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

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著者	Yamamoto Hisanao
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**Synthesis and Characterization of Novel Liquid Crystalline
Epoxy Resin with Low Melting Point**

Hisanao YAMAMOTO

**Kansai University
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《氏名》 山本 久尚

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

(低融点液晶性エポキシ樹脂の合成とキャラクターゼーション)

《概要》

エポキシ樹脂は優れた機械的、電気的特性を示すことから、電気電子、塗料、各種コンポジット用途など工業的に広く利用されている。しかしながら、その応用技術の急速な発展に伴いエポキシ樹脂に対しては常に高い特性が求められ続けている。特にエポキシ樹脂は比較的脆い点が指摘されており、強靱性の改良は強く望まれている特性の一つである。

そのような中で近年、液晶性エポキシ樹脂（LCE）が優れた熱的・力学的特性を発現することから注目されてきている。このアプローチは、液晶性（LC）を有するエポキシ樹脂モノマーを硬化中に分子鎖配向させていき、秩序性の高い三次元構造を形成させることにより、強靱性の高い硬化物を得る手法であり、その実用化が期待されている。しかしながら、現在報告されている液晶性エポキシ樹脂は樹脂モノマーの融点が高い傾向にあるため、広く実用化されるには課題がある。本研究の目的は融点の低い液晶性エポキシ樹脂を設計し、強靱性の高い硬化物を創出するとともにその発現メカニズムを解明することにある。

本研究では、液晶性を発現するために必要な剛直なメソゲン骨格の両端に適切な構造のスペーサーを導入することにより、融点の低い新規の液晶性エポキシ樹脂モノマーを創出することができた。そして、通常のエポキシ樹脂硬化物は力学試験において降伏点を示すことなく脆性破壊を示すのに対して、本研究で創出した低融点液晶性エポキシ樹脂モノマーの硬化物は、降伏点を示すほど柔軟な特性を示すことが確認された。さらに、大型放射光施設（SPring8）にて引張試験中にSAX/WAX時分割測定を行うことにより、引張試験中にネットワーク分子鎖が配向するとともに、系内に形成された高度な規則性を有する層状構造体が崩壊していく挙動が観察され、これらの構造変化によるエネルギー損失が高い強靱性を発現する源泉であることを明らかにした。

《各章の要旨》

第1章では、低融点の液晶性エポキシ樹脂の合成とキャラクターゼーションを示す。比

較的低温領域で液晶性を示すことが報告されているメソゲン基である α -メチルスチルベン構造の両側に炭素数2のスペーサーを導入することにより、72℃という液晶性エポキシ樹脂としては融点の低い樹脂モノマー（DGE(C2-MS-C2)）を合成することができた。スペーサーを導入していない樹脂モノマー（DGEDHMS）の融点は128℃であり、スペーサーの導入により56℃の低融点化ができた。DGE(C2-MS-C2)は樹脂モノマーの融点が高いことにより温和な硬化条件で硬化できるため、従来の液晶性エポキシ樹脂では硬化できなかった脂肪族アミン系硬化剤とも硬化して均一な硬化物を得ることができることを示す。

第2章では、DGE(C2-MS-C2)およびDGEDHMSはジアミノジフェニルエーテル（DDEt）を用いて低温で硬化することにより液晶性（LC）硬化物を、高温で硬化することにより等方性（Iso）硬化物を形成することを示した。さらにそれぞれのLC硬化物として、ネマティック状の配向組織と秩序性の高い層状構造物であるスメクティック状組織からなる構造体の混合組織を提案した。DGE(C2-MS-C2)はLC硬化物、Iso硬化物ともに対応するDGEDHMS硬化物よりも、引張試験において靱性が高いことが確認された。さらに、スペーサーの有無に拘わらずLC硬化物はIso硬化物よりも強靱な特性を示した。DGE(C2-MS-C2)のDDEt硬化物の強靱化メカニズムが分子鎖の配向挙動にあることを提案した。

第3章では、DGE(C2-MS-C2)/DDEt系のLC硬化物、およびIso硬化物の加熱時のネットワーク分子鎖の挙動について調査した。加熱XRD解析の結果、LC硬化物中に形成された秩序性の高い層状構造は250℃まで維持されることが判った。一方、動的粘弾性（DMA）の周波数依存性評価結果に基づいて、LC硬化物中のネマティック状組織およびIso硬化物はT_gよりわずかに高い温度帯でメチルスチルベン骨格の局部運動が生じるという特異的現象が生じていることを提案した。また、LC硬化物中のネマティック状組織はT_g（106℃）以上でもその配向は維持され、200℃付近に達した段階で配向が崩れることが、偏光顕微鏡観察（POM）およびDMAの結果から示唆された。

第4章では、DGE(C2-MS-C2)/DDEt系、DGEDHMS/DDEt系のそれぞれのLC硬化物、Iso硬化物（合計4硬化物）の接着特性評価を行い、その接着特性とネットワーク構造の関係を明らかにする。接着試験はせん断接着試験とT型剥離試験を行い、その両試験において引張試験で得られた強靱性評価結果とは異なり、DGE(C2-MS-C2)/DDEt系、DGEDHMS/DDEt系ともにIso硬化物の方がLC硬化物よりも高い接着強度を示した。特にDGE(C2-MS-C2)/DDEt系のIso硬化物は他の硬化系に比較して非常に高い接着強度を示し、その原因が低い内部応力にあることを明らかにした。DGE(C2-MS-C2)/DDEt系のIso硬化物が低い内部応力を示すことの理由として樹脂硬化物のT_gより約30℃低い温度領域において応力緩和を起こすことが想定され、応力緩和評価試験においてその挙動傾向が観察された。

第5章では、種々のスペーサー構造（炭素数0、炭素数2、炭素数3（直鎖）、および炭素数3（分岐））を持つメソゲンエポキシ樹脂モノマーを合成し、スペーサー構造と樹脂モノマーおよび硬化物の関係を明らかにした。スペーサー長が長いほど樹脂モノマーの融点が低下した。分岐スペーサー構造は直鎖構造よりも効率的に融点を低下させたが、液

晶性は確認できず、液晶相硬化物も形成されなかった。エポキシ樹脂モノマーの融点が低いほど低温で硬化することが可能となり、液晶相を形成するスペーサー構造が炭素数 0、炭素数 2、炭素数 3（直鎖）の 3 種のエポキシ樹脂モノマー（DGEDHMS, DGE(C2-MS-C2), DGE(C3-MS-C3)）に関しては低温で硬化できるエポキシ樹脂モノマーほどより規則性の高い層状構造が形成されることが示された。

引張試験における破壊強度はスペーサー長が炭素数 2 のエポキシ樹脂モノマー（DGE(C2-MS-C2)）が最も高い破壊エポキシ樹脂エネルギーを示した。引張試験中の WAX 時分割測定を行ったところ、上記 3 種の硬化物は弾性領域においては差異を示さなかったが、塑性変形領域において DGE(C2-MS-C2) 中が最も大きな配向挙動を示すことが判明した。DGE(C2-MS-C2) 中のメソゲン基の方向変化によるエネルギー散逸が大きな破壊エネルギーを発現する理由であることが示唆された。

第 6 章では、スペーサー構造が炭素数 2（DGE(C2-MS-C2)）の DDEt 硬化物、およびスペーサー構造が炭素数 0、炭素数 2、炭素数 3（直鎖）の 3 種のエポキシ樹脂モノマー（DGEDHMS, DGE(C2-MS-C2), DGE(C3-MS-C3)）のメタフェニレンジアミン（m-PD）から形成された LC 硬化物中の規則性の高い層状構造体であるスメクティック状組織の引張試験中の挙動解析を SAX 時分割測定により行った。その結果、各系内に形成された高度な規則性を有する層状構造体の規則性が壊れていく様子が観察され、特に DGE(C2-MS-C2)/DDEt 硬化物中の層構造の規則性が壊滅的に消失することが確認され、このことも高い破壊エネルギーに関連することが示唆された。

以 上

CONTENTS

	Page
GENERAL INTRODUCTION	1
 Part I	
Introduction of Spacers with Carbon Number Two Outside Methylstilbene Structure in the Liquid Crystalline Epoxy Resin	9
 Chapter 1	
Synthesis and Characterization of Novel Liquid Crystalline Epoxy Resin with Low Melting Point	
I-1-1. INTRODUCTION	10
I-1-2. EXPERIMENTAL	10
I-1-3. RESULTS AND DISCUSSION	13
I-1-3-1. Characterization of DGE(C2-MS-C2)	13
I-1-3-2. Characterization of DGE(C2-MS-C2) cured with DDEt	15
I-1-3-3 Curing with aliphatic amine	17
I-1-4. CONCLUSIONS	19
I-1-5. REFERENCES	19
 Chapter 2	
Toughening Mechanism of Liquid Crystalline Epoxy Resin with Spacers Outside the Mesogenic Group	21
I-2-1. INTRODUCTION	21
I-2-2. EXPERIMENTAL	22
I-2-3. RESULTS AND DISCUSSION	25
I-2-3-1. Network structures formed after curing with DDEt	25
I-2-3-2. Mechanical properties	28
I-2-3-3 Fracture toughness	29
I-2-3-4 Toughening mechanism	30
I-2-4. CONCLUSIONS	35
I-2-5. ACKNOWLEDGEMENT	35
I-2-6. REFERENCES	36

Chapter 3

Thermal Behavior of Molecular Chains in a Liquid Crystalline Network with Spacers

I-3-1. INTRODUCTION	39
I-3-2. EXPERIMENTAL	39
I-3-3. RESULTS AND DISCUSSION	41
I-3-3-1. Dynamic mechanical analysis	41
I-3-3-2. Thermal behavior of LC networks	46
I-3-3-3. Thermal behavior of the LC DGE(C2-MS-C2)/DDEt network	47
I-3-3-4. Thermal behavior of the Iso DGE(C2-MS-C2)/DDEt network	50
I-3-3-5. Thermal behavior of LC and Iso DGEDHMS/DDEt networks	51
I-3-4. CONCLUSIONS	52
I-3-5. REFERENCES	52

Chapter 4

Adhesive Properties of Liquid Crystalline Epoxy Resin Having a Low Melting Point by Introducing Flexible Spacers

I-4-1. INTRODUCTION	55
I-4-2. EXPERIMENTAL	55
I-4-3. RESULTS AND DISCUSSION	59
I-4-3-1. Evaluation of adhesive strength of LC and Iso networks formed from DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt systems	59
I-4-3-2. The surface free energy of LC and Iso networks formed from DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt systems	61
I-4-3-3. Internal stress of LC and Iso networks formed from DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt systems	62
I-4-3-4. Comparison of calculated value and measured value on the internal stress of LC and Iso networks formed from DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt systems	66
I-4-3-5. Evaluation of stress relaxation behavior of LC and Iso networks formed from DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt systems	67
I-4-4. CONCLUSIONS	69
I-4-5. REFERENCES	70

Part II

Influence of Spacer Structures on the Physical Properties of Spacer-introduced Liquid Crystalline Epoxy Resins	71
---	-----------

Chapter 5

Influence of Spacer Structure on the Physical Properties of Cured and Uncured Spacer-introduced Liquid Crystalline Epoxy Resins	72
II-5-1. INTRODUCTION	72
II-5-2. EXPERIMENTAL	72
II-5-3. RESULTS AND DISCUSSION	77
II-5-3-1. Characterization of mesogenic epoxy resin monomers	77
II-5-3-2. Characterization of mesogenic epoxy resins cured with m-PD	79
II-5-3-3 Mechanical properties and the behavior of molecular chains in the LC networks during tensile tests.	82
II-5-4. CONCLUSIONS	86
II-5-5. ACKNOWLEDGEMENT	87
II-5-6. REFERENCES	87

Chapter 6

Study on the Structural Change of the Smectic-like Structure in the LC Networks with and without Spacers during Tensile Tests	89
II-6-1. INTRODUCTION	89
II-6-2. EXPERIMENTAL	90
II-6-3. RESULTS AND DISCUSSION	94
II-6-3-1. DDEt cure system	94
II-6-3-2. m-PD cure system	102
II-6-4. CONCLUSIONS	109
II-6-5. ACKNOWLEDGEMENT	110
II-6-6. REFERENCES	110
CONCLUDING REMARKS	111
LIST OF PUBLICATIONS	115
ACKNOWLEDGEMENT	119

GENERAL INTRODUCTION

This work has dealt with the fundamental research in the cured and uncured liquid crystalline (LC) epoxy resins (LCEs) with low melting points, and has placed the focus on the thermal and mechanical behavior of the molecular chains in the LC networks.

Epoxy resins are widely used in the industrial applications such as encapsulants for electronics or electrical devices, adhesives, coatings, matrices for composites, because of their excellent thermal, electrical and chemical properties. On the other hand, epoxy resins are still needed further improvement with the evolution and emerging of advanced application technology. So, great deals of developments have been performed to respond to and to satisfy these requirements. As the results, in these decades of years so many numbers of epoxy resin monomers have been developed.

Most of these developments were conducted based on the consideration how the backbone structure of monomers affect the performance of network. One of the major requirements for epoxy resin is improvement of brittleness. However there was little outcome such as the epoxy resins which show yielding behavior with high crosslinking density as far as rubber modification manners were not applied. We considered that one of barriers to achieve the issue was that we could not exactly design the network structure, especially three-dimensional (3D) structure. This is because the networks usually do not melt nor dissolve in any solvents. So we cannot realize how the network is being formed. Furthermore we cannot analyze nor monitor the behavior of network structure while external stress is applied.

On the other hand, in early 1990s it was reported that epoxy resins with rigid moiety generate highly oriented networks [1, 2], and the new approach to generate liquid crystalline (LC) networks was reported [3-11]. The approach of LC network is the novel investigation that the mesogenic groups included in the epoxy resin monomer orient to generate meso-phase during curing reaction according to self-alignment property of mesogenic groups, then finally form oriented or ordered structures. This LCE approach, so to speak, is also much different from conventional approach in terms that the LCE approach tries to design and control three-dimensional (3D) structure of the generated network. It has been already reported that several liquid crystalline epoxy resins (LCEs) have excellent thermal and mechanical properties, such as a high T_g, high fracture toughness, and increased bonding strength [12-19]. These inventions would enhance the potential of epoxy resins as seen in the utilization for high thermal conductive encapsulants.

However, it is sometimes troublesome to utilize LCEs for industrial applications because almost all of LCEs have high melting points. When the LCEs are formulated with some curing agents or additives such as fillers, curing reaction would initiate

before the resin composition become inhomogeneous. On the other hand, some researchers reported that more highly-layered structures are formed as the LCEs are cured at lower temperatures [20].

