

Structures and Properties of Liquid Crystalline Materials Oriented under Magnetic Field

Koichiro Yonetake, Hiroshi Awano, Osamu Haba and Junji Kido
 Yamagata University, 4-3-16 Jonan, Yonezawa Yamagata, 992-8510 Japan
 Fax: 81-238-26-3045, e-mail: yone@yz.yamagata-u.ac.jp

High magnetic field can form a variety of molecular orientation structures in liquid crystalline(LC) materials. Poly(propyleneimine) dendrimers having peripherally mesogenic groups exhibited a smectic liquid crystalline nature. Application of the magnetic fields to the LC dendrimers aligned the mesogenic groups in various field directions. The dielectric constant could be changed by the magnetic orientation. Liquid crystalline structures of UV curable LC can be fixed in the film by photo-polymerization. Using the procedure, the magneto-oriented structures of UV curable LC were fixed in the film: homogeneous, homeotropic, and bend oriented structures. UVlight irradiated to the monomers through a photomask in the magnetic field to fix the molecular orientation in only the part of the photomask's pattern. The pattern could be recorded in the film by molecular orientation.

Key words: magnetic field, liquid crystalline dendrimer, UV curable liquid crystal, photo-polymerization

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. Thus, in particular, liquid crystalline materials are highly oriented under magnetic field because they have high anisotropic diamagnetic susceptibility.[1-9] However, it is hard to fix the magneto-oriented structures of low molecular weight liquid crystals. On the other hand, liquid crystalline dendrimers have unique steric structures and comparatively high glass transition temperature so that they produce stable smectic structures in ambient temperature.[10-13] It is possible to keep the smectic structure arranged under magnetic field. Photo-curable liquid crystal is easily oriented under comparatively low magnetic field, and the oriented liquid crystalline structures can be fixed by photo-polymerization.

In this paper, we have proposed a variety of magnetic field processings using liquid crystalline dendrimers and UV-curable liquid crystals, and have investigated the structures and properties of the magneto-oriented samples.

2. EXPERIMENTAL

Samples

Liquid crystalline dendrimers(LCD) used are shown in Fig.1. Poly(propylene-imine) dendrimers of 2nd and 3rd generations were peripherally modified with a cyanobiphenyl and difluorobiphenyl mesogenic groups to prepare liquid crystalline dendrimers (LCDs).

Ultra violet (UV) curable liquid crystal (LC) and photo-initiator used are shown in Fig.2.

Measurements

The structural characterization was carried out using differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD) methods. Heating and cooling rates of the DSC measurement were 10 °C min⁻¹. POM observation was carried out by an OLYMPUS BX50-33P equipped with a heating stage. X-ray diffraction experiments were

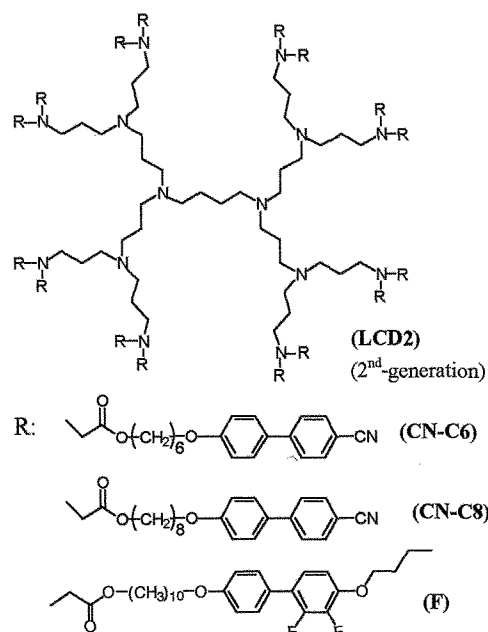


Fig.1 Structural formula of LC dendrimers

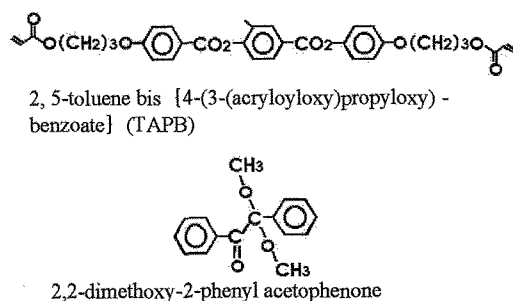


Fig.2 Structural formula of UV curable liquid crystal and photo-initiator

carried out by a MicroMax007 diffractometer (Rigaku Denki Co. Ltd.) operated at 40kV and 20mA. CuK α X-ray beams monochromatized with a confocal mirror were shone onto the specimen through a pinhole collimator of 0.3 mm in diameter. As an X-ray detector, the imaging plate (IP) system was utilized. Orientation coefficients of the magnetically oriented samples were

