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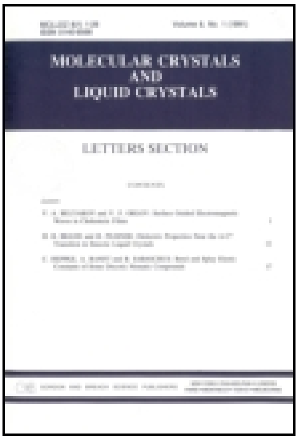

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# Synthesis and Characterization of Novel Liquid Crystalline Epoxy Resin with Low Melting Point

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*A liquid crystalline epoxy resin (LCE) having α-methylstilbene as a mesogenic unit and an ethylene-oxy unit as a spacer (DGE(C2-MS-C2)) was synthesized and characterized. DGE (C2-MS-C2) has a lower melting point (MP) compared to the diglycidylether of 4,4′-dihydroxy-α-methylstilbene (DGEDHMS). The curing of DGE (C2-MS-C2) with diaminodiphenylethane (DDEt) in a mesophase generated a liquid crystalline (LC) network, which have a more highly layered structure than DGEDHMS. The LC network showed extensively large fracture energy on a tensile test. Introducing spacers outside the mesogen unit promotes the mesogen unit to form a highly ordered structure, which enhances the versatility of LC epoxy resins.*

**Keywords** Fracture toughness; layered structure; LC thermosets; liquid crystalline epoxy resin

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## 1. Introduction

It has been reported that liquid crystalline (LC) epoxy resins (LCEs) have excellent thermal and mechanical properties, such as a high $T_g$, high fracture toughness, and increased bonding strength [1–7,8]. These characteristics would have a good potential to expand and create new use of epoxy resins, which have already been widely used for electronics, composites, adhesives, etc. The origin of these unique properties of LCEs, such as fracture toughness, was interpreted in terms of their highly oriented or layered structure [3–6]. Q. Lin et al. [9] researched the relationship between the curing temperature and resulting network structure of DGDHMS. They demonstrated that as the DGEDHMS is cured at a lower temperature, a more high-layered structure is formed. This research result implies the possibility that LCEs would have even more remarkable its unique properties if the resins are cured under milder conditions such as below 100°C.

However, it is not very easy to cure LCEs at moderate temperature because curing at a lower temperature would lead to the generation of a segmental crystalline monomer or oligomers in the matrices during or before the curing reaction. Some researchers showed a molecular design that decreases the clearing temperature by introducing spacers between

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two mesogenic groups [2,9,10]. Another approach is introducing spacers between the mesogenic group and also outside of the glycidyl groups [11,12].

In this article, the latter approach was taken using the 4,4′-dihydroxy-$\alpha$-methylstilbene (DHMS) moiety, and then the LCE was synthesized and characterized.

## 2. Experimental Part

### 2.1. *Materials*

DHMS and the diglycidylether of DHMS (DGEDHMS) were synthesized according to the procedures described in a patent [7]. The 1,3-Diaminopropane (DAP) was purchased from Tokyo Chemical Industry Co., Ltd. Ethylencarbonate (EC), $K_2CO_3$ and other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. These reagents were used without further purification.

### 2.2. *Measurements*

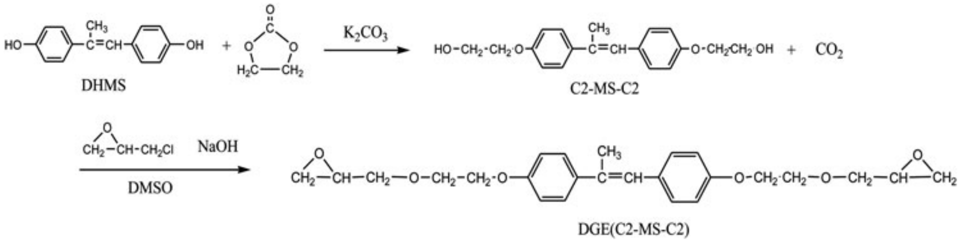
The molecular weight distribution was measured by Gel Permeation Chromatography (GPC, Shimazdu CBM-20A) using Shimadzu RID-10A reflex indicator and Shodex$^{TM}$ LF804 × 2 columns at 40°C. The $^1$H NMR spectra were recorded using a JNM-EX400 (JEOL Ltd.) spectrometer working at 400 MHz using tetramethylsilane (TMS) as the internal standard. DMSO-$d_6$ and $CDCl_3$ were used as the solvents for the C2-MS-C2 and DGE(C2-MS-C2), respectively.