It is known that even conventional epoxy resins would show tougher properties when they cured at a lower temperature compared with the cured resins cured at higher temperatures. We consider that this is resulted from the reduced internal stress inside the generated network because the molecular chains under curing reaction take the relatively stable conformation from the thermodynamic point of view. Furthermore, when the LCEs were cured at lower temperature, the generation of highly ordered structure would be encouraged, so that we expected that the unique properties of LC network would become more remarkable.

From these points of view, we initiated a research work to decrease the melting points of LCEs, and then evaluated the cured and uncured properties.

Concerning mechanism of specific mechanical properties for LC networks, some researchers proposed the mechanism of fracture toughness, which is interpreted from the morphology [12, 16-21]. Then, for example, the microscopic void formation ahead of the crack tip, which leads to the plastic deformation, or deflection, bifurcation etc. of crack propagation are proposed as the toughening mechanism [12, 16]. However there are little reports which investigated the toughening mechanism from the aspect of behavior of molecular chains or behavior of layered structure generated in the networks. We considered that we may observe behavior of the network chains and the structural change of layered structures during tensile test by means of time-resolved small- and wide- angle X-ray scattering (SAXS/WAXS) using synchrotron radiation. Especially, we tried to understand the influence of the distance between crosslinking point and mesogenic group on the physical properties by comparing behaviors of LC networks with analogous spacers while external stress was applied.

The aim of this work is to generate LCE with low melting points which perform specific physical properties such as high fracture toughness etc., and to understand the thermal and mechanical behavior of the molecular chains in the network.

A brief summary of the series of studies conducted on the cured and uncured properties of the liquid crystalline with low melting point is as follows;

In Part I, involving Chapter 1,2,3, and 4, the properties of cured and uncured properties of LCE with flexible spacers of carbon number two is described.

In Part II, involving Chapter 4 and 5, the influence of spacer structures on the physical properties of spacer-introduced LCE is described.

Chapter 1. Synthesis and Characterization of Novel Liquid Crystalline Epoxy Resin with Low Melting Point

In this chapter, a liquid crystalline epoxy resin 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) proved to have a lower melting point (MP) compared to the diglycidylether of 4,4'-dihydroxy- α -methylstilbene (DGEDHMS). DGE(C2-MS-C2) and DGEDHMS were cured with diaminodiphenylethane (DDEt) to generate networks showing LC or isotropic (Iso) phase depending on the curing temperatures.

LC network generated from DGE(C2-MS-C2) had a more sequentially layered structure than LC network generated from DGEDHMS. Both of LC and ISO network of DGE(C2-MS-C2) showed larger fracture energy on a tensile test than corresponding network of DGEDHMS. Furthermore, regardless of whether spacer is introduced or not, LC network showed larger fracture energy than Iso network.

It was also demonstrated that curing DGE(C2-MS-C2) with 1,3-diaminopropane (DAP) generated to form LC network.

Chapter 2. Toughening Mechanism of Liquid Crystalline Epoxy Resin with Spacers Outside the Mesogenic Group.

In this chapter, the behavior of molecular chains of LC and Iso networks during tensile tests in a glass region was investigated by time-resolved wide angle X-ray diffraction (WAX) measurements. It was found that the LC network of DGE(C2-MS-C2)/DDEt was more highly orientated than the isotropic (Iso) network formed from the same resin composition. The dissipation energy, which would be generated during the reorientation process of the network chains in a glass region, is proposed as the source of the high fracture toughness of the DGE(C2-MS-C2)/DDEt network during the tensile test.

Chapter 3. Thermal Behavior of Molecular Chain in a Liquid Crystalline Network with Spacers

In this chapter, the thermal behavior of molecular chains in the LC and Iso network of DGE(C2-MS-C2) cured with DDEt was studied. It was proposed that each network two relaxation behaviors; one is α relaxation behavior which is attributed to the micro-Brownian motion of flexible section except for the methylstilbene moiety, another is α' relaxation behavior which is attributed to the local mode motion of the

methylstilbene moiety.

Concerning the LC network of DGE(C2-MS-C2)/DDEt, the consideration was attempted for each of smectic-like structure and nematic-like structure. The smectic-like layer is maintained to 250 °C, the nematic structure does not disordered at T_g but initiate to disorder at around 200°C.

Chapter 4. Adhesive Properties of Liquid Crystalline Epoxy Resin Having a Low Melting Point by Introducing Flexible Spacers

In this chapter, adhesive properties of LCEs having a low melting point with flexible spacers were investigated. LC and Iso networks with flexible spacers showed higher adhesive strength at the lap share tests and T-peel tests than those without flexible spacers. Furthermore, Iso epoxy networks showed higher adhesive strength than LC networks. It was found that the Iso network has the lower internal stress generated in the curing and cooling process compared with the LC network. In particular, Iso DGE(C2-MS-C2)/DDEt network which performed highest adhesive strength had the lowest internal stress. Relaxation behavior of network chains in the Iso networks was suggested as the reason of the low internal stress and consequently the high adhesive strength of Iso networks.

Chapter 5. Influence of Spacer Structure on the Physical Properties of Cured and Uncured Spacer-introduced Liquid Crystalline Epoxy Resins

In this chapter, the influence of the spacer structures on the physical properties of cured and uncured spacer-introduced liquid crystalline epoxy resins was investigated by introducing various structures of spacers outside of α -methylstilbene backbone.

As the spacers are longer, the MP of the epoxy resin is lower, which makes it possible to cure the mesogenic epoxy resin at a lower temperature to provide more sequentially ordered structure. LC network with spacers of carbon number two, DGE(C2-MS-C2), showed largest fracture energy in the tensile test. The behavior of network chain in the tensile test was analyzed by time-resolved WAX. It was proposed that the plastic deformation of LC network with spacers is composed of deformation of flexible section and the direction change of α -methylstilbene group, and that the dissipation energy which would be generated by the direction change is the main source of the large fracture energy of the LC network of DGE(C2-MS-C2)

Chapter 6. Study on the Structural Changes of the Smectic-like Structures in the LC Networks with and without Spacers during Tensile Tests

In this chapter, the behaviors of the smectic-like structures in the glassy state during tensile test were investigated for the LC networks with and without spacers. Whereas SAX diffraction pattern in the network without spacers did not show distinct feature before break, SAX diffraction patterns of the spacer-introduced type networks exhibit characteristic behaviors.

In the elastic deformation region, the smectic-like structure oriented orthogonal direction to the tensile direction started to decrease, whereas the smectic-like structures oriented along the tensile direction tended to increase.

In the plastic deformation region, the smectic-like structure oriented orthogonal to the tensile direction continued to decrease in the plastic deformation region. Concerning smectic-like structure oriented along the tensile direction, the layered structure consisted of less flexible section decreased remarkably, the layered structure consisted of much flexible section maintain or even increase. These phenomena were understood from the aspect of the behavior of network chains.

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Part I

Introduction of Spacers with Carbon Number Two Outside Methylstilbene Structure in the Liquid Crystalline Epoxy Resin

Chapter 1

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

I-1-1. 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, 9} 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.⁸ researched the relationship between the curing temperature and resulting network structure of DGDHMS. They demonstrated that as the DGDHMS is cured at a lower temperature, a more highly-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 which decreases the clearing temperature by introducing spacers between 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 chapter, the latter approach was taken using the 4,4'-dihydroxy- α -methylstilbene (DHMS) moiety, and then the LCE was synthesized and characterized.

I-1-2. EXPERIMENTAL

I-1-2-1. Materials

Dihydroxy- α -methylstilbene (DHMS) and the diglycidylether of DHMS (DGEDHMS) were synthesized according to the procedures described in a patent.⁷ 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.

I-1-2-2. Measurements

The molecular weight distribution was measured by GPC (Shimadzu CBM-20A) using Shimadzu RID-10A reflex indicator and ShodexTM LF804 x 2 columns at 40°C. The 1H NMR spectra were recorded using a JNM-EX400 (JEOL Ltd.) spectrometer working at 400MHz using 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.) at the heating and cooling rate of 5°C/min. Optical anisotropy of the epoxy was observed using an optical microscope (BH-2, Olympus Corporation) 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).

The tensile tests were performed as per the ISO 527-1 and 527-2 standards using a tabletop precision universal tester (Autograph AGS-J, Shimadzu, Japan) equipped with a noncontact digital video extensometer (TRViewX55S, Shimadzu, Japan); the crosshead speed was 2 mm/min. The dumbbell-shaped specimens were prepared according to type 1BB of the ISO 527-2 standard. The strain was determined as the ratio of the change in the distance between the gage marks versus the original distance. The fracture energies of the cured LCE resin systems were evaluated from the area under the stress-strain curves obtained from the tensile tests.

I-1-2-3. Sample preparation

Synthesis of C2-MS-C2

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

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 1Hr. 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 1H 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, CH_2 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), 7.48 ppm (2H, d, aromatic).

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% NaOH aq. (64 g) solution was added dropwise to the reactor over 30 min. One hour after completion of the 50 wt% NaOH aq. 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 5 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% NaOH aq. 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. ¹H NMR (CDCl₃): 2.25 ppm (3H, s, CH₃ of stilbene), 2.66 ppm (2H, dd, CH₂ of glycidyl), 3.83 ppm (2H, t, CH₂ of glycidyl), 3.22 ppm (2H, m, CH of glycidyl), 3.52 ppm (2H, dd, CH₂ of glycidyl), 3.86-3.96 ppm (6H, m, CH₂ of ethylene-oxy, CH₂ 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), 7.45 ppm (2H, d, aromatic).

I-1-2-4. 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 prepare LC network, the oven temperature was regulated as low as possible within the range of no crystal generation in the reaction system.

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

I-1-3. RESULTS AND DISCUSSION

I-1-3-1. Characterization of DGE(C2-MS-C2)

A DSC thermogram of DGE(C2-MS-C2) is shown in Figure 1-1. 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 liquid crystalline transitions, because the POM observation indicates the existence of a nematic phase in the range of 48 °C to 40 °C (Figure 1-2). 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 48-40 °C. So small exothermic peak at 38°C on DSC corresponds to an isotropic-nematic transition.

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

Figure 1-2. POM photograph of DGE(C2-MS-C2)

The thermal transitions of DGE(C2-MS-C2) and DGEDHMS are summarized in Table 1-1. 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 diglycidyl group decreased the clearing point from 257 °C to 240 °C.

Figure 1-3. XRD patterns of (a) DGE(C2-MS-C2) and (b) DGEDHMS

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

Chemical structure	Heating	Cooling	
	Ti ^a	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.

The XRD patterns at room temperature of DGE(C2-MS-C2) and DGEDHMS are shown in Figure 1-3. Figure 1-3 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 5 Å, 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.

I-1-3-2. Characterization of DGE(C2-MS-C2) cured with DDEt

Lowering melting point 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 (Figure 1-4(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 hr. followed by 160 °C for 30 min., then an opaque matrix without crystal was obtained (Figure 1-4(b)). Figure 1-4(a) and Figure 1-4(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.

Figure 1-4. XRD patterns of (a)DGE(C2-MS-C2) cured with 4,4'-diaminodiphenylethane and (b)DGEDHMS cured with 4,4'-diaminodiphenylethane.

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 (Iso) networks. For this purpose DGE(C2-MS-C2) / DDEt system was cured at at 170 °C for 1.5 hr, DGEDHMS/DDEt system was cured at 160 °C for 3.0 hr. Figure 1-5 and Table 1-2 shows

Figure.1-5. Stress-strain curves of the DGE(C2-MS-C2)/DDEt and DGEDHMS/DDEt systems.

- (a) LC network of DGE(C2-MS-C2)/DDEt
- (b) Iso network of DGE(C2-MS-C2)/DDEt
- (c) LC network of DGEDHMS/DDEt
- (d) Iso network of DGEDHMS/DDEt

Table 1-2. Tensile test data for DGEDHMS / DDEt and DGE(C2-MS-C2) / DDEt system.

Resin system	Curing condition	Stress at break	Strain	Fracture energy	Structure
DGE(C2-MS-C2) /DDEt	90°C 3.5hr +170°C 20min	52 [MPa]	33 [%]	15.8 [MPa]	LC
	170°C 1.5hr	51 [MPa]	16 [%]	7.3 [MPa]	Iso
DGEDHMS /DDEt	110°C 2.5hr +160°C 0.5hr	74 [MPa]	17 [%]	9.9 [MPa]	LC
	160°C 3.0hr	68 [MPa]	10 [%]	4.8 [MPa]	Iso

both of cured DGE(C2-MS-C2)s 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.

I-1-3-3. Curing with aliphatic amine

A lower melting point 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-diaminopropane (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 (Figure 1-6). Figure 1-6 shows that the curing reaction initiates below 60 °C.

Figure 1-6. DSC thermogram of DGE(C2-MS-C2) formulated with DAP

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 Figure 1-7. At the beginning, the system is isotropic (Figure 1-7(a)). An emerging birefringence is then observed at 17 min. (Figure 1-7(b)), and at 26 min., formation of the oriented structure is confirmed (Figure 1-7(c)). Next, DGE(C2-MS-C2) was cured with DAP at 60°C for 3 hr followed by curing at 100°C for 1hr, then an XRD analysis of the cured material was completed (Figure 1-8). Figure 1-8 suggests the existence of a smectic-like structure in the resulting network.

Figure 1-7. POM photographs of DGE(C2-MS-C2) and DAP system during isothermal curing at 60 °C

Figure 1-8. XRD pattern of DGE(C2-MS-C2) cured with DAP.

I-1-4. CONCLUSIONS

An LCE of DGE(C2-MS-C2), which have 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.

I-1-5. REFERENCES

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Chapter 2

Toughening Mechanism of Liquid Crystalline Epoxy Resin with Spacers Outside the Mesogenic Group

I-2-1. INTRODUCTION

It has been reported that liquid crystalline epoxy resins (LCEs) have excellent thermal and mechanical properties, such as a high glass-transition temperature (T_g), high fracture toughness, and increased bonding strength [1-8]. Their unique properties suggest that there is great potential to expand the use of epoxy resins, which are already being employed widely as encapsulants for electronics devices, as composites, and as adhesives. The origin of these unique properties of LCEs, such as their high fracture toughness, can be attributed to terms of their morphology or network structure. Ortiz et al. [2] demonstrated that a highly ordered network exhibited a higher deformation in compression tests. Lin et al. [9] researched the relationship between the curing temperature and the resulting network structure of the diglycidyl ether of 4,4'-dihydroxy- α -methylstilbene (DGEDHMS). They demonstrated that when DGEDHMS is cured at a lower temperature, a more highly layered structure is formed. These results imply that LCEs would have even more remarkably unique properties if they were to be cured under milder conditions, such as temperatures lower than 100°C.

