

# Thermal Conductivity of Homogeneous Alignment Networks Formed with Mono- and Bi-functional Polymerizable Liquid Crystals

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**ABSTRACT:** Mixtures consisting of mono-functional polymerizable liquid crystals (PLC) having a polymerizable moiety on the molecular short axis terminal and a bi-functional PLC having the polymerizable moieties on the molecular long axis terminals were prepared. These mixtures had a wide liquid crystal range. Uniaxially aligned films were prepared from the PLC mixtures by photo polymerization after aligning the molecular directions by the rubbing method. The thermal conductivity of the films

increased from 0.45 to 0.68 W/m · K with the increase of the content of the bi-functional PLC. The relation between the thermal conductivity and the PLC network styles was investigated from the aspect of the molecular order. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3453–3458, 2007

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

## INTRODUCTION

Liquid crystalline polymers immobilizing the uniaxial molecular alignment, for example, the fibers and the injection molding films prepared from the thermotropic liquid crystal polymers,<sup>1,2</sup> the liquid crystal polymers cured under the magnetic field,<sup>3</sup> and the thin film on the silicon wafer,<sup>4</sup> and the free-standing films prepared from the PLCs by the rubbing method,<sup>5–7</sup> have a high thermal conductivity. These PLCs have the character that the molecular alignment can be arranged before the polymerization. In aiming for high performance with the PLCs, it is useful to apply liquid crystal mixtures consisting of the PLCs, because their properties, namely the mesophase temperature range, the refractive index anisotropy, the dielectric anisotropy, and the magnetic anisotropy can be diversely arranged. The thermal conductivity of the films prepared with the PLC mixtures, which consisted of the mono- and bi-functional PLC monomers having the polymerizable moiety on the molecular long axis terminal(s), has been investigated in our previous report.<sup>7</sup> The mono-functional PLCs having the

polymerizable moiety at the molecular short axis that induced another type of the side chain polymer, has already been reported.<sup>8–14</sup> In this work, the PLC mixtures were prepared from the mono-functional acrylic PLCs having the polymerizable moiety on the molecular short axis terminal and the bi-functional acrylic PLCs with the polymerizable moiety on the long axis terminals. The relation between the thermal conductivity and the network styles has been investigated with free-standing homogeneous alignment films consisting of the main and the side chain fractions.

## EXPERIMENTAL

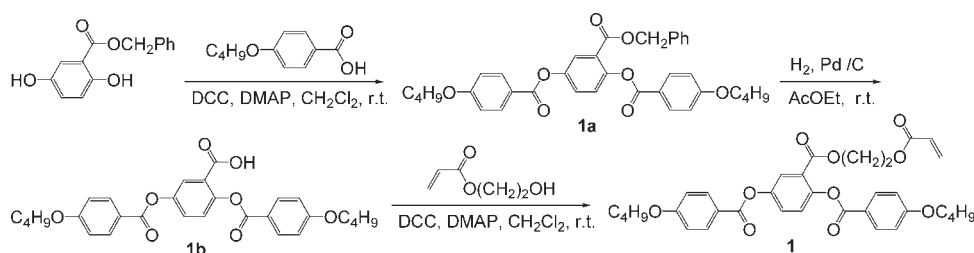
### Materials

2-Acryloyloxyethyl 2,5-bis(4-butoxybenzoyloxy)benzoate (**1**) was synthesized according to the method of Thomsen et al.<sup>13</sup> with modifications (Scheme 1). 1,4-Bis[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (**2**) was synthesized according to the methods of Kato et al.<sup>5</sup> (Fig. 1).

### Synthesis of benzyl 2,5-bis(4-butoxybenzoyloxy)benzoate (**1a**)

To a mixture of 4-*n*-butoxybenzoic acid (122.5 g, 631 mmol), benzyl 2,5-dihydroxybenzoate (70.0 g, 287 mmol), 4-dimethylaminopyridine (DMAP) (21.0 g,

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**Scheme 1** Synthesis of 2-acryloyloxyethyl 2,5-bis(4-butoxybenzoyloxy)benzoate (**1**).

