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Temperature Dependence of Helical Structure of Polymer-Stabilized Antiferroelectric Liquid Crystals

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In an antiferroelectric liquid crystalline SmC_A^* phase, the helical structure of molecular alignment depends strongly on temperature. It is well known that in the SmC_A^* phase of optically pure MHPOBC, the helical pitch increases to infinity and then the right or left helical handedness changes to the other as temperature decreases after the phase transition to the SmC_A^* phase. In this study, we have investigated the temperature dependence of the helical structure of polymer-stabilized antiferroelectric liquid crystals (PS-AFLCs) in terms of circular dichroism (CD) and optical rotatory power (ORP), and discuss the effect of introducing the polymer network into the AFLC medium upon the helical structure. It is found that the both of helical pitch and handedness can be fixed by polymer stabilization over a wide range of temperature.

Keywords: antiferroelectric liquid crystal; circular dichroism; handedness; helical pitch; optical rotatory power; polymer stabilization

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INTRODUCTION

Antiferroelectric liquid crystals (AFLCs) are attractive materials for device application because of their unique characteristics such as high speed response and monostability [1]. Furthermore, it is academically interesting that AFLC materials have various liquid crystalline phases in the phase sequence and show a complicated phase series, and moreover that in the antiferroelectric liquid crystalline SmC_A^* phase, the helical structure of molecular alignment depends strongly on temperature. It is well known that in the SmC_A^* phase of optically pure MHPOBC in which antiferroelectricity was happened to see for the first time [1], the helical pitch increases to infinity and then the right or left helical handedness changes to the other as temperature decreases after the phase transition to the SmC_A^* phase [2–5]. For an application of AFLC, it is important to control the temperature dependence of the helical structure.

Polymer stabilization techniques are useful for the control of molecular alignment structure of liquid crystals. In previous papers our research group reported many types of polymer-stabilized ferroelectric liquid crystals (PS-FLCs) fabricated by a UV photocure of doped photocurable monoacrylates which have mesogenic side chains [6–13]. In this paper, we propose a polymer-stabilized AFLC (PS-AFLC) and report the effect of introducing the polymer network into the AFLC medium upon the helical structure discussed form the temperature dependence of the helical structure of PS-AFLCs in terms of circular dichroism (CD) and optical rotatory power (ORP).

EXPERIMENTAL DETAILS

The materials used in this research were as follows: the AFLC was CS-4001 [14] (Chisso Petrochemicals); the photocurable mesogenic monoacrylate was UCL-001 [6–14] which were doped with 1 wt% photoinitiator; and the LC alignment film was polyimide SE-1211 (Nissan Chemical Industries) which induced a homeotropic alignment. The relevant properties of CS-4001 given by the catalogue are shown in Table 1.

A solution of polyimide was spun on glass substrates coated with indium-tin-oxide (ITO) and then baked. The AFLC, which was doped with the photocurable mesogenic monomer (1–5 wt%), was injected in the isotropic phase via capillary action into an empty cell in which the cell gap was 50 μm. After the injection, the cell was cooled gradually to the temperature T where the LC medium is in the SmC_A^* phase. Next, the LC medium was photocured with a UV light source (365 nm,

TABLE 1 Properties of CS-4001

Properties	
Phase sequence	Iso.(88.8)SmA(71.5)SmC*(70.2)AF(68.8) SmC^*_γ (67.8)SmC^*_A (< −70)Cryst. [°C]
Spontaneous polarization	79.7 nC/cm^2 (25°C)
Tilt angle	25° (25°C)
Switching time	79.5 μs (E = 10 V/μm, 25°C)

2 mW/cm^2) at the temperature of $T-T_c = 10$°C under the quiescent condition, where Tc is the phase transition temperature to SmC^*_A phase under the cooling process.

The CD and ORP data of the AFLC cells fabricated by this method were measured with a spectropolarimeter J-720WI (JASCO), in which the range of measurement wavelength were between 200 and 900 nm, before and after UV photocure. The information of helical pitch and handedness can be obtained from the CD and ORP data. Although the helical pitch can be calculated from the wavelength of the selective