$$\langle P_2 \rangle = \frac{1}{2} (3 \langle \cos^2 \theta \rangle - 1) \quad (1)$$

$$\langle \cos^2 \theta \rangle = \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi}$$

estimated by the X-ray diffraction method using following equation (1).

where $\langle P_2 \rangle$ is an orientation coefficient, θ an angle between molecular axis and magnetic field, $I(\phi)$ an azimuthal intensity distribution.

Magnetic field processing

The sample was heated up to the isotropic melt state (120°C), and the magnetic fields of 2.4 T or 10 T were applied by using an electromagnet TM-WV8615MRC-156 (Tamagawa Co.) or a superconducting magnet JMTD-10T 100M (Japan Magnet Technology Ltd.). The sample was cooled at 0.5°C min⁻¹ to room temperature under the magnetic field. The magnetic fields were applied parallel, vertical, or tilt to the samples.

The magnetic field was applied to the UV curable LC to form a highly oriented structure, and then UV light was irradiated to the magneto-oriented sample to fix the oriented structure.

3. RESULTS AND DISCUSSION

3.1 Magnetic orientation of LC dendrimers

Poly(propyleneimine) dendrimers of 2nd generation having peripherally cyanobiphenyl mesogenic groups (LCD2-CN-C6 and LCD2-CN-C8) exhibited a liquid crystalline smectic A (SA) phase. The isotropic (I) to SA phase transitions of LCD2-CN-C6 and LCD2-CN-C8 occurred at 74.0°C and 79.0°C, respectively. On the other hand, Poly-(propyleneimine) dendrimers of 3rd generation with difluorobiphenyl groups (LCD3-F) exhibited smectic E (SE) and SA phases. The phase transition temperatures of I/SE and SE/SA were 86.3°C and 50.8°C, respectively.

In general, magneto-orientation occurs when the magnetic field is applied to the sample during slow cooling process from the melt. The magneto-orientation requires low viscosity and mesomorphic structure.[10] Therefore, the magnetic field of 2.4 T was applied to the LC dendrimers during cooling process of 1 °C/min from the isotropic melt. The X-ray diffraction patterns of the magneto-oriented LCD2-CN-C6's are shown in Fig.2 where the temperature denotes the starting temperature of the magnetic field application. On cooling from 120°C, the magnetic field of 2.4T kept be applied to LCD2-CN-C6 from an elevated temperature to room temperature. The samples to which magnetic field was applied above 80°C showed oriented X-ray diffraction patterns. Orientation coefficients $\langle P_2 \rangle$ of samples to which magnetic field was applied above

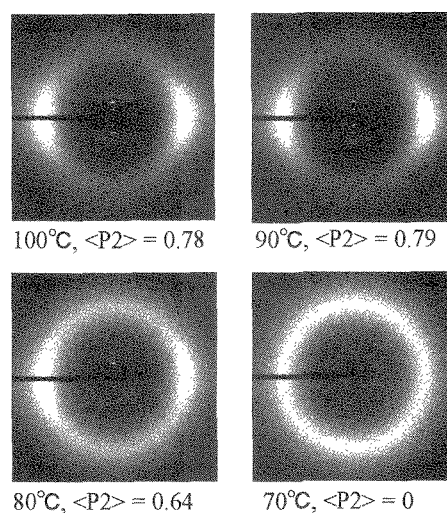


Fig.3 X-ray diffraction patterns of magneto-oriented LC dendrimers, LCD2-CN-C6.