172 mmol), and 1000 mL of  $\text{CH}_2\text{Cl}_2$  was added dropwise a mixture of dicyclohexylcarbodiimide (DCC) (130.0 g, 631 mmol) and 500 mL of  $\text{CH}_2\text{Cl}_2$  over an ice bath. After 1 h of stirring at the ice bath 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 dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel eluted with toluene/ethyl acetate (4 : 1) to give 150.0 g (87%) of **1a**. The  $^1\text{H}$  NMR spectrum was identical to the desired structure. **1a** was used in the next step without the further purification.  $R_f = 0.81$  (toluene/ethyl acetate (4 : 1)). IR (KBr):  $\nu = 2962\text{ cm}^{-1}$ , 2936, 2876, 1734, 1609, 1514, 1253, 1172, 1131, 1081, 1006, 845, 760, 735, 690, 652.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 1.00 ( $t$ ,  $^3J = 7.1\text{ Hz}$ , 3 H), 1.01 ( $t$ ,  $^3J = 7.1\text{ Hz}$ , 3 H), 1.51 (quint,  $^3J = 7.1\text{ Hz}$ , 2 H), 1.54 (quint,  $^3J = 7.1\text{ Hz}$ , 2 H), 1.78–1.86 (m, 4 H), 4.06 ( $t$ ,  $^3J = 6.4\text{ Hz}$ , 4 H), 5.19 (s, 2 H), 6.92 (d,  $^3J = 8.8\text{ Hz}$ , 2 H), 6.98 (d,  $^3J = 8.9\text{ Hz}$ , 2 H), 7.23–7.25 (m, 5 H), 7.26 (d,  $^3J = 8.8\text{ Hz}$ , 1 H), 7.46 (d,  $^3J = 8.8\text{ Hz}$ ,  $^4J = 2.8\text{ Hz}$ , 1 H), 7.90 (d,  $^4J = 2.8\text{ Hz}$ , 1 H), 8.07 (d,  $^3J = 8.8\text{ Hz}$ , 2 H), 8.13 (d,  $^3J = 8.9\text{ Hz}$ , 2 H).

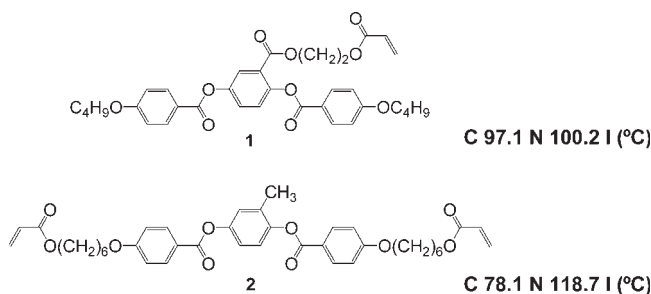
### Synthesis of 2,5-bis(4-butoxybenzoyloxy)benzoic acid (**1b**)

A mixture of **1a** (150.0 g, 251 mmol), 5 wt % PdC (15.0 g) and 1000 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 crystallized from toluene/tetrahydrofuran (2 : 1) to give 100.0 g (79%) of **1b** as colorless crystals. Phase transition temperature: C 182.6 I ( $^\circ\text{C}$ ) (heating rate:  $5^\circ\text{C}/\text{min}$ ). IR (KBr):  $\nu = 2962\text{ cm}^{-1}$ , 2931, 2874, 1729, 1701, 1686, 1608, 1511, 1189, 1172, 1073, 969, 845, 759, 691.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 0.99 ( $t$ ,  $^3J = 7.3\text{ Hz}$ , 3 H), 1.00 ( $t$ ,  $^3J = 7.3\text{ Hz}$ , 3 H), 1.48–1.57 (m, 4 H), 1.78–1.85 (m, 4 H), 4.05 ( $t$ ,  $^3J = 6.5\text{ Hz}$ , 2 H), 4.06 ( $t$ ,  $^3J = 6.5\text{ Hz}$ , 2 H), 6.95 (d,  $^3J = 8.9\text{ Hz}$ , 2 H), 6.98 (d,  $^3J = 8.9\text{ Hz}$ , 2 H), 7.29 (d,  $^3J = 8.8\text{ Hz}$ , 1 H), 7.50 (d,  $^3J = 8.8\text{ Hz}$ ,  $^4J = 3.0\text{ Hz}$ , 1 H), 7.93 (d,  $^4J$

