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Formation of LC Oriented Films by Polymerization of Nonmesomorphic Monomers

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Two monomers with methacrylate and aziridine units were synthesized. Liquid-crystalline oriented films were obtained by the thermal polymerization of these monomers in a sandwich cell without alignment treatment. The methacrylate monomers with a chiral center did not exhibit a liquid-crystalline phase. A liquid-crystalline oriented film with a cholesteric helical structure was obtained by the thermal polymerization of the methacrylate monomers in the cell. The aziridine monomer with a nitro terminal group did not exhibit a mesophase. The oligomers and polymers obtained by the polymerization of the aziridine monomer formed a smectic A phase. A homeotropic structure was spontaneously formed by the adsorption of a hydrophilic polyamine unit in the smectic A temperature range. The formation of the homeotropic structure was clearly characterized by a uniaxial-conoscopic interference figure.

Key words: Liquid Crystal, Polymer, Oriented Film, Smectic, Cholesteric

1. INTRODUCTION

Thermotropic liquid crystals have been widely utilized in the field of functional systems. The orientation control of the anisotropic phases is an important subject from scientific and technological viewpoints. Liquid crystalline polymers and cross-linked polymers can easily form anisotropic glasses having liquid crystalline orientations. Anisotropic glasses with a monodomain structure can be obtained by the polymerization of monomers in the liquid crystalline states [1-5].

The imine ring of the aziridine monomers exhibits high reactivity and polymerizes easily in solutions or bulk states at temperatures above the melting points. Furthermore, methacrylate monomers can form polymers by thermal polymerization. This paper describes the thermal polymerization of nonmesomorphic monomers occurring at isotropic phases in sandwich cells, and also reports the formation of a uniform alignment. The liquid crystal formation and the orientation of the cross-linked polymers are also discussed.

2. EXPERIMENTALS

Synthesis of monomers

The synthetic scheme of a monomer with an aziridine unit is shown in Fig. 1. The synthesis of 12-Bromo-1-(4-(2-methyl-4-nitrophenylazo)phenoxy) alkane (**Br12MN**) was achieved by the reaction of 4-(2-methyl-4-nitrophenylazo)phenol and 1,12-bromododecane. By reaction of **Br12MN** and 2-methylaziridine, an aziridine monomer was obtained. **Br12MN**, triethylamine and 2-methylaziridine were dissolved in tetrahydrofuran (THF) [6]. The THF solution was then stirred at 25 ℃ for three weeks. After the reaction, the residue was dissolved in chloroform and washed with water. The chloroform solution was dried with $MgSO_4$. Chloroform was evaporated and a crude monomer was obtained. This monomer was purified by recrystallization from the hexane solution. Fig. 2 shows the synthetic scheme of chiral methacrylates. The chiral methacrylate monomers were synthesized by esterification of materials. 4-Hydroxybenzoic acid and sodium hydroxide were dissolved in water. A methacryloyl chloride-THF solution was added dropwise to this water solution, and the solution was

stirred for 5 h. After the reaction, THF and water were evaporated at room temperature, and the crude product was dissolved in water. The water solution was acidified by the addition of hydrochloric acid, and the 4-(methacryloyloxy)benzoic acid precipitate was filtered off and washed with cold water.

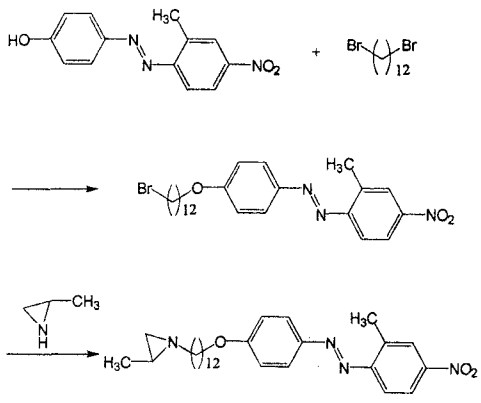

Fig. 1. Synthetic scheme of the aziridine monomer.

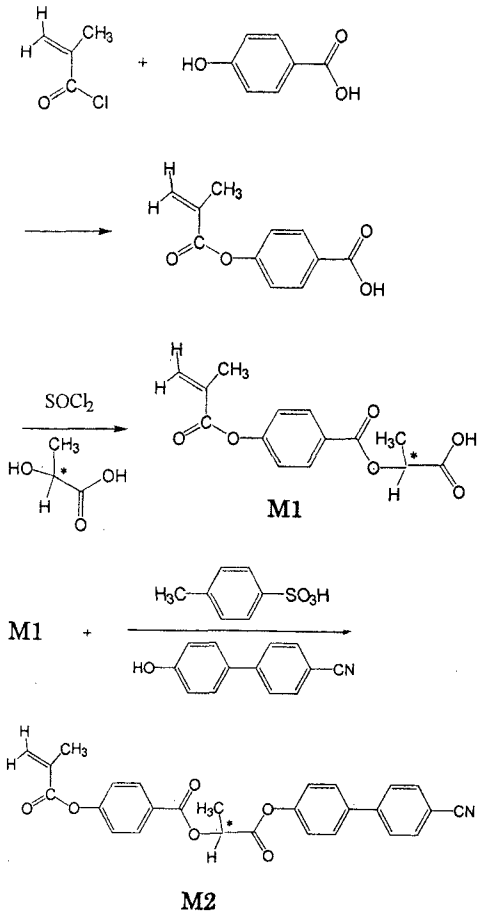

Fig. 2. Synthetic scheme of the chiral methacrylate monomers.

