Relation between Thermal Conductivity and Network Formation with Polymerizable Liquid Crystals

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ABSTRACT: The molecules with the mono- and bi-function at the sides in the acrylic PLC mixtures were aligned by the rubbing method. The alignment was immobilized by the photo polymerization to result the homogeneous acrylic films, which have good alignment with the higher order parameters. The thermal conductivity along the molecular long axis direction showed the larger magnitude of 0.62 W/m · K, which is independent on ratio of the main chain and the side chain fractions. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3169–3174, 2007

Key words: thermal conductivity; polymerizable liquid crystal; network; rubbing

INTRODUCTION

Liquid crystalline molecules having the ability for self-assembly are able to align under rubbing and external fields such as an electric field and a magnetic field. The molecular alignment induces anisotropies, i.e., the optical anisotropy and the anisotropy of the thermal conductivity. It is reported that the thermal transmission along the aligned molecular long axis direction is higher than that in the across direction, for example, 0.2 W/m · K (long axis) and 0.1 W/m · K (short axis).[1–6] The thermal conductive anisotropy of polymers have been investigated, for example, in the fibers and the films with the injection molding of the thermotropic liquid crystals,[7,8] the liquid crystal polymers cured under the magnetic field,[9] and the thin film on the silicon wafer,[10] and the free-standing films prepared with polymerizable liquid crystals (PLCs) by the rubbing method.[11] Up to now, the thermal conductivity of the main chain type polymers prepared from only bi-functional liquid crystals has been investigated. It can be useful to apply liquid crystal mixtures, because the properties such as the mesophase temperature range, the refractive index anisotropy, the dielectric anisotropy, and the magnetic anisotropy are able to be diversity arranged. In addition, it is expected to create the unique properties with the PLC mixtures.[12–14] However, there is no investigation about thermal conductivity of a polymer prepared with PLC mixtures that are prepared from mono- and bi-functional PLC monomers. In this work, the thermal conductivity of the homogeneous alignment polymers consisting of the main- and the side-chain fractions, that are prepared from mixtures containing the mono- and the bi-functional benzoate type PLC monomers, has been investigated.

EXPERIMENTAL

Synthesis of polymerizable liquid crystalline monomers (1) and (2)

The mono-functional compound 1-[4-(6-acryloyloxy-hexyloxy)benzoyloxy]-4-(4-hexyloxybenzoyloxy)ben-zene (**1**) and the bi-functional compound 1, 4-bis[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzene (**2**) have been synthesized according to the methods of Borer[15] and Kato[11] with modifications (Schemes 1 and 2).

4-Benzyloxyphenyl 4-hexyloxybenoate (1a)

To a mixture of 4-hexyloxybenzoic acid (24.4 g, 110 mmol), 4-benzyloxyphenol (20.0 g, 100 mmol), 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (13.4 g, 110 mmol) and 300 mL of THF, 1-ethyl-3-(3-dimethylami-nopropyl)carbodiimide hydrochloride (EDC) (34.5 g, 180 mmol) was added over an ice bath. After 1 h of stirring at the temperature, the resulting mixture was stirred additionally at room temperature for 12 h. The resulting precipitates were removed by filtration, and water was added to the filtrate. The mixture was extracted with ethyl acetate and was washed with dilute hydrochloric acid and water, and then was dried over anhydrous MgSO$_4$. The solvent was
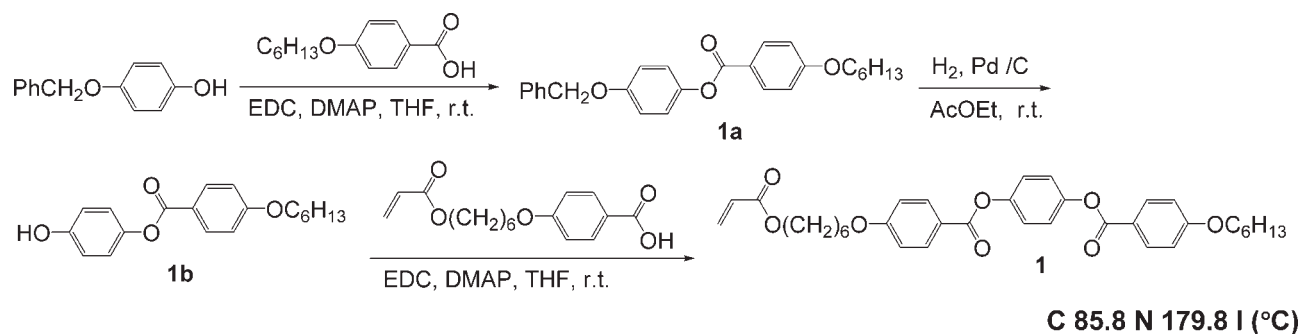
Scheme 1 Synthesis of 1-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-4-(4-hexyloxybenzoyloxy) benzene (**1**).