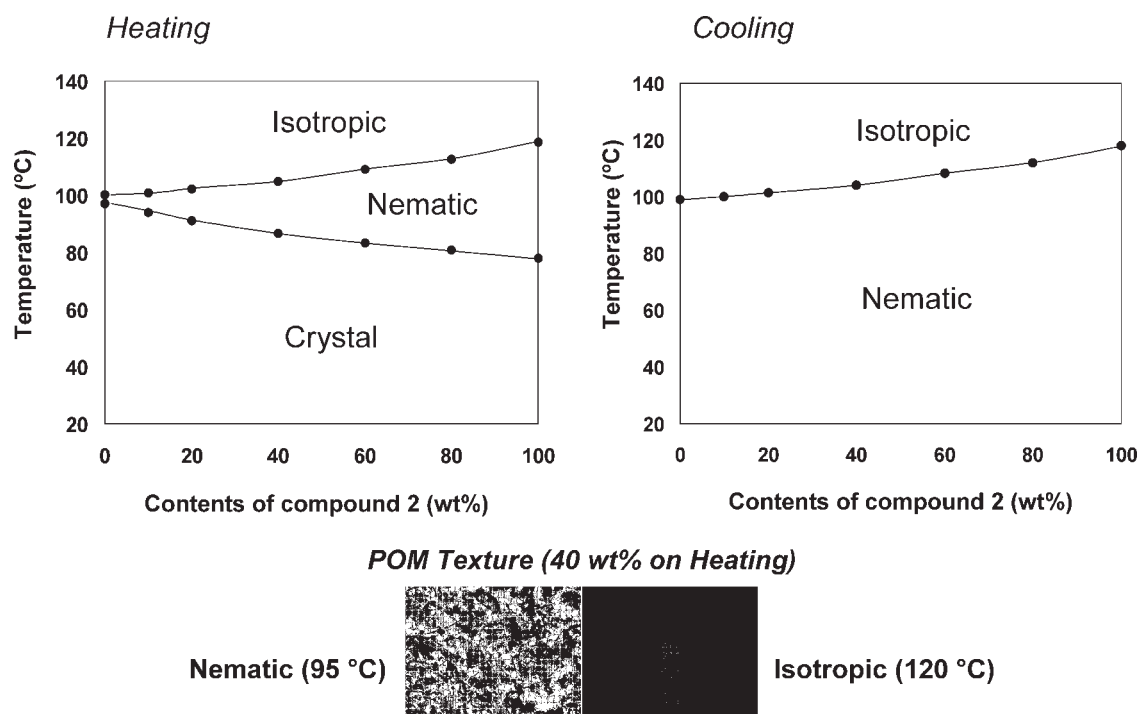
= 3.0 Hz, 1 H), 8.12 (d,  $^3J = 8.9\text{ Hz}$ , 2 H), 8.14 (d,  $^3J = 8.9\text{ Hz}$ , 2 H).