4-(Methacryloyloxy)benzoic acid was dissolved in thionyl chloride, and a small amount of DMF was added to the solution, which was subsequently stirred for 3 h. After the reaction, the excess thionyl chloride was evaporated under reduced pressure. The product was dissolved in THF, and a mixture of L-lactic acid and triethylamine was added to the THF solution. THF was evaporated after 7 h, and the crude product was dissolved in chloroform. The chloroform solution was washed with water and dried with $MgSO_4$. Subsequently, chloroform was evaporated from the chloroform solution. M1, 4-hydroxy-4'-cyanobiphenyl, and *p*-toluene sulfonic acid were dissolved in THF, and 2,6-di-*tert*-butyl-*p*-cresol was added in this THF solution. The THF solution was refluxed for 12 h, and after the reaction, THF was evaporated. The crude product was dissolved in chloroform. The chloroform solution was washed with water and dried with $MgSO_4$. Subsequently, chloroform was evaporated, and the product (M2) was obtained.

Thermal polymerization and measurements

A sandwich glass cell (cell thickness = 6 μm) was used for the thermal polymerization. Trimethylolpropane tris(2-methyl-1-aziridine-propionate) (TMA) with three imine rings, which was purchased from Sigma-Aldrich Co., was used as a cross-linker. The aziridine monomer and 5 wt% of TMA were dissolved in THF. The mixture (A1) was obtained by evaporation of THF solvent. In the case of the thermal polymerization for the chiral methacrylate monomer, the mixture (MM) of M1 (5 wt%) and M2 was prepared.

The phase transitions were estimated using a Shimadzu differential scanning calorimeter (DSC60), a Mettler Thermosystem 3000, and an Olympus polarizing microscope with equipped with a Mettler FP900 system.

RESULTS AND DISCUSSION

Chiral methacrylate monomers (M1, M2, and MM) did not exhibit a liquid crystalline phase. A cholesteric phase was obtained by the thermal polymerization of MM at an isotropic phase. MM (the mixture of M1 with M2) was introduced in the sandwich cell without surface treatments by the

capillary method at 100 ℃ (an isotropic fluid) and maintained at 130 ℃. After 3 min, droplets were formed within the isotropic fluid phase and their number increased in the cell. After 30 min, the cholesteric phase with a finger-print texture was completely filled in the cell (Fig. 3). This finger-print texture shows that oligomers and polymers obtained from MM form the cholesteric phase. MM smoothly polymerized at temperatures above 130 ℃. At temperatures below 130 ℃, however, the thermal polymerization of MM very slowly proceeded. The isotropization temperature increased with polymerization time (Fig. 4). This is related to the molecular weight of the polymer. The gel permeation chromatography (GPC) curves are exhibited in Fig. 5. The molecular weight increased with an increase in the polymerization time. After 0.5 h and 1.0 h, the methacrylate monomers component remained in the sample. The sample polymerized for 2 h scarcely had the methacrylate monomer component. Polymers with the molecular weight above 10,000 were obtained after 2 h. The liquid crystalline formation for the MM polymerization system arises from the production of the oligomers. This corresponds to the polymer effects and is generally a well-known experimental fact that the increase in the molecular weight enhances the ability of the liquid crystal formation [7].

The temperature dependence of the cholesteric pitch for the polymethacrylate sample obtained by polymerization for 2 h is shown in Fig. 6. The cholesteric pitch is constant in the temperature range below 200 ℃ and immediately increases above 200 ℃.

In the case of the thermal polymerization of A1 without a mesophase, which is the mixture of the aziridine monomers, batonnets that were initially formed by the production of oligomeric materials were homeotropically aligned (100 ℃). The liquid-crystalline homeotropic domain increased with an increase in the polymerization time. When the non-treatment cell was filled by the smectic A-fluid state, the homeotropic structure was clearly observed, and the other optical textures such as oily streak and focal conic fan textures did not exist. The homeotropic structure exhibited a conoscopic

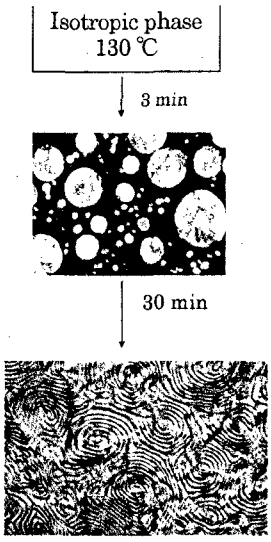

Fig. 3. Formation of the cholesteric phase by thermal polymerization of **MM**.