However, it is not easy to cure LCEs at moderately high temperature because curing at lower temperatures leads to the generation of crystalline monomers or oligomers in the system during or even before the curing reaction. A few researchers have shown that introducing spacers outside the mesogenic groups decreases the melting points of LCEs [10-15]. Broer et al. [10] and Jahromi et al. [12] synthesized LCEs with low melting points by introducing spacers outside the phenylbenzoate moiety and demonstrated that photoinitiated polymerization could occur even at low temperatures.

We had previously synthesized the LCE DGE(C2-MS-C2), whose clearing temperature is 72°C and had found that cured DGE(C2-MS-C2) exhibits a higher strain than does cured DGEDHMS, and that the LC networks of both DGE(C2-MS-C2) and DGEDHMS exhibit greater toughness than do the Iso networks of the corresponding same resin compositions [16].

In this study, we performed time-resolved wide-area X-ray diffraction (WAXD) measurements during tensile tests in order to observe the movement of the network chains. Using time-resolved X-ray diffraction analysis, Shiota et al. [17] found that the

structures with a smectic-like network align in the rubbery state under static stress. However, there are few reports concerning the movement of the network chains in the glass region when an external force is applied such during a mechanical test.

In this chapter, the orientation behaviors of the network chains in the glass state were observed using WAXD measurements performed during tensile tests. In addition, a mechanism for the toughening exhibited by the mesogenic epoxy resin with spacers is suggested.

I-2-2. EXPERIMENTAL

I-2-2-1. Materials

The chemical structures of the materials used in this study are given in Figure 2-1.

Figure 2-1. Chemical structures used in this study

DGE(C2-MS-C2) was synthesized as described in the literature [16]. 4,4'-Dihydroxy- α -methylstilbene (DHMS) and the diglycidyl ether of 4,4'-dihydroxy- α -methylstilbene (DGEDHMS) were synthesized according to the procedures described in a patent [18]. The transition temperatures of the LC epoxy resins are listed in Table 2-1. Diaminodiphenylethane (DDEt) was purchased from Wako Pure Chemical Industries, Ltd. All the reagents were used without further purification.

Table 2-1. Transition temperatures of the LCE resins

LCE resin	Heating	Cooling	
	Ti ^a	Tin ^b	Tc ^c
DGE(C2-MS-C2)	72	48	40
DGEDHMS	128	107	53

^aTi denotes isotropization temperature [°C].

^bTin denotes isotropic to nematic transition temperature [°C].

^cTc denotes nematic to crystal transition temperature [°C].

I-2-2-2. Measurements

The T_g values were determined from the tops of the peaks of the tan δ curves obtained from dynamic mechanical analysis (DMA), which was performed using an automatic dynamic viscoelastometer (Rheogel DVE-V4, UBM Co. Ltd., Japan). Samples with dimensions of 30 × 4 × 0.4 mm³ were tested in the tensile mode by applying mechanical vibrations with an amplitude of 25 μ m at a frequency of 10.0 Hz while raising the temperature at the rate of 2°C/min. The optical anisotropy of the cured epoxy resins was observed using an optical microscope (BH-2, Olympus Corporation, Japan) under cross-polarized light.

Fracture toughness was measured according to ASTM E-399 using the three point bending method. The sample dimensions were 2.2×4.4×19.6 mm. The pre-crack was formed by tapping with fresh razor blade. The specimen was mounted in an Instron-type tensile machine (Autograph AG-20/50KINIS MO Shimadzu, Japan) and loaded at a constant crosshead speed of 0.5 mm/min.

The time-resolved WAXD measurements made during the tensile tests were performed at the Spring 8, synchrotron radiation facility. The sample specimens were prepared according to type 1BB and then tuned to the appropriate thickness for a load cell of 5 N. The tensile tests were conducted at the crosshead speed of 6 mm/min (Figure 2-2).

The strain was determined by the ratio of the change in the distance between the grips that hold the test specimens versus the original distance. The wavelength of the incident X-ray beam was 0.06 nm, and the sample-to-detector distance during the WAXD measurements was 88.5 mm. The accumulation time of each shot and the time interval between the measurements were 500 and 1350 ms, respectively. The two-dimensional (2D) WAXD patterns were detected with a flat-panel detector (C9827DK-10, Hamamatsu Photonics, Japan). The obtained WAX patterns were averaged circularly and corrected for the scattering from air and the dark current of the detector. A dumbbell-shaped specimen was placed between the crossheads of the tensile test unit with a load cell. The tensile unit was then mounted on the synchrotron beam line.

Figure 2-2. Scheme for experiment of time-resolved WAX measurement during the tensile test of LC epoxy resin.

The 2D data were transformed into one-dimensional (1D) analytical data by integration and averaged in a defined direction using Eq. (1)

$$I_{\phi_s < \phi < \phi_e}(2\theta) = \frac{1}{(\phi_e - \phi_s)P} \int_{\phi_s}^{\phi_e} \frac{I(2\theta, \phi)}{\cos^3 2\theta} d\phi \quad (1)$$

where ϕ is the angle clockwise from the direction of the meridian (Figure 2-2) and θ denotes the Bragg angle. Further, P , which denotes the polarization factor, was assumed to be 1, and ϕ_s and ϕ_e were assumed to be $(\phi+5)^\circ$ and $(\phi-5)^\circ$ respectively.

I-2-2-3. Curing of epoxy resins

DGE(C2-MS-C2) and DGEDHMS were cured with stoichiometric amounts of DDEt. To prepare the networks, a molten mixture of LCE and DDEt was transferred to an oven, and cured under predefined conditions. The mixture of DGE(C2-MS-C2) and DDEt was homogenized at 110° , while the mixture of DGEDHMS and DDEt was

homogenized at 140°C. To prepare the LC networks, the oven temperature was kept as low as possible such that no crystals were formed in the reaction systems. The curing conditions employed, which are denoted as conditions (i) to (iv), were as follows.

DGE(C2-MS-C2) /DDEt:

- (i) LC network: 90°C and 3.5 h + 170°C and 0.3 h
- (ii) Iso network: 170°C and 1.5 h

DGEDHMS /DDEt:

- (iii) LC network: 110°C and 2.5 h + 160°C and 0.5 h
- (iv) Iso network: 160°C and 3.0 h

I-2-3. RESULTS AND DISCUSSION

I-2-3-1. Network structures formed after curing with DDEt

Both DGE(C2-MS-C2)/DDEt cured under condition (i) and DGEDHMS/DDEt cured under condition (iii) had an opaque appearance. Further, birefringent patterns were observed in polarized optical microscopy (POM) images of the samples (Figures 2-3(a) and 2-3(c)).

(a) Network of DGE(C2-MS-C2)/DDEt cured under condition (i)

(b) Network of DGE(C2-MS-C2)/DDEt cured under condition (ii)

(c) Network of DGEDHMS/DDEt cured under condition (iii)

(d) Network of DGEDHMS/DDEt cured under condition (iv)

Figure 2-3. POM photographs of networks of DGE(C2-MS-C2)/DDEt system and DGEDHMS/DDEt system at room temperature.

On the other hand, both resin systems when cured under conditions (ii) and (iv) had a clear appearance and did not exhibit birefringence (Figures 2-3(b) and 2-3(d)). These results suggest that both resin composition systems produce LC networks when they are cured at lower temperatures, that is, under conditions (i) and (iii), and produce Iso networks when they are cured at higher temperatures, that is, under conditions (ii) and (iv).

The XRD patterns of the networks of DGE(C2-MS-C2)/DDEt and DGEDHMS/DDEt indicated that both the cured resins have an LC network containing a smectic-like structure, as reported in a previous paper [16]. The d-spacings calculated from the smectic peaks of DGE(C2-MS-C2)/DDEt and DGEDHMS/DDEt were 19 and 16 Å, respectively. These values were almost half the lengths of the repeating units of the resins, which include one each of the epoxy and curing agent molecules. The lengths, which were determined using Chem3D, were 37 and 32 Å, respectively.

Figure 2-4. Proposed layered structure of DGE(C2-MS-C2) cured with DDEt in the mesophase.

Figure 2-5. Proposed layered structure of DGEDHMS cured with DDEt in the mesophase.

On the basis of these results, we could produce schematic illustrations of the layered structures of DGE(C2-MS-C2)/DDEt (Figure 2-4) and DGEDHMS/DDEt (Figure 2-5). We propose that a layered structure in which both methylstilbene units and diphenylethylene units exist in the same layer is formed as the lengths of the units are approximately the same. Such a layered structure is consistent with the lack of diffraction peaks corresponding to the individual units of the methylstilbene group and diphenylethylene. Regarding the volume fraction of the layered structure, the relatively small peaks noticed in the small-angle region in the XRD patterns of DGE(C2-MS-C2)/DDEt and DGEDHMS/DDEt suggest that the volume fraction of the smectic-like phase in the network was small [16]. Therefore, we propose that these networks are composed of a major phase with a nematic-like structure which include some amount of isotropic phase, and a minor phase with a smectic-like structure. Figure 2-6 shows a schematic illustration of the LC network of DGE(C2-MS-C2)/DDEt. The nematic-like structure, which forms the main phase, is considered to be aggregate of nematic domains. The nematic-like structure might include some amount of isotropic phase between domains. In the nematic domain, the mesogenic units are aligned in one direction, but are not stacked on top of each other in a single domain. On the other hand, the smectic-like structures, which form the minor phase, are dispersed in the nematic-like structure. A polydomain structure would thus be formed because none of the domains exhibits regularity in terms of the alignment direction.

Figure 2-6. Schematic illustration of the LC network formed in the DGE(C2-MS-C2)/DDEt system.

I-2-3-2. Mechanical properties

The results of the tensile tests are reported in the chapter 1, and the summary of the results are shown in Table 2-2. The T_g values of all the examined networks were higher than 100°C (Table 2-2). Thus, it can be surmised that the tensile test was performed when the specimens were in their glassy state. Therefore, it is reasonable to assume that the initial moduli of all the networks are almost the same.

Table 2-2. T_g values and tensile-test results of LCE resins cured with DDEt

Resin system	Structure	T _g	Stress at break	Strain	Fracture energy
DGE(C2-MS-C2)/DDEt	LC	100 [°C]	52 [MPa]	33 [%]	15.8 [MPa]
	Iso	106 [°C]	51 [MPa]	16 [%]	7.3 [MPa]
DGEDHMS/DDEt	LC	160 [°C]	74 [MPa]	17 [%]	9.9 [MPa]
	Iso	170 [°C]	68 [MPa]	10 [%]	4.8 [MPa]

However, there are significant differences in the strains at break and fracture energies of the examined networks; the LC and Iso networks of DGE(C2-MS-C2)/DDEt have higher strains and fracture energies than those of the corresponding networks of DGEDHMS/DDEt. It would be natural to assume that these results are attributable to the flexible unit introduced in the former system. Flexible spacers would increase the mobility of the networks. Furthermore, in both the epoxy resin systems, the networks with the LC-like ordered structure exhibited higher strains and fracture energies than did the Iso networks. In the case of the DGE(C2-MS-C2)/DDEt system, the strain of the LC network is 33% and the fracture energy of the LC network is 15.8 MPa; these values are almost twice as high as those of the Iso network (16% and 7.3 MPa, respectively). The same phenomenon is also observed in the DGEDHMS/DDEt system.

In the case of isotropic system (Figure 2-7(a)), applied stress would be concentrated at some structural defects. Then micro-cracks would generate and propagate easily at a relatively lower strain. In the case of LC system (Figure 2-7(b)), there thought to be numerous amounts of LC domains in the whole matrix. Then their moduli are thought to be different from each other. So it is likely that the applied stress would be concentrated on the boundary regions of the domains, and which results in the uniform dispersion of the stress concentration. This phenomenon would prevent the generation and the propagation of the micro-cracks because the stress concentration on the structural defect would be decreased. Consequently LC system would undergo a higher plastic deformation prior to failure.

Figure 2-7. Schematic illustration for toughening mechanism of LC network.

I-2-3-3. Fracture toughness

Figure 2-8 shows the result of fracture toughness test. It is noted that each of LC and Iso network from DGE(C2-MS-C2)/DDEt system shows much higher crack opening displacement, and then higher elastic-plastic fracture toughness value than corresponding DGEDHMS/DDEt system.

Figure 2-8. Elastic-plastic fracture toughness of DGEDHMS / DDEt and DGE(C2-MS-C2) / DDEt systems.

Furthermore, regardless of whether spacers are introduced or not, LC systems exhibit higher crack opening displacement and higher load, and consequently, LC systems exhibit higher elastic-plastic fracture toughness value than corresponding isotropic systems. This result implied that LC domains would prevent propagation of crack and large plastic deformation would occur at failure.

So, the morphology of the fracture surface was examined (Figure 2-9). Each of LC and Iso network generated from DGE(C2-MS-C2)/DDEt system shows rougher surface than corresponding network from DGEDHMS/DDEt system. Especially, LC network of DGE(C2-MS-C2)/DDEt system exhibits a distinct rough and highly-deformed fracture surface. This result suggests that LC network shows large plastic deformation at failure.

Figure 2-9. Fracture surface after fracture toughness test.

I-2-3-4 Toughening mechanism

Time-resolved WAXD and small-angle X-ray diffraction (SAXD) measurements were performed during the tensile tests to elucidate the toughening mechanism of the LCE resins by observing the motion of the molecular chains in the networks. Figure 2-10 shows the strain-stress curves obtained during the X-ray diffraction measurements. The LC network formed from in DGE(C2-MS-C2) showed exhibited greater toughness than did the LC network of DGEDHMS. The LC network of DGE(C2-MS-C2) also showed a higher strain at break and fracture energy than did the Iso network of DGE(C2-MS-C2). Although the thickness of the specimens and crosshead speed deviate

from those in the ISO 527-2 standard, these results are almost consistent with the results achieved as per the standard, which are shown in Chapter 1.

Figure 2-10. Stress-strain curves of (a) LC network of the DGE(C2-MS-C2)/DDEt system, (b) Iso network of the DGE(C2-MS-C2)/DDEt system, and (c) LC network of the DGEDHMS/DDEt system.