### Synthesis of 2-acryloyloxyethyl 2,5-bis(4-butoxybenzoyloxy)benzoate (**1**)

To a mixture of **1b** (57.0 g, 113 mmol), 2-hydroxyethyl acrylate (14.4 g, 124 mmol), DMAP (4.1 g, 34 mmol), and 500 mL of  $\text{CH}_2\text{Cl}_2$  was added dropwise a mixture of DCC (25.5 g, 124 mmol) and 100 mL of  $\text{CH}_2\text{Cl}_2$  over an ice bath. After 1 h of stirring at the ice bath 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  $\text{MgSO}_4$ . The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel eluted with toluene/ethyl acetate (4 : 1) and was recrystallized from ethanol/toluene (4 : 1) to give 55.0 g (80%) of **1** as colorless crystals.  $R_f = 0.69$  (ethanol/toluene (4 : 1)), Phase transition temperatures: C 97.1, N 100.2 I ( $^\circ\text{C}$ ) (heating rate:  $5^\circ\text{C}/\text{min}$ ). IR (KBr):  $\nu = 2953\text{ cm}^{-1}$ , 2868, 1728, 1607, 1512, 1413, 1298, 1250, 1181, 1164, 1073, 1007, 843, 758, 685, 640.  $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 1.00 ( $t$ ,  $^3J = 7.5\text{ Hz}$ , 6 H), 1.48–1.57 (m, 4 H), 1.78–1.85 (m, 4 H), 4.05 ( $t$ ,  $^3J = 6.4\text{ Hz}$ , 2 H), 4.06 ( $t$ ,  $^3J = 6.4\text{ Hz}$ , 2 H), 4.22–4.24 (m, 2 H), 4.40–4.43 (m, 2H), 5.81 (d,  $^3J = 10.1\text{ Hz}$ ,  $^2J = 1.2\text{ Hz}$ , 1 H), 6.05 (d,  $^3J = 17.5\text{ Hz}$ ,  $^3J = 10.1\text{ Hz}$ , 1 H), 6.38 (d,  $^3J = 17.5\text{ Hz}$ ,  $^2J = 1.2\text{ Hz}$ , 1 H), 6.97 (d,  $^3J = 9.0\text{ Hz}$ , 2 H), 6.99 (d,  $^3J = 9.0\text{ Hz}$ , 2 H), 7.28 (d,  $^3J = 8.7\text{ Hz}$ , 1 H), 7.48 (d,  $^3J = 8.7\text{ Hz}$ ,  $^4J = 2.9\text{ Hz}$ , 1 H), 7.91 (d,  $^4J = 2.9\text{ Hz}$ , 1 H), 8.15 (d,  $^3J = 9.0\text{ Hz}$ , 4 H).



**Figure 1** Chemical structures of compounds **1** and **2**.



**Figure 2** Phase diagrams of the mixture consisting of compounds 1 and 2. Polarized optical micrographs of the mixture containing 40 wt % of compound 2 in the heating process. Magnification:  $\times 200$ .

### Measurement

The thermal diffusivity of the free-standing acrylic films, in which the mesogens align homogeneously, has been measured according to the method of Kato.<sup>5-7</sup> Thermal conductivity ( $\lambda$ ) was calculated with the eq. (1):

$$\lambda = \alpha \rho c$$

where  $\alpha$ ,  $\rho$ , and  $c$  represent the thermal diffusivity, density, and specific heat at 25°C, respectively.  $\alpha$  was estimated with the half-time method of the laser flash analysis using a laser flash thermal constant analyzer TC-7000 (ULBAC Co., Ltd.), 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.<sup>15</sup>

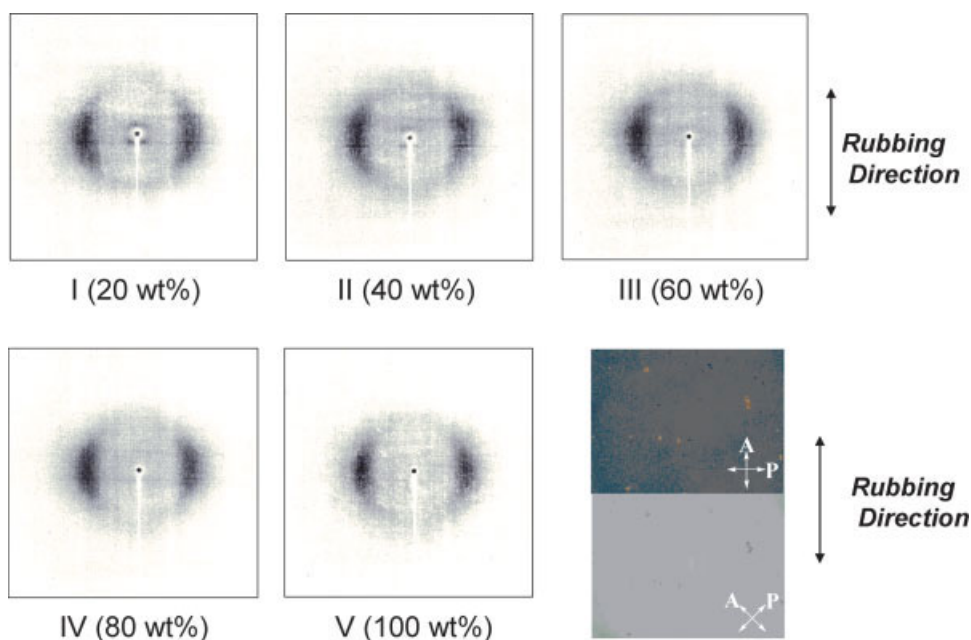
Textures of the synthesized compounds, the mixtures and the films were observed with a polarized optical microscope (POM) (BH-2, Olympus Co., Ltd.). Phase transition temperatures were determined by differential thermal analysis with DSC (Diamond DSC, PERKIN-ELMER Co., Ltd.) in 5°C/min. X-ray diffraction patterns were obtained by wide-angle X-ray diffraction (WAXD, R-AXIS RIGAKU Co., Ltd.) using Ni-filtered Cu K $\alpha$  radiation at 25°C.