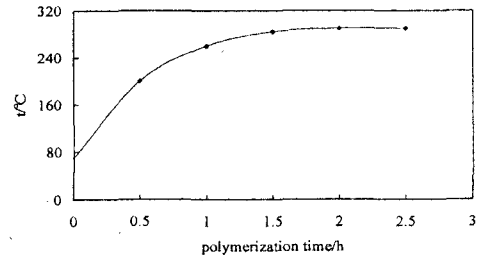

Fig. 4. Polymerization time dependence of Isotropization temperature for **MM**.

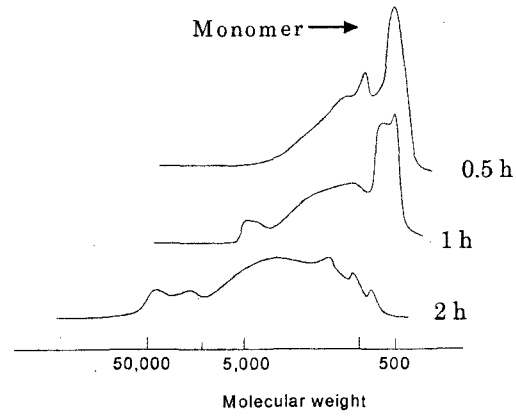

Fig. 5. Polymerization time dependence of molecular weight for **MM**.

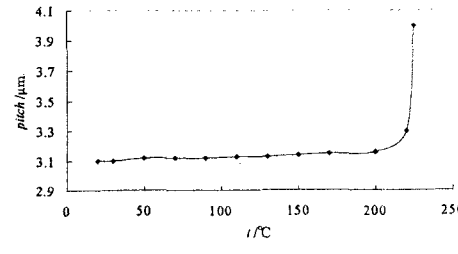

Fig. 6. Temperature dependence of cholesteric pitch for sample obtained by polymerization of **MM** for 2 h.

interference figure with an optical-uniaxial property. A fan texture was formed upon an application of shearing stress for the homeotropic structure. The homeotropic structure and the fan texture show the formation of the smectic A phase.

Fig. 7 is a schematic illustration of the liquid crystal formation in A1. A1 was not a liquid crystalline system; it merely exhibited the isotropic fluid phase above the melting point. In the isotropic phase, the molecules are aligned at random and have no direction. The oligomers and polymers form the liquid crystalline alignment. Moreover, the amine units of the oligomer are adsorbed on the non-treatment glass plate of the cell and the mesogenic side groups are perpendicularly aligned (Fig. 8) [8]. In this case, the oligomer with a hydrophilic chain effectively acts as a surfactant of the perpendicular alignment agent, and the homeotropic mesophase structure (the perpendicular structure) is spontaneously formed in the non-treatment cell.

4. CONCLUSIONS

The liquid-crystalline polymer films with helical and homeotropic structures were obtained by the thermal polymerization of nonmesomorphic monomers in the glass cells. Physical adsorption is effectively used for the spontaneous formation of the homeotropic structure.

5. REFERENCES

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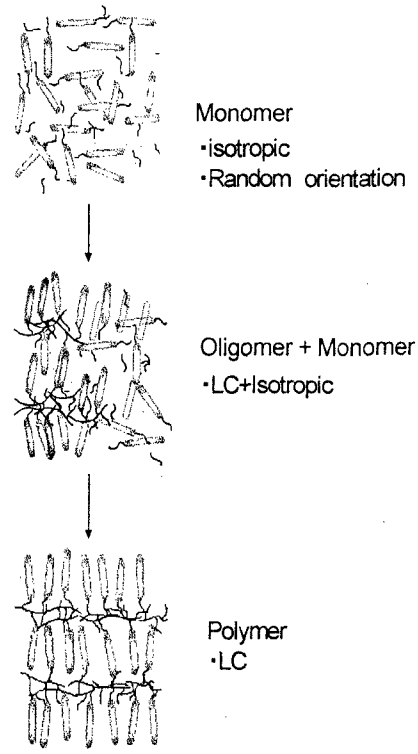

Fig. 7. Illustration of liquid crystal formation by thermal polymerization.

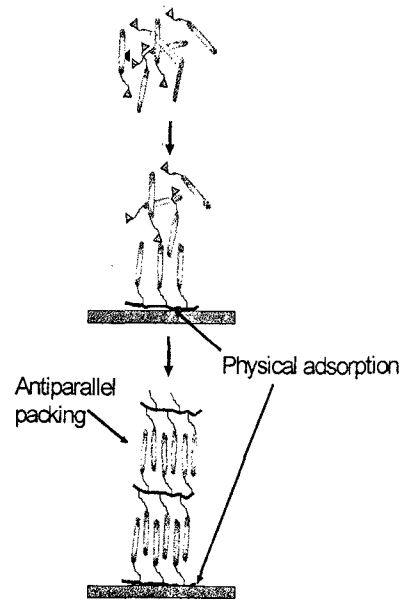

Fig. 8. Spontaneous formation of homeotropic structure.

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