Thermal analysis of the synthesized materials was carried out using a DSC (DSC7020 Seiko Instrument, Inc. Chiba, Japan) at the heating and cooling rate of 5°C min$^{-1}$. Optical anisotropy of the epoxy was observed using an optical microscope (BH-2, Olympus Corporation, Tokyo, Japan) under cross-polarized light. The observation under the polarized microscope was employed for the sample film mounted on a hot stage. The XRD was measured using a RINT-Ultima III (Rigaku Corporation).

Tensile test was conducted using an Instron-type tensile machine (Shimadzu Autograph, AGS-J) according to ISO 527-1 and 527-2. The tensile strength and elongation of the epoxy resin systems were measured with the dumb-bell-shaped specimen according to ISO 37 type 3, at a crosshead speed of 2 mm min$^{-1}$. Fracture energies of the cured epoxy resin systems were evaluated from the area under the stress–strain curves in the tensile test.

### 2.3. *Sample Preparation*

*2.3.1. Synthesis of C2-MS-C2.* The synthesis pathways of (C2-MS-C2) and DGE(C2-MS-C2) are shown in Scheme 1.



**Scheme 1.** Pathway for the synthesis of DGE (C2-MS-C2).

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EC (59.4 g, 0.675 mol) and DHMS g (70.7 g, 0.313 mol) were placed in a separate flask equipped with a stirrer blade, thermometer and cooling condenser. The reaction media was heated to 120°C and then 2.04 g of 50 wt% $K_2CO_3$aq was added. The reaction was carried out at 170°C for 1 hr. The obtained crude C2-MS-C2 was purified twice by crystallization from an MEK solution. The purified C2-MS-C2 (yield 65%) was confirmed by $^1$H NMR (DMSO-$d_6$): 2.18 ppm (3H, s, $CH_3$ of stilbene), 3.72 ppm (4H, m, $CH_2$ of ethylene-oxy), 4.00 ppm (4H, m, CH2 of ethylene-oxy), 4.87 ppm (2H, m, OH), 6.76 ppm (1H, s, CH stilbene), 6.96 ppm (4H, dd, aromatic), 7.30 ppm (2H, d, aromatic), and 7.48 ppm (2H, d, aromatic).

*2.3.2. Synthesis of DGE (C2-MS-C2).* C2-MS-C2 (50.2 g, 0.16 mol), epichlorohydrin (178 g, 1.91 mol), and dimethylsulfoxide (DMSO, 124 g) were added to a reactor and heated at 50°C with stirring. A 50 wt% NaOHaq. (64 g) solution was added dropwise to the reactor over 30 min. One hour after completion of the 50 wt% NaOHaq. addition, toluene (250 g) and water (250 g) were added to the reaction mixture, then the stirring was stopped and the aqueous layer was discharged. The separated organic layer was washed five times with water (250 g) at 70°C, then rotary evaporated under vacuum for 30 min. at 80°C, then 1 hr at 120°C. The product (70.8 g) underwent the same treatment as above using 250 g of epichlorohydrin, 175 g of DMSO and 20.0 g of 50 wt% NaOHaq. for completion of the glycidylation. The obtained crude DGE (C2-MS-C2) (75 g) was purified by crystallization from a methylisobutylketone solution, yielding 58 g (85%), mp 72°C (DSC). According to the GPC, the obtained DGE (C2-MS-C2) contained 7% of other components with a higher molecular weight, some of which were the result of the step-growth polymerization. $^1$H NMR ($CDCl_3$): 2.25 ppm (3H, s, $CH_3$ of stilbene), 2.66 ppm (2H, dd, $CH_2$ of glycidyl), 3.83 ppm (2H, t, $CH_2$ of glycidyl), 3.22 ppm (2H, m, CH of glycidyl), 3.52 ppm (2H, dd, $CH_2$ of glycidyl), 3.86–3.96 ppm (6H, m, $CH_2$ of ethylene-oxy, $CH_2$ of glycidyl), 4.18 ppm (4H, t, CH2 of ethylene-oxy), 6.73 ppm (1H, s, CH stilbene), 6.93 ppm (4H, dd, aromatic), 7.29 ppm (2H, d, aromatic), and 7.45 ppm (2H, d, aromatic).