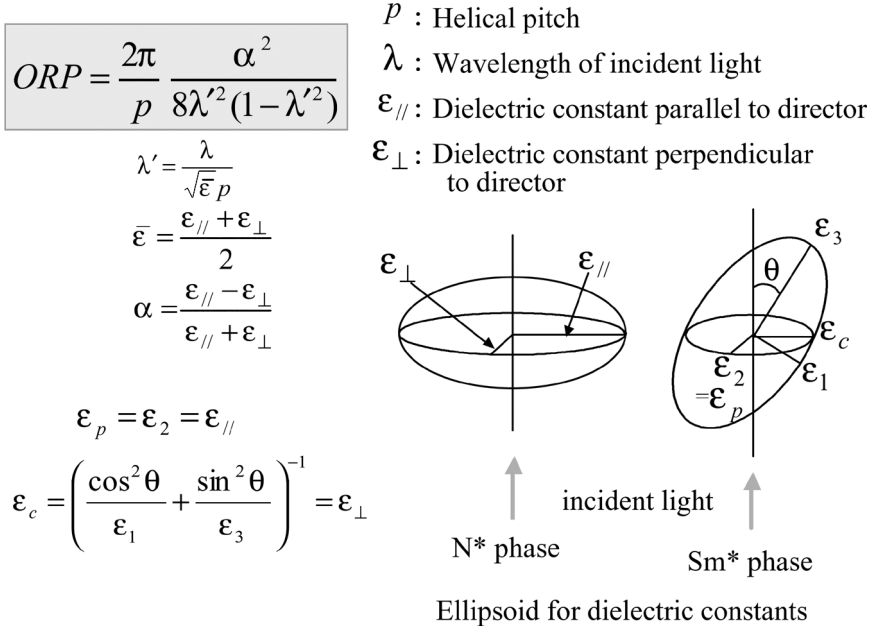

FIGURE 1 de Vries theory extended to smectic phase: the inclined ellipsoid for dielectric constants rotates along the helical axis in the chiral smectic phase.

reflection which can be measured directly from the CD spectrum; if the wavelength is over 900 nm, the helical pitch cannot be obtained from the CD data in this research. In this case, we used the de Vries theory extended to the chiral smectic phase, as shown in Figure 1 [5,15]. The helical pitch can be calculated from the ORP data by using this theory.

RESULTS AND DISCUSSION

Figure 2 demonstrates the temperature dependence of the helical pitch in a conventional AFLC of CS-4001. After the phase transition from the ferrielectric liquid crystalline SmC^*_γ phase to SmC^*_A phase under the cooling process; the helical pitch with right handedness increases to infinity, the right helical handedness changes to the left, and then the helical pitch with left handedness decreases as the temperature decreases.

Figure 3 shows the temperature dependence of the helical structure in PS-AFLC fabricated using 1 wt% monomer. It is found that the temperature at which the reversal of helical handedness occurs shifts to a lower temperature region after the photocure, and thus the helical handedness which forms at the temperature where the photocure has been done may stabilize even by a lower concentration of the polymer network (1 wt%). Figure 4 shows the case of 2 wt% doping. In addition to the shift of the temperature at which the reversal of helical handedness occurs, the helical pitch having right handedness

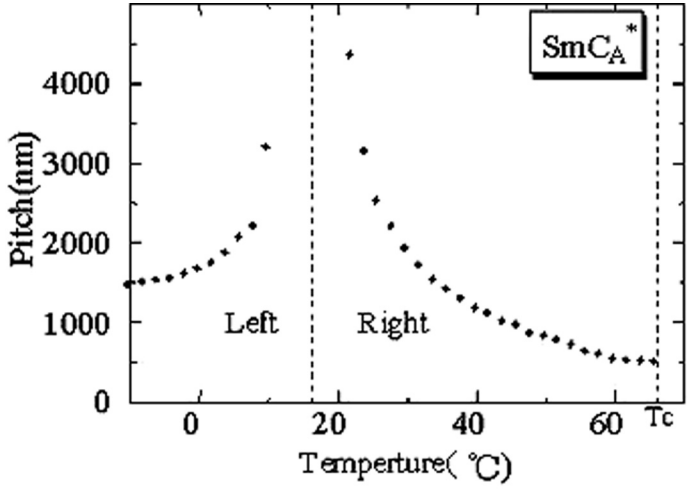

FIGURE 2 Temperature dependence of helical pitch in CS4001.

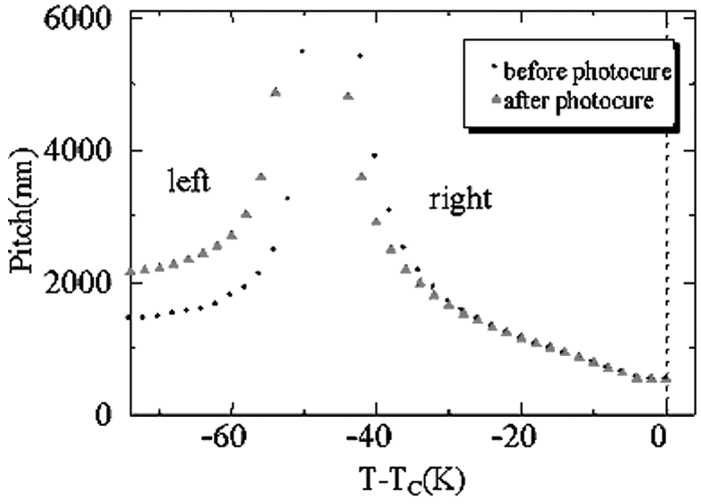

FIGURE 3 Temperature dependence of helical structure of PS-AFLC in monomer density 1wt%: Tc is 66°C before and after the photocure, and the temperature where the photocure is done is 56°C.