The results of the time-resolved WAXD measurements are discussed because the major mechanical properties of these LC networks would be determined by the nematic-like structure. The WAXD 2D images of the LC networks of DGE(C2-MS-C2) obtained during the tensile test are shown in Figure 2-11. At the beginning of the tensile test, a uniform round image was observed (Figure 2-11(a)), whereas, for a strain of 52%, an increase in the intensity in the direction of $\varphi = 90^\circ$ and a decrease in the intensity in the direction of $\varphi = 180^\circ$ were observed (Figure 2-11(b)). The 2D WAXD data were transferred into 1D data so that they could be evaluated quantitatively; the obtained WAXD data were averaged sector wise according to the predefined direction, φ , and then corrected by transforming the thickness with the increase in the strain on the basis of the assumption that the Poisson's ratio is 0.33 (Figure 2-12). The obtained 1D WAXD patterns are shown in Figure 2-12. An increase in the intensity in the direction of $\varphi = 90^\circ$ and a decrease in the intensity in the direction of $\varphi = 180^\circ$ were observed with increasing strain. This means that the network chains were oriented along the stress

direction during the tensile test.

Figure 2-11. WAXD diffraction images corresponding to (a) 0% and (b) 52% deformation of the LC network of the DGE(C2- MS-C2)/DDEt system.

Figure 2-12. Transforming the WAXD pattern of the LC network of the DGE(C2- MS- C2)/DDEt as a function of the increasing strain for (a) the stress direction $\phi = 180^\circ$ and (b) $\phi = 90^\circ$. The numbers in the figures denote strain values.

In addition, the peak areas under each of the diffraction patterns for $\phi = 180^\circ$ and $\phi = 90^\circ$, which are denoted as A_{180} and A_{90} , respectively, were plotted versus the strain (Figure 2-13(a)). As can be seen from Figure 2-13(a), the increase in A_{90} with the increase in the strain is almost equal to the decrease in A_{180} for the same process. We illustrated supposed behavior of nematic-like structure in the DGE(C2-MS-C2)/DDEt LC network during tensile test in Figure 2-14(a). In the initial stage of the tensile tests, the mesogenic groups are aligned in each of the domains; however, there is no regularity between the domains. Thus, there is no macroscopic orientation.

It is conceivable that the LC network of DGE(C2-MS-C2)/DDEt which has high crosslink density is elongated to large strain of 50% without structural damage if it is considered that the network deforms as follows;

Even though the network is in the glass region, because the boundary region of the domain would be consisted of flexible structures the nematic domains would be able to changes their shape and the direction toward the elongated direction. Besides, the mesogenic group would provide some mobility because the distance between the methylstilbene group and the crosslink point is rather large. Therefore, the methylstilbene groups in the nematic domains could change their directions and become oriented along the elongation direction while maintaining their alignment with the increasing strain. As a result, the network chains became macroscopically oriented (Figure 2-14(a)). Thus LC network of DGE(C2-MS-C2)/DDEt undergoes, during tensile test, dispersion of stress concentration in the macroscopic point of view as illustrated in the Figure 2-7(b). On the other hand, when this resin is considered by a molecular level, orientation behavior has been caused during the tensile test.

The dissipation energy, which is supposed to be generated in the above-described process, is likely responsible for the toughness for the LC network of DGE(C2-MS-C2)/DDEt.

The same analytical scheme was then applied for the Iso network of

DGE(C2-MS-C2)/DDEt and the LC network of DGEDHMS/DDEt (Figure 2-13(b), and Figure 2-13(c), respectively).

Figure 2-13(b) shows that the Iso network of DGE(C2-MS-C2)/DDEt also exhibits behavior similar to that of the LC network of DGE(C2-MS-C2)/DDEt. We defined the parameter S as shown in Eq. (2) in order to be able to compare the orientation behaviors of the molecular chains in the LC and Iso networks. The dependence of S on the deformation ratio for each network is shown in Figure 2-15. Figure 2-15 shows that, as far as the same deformation ratio is concerned, there was only a slight difference in the S values of the LC and Iso networks. It can also be seen that the LC network of DGE(C2-MS-C2)/DDEt exhibits a higher degree of orientation before the break during the tensile test.

$$S = A_{90}/A_{180} \quad (2)$$

Regarding the reasons why the LC network of DGE(C2-MS-C2)/DDEt exhibited a higher degree of orientation, we consider, that is because LC network undergoes dispersion of stress concentration due to the inhomogeneity of the matrix as discussed in the section I-2-3-2.

Figure 2-14. Schematic illustration of the change in the network structure with an increase in the strain: (a) LC network of DGE(C2-MS-C2)/DDEt and (b) LC network of DGEDHMS/DDEt.

In the case of the LC network of DGEDHMS/DDEt LC, it can be seen from Figure 2-13(c) that A_{90} changes slightly compared to those for the LC and Iso networks of DGE(C2-MS-C2)/DDEt. This implies that the LC network of DGEDHMS/DDEt no longer has a sufficiently high mobility for the methylstilbene groups to change their direction towards the elongation direction; this is owing to the lack of spacers. Thus, the network would fail without exhibiting a large-scale deformation.

Figure 2-15. Orientational behavior of the LC and Iso networks of the DGE(C2-MS-C2)/DDEt system during the tensile tests.

I-2-4. CONCLUSIONS

The toughening mechanism of the glass state of the LCE DGE(C2-MS-C2) cured with DDEt was studied through time-resolved WAXD measurements performed during tensile tests. The molecular chains in both the LC networks and the Iso networks of the DGE(C2-MS-C2)/DDEt system showed an orientation towards the stress direction, while the LC network of DGEDHMS/DDEt, which did not contain spacers, was only slightly oriented in this direction. A possible toughening mechanism was proposed. This mechanism assumes that the dissipation energy, which is generated during the process of molecular chain deformation during the tensile tests, is responsible for the toughness of the networks. We also proposed a layered structure, which consists of a mesogenic group and a hardener.

I-2-5. ACKNOWLEDGEMENT

The time-resolved WAXD measurements made during the tensile tests were performed at the second hutch of SPring-8 BL03XU, which has been constructed by the Advanced Soft Material Beamline Consortium (FSBL), with the proposal number 2012B7251, 2013A7201, and 2013B7251.

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Chapter 3

Thermal Behavior of Molecular Chains in a Liquid Crystalline Network with Spacers

I-3-1. INTRODUCTION

In the last two decades, many researchers have reported various liquid crystalline epoxy resins (LCEs) with excellent properties, such as high fracture toughness and thermal conductivity.¹⁻²¹ However, almost all LCEs have relatively high melting points, which inhibits their use for versatile industrial applications.

In the Chapter 1, we synthesized the LCE DGE(C2-MS-C2), which has a clearing temperature of 72 °C, by introducing flexible spacers outside α -methylstilbene moiety. We found that cured DGE(C2-MS-C2) exhibits a higher strain and higher fracture toughness than cured DGEDHMS.²²

In the Chapter 2, the toughening mechanism of the LCE DGE(C2-MS-C2) cured with DDEt was studied through time-resolved wide-angle X-ray diffraction (WAXD) measurements performed during tensile tests. The molecular chains in the LC networks of the DGE(C2-MS-C2)/DDEt system showed greater orientation toward the stress direction than the LC networks of DGEDHMS/DDEt or the isotropic (Iso) networks of DGE(C2-MS-C2)/DDEt. A possible toughening mechanism proposed that the dissipation energy, which is generated by the process of molecular chain deformation during the tensile tests, is responsible for the toughness of the networks.²³

In this chapter, we investigated the thermal behavior of the molecular chains in the LC and Iso networks of DGE(C2-MS-C2).

I-3-2. EXPERIMENTAL

I-3-2-1. Materials

The chemical structures of the materials used in this study are given in Figure 3-1.

Figure 3-1. Chemical structures used in this study

DGE(C2-MS-C2) was synthesized as described in the literature.²² 4,4'-Dihydroxy- α -methylstilbene (DHMS) and the diglycidyl ether of 4,4'-dihydroxy- α -methylstilbene (DGEDHMS) were synthesized according to the procedures described in a patent.²⁰ The transition temperatures of the LCEs are listed in Table 3-1. Diaminodiphenylethane (DDEt) was purchased from Wako Pure Chemical Industries, Ltd. All the reagents were used without further purification.

Table 3-1. Transition temperatures of the LCEs

LCE resin	Heating	Cooling	
	Ti ^a	Tin ^b	Tc ^c
DGE(C2-MS-C2)	72	48	40
DGEDHMS	128	107	53

^aTi denotes isotropization temperature [$^{\circ}\text{C}$].

^bTin denotes isotropic to nematic transition temperature [$^{\circ}\text{C}$].

^cTc denotes nematic to crystal transition temperature [$^{\circ}\text{C}$].

I-3-2-2. Measurements

Dynamic mechanical analysis (DMA) was carried out using an automatic dynamic viscoelastometer (Rheogel DVE-V4, UBM Co. Ltd., Japan) while raising the temperature at a rate of $2^{\circ}\text{C}/\text{min}$. The Tg values were determined from the tops of the peaks of the $\tan \delta$ curves at a frequency of 10.0 Hz. Samples with dimensions of $30 \times 4 \times 0.4$ mm were tested in the tensile mode by applying mechanical vibrations with an amplitude of 25 μm . The optical anisotropy of the cured epoxy resins was observed under cross-polarized light using a polarized optical microscope (BX53, Olympus Corporation, Japan) equipped with a heating stage (Linkam 10084, Linkam Scientific

Instruments, Ltd., UK). X-ray diffraction (XRD) measurements were performed on a small-angle scattering apparatus (Nano-Viewer, Rigaku Co., Japan).

1-3-2-3. Preparation of LC and Iso networks and proposed network structure

A stoichiometric amount of DDEt was used to prepare networks of DGE(C2-MS-C2) or DGEDHMS. LC and Iso networks were obtained for both DGE(C2-MS-C2) and DGEDHMS, as described in Chapter 2. The curing conditions are shown below.

DGE(C2-MS-C2)/DDEt:

- (i) LC network: 90 °C for 3.5 h + 170 °C for 0.3 h
- (ii) Iso network: 170 °C for 1.5 h

DGEDHMS/DDEt:

- (iii) LC network: 110 °C for 2.5 h + 160 °C for 0.5 h
- (iv) Iso network: 160 °C for 3.0 h

For LC DGE(C2-MS-C2)/DDEt, we proposed a network structure that includes the main components of a nematic-like phase and an isotropic phase, as well as minor components of a smectic-like phase (Figure 3-2).

Figure 3-2. LC network structure formed from the DGE(C2-MS-C2)/DDEt system.

I-3-3. RESULTS AND DISCUSSION

I-3-3-1. Dynamic mechanical analysis

The DMA results for the LC and Iso networks of both DGE(C2-MS-C2)/DDEt and DGEDHMS/DDEt are shown in Figure 3-3. Neither the LC or Iso networks of

DGEDHMS/DDEt show distinct decreases in the storage moduli or clear $\tan \delta$ peaks. This result implies that micro-Brownian motion is constrained owing to the oriented and closely packed structure of the methylstilbene moiety, as discussed in previous reports.^{1, 4, 5} On the other hand, both the LC and Iso networks of DGE(C2-MS-C2)/DDEt show distinct decreases in the storage moduli at lower temperatures. This result indicates that the mobility of the network chains was increased by the introduction of flexible spacers because the distance between the methylstilbene group and the crosslinks increased.

Figure 3-3. Dynamic mechanical properties of DGEDHMS / DDEt and DGE(C2-MS-C2) / DDEt systems.

It is also noted that the $\tan \delta$ curves of both the LC and Iso networks of DGE(C2-MS-C2)/DDEt show broad and asymmetric peaks around 100 °C. This observation indicates that these peaks are the multi-complex peaks superimposed with different relaxation mechanisms. Therefore, the frequency dependence of the $\tan \delta$ curves was examined. As shown in Figure 3-4, these peaks became broader with increasing frequency and shoulders were observed on the higher temperature side of the peaks.

(a) LC network of the DGE(C2-MS-C2)/DDEt system (b) Iso network of the DGE(C2-MS-C2)/DDEt system

Figure 3-4. Frequency dependence of the $\tan \delta$ curves of the DGE(C2-MS-C2)/DDEt system.

As we consider these peaks to consist of multiple peaks, we separated the $\tan \delta$ peaks for each frequency into two peaks, denoted here α and α' relaxations, using a Gaussian function (Figure 3-5). Both the $\tan \delta$ peaks of the LC and Iso DGE(C2-MS-C2)/DDEt networks include a larger α peak and a smaller α' peak. However, even the larger α peak is smaller than conventional $\tan \delta$ peaks, such as the α peaks of the network generated from the diglycidyl ether of bisphenol A.¹ This result means that any relaxation of DGE(C2-MS-C2)/DDEt networks is considerably constrained or a local mode motion.

Figure 3-5. Peak separation for the $\tan \delta$ curves of DGE(C2-MS-C2)/DDEt systems using a Gaussian function.

We plotted the logarithmic frequency ($\ln f_{\max}$) against the reciprocal of the peak temperatures for the α and α' relaxations ($T\alpha$ and $T\alpha'$ respectively; Figure 3-6) to evaluate the activation energy value of each peak. The relation between $\log f_{\max}$ and the reciprocal temperature is linear, and the activation energies of the α and α' relaxations estimated using the following equation are shown in Table 3-2.

$$\Delta E_a = -R \left[\frac{d(\ln f)}{d(1/T)} \right]$$

Figure 3-6. Relation between frequency and peak temperature in DGE(C2-MS-C2)/DDEt systems.

Table 3-2. Activation energies of DGE(C2-MS-C2)/DDEt systems.

System	State	Activation energy (kJ/mol)	
		α	α'
DGE(C2-MS-C2) /DDEt	LC	530	250
	Isotropic	520	260

The activation energy values of the α and α' relaxations for the LC network of DGE(C2-MS-C2)/DDEt are 530 and 250 kJ/mol respectively. The activation energy value of the micro-Brownian motion of main chain segments is known to be as large as several hundred kJ/mol, whereas the value associated with local motion is one or two orders of magnitude smaller.^{24, 25} Barral et al.²⁶ reported an activation energy value of 345.5 kJ/mol for the micro-Brownian motion of a diglycidyl ether of bisphenol A

(DGEBA) cured with 1,3-bis(aminomethyl)cyclohexane (1,3-BAC). We evaluated the activation energy value of micro-Brownian motion for DGEBA cured with diaminodiphenylmethane (DDM) as 655 kJ/mol. The activation energy value of the α relaxation for LC DGE(C2-MS-C2)/DDEt (530 kJ/mol) is large enough to be attributed to the motion of main chain segments. With regard to the α' relaxation for LC DGE(C2-MS-C2)/DDEt, the activation energy value (250 kJ/mol) is smaller than that of the α relaxation but much larger than the activation energy value reported for local mode motion, such as *p*-phenylene groups in an epoxy resin network.²⁴ Therefore, we attribute the α' relaxation to the local motion of a relatively large-scale unit. A very similar tendency was obtained for the Iso network of DGE(C2-MS-C2)/DDEt; a larger activation energy was obtained for the α relaxation (520 kJ/mol) than for the α' relaxation (260 kJ/mol). Because the α' relaxation is observed not only in the LC network but also in the Iso network, the relaxation is not concerned with the morphology. Therefore, we attribute the α' relaxation to the local mode motion of the methylstilbene moiety. Usually, local mode motions are observed at temperatures lower than the glass transition temperature; however, the local mode motion of the methylstilbene moiety may occur at a higher temperature than T_g owing to the rigid and planar structure of methylstilbene. It is also likely that the rigid and planar methylstilbene moiety has a much larger activation energy value than flexible units.