### 2.4. Curing of Epoxy Resins to Prepare LC Network

DGE (C2-MS-C2) and DGEDHMS were cured with a stoichiometric amount of amine. The mixture of the epoxy resin and amine was once melted to make a homogeneous system in an oil bath, then immediately cured in an oven. For the purpose of preparing LC network, the oven temperature was regulated as low as possible within the range of no crystal generation in the reaction system.

## 3. Results and Discussion

### 3.1. Characterization of DGE (C2-MS-C2)

A DSC thermogram of DGE (C2-MS-C2) is shown in Fig. 1. The endothermic peak at 72°C during the heating process indicates a crystal-isotropic transition because no clear mesophase texture was observed on the POM. On the other hand, one small exothermic peak at 38°C, and two large ones at 33°C and 28°C are observed during the cooling process. Some of them are associated with LC transitions, because the POM observation indicates the existence of a nematic phase in the range of 48°C to 40°C (Fig. 2). Taking into account the fact that the sample on the hot stage of the POM is exposed to air, it's natural that the temperature region where the birefringence was observed is slightly lower range than

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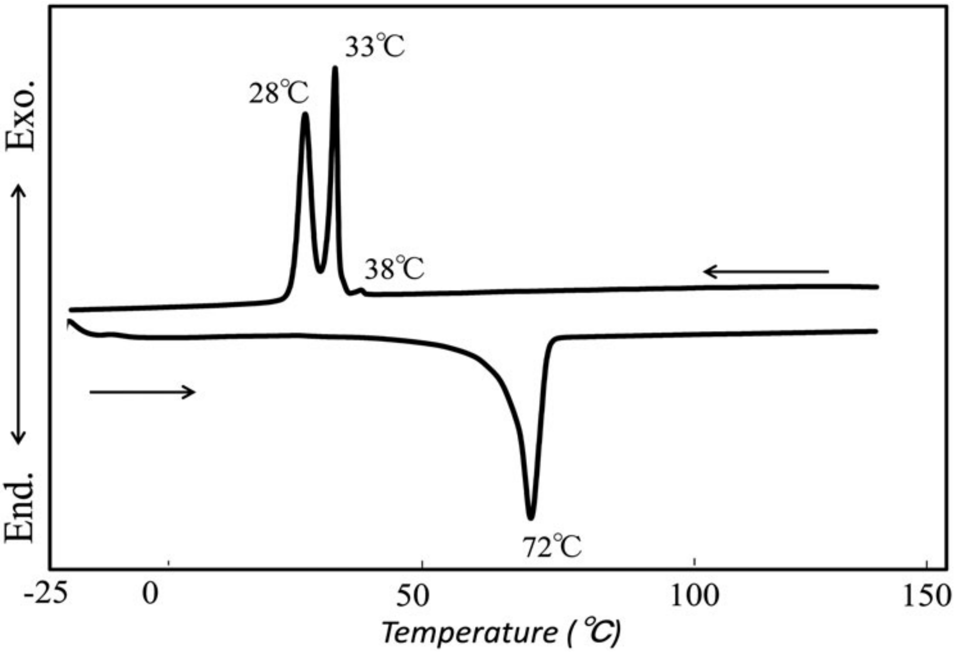