90°C are higher than that of the samples at 80°C. Thermal condition of the magnetic orientation for LCD2-CN-C6 was effective in around 90°C. Note that LCD2-CN-C6 was oriented at temperature close to the SA phase. It is hard to orient the liquid-crystalline polymers around SA transition temperature. The viscosity of LC dendrimer is probably low due to no chain entanglement. No oriented pattern was obtained below 70°C. It is probably due to the higher viscosity since the temperature region corresponds to fully smectic A phase compared with 80°C. Three periodic reflections appeared in the low angle area of the X-ray diffraction pattern: $d = 38.4, 19.2, \text{ and } 1.27 \text{ nm}$. These reflections result from the smectic layer structure. The magnetic field enhanced the long range order of the smectic layer structure.

The dark area and bright texture were observed under POM with crossed polarizers when the sample was kept at elevated temperature in smectic A phase. The conoscopic images showing typical isogyre

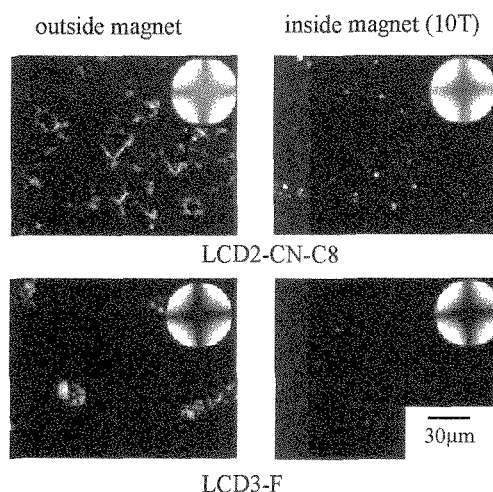


Fig.4 Homeotropic structure of LCD2-CN-C8 and LCD3-F.

pattern was obtained at the dark area. The optical textures and conoscopic images of LCD2-CN-C8 and LCD3-F were shown in Fig.3 (outside magnet). The mesogenic groups perpendicularly stood on the glass substrate in the dark area. Thus, homeotropic structure spontaneously formed on a glass plate. Same findings have been obtained in other LC dendrimers.[12] The magnetic field was perpendicularly applied to the sample. The dark area expanded to the whole sample, and the conoscopic image became clear, as shown in Fig.3 (inside magnet). Thus, the application of vertical magnetic field enhanced the homeotropic orientation. It is possible to form a monodomain under magnetic field.

The magnetic fields were obliquely applied to the samples at angles of 30, 45, and 60 degree. The conoscopic images of the magneto-oriented samples are shown in Fig.5. A cross point of the isogyre has deviated to the right side. This suggests that the mesogenic groups were tilted to the right side on the glass substrate. The deviation of the cross point of the isogyre became large with decreasing in the setting angle of the magnetic field applied. The inclined angle between the mesogen and glass plate was estimated from the deviation. The relationship between the inclined angle and the setting angle was shown in Fig.5. The orientation direction of the mesogen was almost consistent with the magnetic field direction. Thus, the magnetic field can align the LC dendrimers in any direction without contact.

Dielectric constant ϵ' of the magneto-oriented sample has been measured. The LC dendrimer sample was sandwiched between two ITO-coated glass plates. The cell was placed in the magnet, and the magnetic field of 2.4T was applied parallel to the cell. The sample exhibited a streak texture where focalconic fan texture was extended to the magnetic field applied (Fig.6). The ϵ' values of the magneto-oriented and isotropic samples measured are shown in Fig.6. The ϵ' values of magneto-oriented sample are larger than those of the isotropic sample. Cyanobiphenyl has a high dipole moment along to the molecular direction. The ϵ' value depends on the number of movable dipole under electric field. The number of movable dipole component in the magneto-oriented sample is more than that in the isotropic sample because the cyanobiphenyl mesogenic groups aligned parallel to the glass plate in the magneto-oriented sample. Thus, magnetic field orientation can change in the electrical property of the sample.

3.2 Magnetic field processing of UV curable LC

Low molecular weight liquid crystal can be oriented under comparatively low magnetic field due to the high diamagnetic susceptibility and low viscosity. It is hard, however, to fix the magnetic oriented structure.

If UV curable liquid crystalline (LC) monomer is used, the liquid crystalline structure of the monomer can be fixed by the photo-polymerization. UV-curable LC monomer used in this study exhibits the nematic to isotropic phase transition at 126.5°C.