removed under reduced pressure to yield 41 g of **1a**. (Yield 100%) The crude **1a** was used in the next step without further purification. A small portion was recrystallized from ethanol for correcting the phase transition temperatures. IR (KBr): ν = 2934 cm^{-1}, 2871, 1731, 1607, 1509, 1254, 1170, 1079, 1015, 852, 764, 743, 694. ^{1}H-NMR (500 MHz, CDCl$_3$): δ (ppm) = 0.92 (t, ^3J = 7.0 Hz, 3 H), 1.32–1.39 (m, 4 H), 1.44–1.51 (m, 2 H), 1.82 (quint, ^3J = 7.0 Hz, 2 H), 4.04 (t, ^3J = 6.6 Hz, 2 H), 5.07 (s, 2 H), 6.96 (d, ^3J = 9.0 Hz, 2 H), 7.00 (d, ^3J = 9.0 Hz, 2 H), 7.11 (d, ^3J = 9.0 Hz, 2 H), 7.31–7.47 (m, 5 H), 8.12 (d, ^3J = 9.0 Hz, 2 H).

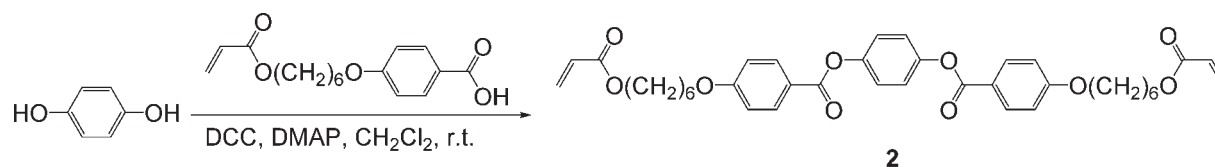Phase transition temperatures: C 121.8 (N 99.3) I (°C) (heating rate: 5°C/min).

4-Hexyloxyphenyl 4-hydroxybenzoate (1b)

A mixture of **1a** (41.0 g, 101 mmol), 5wt%PdC (4.8 g) and 400 mL of ethyl acetate was stirred at room temperature under hydrogen atmosphere for 8 h. The catalyst was removed by filtration, and the solvent was removed from the filtrate under reduced pressure. The residue was recrystallized from heptane to give 25.5 g of **1b** as colorless crystals. (Yield 74%) IR (KBr): ν = 3392 cm^{-1}, 2936, 1703, 1607, 1512, 1261, 1239, 1194, 1169, 1083, 1023, 867, 765, 648. ^{1}H-NMR(500 MHz, CDCl$_3$): δ = 0.92 (t, ^3J = 7.0 Hz, 3 H), 1.32–1.39 (m, 4 H), 1.44–1.51 (m, 2 H), 1.82 (quint, ^3J = 7.1 Hz, 2 H), 4.04 (t, ^3J = 6.5 Hz, 2 H), 5.31 (brs, 1 H), 6.80 (d, ^3J = 8.9 Hz, 2 H), 6.96 (d, ^3J = 8.9 Hz, 2 H), 7.02 (d, ^3J = 8.9 Hz, 2 H), 8.13 (d, ^3J = 8.9 Hz, 2 H).

Phase transition temperature: C 115.2 I (°C) (heating rate: 5°C/min).