**Figure 1.** DSC thermogram of DGE (C2-MS-C2).

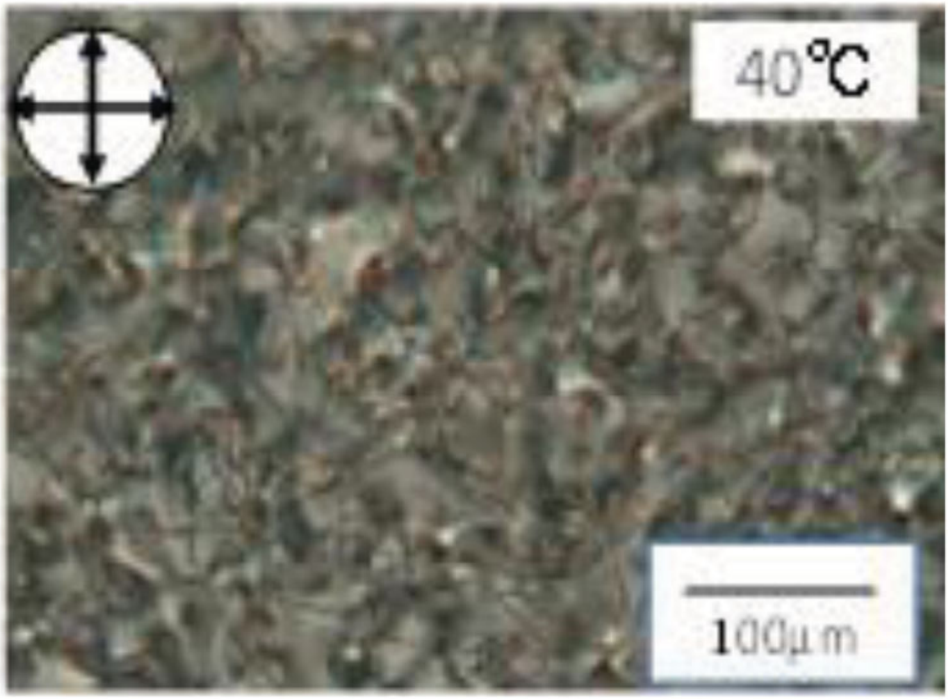

**Figure 2.** POM photograph of DGE (C2-MS-C2).

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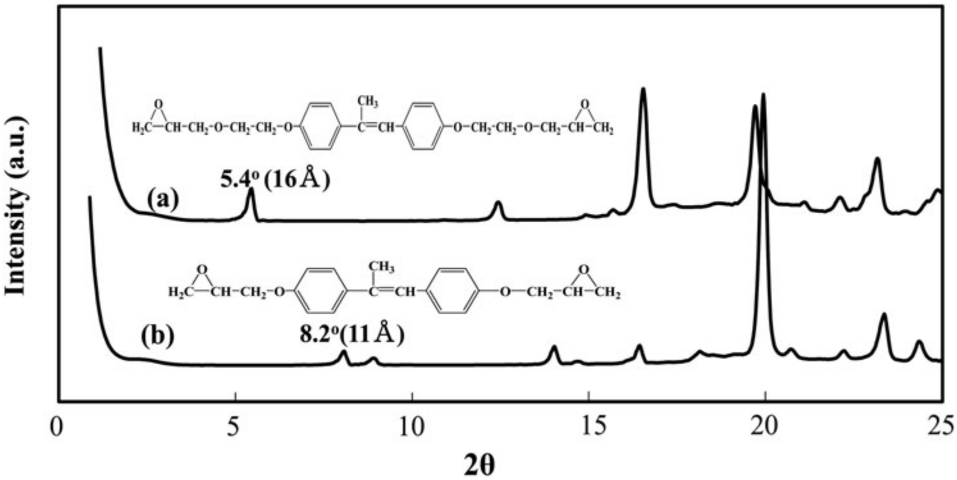

Figure 3. XRD patterns of (a) DGE (C2-MS-C2) and (b) DGEDHMS.

48°C–40°C. So, small exothermic peak at 38°C on DSC corresponds to an isotropic-nematic transition.

The thermal transitions of DGE (C2-MS-C2) and DGEDHMS are summarized in Table 1. Because the clearing temperature of DGEDHMS during the heating process is 128°C, introducing an ethylene-oxy group to DGEDHMS has the effect of decreasing the clearing temperature by 56°C.

This effect is rather remarkable as considered by the report of P. Castell et al. [12]; introducing an ethylene-oxy group between the imine type mesogen unit and digycidyl group decreased the clearing point from 257°C to 240°C.

The XRD patterns at room temperature of DGE (C2-MS-C2) and DGEDHMS are shown in Fig. 3.

Figure 3 shows that DGE (C2-MS-C2) maintains a high crystallinity, and also shows a longer layer spacing than DGEDHMS. The difference in the layer spacing between DGE (C2-MS-C2) and DGEDHMS, which is 5A, approximately corresponds to the length of two oxyethylene units. Therefore, it is natural to consider that oxyethylene units extend along either side of the DHMS units. The increased volume fraction of the flexible unit, including the oxyethylene units and glycidyl unit, in the DGE(C2-MS-C2) molecule effectively decreased the melting point (MP).

### *3.2. Characterization of DGE (C2-MS-C2) Cured with DDEt*

Lowering MP makes it possible to cure the epoxy resin at a lower temperature without crystal generation of the epoxy resin monomer, oligomer nor curing agent during the curing process. The curing of DGE (C2-MS-C2) with DDEt at 90°C for 3.5 hr followed 170°C for 20 min served to generate matrix having layered structure without crystals (Fig. 4(a)).

