New material design for liquid crystals and composites by magneto-processing

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Abstract

We have tried to form a variety of oriented structures in liquid crystalline materials and composites by magneto-processing. Using photo-curable liquid crystal (LC), homogeneous, homeotropic, and bend oriented structures were fixed in the films. Moreover, UV light was irradiated to the LC monomers through a photomask under the magnetic field. The pattern was successfully recorded in the film by molecular orientation. Low viscous branched LC molecules, LCs based on calix [4] resorcinarene and dendrimer, synthesized in this study could be highly aligned under the magnetic fields. The smectic structures of these LC materials were demonstrated from X-ray diffraction results of the magneto-oriented samples. Carbon nanotubes (CNTs) were aligned parallel to the field direction in polycarbonate (PC). Moreover, magneto-oriented CNTs remarkably enhanced the recrystallization of the PC during annealing.

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1. Introduction

The development of high performance materials for structural applications has been driven by the ability to create anisotropy at the molecular level. Aromatic ring has comparatively high diamagnetic susceptibility. In particular, liquid crystalline (LC) materials and carbon nanotube (CNT) are highly oriented under magnetic field because they have high anisotropic diamagnetic susceptibility [1–7]. The magnetic field can be applied to these materials at any directions without contact. In addition, the magnetic field is uniformly applied to the samples.

In this paper, we have proposed a variety of magnetic field processing methods using photo-curable liquid crystals, branched LC molecules: LCs based on calix [4] resorcinarene and dendrimer, and carbon nanotubes (CNTs) in polycarbonate (PC).

1.1. Molecular alignment of liquid crystalline materials by magneto-processing

In general, low molecular weight LCs can be oriented under comparatively low magnetic field. However, it is hard to fix the magneto-oriented structures because of their low viscosity. In the case of photo-curable liquid crystal, on the other hand, the oriented liquid crystalline structures can be fixed by photo-polymerization [8].

Photo-curable LC monomer used in this study (Fig. 1) exhibits the nematic to isotropic phase transition at 126.5 °C [8]. The LC monomer was coated on a glass substrate by spin coat method. The magnetic field of 2.4 T was applied to the sample on cooling from the melt, and then ultraviolet (UV) light of 365 nm was irradiated for 120 s to it around room temperature. The magnetic field was applied to the sample at various setting angles between the magnetic field direction and glass substrate; 0 (parallel), 30, 45, 60, and 90° (vertical). Fig. 1 represents conoscopic images observed under polarizing optical microscope (POM) with crossed polarizers. The center of the isogyre of the conoscopic images deviated with decreasing the setting angle. The inclined angle between the molecule and the glass plate was estimated from the deviation of the center of the isogyre. The inclined angles were almost consistent with the setting angles as shown in Fig. 1. Thus, the oriented structure formed under the magnetic fields can be fixed by photo-polymerization. The intensity of the birefringent light increased with decreasing setting angle and the optical retardation of the films also gradually changed [8].

The photo-curable LC monomer was coated on the glass rod and wrapped into a polyester film to avoid flowing out at elevated temperature. The magnetic field was applied to the
rolled film, and the UV was simultaneously irradiated to the film, as illustrated in Fig. 2. The film peeled from the glass rod exhibited various conoscopic images as shown in Fig. 3. The isogyre patterns were observed at two regions where the magnetic field was vertically applied. The center of the isogyre gradually shifted between two regions as shown in Fig. 3. The result suggests that the molecular orientation direction continuously changed in the film as illustrated in Fig. 4 [9].

The rolled film was placed tilt to the magnetic field line. The conoscopic images of the film were shown in Fig. 5, where the center of the isogyre images gradually changed in a spiral. Thus, the molecules were oriented in a spiral in the film as schematically illustrated in Fig. 6.

As a result, the magneto-processing gives a variety of steric molecular alignments.

2. Patterning of photo-curable liquid crystal using magnetic field and photo-polymerization

We have tried to draw a pattern in a film by photolithographic and magneto-orientation methods [8]. The photo-curable LC monomer was spin-coated on a glass plate. The magnetic field was applied to the film on cooling from the melt, and UV was irradiated through a photomask of pattern ‘Y’ to polymerize the monomer in only the part of the pattern. The molecular orientation was fixed in only the part of the pattern. The magnetic field was applied again. The monomers outside of the pattern were reoriented to the second field direction. The UV light was irradiated to whole of the sample. The second irradiation fixed the molecular orientation outside the pattern ‘Y’. The molecular orientation formed in the film was schematically illustrated in Fig. 7, where the molecular orientation direction inside the pattern ‘Y’ is 45° tilt to that outside the pattern. The film is transparent, as shown in Fig. 7(a). The pattern ‘Y’ was bright under the crossed polarizers when the molecular orientation inside the pattern was in diagonal position, as shown in Fig. 7(b), on the other hand, the pattern was dark in the extinction position in Fig. 7(c).

Thus, the pattern was successfully recorded in the film by molecular orientation.

3. Magneto-orientation of branched liquid crystalline materials

We have prepared novel liquid crystals based on calixarenes and dendrimers [10,11]. The structural formula of calix [4] resorcinarene having mesogenic units (C4RA-LC) is shown in Fig. 8 [10]. It exhibited nematic and smectic A(SmA) liquid crystalline phases. It was hard to demonstrate the SmA layer structure in detail from the X-ray diffraction (XRD) pattern of the isotropic (no-oriented) sample. Thus, the magnetic field of 2.4 T was applied to C4RA-LC to prepare an oriented sample for the XRD measurement. The magneto-oriented sample exhibited sharp reflections at small angle area on the meridian line, as shown in Fig. 9. This XRD pattern reveals a smectic

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Fig. 1. Relationship between setting and inclined angles, and conoscopic images of magneto-oriented samples.

Fig. 2. Magneto-orientation for roll film of photo-curable LC.

Fig. 3. Conoscopic images observed in the magneto-oriented roll film.
A(SmA) with the layer spacing of 5.11 nm. Diffuse arcs appeared at \( 2\theta \) around 5 and 20° on the equator; the d-spacings were estimated to 1.5 and 0.43 nm, respectively. Thus, the oriented XRD pattern and the molecular model of C4RA-LC suggest the smectic layer structure illustrated in Fig. 10, where C4RA-LC forms a cone-like structure, mesogenic units are readily oriented within the molecule, and a partial overlapping of the cyanobiphenyl units occurs.

Poly(propyleneimine) dendrimer of second generation having peripherally cyanobiphenyl mesogenic groups (LCD2-CN-C6) shown in Fig. 11 exhibited a liquid crystalline SmA phase [11]. The isotropic/SmA phase transition of LCD2-CN-C6 occurred at 74.0°C. In general, magneto-orientation requires low viscosity and mesomorphic structure. The magnetic field of 2.4 T was applied to the LC dendrimers during slow cooling at 1 °C/min from the isotropic melt. The DSC trace of LCD2-CN-C6 and XRD patterns of the magneto-oriented samples are shown in Fig. 12, where the temperature denotes the starting temperature of the magnetic field application. The samples applied above 80 °C showed oriented X-ray diffraction patterns. These samples exhibit comparatively high orientation coefficients: \( (P2) \) values were larger than 0.6. Note that LCD2-CN-C6 was oriented at temperature close to the SmA phase. The viscosity of LC dendrimer is probably low due to no chain entanglement. In addition, three periodic reflections appeared in the low angle area of the X-ray diffraction pattern: \( d = 38.4, 19.2, \) and 1.27 nm. It suggests that the magnetic field enhances the formation of a long-range ordered smectic layer structure.

4. Oriented crystallization of polycarbonate by magnetically aligned CNT [6,7]

It is known that polycarbonate (PC) is categorized as amorphous polymer and pure PC crystallizes extremely slowly [12]. In general, CNT has curved structure without having graphitization and orients magnetically [13]. However, the alignment property of graphitized CNT with relatively linear structure under magneto-processing was not fully characterized.

We have recently found that the crystallization of PC was substantially accelerated around 200 °C in the presence of graphitized vapor grown carbon fiber (VGCF, \( d = 100–200 \) nm), having ultra thick multi-walled carbon nanotube (MWCNT) structure with relatively linear form [14]. Fig. 13 shows DSC curves and XRD traces of PC including 5 wt% of
VGCF having annealed prehistory. Dynamic mechanical analysis (DMA) and melt rheological property also suggested the induced crystallization of PC in the presence of VGCF around 200 °C. To examine the accelerated crystallization by VGCF, the effect of pre-graphitized VGCF (amorphous), carbon black (amorphous), and meso-phase pitch based carbon fiber (CF) on the crystallization was evaluated. Amorphous carbon surface did not induce the acceleration of PC crystallization but the graphitized surface, either VGCF or CF, did.

To examine macroscopic PC crystallization structure nucleated by VGCF, the in situ optical microscope observation of PC/VGCF (99.9/0.1 wt ratio) on hot stage (200 °C) was carried out. We have attempted to observe retardation property around VGCF using PC/VGCF composite with randomly

![Fig. 8. Structural formula of C4RA-LC.](image)

![Fig. 9. X-ray diffraction patterns of magneto-oriented C4RA-LC.](image)

![Fig. 10. Smectic layer structure of C4RA-LC.](image)

![Fig. 11. Structural formula of LC dendrimer.](image)

![Fig. 12. DSC trace of LCD2-CN-C6 and XRD patterns of magneto-oriented samples.](image)

![Fig. 13. (a) The first heating DSC curves (lower direction = endothermic, 10 °C/min) (b) XRD traces for annealed PC/VGCF (95:5 wt ratio) composites at various temperatures for 2 h.](image)
dispersed VGCF. However, it was difficult to judge the retardation property around VGCF due to the random orientation of VGCF. Therefore, we have magnetically aligned VGCF toward one direction. Fig. 14 shows the insitu polarized optical micrograph (POM) of PC/VGCF (99.9/0.1 wt ratio) including oriented VGCFs at 200 °C after 2 h. The orientation time of VGCF in molten PC was estimated based on the proposed equation [15] and the anisotropic diamagnetic susceptibility of VGCF (3.11×10⁻⁴). The POM demonstrated that PC crystals were generated at the surface of VGCF and that the crystals oriented along the axial direction of VGCF.

By utilizing this finding, we have magnetically aligned 5 wt% of VGCF in PC at 270 °C, then annealed it at 220 °C for 2 h without magnet. Fig. 15 shows optical micrograph and XRD pattern of the composite film. The optical micrograph showed that the fine VGCF oriented in the direction of the applied magnetic field. In addition, two arc reflections appeared on the equator in the XRD pattern, where the outer and inner reflections were assigned to (002) plane of graphite crystal and (020) of PC crystal, respectively. Thus, VGCF and PC crystallites were oriented under magnetic field. The magneto-processing of CNT composite could open a new material design method for composite systems.

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