1-[4-(6-Acryloyloxyhexyloxy)benzoyloxy]-4-(4-hexyloxybenzoyloxy)benzene (1)

To a mixture of 4-(6-acryloyloxyhexyloxy)benzoic acid (25.6 g, 88 mmol), **1b** (25.0 g, 80 mmol), 4-(N,N-dimethylamino)pyridine (DMAP) (9.7 g, 80 mmol) and 300 mL of THF, EDC (27.4 g, 143 mmol)was added over an ice bath. After 1 h of stirring at the temperature, the resulting mixture was stirred additionally at room temperature for 12 h. The resulting precipitates were removed by filtration, and water was added to the filtrate. The mixture was extracted with ethyl acetate and was washed with dilute hydrochloric acid and water, and then was dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel eluting with toluene/ethyl acetate (8:2) and was recrystallized from ethanol to give 23.0 g of **1** as colorless crystals. (Yield 49%) R_f = 0.75, IR (KBr): ν = 2936 cm^{-1}, 2860, 1727, 1606, 1510, 1258, 1184, 1167, 1072, 1008, 988, 911, 845, 763, 692, 647. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 0.92 (t, ^3J = 7.0 Hz, 3 H), 1.34–1.38 (m, 4 H), 1.44–1.58 (m, 6 H), 1.73 (quint, ^3J = 7.0 Hz, 2 H), 1.79–1.88 (m, 4 H), 4.05 (t, ^3J = 6.5 Hz, 2 H), 4.06 (t, ^3J = 6.4 Hz, 2 H), 4.19 (t, ^3J = 6.6 Hz, 2 H), 5.83 (d,d, ^3J = 10.6 Hz, ^2J = 1.3 Hz, 1 H), 6.13 (d,d, ^3J = 17.5 Hz, ^3J = 10.6 Hz, 1 H), 6.41 (d,d, ^3J = 17.5 Hz, ^2J = 1.3 Hz, 1 H), 6.97 (d, ^3J = 8.9 Hz, 2 H), 6.98 (d, ^3J = 8.9 Hz, 2 H), 7.26 (s, 4 H),

Scheme 2 Synthesis of 1,4-bis[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzene (**2**).

8.14 (d, ^3J = 8.9 Hz, 4 H). Phase transition temperatures: C 85.8N 179.8 I (°C) (heating rate: 5°C/min).

1,4-Bis[4-(6-acryloyloxyhexyloxy)benzoyloxy] benzene (2)

To a mixture of 4-(6-acryloyloxyhexyloxy)benzoic acid (50.0 g, 171 mmol), hydroquinone (8.6 g, 78 mmol), DMAP (5.7 g, 47 mmol), and 500 mL of CH_2Cl_2, a mixture of dicyclohexylcarbodiimide (DCC) (35.3 g, 171 mmol) and 300 mL of CH_2Cl_2 was added dropwise over an ice bath. After 1 h of stirring at the temperature, the resulting mixture was stirred additionally at room temperature for 12 h. The resulting precipitates were removed by filtration, and the filtrate was washed with water and was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel eluting with toluene/ethyl acetate (8:2) and was recrystallized from ethanol to give 44.4 g of 2 as colorless crystals. (Yield 86%) R_f = 0.75, IR (KBr): ν = 2943 cm^{-1}, 2860, 1724, 1632, 1605, 1577, 1511, 1469, 1403, 1299, 1253, 1205, 1164, 1074, 1003, 966, 845, 762, 691, 649. ^{1}H-NMR 500 MHz, CDCl$_3$): δ = 1.45–1.57 (m, 8 H), 1.73 (quint, ^3J = 7.0 Hz, 4 H), 1.85 (quint, ^3J = 7.0 Hz, 4 H), 4.05 (t, ^3J = 6.4 Hz, 4 H), 4.18 (t, ^3J = 6.6 Hz, 4 H), 5.82 (d,d, ^3J = 10.6 Hz, ^2J = 1.3 Hz, 2 H), 6.13 (d,d, ^3J = 17.5 Hz, ^3J = 10.6 Hz, 2 H), 6.41 (d,d, ^3J = 17.5 Hz, ^2J = 1.3 Hz, 2 H), 6.97 (d, ^3J = 8.9 Hz, 4 H), 7.26 (s, 4 H), 8.14 (d, ^3J = 8.9 Hz, 4 H). Phase transition temperatures: C 105.6 (SmC 89.1) N 154.3 I (°C) (heating rate: 5°C/min).