On the other hand, curing DGEDHMS with DDEt generates crystals in the matrix at the same temperature. Therefore, DGEDHMS was cured with DDEt at 110°C for 2.5

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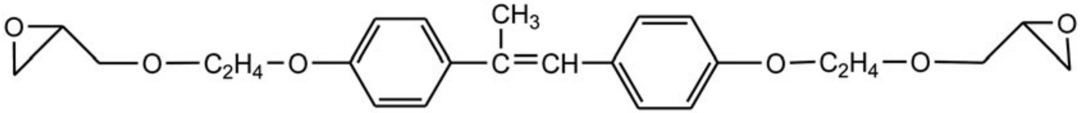
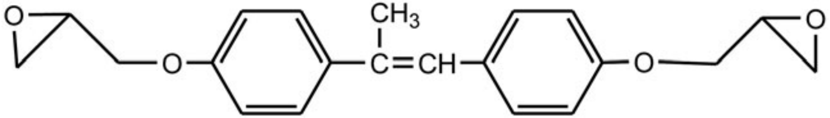
**Table 1.** Comparison of thermal transition temperature between LC epoxy resins with spacer and without spacer

| Chemical structure | Heating Ti[a] | Cooling Tin[b] | Tc[c] |
|---|---|---|---|
|  | 72 | 48 | 40 |
|  | 128 | 107 | 53 |

[a] Ti denotes isotropization temperature.
[b] Tin denotes isotropic to nematic transition temperature.
[c] Tc denotes nematic to crystal transition temperature.

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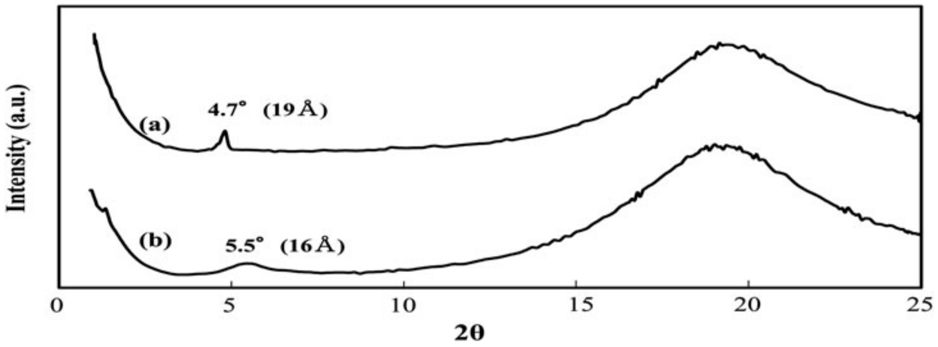

**Figure 4.** XRD patterns of (a) DGE (C2-MS-C2) cured with 4,4′-diaminodiphenylethane and (b) DGEDHMS cured with 4,4′-diaminodiphenylethane.

hr followed by 160°C for 30 min, then an opaque matrix without crystal was obtained (Fig. 4(b)).

Figures 4(a) and (b) show that the cured DGE (C2-MS-C2) with DDEt has a more distinct layered structure than the cured DGEDHMS. The possible reason for this would be (1) curing at a lower temperature of DGE (C2-MS-C2) suppresses the thermal mobility of the molecule and molecular chain during the curing reaction, (2) extended flexible units consisting of an oxyethylene unit and glycidyl group on both sides of mesogen unit prohibit unbound movement of the mesogen unit at an earlier stage, and (3) the longer flexible unit of DGE(C2-MS-C2) makes the mesogen units easily align and stack on each other during later curing stage.

Tensile test was conducted on cured DGE (C2-MS-C2) and DGEDHMS. In order to clarify an effect of a chemical structure and that of a layered structure, each epoxy resin was also cured at higher temperature to prepare isotropic networks. For this purpose, DGE (C2-MS-C2)/DDEt system was cured at 170°C for 1.5 hr, DGEDHMS/DDEt system was cured at 160°C for 3.0 hr. Figure 5 and Table 2 show both of cured DGE (C2-MS-C2)s