## RESULTS AND DISCUSSION

### Phase Transition Temperature of Mixture

Phase diagrams of the mixtures consisting of compounds 1 and 2 are represented in Figure 2. In the

heating process, the crystal - nematic transition temperature ( $T_{CN}$ ) decreases linearly from 97.1°C (0 wt %) to 78.1°C (100 wt %) with the increase of the content of compound 2. On the other hand, the nematic-isotropic transition temperature ( $T_{NI}$ ) increases linearly from 100.2°C (0 wt %) to 118.7°C (100 wt %). The textures of the nematic (95°C) and isotropic textures (120°C) in the mixture containing 40 wt % of compound 2 with POM under crossed nicol were indicated in Figure 2. Similar textures in the corresponding phases were observed in the other mixtures. The nematic temperature range becomes wider from 3.1 to 40.6°C upon the increase of compound 2 content due to the synergistic contributions of the  $T_{CN}$  decrease and the  $T_{NI}$  increase. In the cooling process, while the isotropic-nematic transition temperature ( $T_{IN}$ ) shows the same tendency as the  $T_{NI}$ , the nematic-crystal transition temperature ( $T_{NC}$ ) does not appear until 20°C over all the contents in the DSC measurements (cooling rate: 5°C/min). Crystallization in the mixtures was observed when small portions (5 mg) of the mixtures on the slide glasses washed with acetone were cooled rapidly from 120 to 25°C without the cover glasses. ( $N = 5$ ) Compounds 1 (0 wt %) and 2 (100 wt %) started to crystallize in 7–10 min and 1–2 min after reaching 25°C, respectively. Crystallization in the mixtures with 20, 40, 60, and 80 wt % content of compound 2 started in 6–20, 27–50, 30–50, and 15–30 min, respectively. A longer time was needed for the mixtures to crystallize completely. This result indicates that the inclusion of compound 1



**Figure 3** WAXD patterns of homogeneous alignment films from I to V, which were prepared by the photo polymerization of mixtures consisting of compound 1 and 2. The compound 2 contents for I–V are 20, 40, 60, 80, and 100 wt %, respectively. Polarized optical micrographs of alignment film, which was prepared with the mixture containing 40 wt % of compound 2. P, polarizer; A, analyzer; Magnification:  $\times 40$ .

in the mixtures induces the stabilization of the nematic phase.

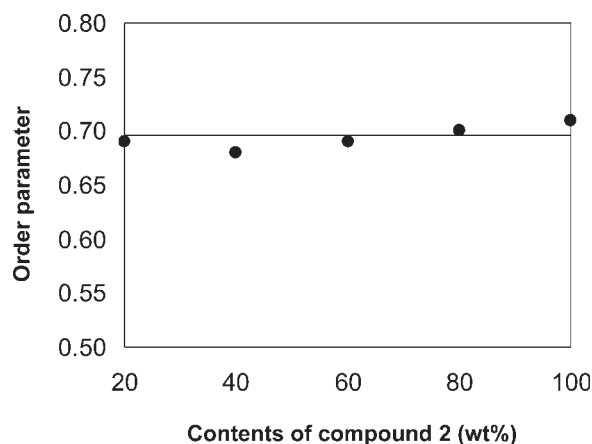
#### WAXD measurement and POM observation of alignment films

The molecular orientation of the mixture was obtained in the nematic state by the rubbing method. The homogeneous free-standing alignment films of 200  $\mu\text{m}$  thickness were prepared from PLC mixtures (0, 20, 40, 60, 80, and 100 wt % compound 2) at 90°C in the nematic phase. The film prepared from 100 wt % of compound 1 exhibited poor mechanical strength, which was not acceptable for the measurements.