The magnetic field was applied to the LC monomer on cooling from the melt, and then UV light of 365 nm was irradiated for 120 sec to it around room temperature. The magnetic field was applied to the sample at various setting angles; 0 (parallel), 30 deg, 45 deg, 60 deg, and

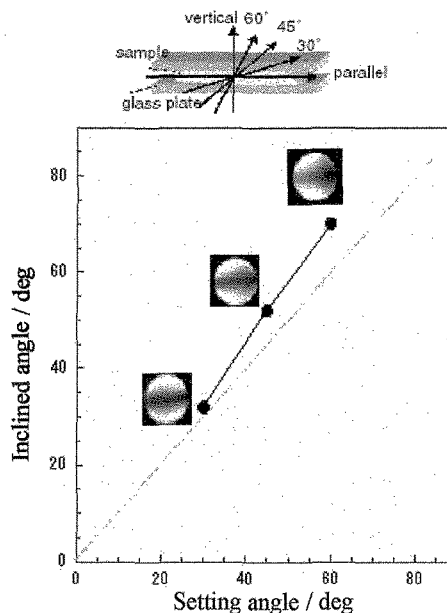


Fig.5 Relationship between inclined angle and setting angle. Conoscopic images of tilt-oriented samples

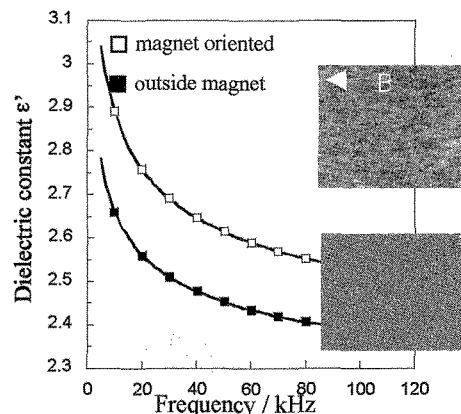


Fig.6 Dielectric constants ϵ' of the magneto-oriented and isotropic samples.

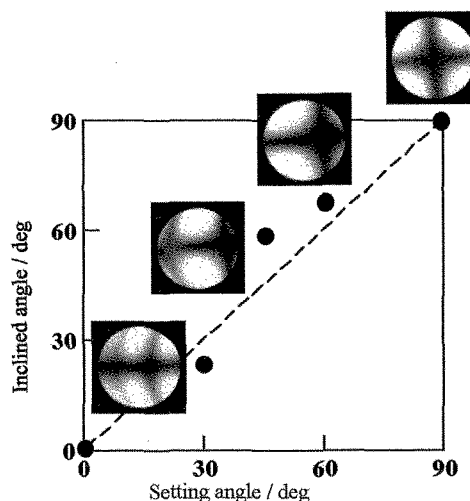


Fig.7 Relationship between setting and inclined angles, and conoscopic images of magneto-oriented samples.

90 deg (vertical). Fig.7 represents conoscopic images observed under POM and the relationship between the inclined and setting angles. The center of the isogyre of the conoscopic images deviated with decreasing the setting angle. The inclined angles were almost consistent with the setting angles. Thus, the oriented structure formed by the magnetic field could be fixed by photo-polymerization.

3.3 Patterning of UC curable LC under magnetic field

We have tried to draw a pattern in a film by photolithographic and magneto-orientation methods. The patterning procedure is illustrated in Fig.8. The magnetic field of 2.4 T applied to the UV-curable LC monomer on cooling from the melt, and then UV was irradiated to the monomer through a photomask in the magnetic field to polymerize the monomer in only the part of the photomask's pattern "Y". The molecular orientation was fixed in only the part of the pattern. The photomask was removed, and the sample was rotated to 45 degree. The magnetic field was applied to the sample again. The monomers outside of the pattern were rearranged to the field direction. The UV light was irradiated to the sample. The 2nd irradiation fixed the molecular orientation outside the pattern "Y".

The molecular orientation formed in the film was schematically illustrated in Fig.9. The molecular orientation direction inside the pattern "Y" is 45° tilt to that outside the pattern. The film is transparent, as shown in Fig.9 (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.9 (b), on the other hand, the pattern is dark in the extinction position in Fig.9 (c). Thus, the pattern could be recorded in the film by molecular orientation.

