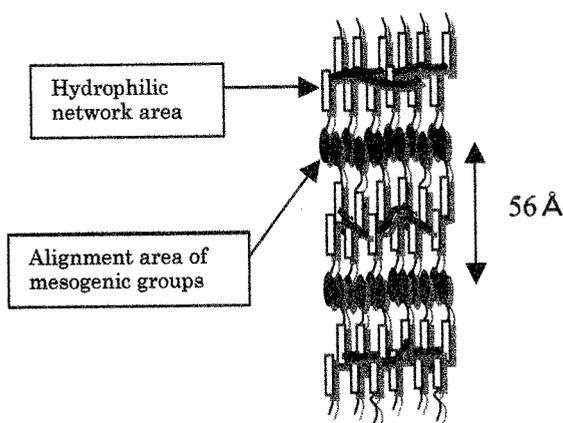


Figure 6. Possible packing model for oriented liquid crystalline polymer films.

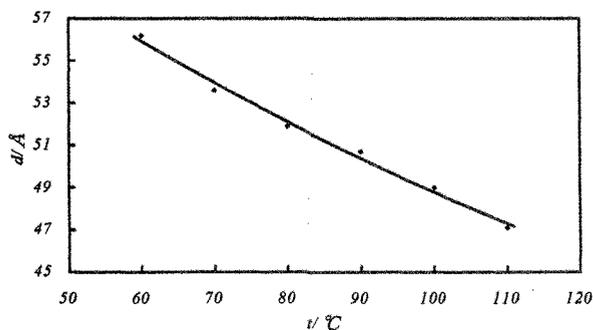


Figure 7. Temperature dependence of layer spacings for the oriented liquid crystalline polymer film with homeotropic structure.

Figure 7 shows a temperature dependence of layer spacings for the oriented film with the homeotropic structure. The smectic layer spacing became narrow with increasing temperature because the stability of the aggregation in the hydrophilic sublayer decreases.

4. CONCLUSIONS

The liquid crystalline polymer films with homeotropic and homogeneous orientational structures were obtained by thermal polymerization in the glass cells. The polymerization in the glass cell without the alignment treatment gave the homeotropic film by the physical adsorption of the ammonium terminal group. In the glass cell with the rubbing treatment, the homogeneous alignment was prepared.

5. REFERENCES

- [1] *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H. -W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol. 3, ch. VI and VII; K.Kanie, T. Yasuda, M. Nishi, S. Ujiie, and T. Kato, *Chem. Lett.*, 2001, 480; *Introduction to soft Matter*, Ian W. Herley, Wiley, 193-259(2000).
- [2] S. Ujiie, Y. Tanaka, and K. Iimura, *Polym. Adv. Technol.*, 11, 450(2000); S. Ujiie and K. Iimura, *Polym. J.*, 25, 347(1993); S. Ujiie and S. Takagi, *High Perform. Polym.*, 20, 347(1999).
- [3] S. Ujiie and Y. Yano, *Chem. Commun.*, 2000, 79; S. Ujiie and Y. Yano, *Mol. Cryst. Liq. Cryst.*, 347, 265(2000).

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