The photos I–V show the WAXD patterns of the alignment films prepared from the mixtures (20, 40, 60, 80, and 100 wt % compound 2) (Fig. 3). The symmetry crescent patterns along the rubbing direction at the wide-angle region represented that the molecules were aligned uniformly along the rubbing direction. The layer space, which corresponds to the space between the molecules, was estimated from  $2\theta$  of the diffraction pattern to be 4.4 Å in each film. Although the polymerization was performed in the nematic state, photos I and II had spots in the short-angle region corresponding to the smectic A phase. The layer space of the smectic A phase can be estimated from  $2\theta$  of the diffraction pattern and the two symmetrical broad spots at the short-angle region to be 29.5 Å. The spot of the short-angle region in photo II was weaker than in photo I. The smectic A phase may

be broken with the increase of compound 2. Since the two symmetrical spots were not observed at the short angle region in photos III, IV, and V, their phases can be regarded as nematic.

The molecular alignment in the film that was prepared from the mixture of 40 wt % compound 2 was investigated optically with POM under the crossed nicol. When the rubbing direction was settled as parallel to either one of the analyzer and the polarizer, dark uniform textures were observed. The brightest uniform textures were observed in rotating the crossed nicol at 45°. The similar textures were observed in the other films. The results of the WAXD



**Figure 4** Order parameters of homogeneous alignment films estimated from WAXD patterns.



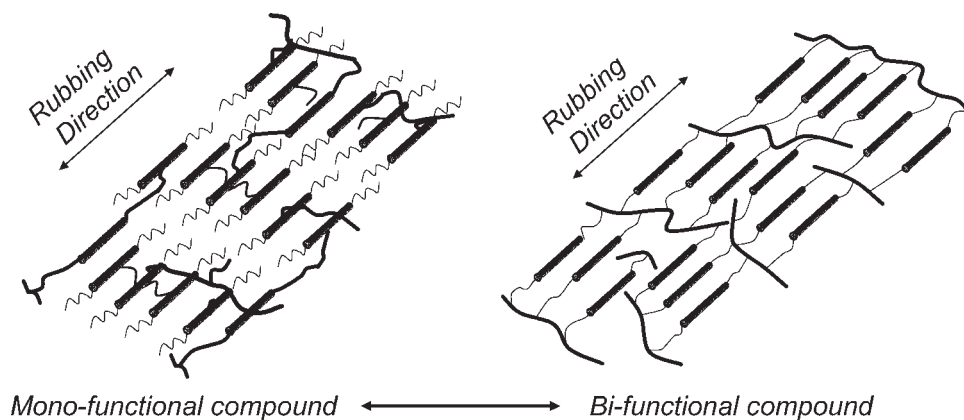


Figure 5 Illustrations of molecular alignment in homogeneous alignment films.

measurement and the POM observation indicated that the molecules were fixed by the polymerization with the homogeneous molecular alignment along the rubbing direction.

The order parameters of the homogeneous alignment films are represented in Figure 4. The order parameter  $S$  was estimated from the WAXD patterns according to the following eq. (2).<sup>16</sup>

$$S = (180 - H)/180$$

where  $H$  indicates the half bandwidth of the angle dispersion peak.