Measurement

The free-standing acrylic films, in which the mesogens align homogeneously, and the sample pieces for the thermal diffusivity analysis have been prepared according to the method of Kato.[11] Thermal conductivity (λ) was calculated using eq. (1):

$$\lambda = \alpha \rho c \tag{1}$$

where α, ρ, and c represent thermal diffusivity, density, and specific heat at 25°C, respectively. α was estimated with the half-time method of the laser flash analysis using a laser flash thermal constant analyzer TC-7000 (ULBAC Co.), in which the laser pulse was flashed on the front surface of the sample, and the temperature increase rate at the rear surface was measured.[16]

Textures of the synthesized compounds, the mixtures, and the films were observed with a polarized optical microscope (POM) (BH-2, Olympus Co.). Phase transition temperatures were measured by differential thermal analysis with DSC (Diamond DSC, PerkinElmer). X-ray diffraction patterns were obtained by wide-angle X-ray diffraction (WAXD, R-AXIS RIGAKU Co.) using Ni-filtered Cu Kα radiation at 25°C.

RESULTS AND DISCUSSION

Phase transition temperature of mixture

The phase diagrams of the mixtures consisting of the compounds 1 and 2 are presented in Figure 1. In the heating process, the crystal–nematic transition temperature (T_{CN}) is constant at around 85°C in 20–80 wt % of the compound 2 content. The nematic–isotropic transition temperature (T_{NI}) decreases linearly from 179.8 to 154.3°C upon the increase of the compound 2 content. In the cooling process, the isotropic–nematic transition temperature (T_{IN}) shows the same tendency
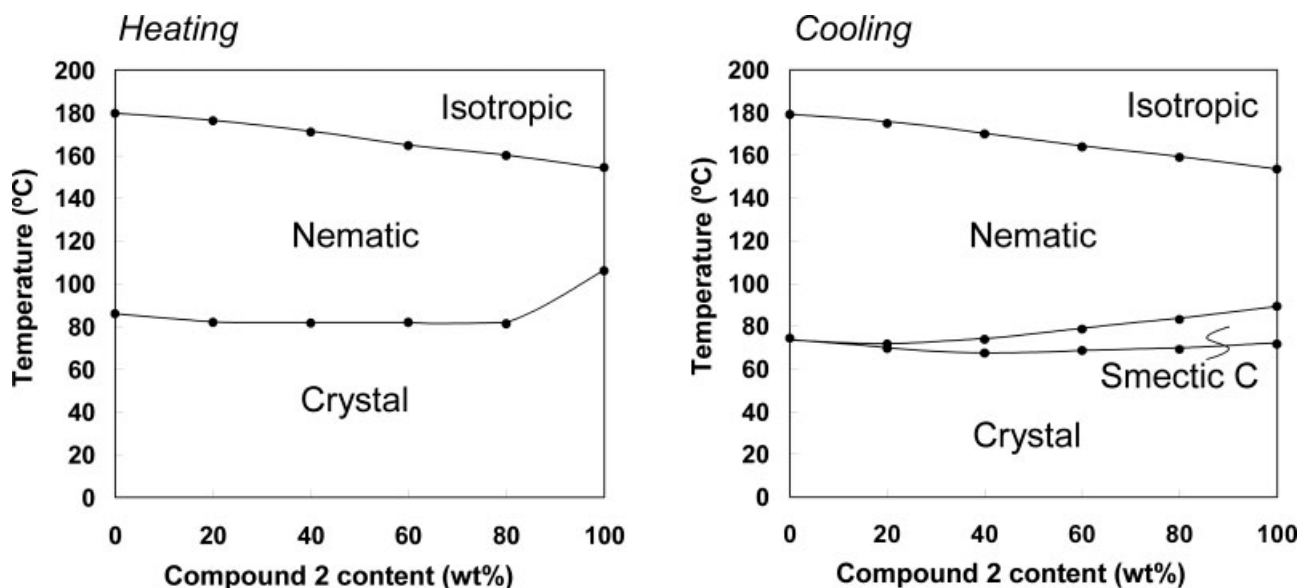