I-3-3-2. Thermal behavior of LC networks

We employed XRD measurements and polarized optical microscopy (POM) observations to understand the thermal behavior of the DGE(C2-MS-C2)/DDEt and DGEDHMS/DDEt networks in conjunction with the DMA results.

Figure 3-7(a). XRD patterns of the LC DGE(C2-MS-C2)/DDEt network at various temperatures.

Figure 3-7(b). XRD patterns in the middle angle range for the LC DGE(C2-MS-C2)/DDEt network at various temperatures.

Figure 3-8(a). XRD patterns of the LC DGEDHMS/DDEt network at various temperatures.

Figure 3-8(b). XRD patterns in the middle angle range for the LC DGEDHMS/DDEt network at various temperatures.

I-3-3-3. Thermal behavior of the LC DGE(C2-MS-C2)/DDet network

XRD measurements at various temperatures were employed to understand the thermal behavior of smectic-like structures in the LC DGE(C2-MS-C2)/DDet network (Figure 3-7(a)). The smectic peak of the LC DGE(C2-MS-C2) network did not disappear up to 250 °C, although the peak broadened with increasing temperature (Figure 3-7(b)). This observation indicates that the layered structure is fundamentally maintained above T_g , although the regularity of the structure decreases. It is noted that the d-spacing of the smectic-like structure in DGE(C2-MS-C2) decreased by 0.5 Å from 120 to 250 °C (Figure 3-9(a)). A decrease of the d-spacing with increasing temperature is attributed to a conformational change of the network chains; some of the extended flexible sections that take a trans-zigzag conformation at room temperature change to a gauche conformation at higher temperatures. On the contrary, the halo diffraction of DGE(C2-MS-C2)/DDet shifts toward smaller angles with increasing temperature. The d-spacing calculated from the halo diffraction, which is considered to reflect the distance between neighboring methylstilbene moieties is plotted against temperature (Figure 3-9(b)). The d-spacing of the LC DGE(C2-MS-C2)/DDet network was found to increase by 0.2 Å from 120 to 250 °C. This change is caused by the thermal motion of flexible sections that include crosslinks, which increases the distance between neighboring methylstilbene moieties (Figure 3-10).

Figure 3-9. Changes in the d-spacing of smectic layer and intermolecular distance for the LC DGE(C2-MS-C2)/DDEt network and LC DGEDHMS/DEEt networks.

Figure 3-10. Schematic illustration of the possible structure change of the smectic-like layer in the LC DGE(C2-MS-C2)/DDEt network with the temperature.

POM observations at various temperatures were employed for both the LC and Iso networks of DGE(C2-MS-C2)/DDEt (Figure 3-11). The POM image in a cross Nicole state at room temperature shows a bright image (Figure 3-11(a)), and the image does not drastically change at T_g (Figure 3-11(b)). When the temperature is increased to 200 °C, the POM image seems slightly darker (Figure 3-11(c)). This observation could be

consistent with the DMA results for the LC DGE(C2-MS-C2)/DDEt network, which showed that the storage modulus of LC DGE(C2-MS-C2)/DDEt decreases slightly around 200 °C.

(a) LC network at room temperature

(b) LC network at 130 °C

(c) LC network at 200 °C

(d) Iso network at room temperature

Figure 3-11. POM images of the LC and Iso networks of DGE(C2-MS-C2)/DDEt at room temperature and 200 °C.

Although these results do not completely clarify the behavior of the network chains in the nematic-phase of DGE(C2-MS-C2)/DDEt, we propose that the thermal behavior of the network in the nematic-phase of DGE(C2-MS-C2)/DDEt could be explained as follows: Most of network chains initiate micro-Brownian motion around 100 °C (Figure 3-12(b)). This relaxation behavior is reflected as the α relaxation. At this temperature, local mode motion of the methylstilbene moiety does not occur. When the temperature reaches ~ 106 °C, the methylstilbene moiety initiates local mode motion, such as vibrations along the oriented direction. One example of the local mode motion of the methylstilbene moiety is shown in Figure 3-12(c). However, the LC network chains in the DGE(C2-MS-C2)/DDEt system do not lose orientational conformation because the

birefringence is maintained to $\sim 180^\circ\text{C}$, as observed by POM. Then orientational conformation becomes disordered around 200°C , as observed by the slight decrease in the storage modulus in the DMA and the slightly darkened POM image (Figure 3-12(d)).

Figure 3-12. Schematic illustration of the possible structural changes in the nematic-like phase of the LC DGE(C2-MS-C2)/DDEt network.

I-3-3-4. Thermal behavior of the Iso DGE(C2-MS-C2)/DDEt network

The storage modulus in the rubbery region for the Iso network of DGE(C2-MS-C2)/DDEt is less than that of the LC network of the same system (Figure 3-3). This difference occurs because the Iso network does not have oriented structures, as confirmed by the lack of birefringence in the POM observation (Figure 3-11(d)). In the DMA, the α relaxation has a peak maximum at a lower temperature of the $\tan \delta$ curve than the α' relaxation and a larger activation energy (520 kJ/mol) than the α' relaxation (260 kJ/mol) (Table 2). Based on these results, the thermal behavior of the network chains in the Iso DGE(C2-MS-C2)/DDEt network is explained as follows:

The network initiates micro-Brownian motion around 100°C (Figure 3-13(b)). The temperature of α relaxation of the Iso network of DGE(C2-MS-C2)/DDEt is slightly higher than that of the LC network of the same resin composition. This phenomenon was also observed in a previous report, although the reason was not discussed.⁵ The methylstilbene moiety is located uniformly throughout the Iso network (Figure 3-13(a)), thus the rigid and planar moiety disturbs the initiation of micro-Brownian motion (Figure 3-13(b)). On the contrary, in the LC network of DGE(C2-MS-C2)/DDEt, there would be localized areas of methylstilbene moieties gathers other localized areas of

flexible moieties, such as spacers (Figure 3-12(a)). Because the molecular chains in the flexible area are separated from the methylstilbene moiety, the α relaxation of the LC network of DGE(C2-MS-C2)/DDEt is observed at a relatively lower temperature than that of the Iso network for the same system. When the temperature increases beyond T_α , the methylstilbene moieties initiate local mode motion, as in the LC network of DGE(C2-MS-C2)/DDEt. One example of local mode motion of the methylstilbene moiety is shown in Figure 3-13(c). The LC network does not include oriented molecular chains, so the network shows a lower storage modulus in the rubbery region than the LC network.

Figure 3-13. Schematic illustration of the possible structural changes in the Iso DGE(C2-MS-C2)/DDEt network.

I-3-3-5. Thermal behavior of LC and Iso DGEDHMS/DDEt networks

The LC and Iso networks of DGEDHMS cured with DDEt do not exhibit distinct decreases in the storage modulus and have broader $\tan \delta$ peaks compared with the LC and Iso networks of DGE(C2-MS-C2)/DDEt. These differences occur because the mobility of the molecular chains in DGEDHMS is tightly constrained because of the short distances between methylstilbene moieties and crosslinking points. The intensity of the smectic-like peak in the XRD pattern of DGEDHMS/DDEt is significantly smaller than that of the DGE(C2-MS-C2)/DDEt network because there is little regularity in the layered structure, as discussed in Chapters 1 and 5. On the other hand, the shape of the smectic peak of DGEDHMS/DDEt does not change much with increasing temperature compared with that of DGE(C2-MS-C2)/DDEt because the mobility of the network chains is more constrained owing to the short distances between methylstilbene moieties and crosslinking points.

I-3-4. CONCLUSIONS

The thermal behavior of the molecular chains in the LC and Iso networks of DGE(C2-MS-C2) cured with DDEt was studied at various temperatures using DMA, XRD, and POM. The broad $\tan \delta$ peak in DMA was separated into two peaks: an α relaxation, which is attributed to the micro-Brownian motion of the flexible sections excluding the methylstilbene moiety, and the α' relaxation, which is attributed to the local mode motion of the methylstilbene moiety.

The LC network of DGE(C2-MS-C2)/DDEt was considered to contain both smectic-like structures and nematic-like structures. The smectic-like layer was maintained up to 250 °C, although the layered structure shrank along the molecular chain axis, and the distance between the molecular chains increased with increasing temperature. The nematic-like structure and the Iso network of DGE(C2-MS-C2)/DDEt exhibited both α and α' relaxations, and the nematic-like structure maintained an oriented structure above T_g but became disordered around 200 °C.

I-3-5. REFERENCES

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Chapter 4

Adhesive Properties of Liquid Crystalline Epoxy Resin Having a Low Melting Point by Introducing Flexible Spacers

I-4-1. INTRODUCTION

Epoxy resins are widely used in certain industrial applications, such as for encapsulants for electronic devices, adhesives, coatings, and matrices for composites, because of their excellent physical, chemical, and electrical properties. Recently, a new category of epoxy resins consisting of a mesogenic group as a rigid moiety was proposed.¹⁻⁸ These epoxy resins are usually expressed as liquid crystalline (LC) epoxy resins (LCEs) because they often generate highly ordered networks. Many researchers have reported that LCEs exhibit excellent thermal and mechanical properties, such as a high T_g, high fracture toughness, and increased bonding strength.¹⁻¹¹ These characteristics would have a good potential to result in the expansion and development of new applications of epoxy resin. However, most LC epoxy resin monomers have relatively higher melting points. Thus, their cured resins sometimes form a macroscopically inhomogeneous matrix because the LC epoxy resin monomers react with hardeners before realizing a homogeneous composition. Such behavior sometimes hinders the versatile applicability of resins, especially in the case of industrial use. From this point of view, we have synthesized an LC epoxy resin monomer DGE(C2-MS-C2) with a low melting point by introducing flexible spacers outside the mesogenic group. We then demonstrated that a smectic-like network was generated and the highly ordered network exhibited high fracture toughness with a higher strain in a tensile test.^{12,13} Ochi et al.⁹ demonstrated that the smectic-like network exhibited a higher adhesive strength due to the larger deformability compared with commercial bisphenol-A type epoxy resin. This result led us to investigate the bonding properties of LC and Iso networks generated from DGE(C2-MS-C2) and DGEDHMS. The mechanism affecting the adhesive strength is discussed.

I-4-2. EXPERIMENTAL

I-4-2-1. Materials

A methylstilbene-type epoxy resin was used with ethylene glycol units DGE(C2-MS-C2) ;

DGE(C2-MS-C2) was synthesized as described previously in the literature.¹² 4,4'-Dihydroxy- α -methylstilbene(DHMS) and diglycidylether of 4,4'-dihydroxy- α -methylstilbene (DGEDHMS) ;

were synthesized according to the procedures described in a patent.⁷ The transition temperatures of the LC epoxy resins are summarized in Table 4-1. Diaminodiphenylethane (DDEt),

was purchased from Wako Pure Chemical Industries, Ltd., and was used as a curing agent. These reagents were used without further purification.

Table 4-1. Transition temperatures of the LCE resins

LCE resin	Heating	Cooling	
	Ti ^a	Tin ^b	Tc ^c
DGE(C2-MS-C2)	72	48	40
DGEDHMS	128	107	53

^aTi denotes isotropization temperature [°C].

^bTin denotes isotropic to nematic transition temperature [°C].

^cTc denotes nematic to crystal transition temperature [°C].

I-4-2-2. Measurements

Optical anisotropy of the epoxy resins was observed using an optical microscope (BH-2, Olympus Corporation) under cross-polarized light. Observations under the polarized microscope were performed for a sample film mounted on a hot stage. X-ray diffraction (XRD) was measured using a NANO-Viewer MicroMax-007HF (Rigaku Corporation) with a R-Axis IV imaging plate (Rigaku Corporation). Diffraction patterns were obtained with Cu K α irradiation generated at 40 kV. The T_g values were determined from the peak tops of the peaks of the tan δ curves obtained from dynamic

mechanical analysis (DMA), which was performed using an automatic dynamic viscoelastometer (Rheogel DVE-V4, UBM Co. Ltd., Japan). Samples with dimensions of $30 \times 4 \times 0.4$ mm were tested in tensile mode by applying mechanical vibrations with an amplitude of 25 μ m at a frequency of 10.0 Hz while raising the temperature at a rate of 2°C/min. The network modulus were determined from the storage modulus values at 25°C obtained from DMA.

Tensile tests were performed as per the according to ISO 527-1 and 527-2 standards using a tabletop precision universal tester (Autograph AGS-J, Shimadzu, Japan) equipped with a noncontact digital video extensometer (TRViewX55S, Shimadzu, Japan). The crosshead speed was 2 mm/min. The dumbbell-shaped specimens were prepared according to type 1BB of the ISO 527-2 standard. The strain was determined as the ratio of the change in the distance between the gauge marks versus the original distance. The fracture energies of cured LCE resin systems were evaluated from the area under the stress-strain curves obtained from the tensile tests. The fracture energies of the cured LCE resin systems were evaluated from the area under the stress-strain curves obtained from the tensile tests.

The lap shear strength of the joints was measured using an Instron-type tensile machine (AG-20/50KINIS MO Autograph, Shimadzu, Japan) at a crosshead speed of 50 mm/min according to ASTM 1002-72. Steel plates were used as a substrate. The steel plate was degreased with acetone vapor, abraded with polishing paper (#240), and then washed again with acetone. The T-peel strength of adhesive joints was measured using a tabletop precision universal tester (Autograph AGS-J, Shimadzu, Japan) in accordance with ISO 11339. Extended aluminum plates (ISO 209-1 A1050, 0.2 mm thickness) were used as a substrate. The aluminum plates were degreased with acetone vapor, abraded with polishing paper (#240), and then washed again with acetone..