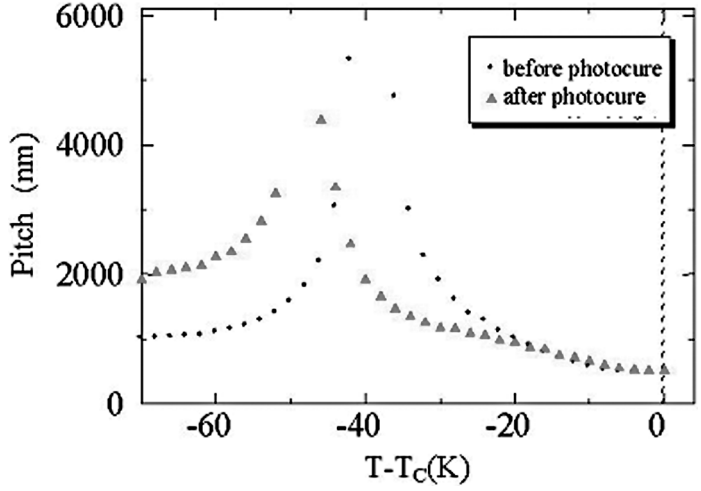

FIGURE 4 Temperature dependence of helical structure of PS-AFLC in monomer density 2wt%: Tc is 58 and 64°C before and after the photocure, respectively, and the temperature where the photocure is done is 48°C.

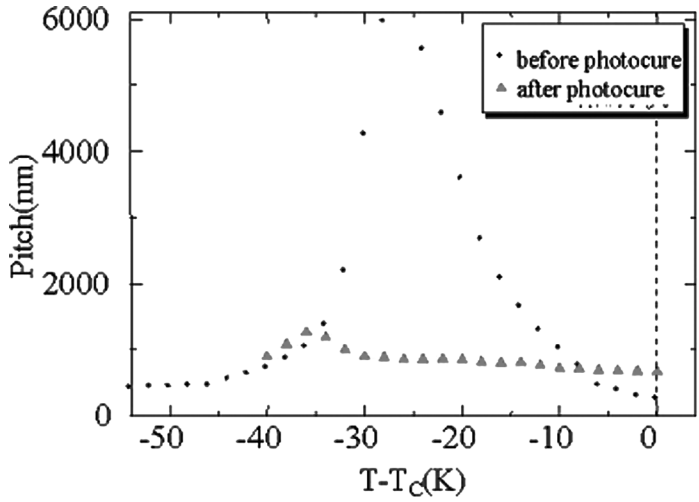

FIGURE 5 Temperature dependence of helical structure of PS-AFLC in monomer density 5wt%: Tc is 48 and 60°C before and after the photocure, respectively, and the temperature where the photocure is done is 38°C. PS-AFLC after photocure does not exhibit the left helical handedness.

tends to settle in the pitch as the photocure has been done. Furthermore, in a relatively high concentration of the polymer (5 wt%), the reversal of helical handedness cannot be observed, and then the both of helical pitch and handedness is almost perfectly fixed to the helical structure, which forms at the photocure temperature, over a wide range of temperature; as shown in Figure 5. It is concluded that the polymer network can strongly stabilize the helical structure of AFLC which forms at the temperature where the photocure has been done and thus the polymer stabilization technique is useful for the control of the helical structure even in AFLC in which the helical structure strongly depends on the temperature.

SUMMARY

In this study, we have investigated the temperature dependence of the helical structure of polymer-stabilized antiferroelectric liquid crystals (PS-AFLCs) in terms of the helical pitch and helical handedness obtained by the measurement of circular dichroism (CD) and optical rotatory power (ORP), and discussed the effect of introducing the polymer network into the AFLC medium upon the helical structure. It has been found that even in a low concentration of the polymer (1wt%),

the temperature of the helical handedness reversal shifts to a lower temperature region after the photocure in which UV irradiation was done at a temperature slightly lower than the phase transition temperature to SmC_A^* ($T-T_c=10^\circ C$), and furthermore, in a relatively high concentration of the polymer (5 wt%), the both of helical pitch and handedness can be fixed to the helical structure, which forms at the temperature where the photocure has been done, over a wide range of temperature. It is concluded that the polymer network can strongly stabilize the helical structure of AFLC.

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