**Figure 1** Phase diagrams of mixtures consisting of compound 1 and 2.

with the T_{NI}. However, the smectic C phase appears in 20–100 wt % of the compound **2** content. The range of the smectic C phase becomes gradually wider from 2°C (20 wt %) to 17°C (100 wt %). The phase transition temperatures of the mixtures exhibiting the smectic C phase are more influenced by the liquid crystallinity of the compound **2**. The smectic C–crystal transition temperature (T_{ScC}) is constant at around 70°C over all the content. The liquid crystal temperature range is wider in the cooling process for 15°C due to the super-cooling of the T_{ScC}.

WAXD measurement and POM observation of alignment films

The molecular orientation of each mixture was obtained at the nematic phase (120°C) by the rubbing method. The molecular orientation was fixed by the UV irradiation to yield the free-standing alignment films with 200 μm of the thickness. Five types of the films were prepared with the PLC mixtures of 20, 40, 60, 80, and 100 wt % of the compound **2** content. The film prepared from 100 wt % of the compound **1** did not have enough mechanical strength, and was not applicable to the measurements.

Figure 2(A–E) show the WAXD patterns of the alignment films that were prepared from the PLC mixtures with 20, 40, 60, 80, and 100 wt % of the compound **2** content. (Fig. 2) The symmetry crescents patterns along the rubbing direction at the wide-angle region in Figure 2(A–E) represented that the molecules were aligned uniformly along the rubbing direction. The layer space that corresponds to the space between the molecules was estimated from 2θ of the diffraction pattern to be 4.4 Å in each film. The layer space of the smectic C phase, that has 50° of the tilt angle to the molecular short axis, can be estimated from 2θ of the diffraction pattern and the symmetrical four spots at the short-angle region to be 29.5 Å. The molecular alignment in the film prepared from the mixture containing 40 wt % of compound **2** was investigated optically with a polarized optical microscope (POM) under the crossed nicol. When the rubbing direction was settled as parallel to either one of the analyzer and the polarizer, the dark uniform texture was observed. Upon rotating the crossed nicol for 45°, the brightest uniform texture was observed. The similar textures were observed in the other films. The results of the WAXD measurement and the POM observation indicated that the molecules were fixed by the polymerization with keeping the homogeneous molecular alignment along the rubbing direction. Results of the WAXD measurements and the POM observation are illustrated in Figure 3. The molecular long axis aligns
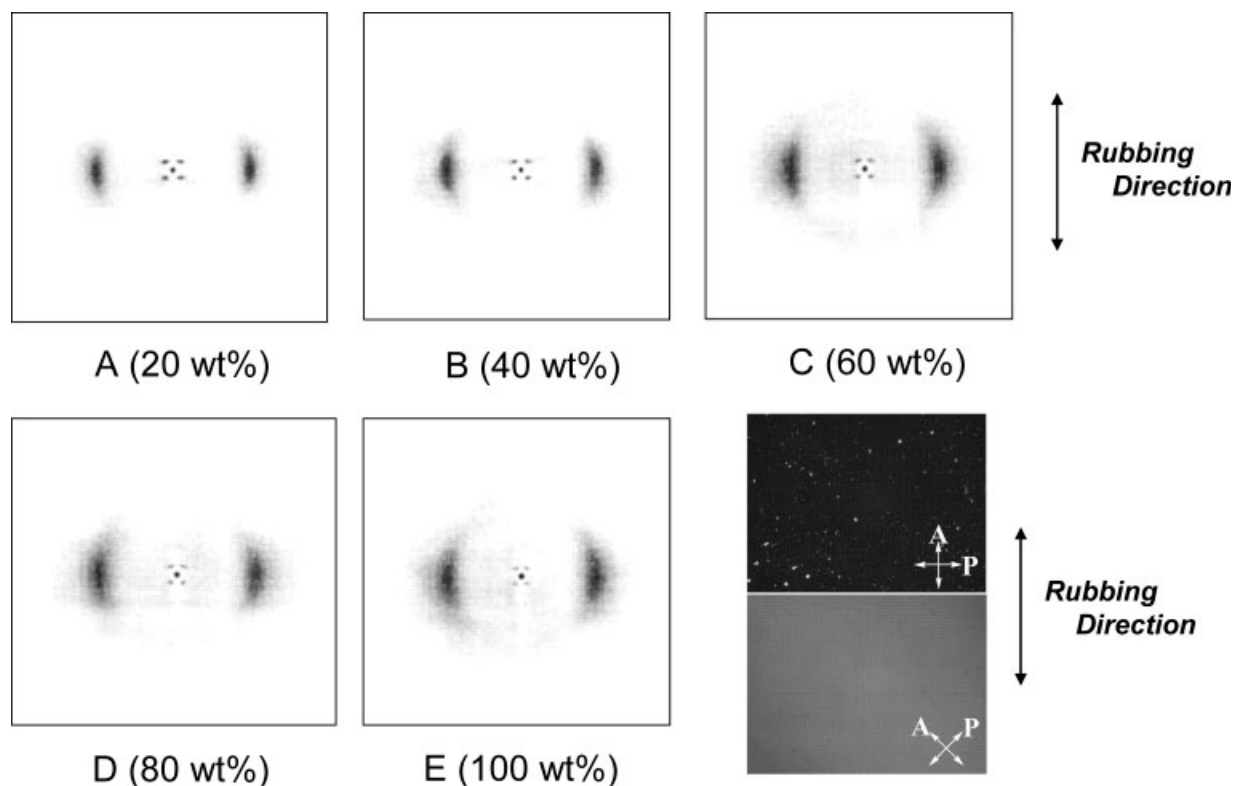
Figure 2 WAXD patterns of homogeneous alignment films (from A to E), which were prepared by photo-polymerization of mixtures consisting of compound **1** and **2**. The compound **2** content from A to E are 20, 40, 60, 80, and 100 wt %, sequentially. Polarized optical micrographs of alignment film, which was prepared with the mixture containing 40 wt % of compound **2**. P, polarizer; A, analyzer; magnification ×100.
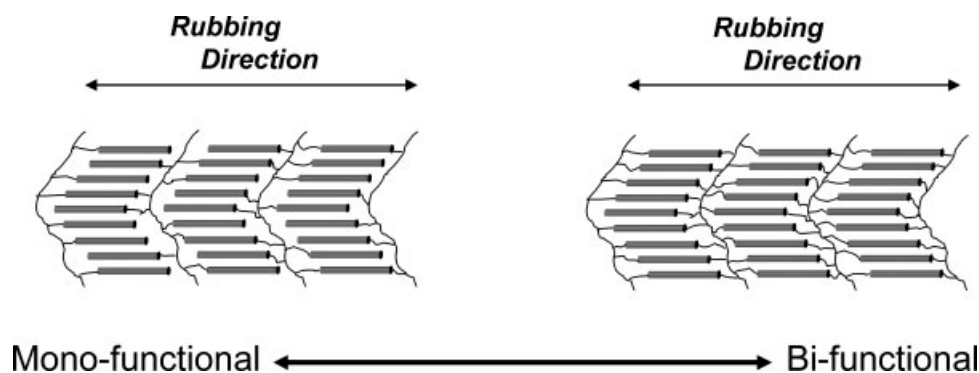
Figure 3 Illustrations of molecular alignment in homogeneous alignment films.

along the rubbing direction, and the smectic C layers tilt to the molecular short axis.

The order parameters of the homogeneous aligned films were represented in Figure 4. The order parameter S was estimated by the following eq. (2) with the WAXD patterns.[17]

$$S = (180 - H)/180 \qquad (2)$$

H indicates the half bandwidth of the angle dispersion peak.