The surface free energy was estimated from the contact angle measured by the sessile method using the contact angle meter (FACE CA-V, Kyowa Interface Science Co., Ltd., Japan) at room temperature for distilled water and diiodomethane.

The internal stress of the cured epoxy resins was estimated from the deformation of the bimetal composed of the phosphor bronze plate (90 x 30 x 0.1 mm) and the cured epoxy resin coatings (Figure 4-1).^{9, 10} With decreasing temperature, the specimen was bent as a consequence of the difference between the thermal expansion coefficient of the phosphor bronze plate and the cured epoxy resin. The amount of displacement δ was measured with a laser displacement detector (LB-01, Keyence Co., Osaka, Japan). The internal stress σ was calculated from:

$$\rho = \frac{l^2}{8\delta} + \frac{\delta}{2} \approx \frac{l^2}{8\delta}$$

$$\sigma = \frac{Eh_1^3}{12h_2} \frac{2}{\rho H} \left\{ 1 + \frac{1}{3} \left(\frac{h_1}{H} \right)^2 \right\}$$

where E is Young's modulus of the phosphor bronze plate (105 GPa), l is the distance from the fulcrum to a measuring point, h₁ and h₂ are the thicknesses of the metal plate and coatings, respectively, H is the total thickness (h₁ + h₂), δ is the displacement, ρ is the radius of curvature, and σ is the internal stress.

Figure 4-1. Measuring method for the internal stress of epoxy resin coatings.

Stress relaxation behavior was evaluated by using a tensile stage with a hot stage (Linkam 10073A, Linkam Scientific Instruments, Ltd. UK). Samples with dimensions of 1 × 30 × 1 mm were tested in the tensile mode. The samples were clamped with a grip distance of 20 mm, adjusted to prescribed temperatures, and then elongated to the strain of 1-1.4% of the grip distance at the rate of 1000 μm/sec. Then the constraint was maintained constant.

I-4-2-3. Curing condition of epoxy resins to prepare LC or Iso network

DGE(C2-MS-C2) and DGEDHMS were cured with a stoichiometric amount of DDEt. The design concept of the curing conditions for LC and Iso networks was described in previous papers.^{11, 12} The curing conditions, denoted as conditions (i) to (iv), are shown as follows.

DGE(C2-MS-C2) /DDEt:

- (i) LC network: 90°C and 3.5 h + 170°C and 0.3 h
- (ii) Iso network: 170°C and 1.5 h

DGEDHMS /DDEt:

- (iii) LC network: 110°C and 2.5 h + 160°C and 0.5 h

(iv) Iso network: 160°C and 3.0 h

The characterization of the four networks of interest, the LC and Iso networks for DGE(C2-MS-C2)/DDEt and the LC and Iso networks for DGEDHMS /DDEt, was reported in a previous paper^{12, 13} and is summarized in Table 4-2.

Table 4-2. Characterization of the LCE resins cured with DDEt

Resin system	Structure	Tg	Stress at break	Strain	Fracture energy
DGE(C2-MS-C2)/DDEt	LC	100 [°C]	52 [MPa]	33 [%]	15.8 [MPa]
	Iso	106 [°C]	51 [MPa]	16 [%]	7.3 [MPa]
DGEDHMS /DDEt	LC	160 [°C]	74 [MPa]	17 [%]	9.9 [MPa]
	Iso	170 [°C]	68 [MPa]	10 [%]	4.8 [MPa]

I-4-3. RESULTS AND DISCUSSION

I-4-3-1. Evaluation of adhesive strength of LC and Iso networks formed from DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt systems

Lap shear strength results are shown in Figure 4-1. Both the Iso and LC DGE(C2-MS-C2)/DDEt systems showed a larger lap shear strength and larger strain. Consequently, the DGE(C2-MS-C2)/DDEt systems had a larger fracture energy than the DGEDHMS/DDEt systems.

It is often stated that a matrix with a higher modulus would show a higher adhesive strength in the lap shear adhesive strength of joint tests. Because we have found that both DGE(C2-MS-C2)/DDEt networks have a lower modulus at room temperature than that for the corresponding network of DGEDHMS/DDEt systems by DMA (Chapter 3, Figure 3-3), the fact that the DGE(C2-MS-C2)/DDEt networks had a higher lap shear strength implies that the introduction of spacers, which adds an increased plastic deformation of the adhesive layers, effectively improves the adhesive properties. On the other hand, regardless of the introduction of the spacer, the Iso networks exhibited a larger lap shear adhesive strength and strain at break than the corresponding LC networks, although the LC networks showed larger strains and larger fracture energies than the corresponding Iso networks in the tensile tests.^{12, 13}

Figure 4-2. Lap shear strength of DGEDHMS / DDEt and DGE(C2-MS-C2) / DDEt systems.

In Chapter 2, we proposed the toughening mechanism, where the applied stress would uniformly disperse in the boundary regions of the numerous LC domains (Chapter 2, Figure 4-7(b)). The toughening mechanism would function effectively in tensile tests as the applied stress is subjected to the entire test specimen. However for the lap shear test, the applied stress is concentrated at the borderline between the adhesive layer and the adherent on the periphery of the adhesive layer (Figure 4-3(a)). As a result, LC adhesives do not perform at higher adhesive strength in the lap shear tests.

We also employed T-peel strength tests for the networks (Figure 4-4), as summarized in Table 4-3. The T-peel strength value for Iso and LC DGE(C2-MS-C2)/DDEt networks are 38 and 14 N/25mm, respectively, which are both larger values than those of Iso and LC DGEDHMS/DDEt networks, corresponding to 11 and 9.5 N/25mm, respectively. As expected, DGE(C2-MS-C2)/DDEt systems show a larger T-peel strength than both DGEDHMS/DDEt systems. The LC networks of DGEDHMS/DDEt and DGE(C2-MS-C2)/DDEt systems showed T-peel strengths of 9.5 and 14 N/25mm, respectively.

Figure 4-3. Illustrations of adhesive strength tests.

Figure 4-4. T-Peel strength of DGEDHMS/DDEt and DGE(C2-MS-C2)/DDEt systems.

These values were lower than those for the corresponding Iso networks, which

were 11 and 38 N/25mm for DGEDHMS/DDEt and DGE(C2-MS-C2)/DDEt systems, respectively. These results are consistent with the results of lap shear tests. A schematic for the T-peel test is illustrated in Figure 4-3(b). It is considered that the applied stress is concentrated on the borderline of the adhesive layer. Thus, it is likely that the mechanism occurring in the tensile test of the LC network is not operative in the T-peel test. Then, the fact that the Iso network, in particular the Iso network of DGE(C2-MS-C2)/DDEt, showed a much higher adhesive strength than that for the LC networks of the same resin composition implies that some other effect, except for the deformability of the adhesive layer, operates in the LC and Iso systems.

I-4-3-2. The surface free energy of LC and Iso networks formed from DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt systems

We evaluated the surface free energy of adhesives calculated through measurements of the contact angle, as shown in Table 4-3 with a summary of tensile and adhesive tests. The surface of the adhesives in the contact failure section in the T-peel test specimens was used for contact angle measurements. We anticipated that LC systems will exhibit much lower values than Iso systems. However, there is almost no difference among these systems. Furthermore, the surface free energy of the LC network of DGE(C2-MS-C2)/DDEt, 46.4 mJ/m², is higher than that of the Iso network of the same resin system, 41.0 mJ/m². The LC network of DGEDHMS/DDEt also shows a higher free energy than the Iso network of the same resin composition. The LC network of DGEDHMS/DDEt, which exhibits the lowest adhesive strength, has a higher surface free energy than the Iso network of DGE(C2-MS-C2)/DDEt, which has the highest adhesive strength. These results suggest that surface free energy is not the controlling factor of the adhesive properties.

Table 4-3. Tensile and adhesion test results and the effect of network phase on adhesion properties.

System	Phase	Tensile test	Adhesive strength		Surface free energy* (mJ/m ²)
		Strain (%)	Lap shear (MPa)	Peel (N/25mm)	
DGEDHMS / DDEt	LC	17.0	12.5	9.5	45.4
	Iso	10.3	15.3	11	43.9
DGE(C2-MS-C2) / DDEt	LC	33.1	15.9	14	46.4
	Iso	16.3	18.1	38	41.0

* Measured by contact angle measurements using sessile drop method.

I-4-3-3. Internal stress of LC and Iso networks formed from DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt systems

It was reported that terephthalylidene-type and biphenol-type LC epoxy resins show improved bonding properties than isotropic bisphenol A type epoxy resins and that the difference can be attributed to the larger deformability of the LC networks.⁹ However, these reports also found that the LC epoxy resins show a much higher adhesive strength at earlier stages of the curing process. The lap shear strength for LC epoxy resins then declines more considerably than that for the isotropic bisphenol A type networks. Thus, these previous reports attributed the origin of the decreased lap shear strength during the curing process to the increased internal stress generated in the adhesive joints. This implies that internal stresses would considerably affect adhesive properties.

Thus, the internal stress generated in the networks during the cooling stage on the curing process for all systems was examined and shown in Figure 4-5.

Figure 4-5. Internal stress of DGEDHMS / DDEt and DGE(C2-MS-C2) / DDEt systems.

The internal stress of all networks was not remarkable above T_g , then increases with the decrease of the ambient temperature below T_g . Concerning DGE(C2-MS-C2) / DDEt systems, it is noted that the increasing ratio of the internal stress for the Iso network is much lower compared to that for the LC network, especially below 80°C. Consequently, the internal stress of the Iso network, 3.02, is approximately half as much as that of the LC networks, 5.90, at room temperature. The same tendency was observed in the DGEDHMS / DDEt system. The internal stress value of 7.07 MPa observed for the Iso network is considerably lower than the value of 10.6 MPa observed for the LC network at room temperature. This would suggest that internal stresses considerably influence adhesive properties.

Figure 4-6. Relationship between T-peel strength and internal stress.

The T-peel strength values and the lap shear strength values are plotted versus internal stress (Figure 4-6). It was clarified that both of the T-peel strength values and the lap shear strength value increase with decreasing internal stress. Thus, it is natural to consider that the adhesive strength is predominantly affected by the value of the internal stress. The lap shear strength value increases gradually with decreasing internal stress. On the other hand, The T-peel strength value increases remarkably when the internal stress become less than 6 MPa. There might be a threshold value around 6 to 7 MPa of the internal stress for the T-peel strength. These differences might be related to the test scheme. For the lap shear test, applied stress would be subjected to nearly the entire adhesive layer area, although most of the stress would be concentrated on the edges, as discussed in relation to Figure 4-3(a). On the other hand, for the T-peel test, the applied stress would be concentrated on the very forefront part of the edge section of the adhesive layer (Figure 4-3(b)). A large J_{IC} for Iso DGE(C2-MS-C2) /DDEt might contribute to the large T-peel strength in conjunction with the small internal stress.

I-4-3-4. Comparison of calculated value and measured value on the internal stress of LC and Iso networks formed from DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt systems

Ochi et al.⁹ reported that LC networks have a higher internal stress than isotropic bisphenol A type epoxy resins. These authors attributed the higher internal stress of LC epoxy resins to the higher glass transition temperatures in these systems. However, the difference in Tg for LC and Iso networks for the DGE(C2-MS-C2)/DDEt system is only 6°C. The corresponding difference for the DGEDHMS/DDEt system is only 10°C. These differences in Tgs cannot explain the difference in internal stress observed in this work.

We examined the relationship between the experimental internal stress σ_{obsd} and the calculated value σ_{calcd} according to eq. (1),¹⁴

$$\sigma_{\text{calcd}} = \int_{T_g}^{T_g} E(\alpha_r - \alpha_s) dT \quad (1)$$

where E is Young's modulus of the network measured by DMA and α_r and α_s are the linear expansion coefficients of the network and substrate, respectively, measured by TMA. The results are shown in the Figure 4-7. It was found that the experimental internal stress σ_{obsd} agrees well with the calculated value σ_{calcd} for the LC network of both DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt systems. On the other hand, σ_{obsd} of the Iso network for both systems shows a much lower value than the corresponding σ_{calcd} . It has been reported that the experimental internal stress values measured by the same method are consistent with the calculated values obtained from eq. (1) for some epoxy resin systems.^{14, 15} There is no report, as far as we know, that provides information on the relaxation mechanism peculiar to the Iso network, including the mesogenic network. However, it is considered that some unusual mechanism would occur in Iso networks consisting of rigid and flat α -methylstilbene moiety. Concerning LC networks, it is reported that the molecular motion of the network chains is highly suppressed in mesogenic epoxy resin networks.¹⁶ We observed that the LC network of DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt do not lose birefringence at the post curing temperature, even at temperatures as high as 200°C. This means that the α -methylstilbene moiety in the LC network of DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt would be constrained even in the curing process at higher temperatures than Tg. It might be possible that the α -methylstilbene moiety in the LC network cannot undergo a relaxation behavior since the moiety has been constrained in

the curing process.

Figure 4-7. Measured internal stress – calculated internal stress of DGEDHMS / DDEt (Iso, LC) and DGE(C2-MS-C2) / DDEt (Iso, LC) systems.

I-4-3-5. Evaluation of stress relaxation behavior of LC and Iso networks formed from DGE(C2-MS-C2) /DDEt and DGEDHMS /DDEt systems

So we attempted to examine stress relaxation behavior of the networks in order to understand the operating mechanism for the lower internal stress in the Iso network. The tests were mainly employed at approximately 30 °C lower temperature than T_g in the cooling process, because the difference between Iso and LC network on internal stress would become obvious at the temperature range (Figure 4-5). The ratio of remaining stress, σ , over initial stress, σ_0 , was plotted against logarithm of time (Figure 4-8). Figure 4-8(a) shows that Iso network of DGE(C2-MS-C2)/DDEt shows lower remaining stress percent than that of LC network of the same resin composition at the temperatures of T_g-40 to T_g-20 . Iso network of DGEDHMS/DDEt also shows that lower remaining stress percent than that of LC network of DGEDHMS/DDEt at the temperatures of T_g-30 to T_g-20 (Figure 4-8(b)). These suggest that Iso network shows

larger stress relaxation behavior at the temperatures range of Tg-30.

Figure 4-8. Stress relaxation curve of DGE(C2-MS-C2)/DDEt and DGEDHMS/DDEt (LC, Iso) systems.