The magneto-orientation technique causes a variety of molecular orientation, and the optical and electrical properties can be changed.

4. CONCLUSION

4.1 Liquid crystalline dendrimer was oriented under the magnetic field of 2.4 T at the temperature close to the isotropic/SA phase transition.

4.2 The mesogenic groups of liquid crystalline dendrimer could be aligned by the magnetic field in any direction.

4.3 The oriented structure of UV-curable LC monomer formed by the magnetic field could be fixed by photo-polymerization.

4.4 The magneto-oriented pattern was successfully recorded in the film using photolithographic method.

REFERENCES

- [1] M. V. Piskunov, S. G. Kostromin, L. B. Stroganov, V. P. Shibaev and N. A. Plate, *Makromol. Chem. Rapid Commun.*, **3**,443(1982)
- [2] N. A. Plate, R. V. Talrose and V. P. Shibaev, *Makromol. Chem. Macromol. Symp.*, **12**,203(1987)
- [3] D. Ferri, D. Wolff, J. Springer, O. Francescangli, M. Laus, A. S. Angeloni, G. Galli and E. Chiellini, *J. Polym. Sci., Polym. Phys. Ed.*, **36**,21(1998)
- [4] H. Oulyadi, F. Laupretre, L. Monnerie, M. Mauzac, H. Richard and H. Gasparoux, *Macromolecules*, **23**,1965(1990)

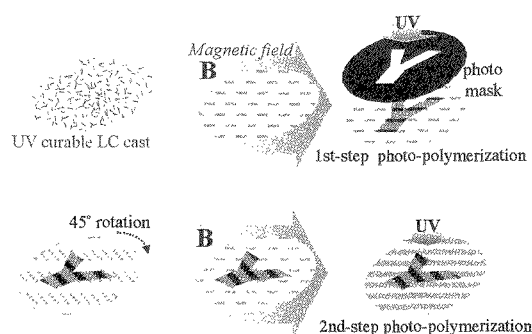


Fig.8 Patterning method using magnetic field and photo-polymerization

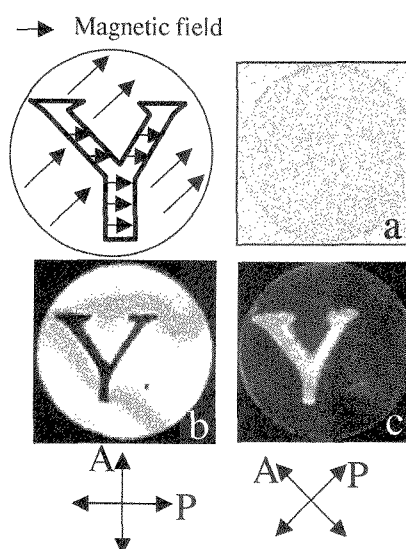


Fig.9 Magneto-patterned film

- [5] F. Lembicz, *Polymer*, **32**,2893(1991)
- [6] J. Allgaier and H. Finkelmann, *Macromol. Chem. Phys.*, **195**,1017(1994)
- [7] P. Roche and Y. Zhao, *Macromolecules*, **28**, 2819 (1995)
- [8] S. G. McNamee, T. J. Bunning, S. S. Patnaik and C. M. McHugh, *LIQUID CRYSTALS*, **18**,787(1995)
- [9] K. Akagi and H. Shirakawa, *Macromol. Symp.*, **104**,137(1996)
- [10] K. Lorenz, D. Holter, B. Stuhn, R. Mulhaupt and H. Frey, *Macromolecules*, **8**,414(1996)
- [11] D. J. Pesak and J. S. Moore, *Angew. Chem. Int. Ed Engl.*, **36**,1636(1997)
- [12] K. Yonetake, K. Suzuki, T. Morishita, R. Nagahata and M. Ueda, *High Perform. Polym.*, **10**,373(1998)
- [13] Z. Bao, K. R. Amundson and A. J. Lovinger, *Macromolecules*, **31**,8647(1998)
- [14] K. Yonetake, T. Masuko, T. Morishita, K. Suzuki, M. Ueda, and R. Nagahata, *Macromolecules*, **32**, 6578(1999)

(Received October 13, 2003; Accepted March 16, 2004)