The order parameters were almost constant around 0.70 independent of the compound 2 content. In the previous work applying the mixtures consisting of the mono- and bi-functional PLCs having the polymerizable moiety(s) at the end of the molecular long axis in the same mesogenic group, the order parameter linearly decreased from 0.87 (20 wt %) to 0.79 (100 wt %) with the increase of the bi-functional compound content, which allowed the molecule to reorient during the polymerization in inhibiting the decrease of the order parameter attributed to the higher mobility of the mesogenic group in the mono-functional compound.<sup>7</sup> However, the reorientation did not effectively generate during the polymerization in this investigation. The high molecular fluctuation may be caused by the link at the end of the molecular short or long axis between compounds 1 and 2. The molecular length of the long axis of compound 1 was estimated at 29.3 Å with the molecular orbital calculation.<sup>17</sup> The value fits to the layer space (29.5 Å) of the smectic A phase. When the double bonds of the acrylic moieties combine to form the main chains, it is difficult to form the chain along the molecular long axis. This is obviously because the basic main chain unit consisting of two double bonds is shorter than the molecular length of the long axis. The main chains were presumed to

form on combining the mesogens along the molecular short axis in the high concentration of compound 1. The networks that combine the mesogens along the molecular long axis are able to form with the increase of the content of compound 2 (Fig. 5).

### Thermal conductivity

The relation between the thermal conductivity of the homogeneous alignment films and the bi-functional compound 2 content was investigated (Fig. 6). The thermal conductivities in the thermal transmission directions perpendicular (white circle) to the molecular long axis were almost constant around 0.20 W/m K, which were independent of the compound 2 content. On the other hand, the thermal conductivity in the case of the parallel direction (black circle) linearly increased from 0.45 to 0.68 W/m · K with the increase of the content of compound 2. In the previous work,

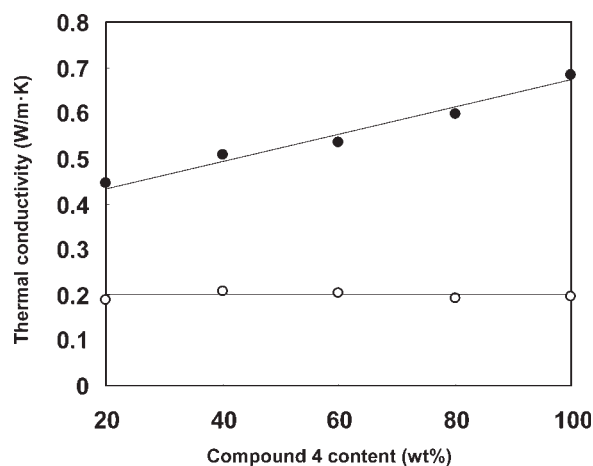


Figure 6 Relationship between the thermal conductivity of homogeneous alignment films and compound 2 content. ●, parallel between the thermal conductive direction and the molecular long axis direction; ○, perpendicular between the thermal conductive direction and the molecular long axis direction.

the thermal conductivities in the thermal transmission directions parallel and perpendicular to the molecular long axis indicated almost constant values of 0.62 and 0.18 W/m · K, respectively, which were independent on the bi-functional compound content. The result represents that the lack of the linkage does not significantly influence the thermal conductivity in the high order parameter (0.87 to 0.79), which the relation between the lack of linkage and the order parameter can be complementary resulting in the keeping of the high thermal conductivity.<sup>7</sup> On the contrary, the lack of the linkages in addition to the lower order parameter (0.70) induced the reduction of the thermal conductivity without the complementary relation in this investigation. The lack of the linkage in the networks without the reactive moiety in the alignment direction influences the thermal conductivity. The relationship shown in this investigation provides the important direction to have the high thermal conductivity with the PLC mixtures. It is necessary in the applications to consider how to optimize the network styles of the aligned polymers applying the mono-functional PLCs without losing their other useful properties, such as the combination of a stable nematic phase in a wide range and the high thermal conductivity of 0.60 W/m · K.

### CONCLUSIONS

Homogeneously aligned acrylic films were prepared by the rubbing method from the mixtures consisting of the mono-functional PLC having the polymerizable moiety at the end of the molecular short axis and the bi-functional PLC with the polymerizable moieties on the long axis. The order parameters of the films were estimated from the WAXD patterns, and they were

almost constant at around 0.70. The thermal conductivity of the homogeneous films increased from 0.45 to 0.68 W/m · K with the increase of the bi-functional PLC content. The results may be attributed with the effect of the lack of linkage in the networks without the reactive moiety in the alignment direction.

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