We measured the density of each network of DGE(C2-MS-C2)/DDEt. The result is 1.19 g/cm^3 for Iso network of DGE(C2-MS-C2)/DDEt and 1.21 g/cm^3 for LC network of DGE(C2-MS-C2)/DDEt respectively. This means that Iso network have larger free volume because the component of Iso and LC network is the same. The behavior of the final curing stage and the cooling process of Iso and LC DGE(C2-MS-C2)/DDEt systems was illustrated in Figure 4-9. For the Iso system, the rigid and large methylstilbene moiety also undergo micro-Brownian motion in the final stage at 170°C , so there should be extremely large free volume around methylstilbene moiety (Figure 4-9(a)). In the cooling system, network chains including methylstilbene moiety stop the micro-Brownian motion and the network chains take thermodynamically the most stable conformation. However there might be still remained the large free volume around methylstilbene moiety because the molecular chains could not fill enough the space around methylstilbene moiety due to the large and rigid moiety. As the result, methylstilbene moiety can shift its position in accordance with the stress generated in the cooling process due to the difference of coefficient of thermal expansion between the network and phosphor bronze plate. This would be origin of the relaxation behavior of the Iso network of DGE(C2-MS-C2)/DDEt system.

On the other hand, for the LC system the motion of the network chains is constrained because the birefringence was not disappeared at 170°C(Figure 4-9(b)). So the free volume in the LC network of DGE(C2-MS-C2)/DDEt would not be so large even at 170°C compared with Iso networks of the same component. Consequently, the free volume in the grassy state is rather small and relaxation behavior was not observed for the LC network of DGE(C2-MS-C2)/DDEt system.

Figure 4-9. Schematic illustration of Iso and LC network for Ep2/DDEt systems.

I-4-4. CONCLUSIONS

LC and Iso epoxy networks with flexible spacers showed higher adhesive strength for lap share and T-peel tests than those without flexible spacers. Furthermore, Iso epoxy networks showed higher adhesive strength than LC networks. There is almost no difference in surface free energy among these systems. On the other hand, Iso network has a lower internal stress generated in the curing and cooling processes compared with LC networks. In particular, the DGE(C2-MS-C2)/DDEt Iso network that performed at highest adhesive strength had the lowest internal stress. The relaxation behavior of network chains in Iso networks was suggested as a origin for the low internal stress and consequently the high adhesive strength of Iso networks.

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Part II

Influence of Spacer Structure on the Physical Properties of Spacer-introduced Liquid Crystalline Epoxy Resins

Chapter 5

Influence of Spacer Structure on the Physical Properties of Cured and Uncured Spacer-introduced Liquid Crystalline Epoxy Resins

II-5-1. INTRODUCTION

It has been reported that liquid crystalline epoxy resins (LCEs) have excellent thermal and mechanical properties, such as a high T_g, high fracture toughness, and increased bonding strength.¹⁻⁸ These characteristics have the potential to expand the use of and create new uses for epoxy resins, which have already been widely used in electronics, composites, adhesives, etc. The origin of these unique properties of LCEs, such as their high fracture toughness, can be attributed to their morphology or network structure. Ortiz et al.² demonstrated that a highly ordered network exhibited a higher deformation in compression tests than the isotropic network of the same composition. Lin et al.⁹ researched the relationship between the curing temperature and the resulting network structure of DGEDHMS. They demonstrated that when DGEDHMS is cured at a lower temperature, a more highly layered structure is formed. From this point of view, we reported that the introduction of flexible spacers into methylstilbene epoxy resins decreases the melting point remarkably and that the epoxy resin could be cured at temperatures lower than 100 °C to provide LC networks with high fracture toughness.¹⁰ Furthermore, it was found that regardless of whether the spacer is introduced or not, LC networks exhibit 1.5 times greater fracture toughness than isotropic (Iso) networks of the same composition. Therefore, in this chapter, we investigated the influence of the spacer structure on the physical properties of cured and uncured spacer-introduced LCEs.

II-5-2. EXPERIMENTAL

II-5-2-1. Materials and sample preparation

The chemical structures of the mesogenic epoxy resins investigated in this study are shown in Figure 5-1. Dihydroxy- α -methylstilbene (DHMS) and the diglycidyl ether of DHMS (DGEDHMS) were synthesized according to the procedures described in a patent.¹² DGE(C2-MS-C2) was synthesized as reported in a previous report.¹⁰

1,3-Diaminopropane (DAP) and propylene carbonate (PC) were purchased from Tokyo Chemical Industry Co., Ltd. Ethylene carbonate (EC), K₂CO₃, *meta*-phenylenediamine (m-PD), tetramethylanmonium chloride (TMAC), 3-bromo-1-propanol, and all other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. These reagents were used without further purification.

Figure 5-1. Chemical structures used in this study

Synthesis of C3-MS-C3

3-Bromo-1-propanol (36.1 g, 0.26 mol), DHMS (22.6 g, 0.1 mol), and DMF (226 g) were placed in a separable flask equipped with a stirrer blade, thermometer, and cooling condenser. The reaction media was heated to 120 °C and then 269 g of K₂CO₃ (1.95 mol) was added. The reaction was carried out under reflux for 1 h. The solid in the reaction mixture was filtered under reduced pressure, and then the filtrate was evaporated. The obtained crude C3-MS-C3 was purified twice by crystallization from a methanol solution. The purified C3-MS-C3 (yield 87%) was confirmed by ¹H NMR (DMSO-*d*₆): 1.83 ppm (4H, m, CH₂ of propylene-oxy), 2.14 ppm (3H, s, CH₃ of α -methylstilbene), 3.52 ppm (4H, m, CH₂ of propylene-oxy), 4.00 ppm (4H, m, CH₂ of propylene-oxy), 4.51 ppm (2H, m, OH), 6.71 ppm (1H, s, CH of α -methylstilbene), 6.85 ppm (4H, m, aromatic), 7.25 ppm (2H, dd, aromatic), 7.42 ppm (2H, dd, aromatic).

Synthesis of DGE(C3-MS-C3)

C3-MS-C3 (20 g, 59 mmol), epichlorohydrin (328 g, 3.54 mol), dimethylsulfoxide (DMSO, 230 g), and TMAC (0.40 g) were added to a reactor and heated at 45 °C with stirring. Finely crushed KOH (33 g, 0.59 mol) was added to the reactor. After 1.5 h, toluene (670 g) and water (400 g) were added to the reaction mixture, then the stirring was stopped and the aqueous layer was discharged. The separated organic layer was washed 5 times with water (250 g) at 70 °C, and rotary evaporated under vacuum for 30 min at 80 °C and then 1 h at 120 °C. The product underwent the same treatment as described above for completion of the glycidylation, and crude DGE(C3-MS-C3) (28 g) was obtained. A 50 wt% DMF solution (8 g) of obtained crude DGE(C3-MS-C3) was poured into water (1200 g) and precipitated. Purified DGE(C3-MS-C3) (2.6 g) was obtained by centrifugal separation accompanied by drying at 120 °C for 2 h in vacuo. The total yield was 71% and mp 25 °C (DSC). According to the GPC, the obtained DGE(C3-MS-C3) contained 6% of components with higher molecular weights, some of which were the result of the step-growth polymerization. ¹H NMR (DMSO): 1.93 ppm (4H, m, CH₂ of propylene-oxy), 2.15 ppm (3H, s, CH₃ of α -methylstilbene), 2.51 ppm (2H, dd, CH₂ of glycidyl), 2.68 ppm (2H, t, CH₂ of glycidyl), 3.07 ppm (2H, m, CH of glycidyl), 3.21 ppm (2H, dd, CH₂ of glycidyl), 3.56 ppm (4H, m, CH₂ of propylene-oxy, CH₂ of glycidyl), 3.68 ppm (2H, dd, CH₂ of glycidyl), 4.00 ppm (4H, t, CH₂ of propylene-oxy), 6.71 ppm (1H, s, CH of α -methylstilbene), 6.90 ppm (4H, dd, aromatic), 7.26 ppm (2H, d, aromatic), 7.43 ppm (2H, d, aromatic).

Synthesis of C2C-MS-C2C

PC (110 g, 1.08 mol) and DHMS (113 g, 0.5 mol) were placed in a separable flask equipped with a stirrer blade, thermometer, and cooling condenser. The reaction media was heated to 120 °C and then 3.0 g of 50 wt% of aqueous K₂CO₃ was added. The reaction was carried out at 170 °C for 2 h. The obtained crude C2C-MS-C2C was purified by crystallization from a mixed solution of DMF (150 g) and methanol (850 g). The purified C2C-MS-C2C (yield 60%) was confirmed by ¹H NMR (DMSO-*d*₆): 1.14 ppm (6H, d, CH₃ of propylene-oxy), 2.17 ppm (3H, s, CH₃ of α -methylstilbene), 3.82–3.94 ppm (6H, m, CH₂ of propylene-oxy, CH of propylene-oxy), 4.86 ppm (2H, m, OH), 6.74 ppm (1H, s, CH of α -methylstilbene), 6.92 ppm (4H, dd, aromatic), 7.29 ppm (2H, d, aromatic), 7.46 ppm (2H, d, aromatic).

Synthesis of DGE(C2C-MS-C2C)

C2C-MS-C2C (100 g, 0.3 mol), epichlorohydrin (325 g, 3.5 mol), and

dimethylsulfoxide (DMSO, 228 g) were added to a reactor and heated at 50 °C with stirring. Sodium hydroxide (60 g, 1.5 mol) dissolved in distilled water (60 g) was added dropwise to the reactor over 30 min. One hour after the completion of the aqueous sodium hydroxide 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 5 times with water (250 g) at 70 °C then rotary evaporated under vacuum for 30 min at 80 °C and then 1 h at 120 °C. The product (141 g) underwent the same treatment as above using 454 g of epichlorohydrin, 318 g of DMSO, and 47.9 g of 50 wt% aqueous NaOH for completion of the glycidylation. DGE(C2C-MS-C2C) was obtained, yielding 127 g (85%). According to the GPC, the obtained DGE(C2C-MS-C2C) contained 4.5% of components with higher molecular weights, some of which were the result of the step-growth polymerization. The obtained DGE(C2C-MS-C2C) was crystallized at 4 °C over a few days, and the melting point by DSC was 24 °C. ¹H NMR (CDCl₃): 1.29 ppm (6H, m, CH₃ of propylene-oxy), 2.23 ppm (3H, s, CH₃ of α -methylstilbene), 2.63 ppm (2H, m, CH₂ of glycidyl), 2.79 ppm (2H, m, CH₂ of glycidyl), 3.16 ppm (2H, m, CH of glycidyl), 3.57–4.01 ppm (10H, m, CH₂ of glycidyl, CH₂ of propylene-oxy, CH of propylene-oxy), 6.70 ppm (1H, s, CH of α -methylstilbene), 6.90 ppm (4H, m, aromatic), 7.25 ppm (2H, m, aromatic), 7.42 ppm (2H, m, aromatic).

II-5-2-2. Measurements

The molecular weight distribution was measured by GPC (Shimadzu CBM-20A, Japan) using a Shimadzu RID-10A reflex indicator and Shodex LF804 $\times$ 2 columns at 40 °C. The ¹H NMR spectra were recorded using a 400 MHz JNM-EX400 spectrometer (JEOL Ltd. Japan) using TMS as the internal standard. DMSO-*d*₆ and CDCl₃ were used as the solvents. Thermal analysis of the synthesized materials was carried out using a DSC (DSC7020, Seiko Instrument, Inc., Japan) with a heating and cooling rate of 5 °C/min. The optical anisotropies of the epoxies were observed using an optical microscope (BH-2, Olympus Corporation, Japan) under cross-polarized light. The polarized microscope was employed to observe sample films mounted on a hot stage. X-ray diffraction (XRD) patterns were measured using a Nano-Viewer MicroMax-007HF (Rigaku Co. Ltd., Japan). Tensile tests were conducted using an Instron-type tensile machine (Autograph, AGS-J Shimadzu, Japan) according to ISO 527-1 and 527-2. The tensile strength and elongation of the epoxy resin systems were measured using a dumb-bell-shaped specimen according to ISO 37 type 3 at a crosshead speed of 2 mm/min. The fracture energies of the cured epoxy resin systems were

evaluated from the area under the stress-strain curves in the tensile test. The T_g values were determined from the peak maxima in the $\tan \delta$ curves obtained from dynamic mechanical analysis (DMA). DMA was performed using an automatic dynamic viscoelastometer (UBM DDV-25FP, A&D Company Ltd., Japan). Samples with dimensions of $30 \times 4 \times 0.4 \text{ mm}^3$ were tested in the tensile mode by applying mechanical vibrations with an amplitude of $25 \text{ }\mu\text{m}$ at a frequency of 10.0 Hz while raising the temperature at a rate of $2 \text{ }^\circ\text{C/min}$.

The time-resolved WAXD measurements made during the tensile tests were performed at the SPring-8 synchrotron radiation facility. The sample specimens were prepared according to type 1BB and then tuned to the appropriate thickness for a load cell of 5 N . The tensile tests were conducted at a crosshead speed of 6 mm/min . The strain was determined from the ratio of the change in the distance between the grips that hold the test specimens and the original distance. The wavelength of the incident X-ray beam was 0.06 nm , and the sample-to-detector distance during the WAXD measurements was 81.6 mm . The accumulation time of each shot and the time interval between the measurements were 500 and 850 ms , respectively. The two-dimensional (2D) WAXD patterns were detected with a flat-panel detector (C9827DK-10, Hamamatsu Photonics, Japan). The obtained WAX patterns were averaged circularly and corrected for the scattering from air and the dark current of the detector.

II-5-2-3. Curing procedure for the epoxy resins

Epoxy resins were cured with a stoichiometric amount of *meta*-phenylenediamine (m-PD). A mixture of the epoxy resin and m-PD was melted to obtain a homogeneous system, and then immediately transferred and cured in an oven. For the purpose of preparing LC networks, the oven temperature was regulated as low as possible within the temperature range where no crystal generation occurs in the reaction system. The curing conditions employed are shown in Table 5-1. When the composition of DGE(C3-MS-C3) and m-PD was cured at temperatures lower than $60 \text{ }^\circ\text{C}$, crystals that could be oligomers of DGE(C3-MS-C3) and m-PD were generated in the cured system in the initial stage. Therefore, this composition was cured at $60 \text{ }^\circ\text{C}$ to avoid crystal generation during the initial stage, and then cured at a lower temperature in the following curing stage.

Table 5-1. Curing conditions for the preparation of LC networks of mesogenic epoxy resins.

System	Curing condition
DGEDHMS / m-PD	110 °C 2.5 h + 160 °C 0.5 h
DGE(C2-MS-C2) / m-PD	80 °C 4 h + 120 °C 1 h
DGE(C3-MS-C3) / m-PD	60 °C 2 h + 50 °C 2 h + 40 °C 20 h + 120 °C 1.0 h

Figure 5-2. DSC thermograms of mesogenic epoxy resin monomers.