The order parameter lineally decreased from 0.87 to 0.79 with the increase of the bi-functional compound **2** content. The side chain type networks (greater compound **1** content) have the higher mobility of the mesogenic groups than the main chain type (less content of the compound **1**), which allows the molecules to reorient during the polymerization resulting the enhancement of the order parameter.

Thermal conductivity

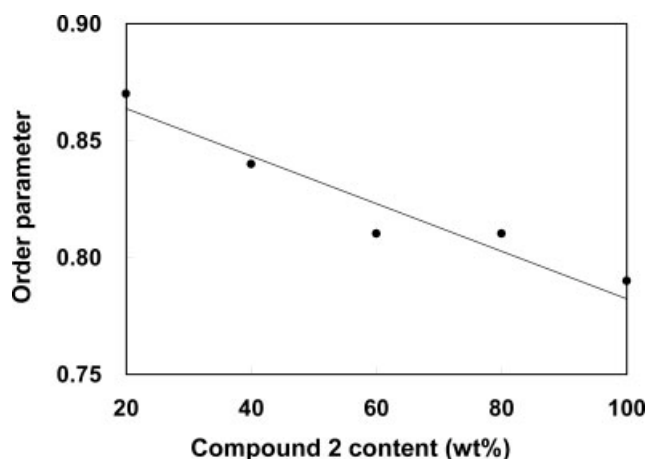Relation between the anisotropy of the thermal conductivity and the bi-functional compound **2** content in the homogeneous alignment films was investigated. (Fig. 5) The thermal conductivities in the thermal transmission directions perpendicular and parallel to the molecular long axis were 0.18 and 0.62 W/m·K, respectively, which were independent on the compound **2** content. The magnitude 0.18 W/m·K is similar to that of poly(methyl methacrylate) [0.19 W/m·K].[18] The thermal conductivity of 0.62 W/m·K (parallel) is 3.4 times greater than that of 0.18 W/m·K (perpendicular). It has been reported that the larger order parameter induces greater magnitude of the thermal conductivity.[6,8] The order parameter of the prepared homogeneous aligned films decreases from 0.87 to 0.79 with the increase of the compound **2** content. However, there is no remarkable relation between the thermal conductivity and the order parameter of the prepared films in the high order parameter. This means that some order fluctuations of the molecules in the high order parameter almost do not have the influence on the thermal conductivity. This result allows PLC mixtures containing various mono-functional liquid crystals to be applied for optimizing other liquid crystalline properties without depressing the thermal conductivity.
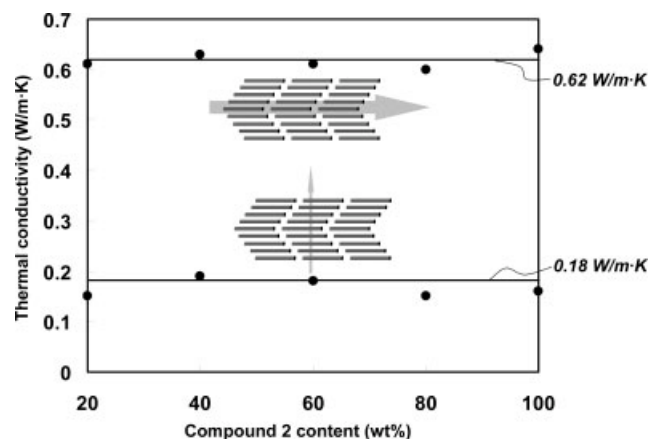

Figure 4 Order parameter of homogeneous alignment films estimated with WAXD patterns.

Figure 5 Relation between the anisotropy of the thermal conductivity of the homogeneous alignment films and compound **2** content.

CONCLUSIONS

The molecules with the mono- and bi-function at the sides in the PLC mixtures were aligned by the rubbing method. The alignment was immobilized by the photo polymerization to result the homogeneous acrylic films. The WAXD measurements indicate that the films have good alignment with the high order parameters of 0.87–0.79. The thermal conductivity along the molecular long axis direction showed the larger magnitude of 0.62 W/m·K in comparison with that across the molecular long axis [0.18 W/m·K]. The thermal conductivity of the films is independent on ratio of the main chain and the side chain fractions.

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