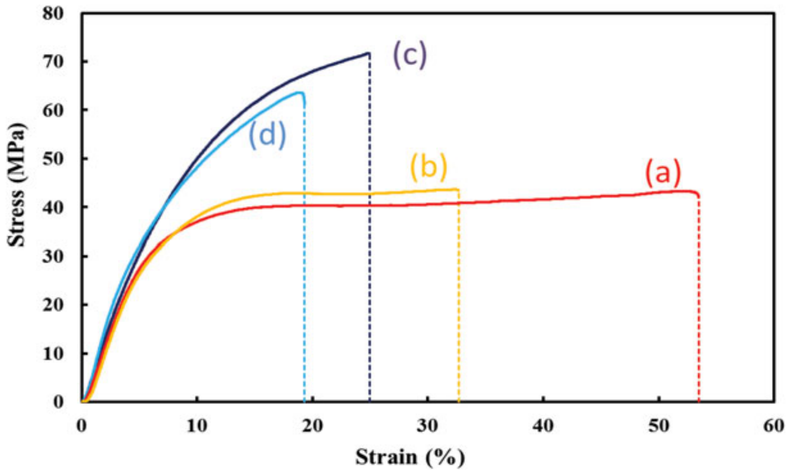

**Figure 5.** Stress–strain curve of DGE (C2-MS-C2)/DDEt and system DGEDHMS/DDEt. (a) LC network of DGE (C2-MS-C2)/DDEt. (b) Isotropic network of DGE (C2-MS-C2)/DDEt. (c) LC network of DGEDHMS/DDEt. (d) Isotropic network of DGEDHMS/DDEt.

**Table 2.** Tensile test data for DGEDHMS/DDEt and DGE(C2-MS-C2)/DDEt system

| Curing system | Curing condition | Stress [MPa] | Strain [%] | Fracture energy [kJ m$^{-2}$] | Phase |
|---|---|---|---|---|---|
| DGE(C2-MS-C2)/ DDEt | 90°C 3.5 hr + 170°C 20 min | 43.1 | 54.5 | 211 | LC |
| | 170°C 1.5 hr | 42.2 | 38.3 | 143 | Isotropic |
| DGEDHMS/DDEt | 110°C 2.5 hr + 160°C 0.5 hr | 71.9 | 24.9 | 134 | LC |
| | 160°C 3.0 hr | 66.6 | 19.8 | 91 | Isotropic |

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perform larger strain and increased fracture energy compared with cured DGEDHMSs. This result is natural to consider DGE (C2-MS-C2) have flexible unit. Furthermore, in both epoxy resin system, matrix with layered structure shows increased fracture energy than isotropic networks. We consider that networks which have layered structure include local region consisted with predominantly flexible units without rigid moieties such as methylstilbene unit and phenylene unit. Such a region without rigid moiety contributes to larger deformation compared with a region comprised both of flexible units and rigid units. Other possible reason is that curing at a lower temperature served to generate a network with less defect point on crosslink.

### *3.3. Curing with Aliphatic Amine*

A lower MP makes it possible to formulate the resin with curing agents with a high reactivity with an epoxy group such as aliphatic amines. Conventional LCEs are usually difficult to cure with such curing agents, because most LCEs have a higher clearing point. A mixture of an epoxy resin and a curing agent has to once form a homogeneous system in molecular order before the curing reaction initiates. However, when a curing agent with a high reactivity is used, the LCEs would not make a macroscopically homogeneous system because the reaction initiates before the LCEs completely melt at elevated temperature.

In this study, 1,3-DAP was used as the curing agent with a high reactivity with an epoxy group.

Indeed, DGEDHMS with a stoichiometric amount of DAP immediately generates a nonhomogeneous gel during the melting operation before the curing process. The DGE (C2-MS-C2) makes a homogeneous clear liquid system in a minute with DAP at 90°C as expected. After cooling the mixture to room temperature, the DSC of the mixture was measured (Fig. 6).

Figure 6 shows that the curing reaction initiates below 60°C.

When the POM observation is carried out, a homogeneous liquid mixture generated in an oil bath at 90°C was put on a hot stage preheated at 60°C. The result of the POM observation during isothermal curing at 60°C is shown in Fig. 7. At the beginning, the system is isotropic (Fig. 7(a)). An emerging birefringence is then observed at 17 min. (Figure 7(b)), and at 26 min., formation of the oriented structure is confirmed (Fig. 7(c)). Next, DGE (C2-MS-C2) was cured with DAP at 60°C for 3 hr followed by curing at 100°C for 1 hr, then an XRD analysis of the cured material was completed (Fig. 8). Figure 8 suggests the existence of a smectic-like structure in the resulting network.

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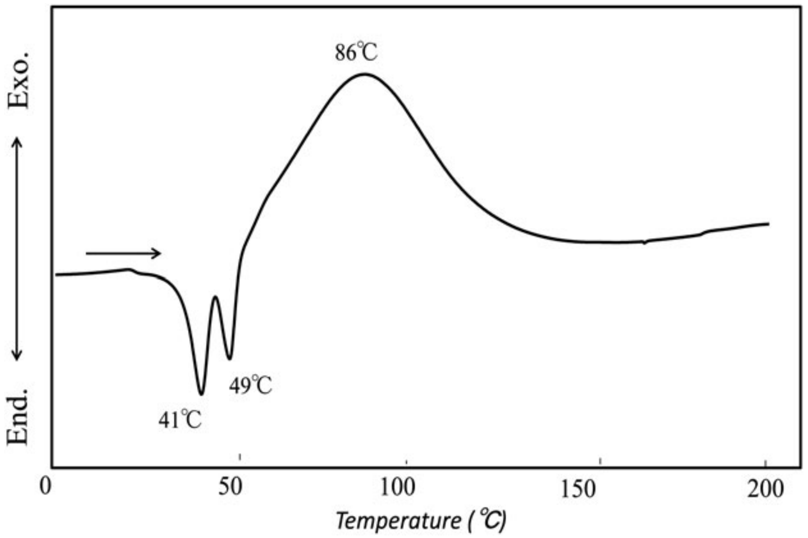
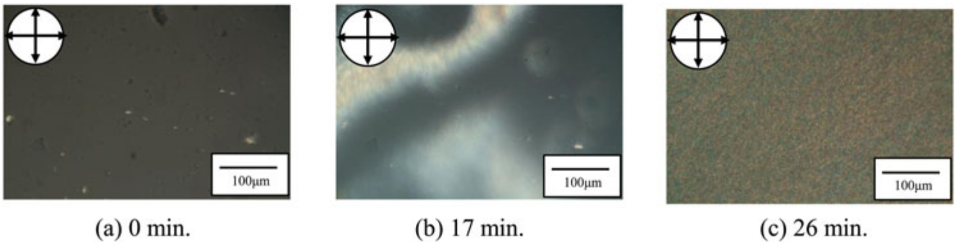


**Figure 6.** DSC thermogram of DGE (C2-MS-C2) formulated with DAP.



(a) 0 min.
(b) 17 min.
(c) 26 min.

**Figure 7.** POM photographs of DGE (C2-MS-C2) and DAP system during isothermal curing at 60°C.

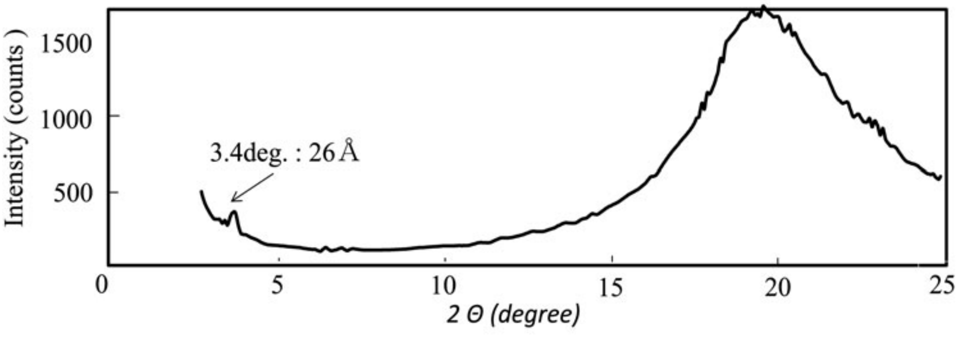


**Figure 8.** XRD pattern of DGE (C2-MS-C2) cured with DAP.

## 4. Conclusions

An LCE of DGE (C2-MS-C2), which has spacers outside the mesogenic unit, was synthesized and characterized. It was found that DGE (C2-MS-C2) has a low clearing point. DGE (C2-MS-C2) cured with DDEt produced a more distinct layered structure compared to DGEDHMS without spacers, nevertheless DGE (C2-MS-C2) has a rather limited mesophase. DGE (C2-MS-C2), especially having layered structure, showed large fracture energy on a tensile test.

We have also demonstrated the DGE (C2-MS-C2) is cured with DAP at a low temperature and forms an ordered network. The cured properties of DGE (C2-MS-C2) with a versatile curing agent are currently being investigated.

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