II-5-3. RESULTS AND DISCUSSION

II-5-3-1. Characterization of mesogenic epoxy resin monomers

The DSC thermograms of the obtained epoxy resins are shown in Figure 5-2. The endothermic peaks in the heating process, which indicate melting points, were observed

at 128, 72, and 35 °C for DGEDHMS, DGE(C2-MS-C2), and DGE(C3-MS-C3), respectively. These results demonstrate that longer spacers decrease the melting point more remarkably. The melting point of DGE(C2C-MS-C2C) (24 °C) was lower than that of DGE(C3-MS-C3), which suggests that the branching structure of DGE(C2C-MS-C2C) efficiently decreases crystallinity. DGEDHMS and DGE(C2-MS-C2) showed multiple peaks in the DSC cooling process and also showed birefringence in the POM observation, as reported in Chapter 1. On the other hand, DGE(C3-MS-C3) showed one exothermic peak at a lower temperature (11 °C) and DGE(C2C-MS-C2C) showed no exothermic peak in the cooling process. Because both DGE(C3-MS-C3) and DGE(C2C-MS-C2C) did not exhibit birefringence in the POM observation, these two mesogenic epoxy resins do not exhibit liquid crystallinity. (Table 5-2).

Table 5-2. Transition temperatures of the mesogenic epoxy resins

Epoxy resin	Heating	Cooling		
	Ti ^a	Tin ^b	Tnc ^c	Tic ^d
DGEDHMS	128	107	53	-
DGE(C2-MS-C2)	72	48	40	-
DGE(C3-MS-C3)	35	-	-	11
DGE(C2C-MS-C2C)	24	-	-	-

^aTi denotes isotropization temperature [°C].

^bTin denotes isotropic to nematic transition temperature [°C].

^cTnc denotes nematic to crystal transition temperature [°C].

^dTic denotes isotropic to crystal transition temperature [°C].

Figure 5-3. Optical photographs, POM and XRD patterns of the LC networks.

II-5-3-2. Characterization of mesogenic epoxy resins cured with m-PD

The optical photographs, polarized light optical micrographs, and XRD patterns for the networks of DGEDHMS/m-PD, DGE(C2-MS-C2)/m-PD, and DGE(C3-MS-C3)/m-PD are shown in Figure 5-3.

All of these networks are opaque, show birefringence in a cross Nicole state, and show a smectic peak in the XRD patterns. These results suggest that these networks are all LC networks that include smectic-like structures. On the other hand, the DGE(C2C-MS-C2C)/m-PD system did not provide an LC network. The d-spacing of the DGEDHMS/m-PD, DGE(C2-MS-C2)/m-PD, and DGE(C3-MS-C3)/m-PD networks were calculated as 20, 25, and 28 Å, respectively. These values are consistent with the estimated length of the units, which are composed of one epoxy resin and one curing agent (Figure 5-4). It should be noted that DGE(C3-MS-C3)/m-PD provides an LC network including smectic-like structure, although DGE(C3-MS-C3) itself does not exhibit liquid crystallinity. Furthermore, the smectic peak for this system is significantly sharper than that for DGEDHMS/m-PD. These results are ascribed to the effects of lower temperature curing on the DGE(C3-MS-C3) system.

Figure 5-4. Suggested layered structures in the LC networks.

A schematic illustration of LC network formation for a spacer-introduced mesogenic epoxy resin/m-PD system during the curing reaction is shown in Figure 5-5. Regardless of whether the epoxy resin itself is LC, the combined epoxy resin and curing agent results in an isotropic composition during the initial stage of the curing reaction. The molecular chains then align, and a nematic phase is generated as the curing reaction proceeds. In the next stage, some methylstilbene groups are stacked on top of each other, and consequently smectic-like structures are generated. In this stage, the spacers might help the mesogenic groups to adjust their position; therefore, a more ordered structure might be generated compared with a network without spacers. This is especially the case for DGE(C3-MS-C3), which was cured at a lower temperature. At a lower temperature, it might be easier to form stacks of methylstilbene groups owing to the decreased thermal motion of the molecular chains. As a result, a neatly ordered structure would be generated, even though the monomer itself did not exhibit liquid crystallinity.

A suggested LC network structure with spacers is shown in Figure 5-6. Because the intensity of the smectic peak is not predominant in the XRD patterns, the major structure is considered to be a nematic-like structure, and the smectic-like structure is considered to be a minor structure.

Figure 5-5. Schematic illustration of LC network formation during the curing reaction for spacer-introduced mesogenic epoxy resin/ m-PD systems.

Figure 5-6. Suggested structure of LC networks of spacer-introduced mesogenic epoxy resin/m-PD systems.

Figure 5-7. Dynamic mechanical analysis of the LC networks cured with m-PD.

DMA results are shown in Figure 5-7. The DGEDHMS/m-PD network did not show a clear T_g . On the other hand, the DGE(C2-MS-C2)/m-PD and

DGE(C3-MS-C3)/m-PD networks show distinct T_g values at lower temperatures. These results suggest that the introduction of spacers increases the mobility of the network chains remarkably.

Curing system	Stress [MPa]	Strain [%]	Fracture energy [MPa]	T _g [°C]
DGEDHMS/ m-PD	81.5	7	3.9	194
DGE(C2-MS-C2) / m-PD	63.6	19	10.0	84
DGE(C3-MS-C3) / m-PD	45.5	22	7.9	76

Figure 5-8. Stress-strain curves and fracture energies of LC networks cured with m-PD.

II-5-3-3. Mechanical properties and the behavior of molecular chains in the LC networks during tensile tests

The results of the tensile tests are shown in Figure 5-8. The T_g of each network is higher than 70 °C, thus these tensile tests were carried out on the glassy state. The initial modulus of each network is almost the same; however, DGE(C2-MS-C2)/m-PD and DGE(C3-MS-C3)/m-PD showed higher strain and larger fracture energies than DGEDHMS/m-PD, with the DGE(C2-MS-C2) system showing the largest fracture energy. This result is attributed to the effect of the flexible spacers in the DGE(C2-MS-C2) and DGE(C3-MS-C3) systems. Because fracture energy is anticipated to be associated with the behavior of the network chains during the tensile test, time-resolved XRD measurements were conducted during the tensile tests at the SPring-8 synchrotron radiation facility (Figure 5-9(a)). The S-S curve and WAX images for the LC network of DGE(C2-MS-C2) cured with m-PD are shown in Figure 5-9(b).

(a) Scheme for X-ray diffraction experiment (b) S-S curve and WAX images for LC network of DGE(C2-MS-C2) cured with m-PD

Figure 5-9. Scheme of the X-ray diffraction experiment during the tensile test and the results for the LC network of DGE(C2-MS-C2) cured with m-PD.

Initially, a uniform round image was observed. Then, a decrease in intensity in the machine direction ($\phi = 0^\circ$) was observed with increasing strain. The 2D WAXD data were transferred into 1D for quantitative evaluation. The obtained WAXD data were averaged sector-wise according to the predefined direction, ϕ , and then corrected by transforming the thickness with the increase in the strain by assuming that Poisson's ratio is 0.33. The obtained 1D WAXD patterns are shown in Figure 5-10. An increase in the intensity in the direction of $\phi = 90^\circ$ and a decrease in the intensity in the direction of $\phi = 0^\circ$ were observed with increasing strain. Furthermore, the observed decrease and increase along these directions were almost equal, which indicates that the network chains were oriented along the stress direction during the tensile test. Therefore, the parameter S was defined according to Equation (1):

Figure 5-10. Intensity Max profile along $\phi=0^\circ$ and 90° for the LC network of DGE(C2-MS-C2)/m-PD during the tensile test.

$$S = \frac{\text{Im}_{90}}{\text{Im}_0} \quad \text{Im : Intensity Max} \quad \text{Eq. (1)}$$

The same analysis scheme was applied to each network and the obtained S values were plotted against strain (Figure 5-11). The DGEDHMS/m-PD system showed some orientation before failure. This early failure occurs because of the absence of flexible spacers. There is almost no difference among the networks in the elastic deformation region. However, differences become obvious in the plastic deformation region. In this region, DGE(C2-MS-C2)/m-PD shows greater orientation than DGE(C3-MS-C3)/m-PD.

Figure 5-11. Orientational behavior of LC networks during tensile tests.

Based on these analytical results, the behavior of an LC network with spacers in the plastic deformation region during the tensile test is shown in Figure 5-12. We consider the time-resolved WAX measurements to indicate the behavior of the α -methylstilbene groups. The plastic deformation comprises the deformation of the flexible section and the directional change of the mesogenic groups, which reflects the change of the WAX pattern. Oriented α -methylstilbene groups in the nematic-like structure were *not* assumed to change direction while maintaining their position relative to the neighboring group, but were assumed to change direction and change their position relative to the neighboring group along the oriented direction. Such a change in position relative to a neighboring α -methylstilbene group would generate considerable dissipation energy through the friction between the groups. Because the spacer of DGE(C3-MS-C3) is longer than that of DGE(C2-MS-C2), the deformation in the flexible section is larger than that in DGE(C2-MS-C2) for the same strain. On the contrary, the directional change of the mesogenic groups in DGE(C3-MS-C3) is smaller than that in DGE(C2-MS-C2), as suggested in Figure 5-11. The larger dissipation energy of DGE(C2-MS-C2), which is generated by the directional change of the mesogenic groups, is the source of the larger fracture energy of the DGE(C2-MS-C2) network.

Figure 5-12. Suggested behavior of an LC network with spacers in the plastic deformation region during the tensile test.

II-5-4. CONCLUSIONS

The influence of spacer structure on the physical properties of cured and uncured spacer-introduced LCEs was investigated by introducing various spacers around the α -methylstilbene backbone.

When the spacer is longer, the mp of the epoxy resin is lower, which makes it possible to cure the mesogenic epoxy resin at a lower temperature to provide a more sequentially ordered structure. The LC network with spacers consisting of two carbon atoms, DGE(C2-MS-C2), had the largest fracture energy in the tensile test. The behavior of network chains in the tensile test was analyzed. As the result, the plastic deformation of LC networks with spacers was proposed to consist of deformations of the flexible sections and directional changes of the α -methylstilbene groups. The dissipation energy that would be generated by the directional change is the main source of the large fracture energy for the LC network of DGE(C2-MS-C2)/m-PD.

II-5-5. ACKNOWLEDGEMENT

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Chapter 6

Study on the Structural Changes of the Smectic-like Structures in the LC Networks with and without Spacers during Tensile Tests

II-6-1. INTRODUCTION

LC epoxy resins (LCEs) with and without spacers outside methylstilbene moiety (DGEDHMS, DGE(C2-MS-C2), and DGE(C3-MS-C3)) were evaluated in Chapters 1 and 5. We have also found that cured DGE(C2-MS-C2) exhibits a higher fracture toughness than the cured diglycidyl ether of 4,4'-dihydroxy- α -methylstilbene (DGEDHMS), and that LC networks exhibit higher toughness than isotropic (Iso) networks of the same resin composition.^{1,2} Therefore, we investigated the toughening mechanism using time-resolved X-ray diffraction (XRD) measurements. We used wide angle X-ray (WAX) diffraction measurement in Chapters 2 and 5 because a nematic-like structure was considered to be the main structure in the generated LC networks. As a result, orientational behavior was suggested as the main source of the large fracture toughness of the LC networks. We also consider it worthwhile to measure the time-resolved small angle X-ray (SAX) diffraction during the tensile test in order to obtain a comprehensive understanding of the behavior of the smectic-like structures in the network and to design even tougher networks. Shiota et al.³ investigated the stress-strain behavior in the rubbery region for crosslinked smectic-like networks using real-time X-ray diffraction measurements under a static stress, and showed that the smectic-like structures in the rubbery region exhibited a tilting phenomenon but maintained the layered structure under stress. However, there are few reports concerning the behavior of the network chains in the glassy state when an external force is applied. Therefore, in this chapter, the behavior of smectic-like structures in the glassy state was investigated during tensile tests.

II-6-2. EXPERIMENTAL

II-6-2-1. Materials

The chemical structures of the materials used in this study are given in Figure 6-1.

Figure 6-1. Chemical structures of epoxy resins and curing agents used in this study

4,4'-Dihydroxy- α -methylstilbene (DHMS) and the diglycidyl ether of 4,4'-dihydroxy- α -methylstilbene (DGEDHMS) were synthesized according to the procedures described in a patent.⁴ DGE(C2-MS-C2), DGE(C2-MS-C2), and DGE(C2C-MS-C2C) were synthesized as described in the literature.^{1, 2} The transition temperatures of the LC epoxy resins are listed in Table 6-1. Diaminodiphenylethane (DDEt) and *meta*-phenylenediamine (m-PD) were purchased from Wako Pure Chemical Industries, Ltd. All the reagents were used without further purification.

Table 6-1 Transition temperatures of the mesogenic epoxy resins

LCE resin	Heating	Cooling		
	Ti ^a	Tin ^b	Tnc ^c	Tic ^d
DGEDHMS	128	107	53	-
DGE(C2-MS-C2)	72	48	40	-
DGE(C3-MS-C3)	35	-	-	11

^aTi denotes isotropization temperature [°C].

^bTin denotes isotropic to nematic transition temperature [°C].

^cTnc denotes nematic to crystal transition temperature [°C].

^dTic denotes isotropic to crystal transition temperature [°C].

II-6-2-2. Measurements

The time-resolved SAX measurements made during the tensile tests were performed at the SPring-8 synchrotron radiation facility. The sample specimens were prepared according to type 1BB in ISO 527-2 and then tuned to the appropriate thickness for a load cell of 5 N. The tensile tests were conducted at a crosshead speed of 6 mm/min (Figure 6-2). The strain (λ) was determined from the ratio of the change in the distance between the grips that hold the test specimens (ΔL) and the original distance (L_0).

$$\lambda = \Delta L / L_0 \quad (6-1)$$

Figure 6-2. Scheme of the time-resolved X-ray diffraction measurement during the tensile test.

The wavelength of the incident X-ray beam was 0.06 nm, and the sample-to-detector distance during the SAX measurements was 678 mm. The accumulation time of each shot and the time interval between the measurements were 1000 and 1350 ms, respectively. The two-dimensional (2D) X-ray scattering patterns were detected using an image intensifier with the cooled CCD (II CCD; Hamamatsu Photonics, V7739P + ORCA R2). The obtained SAX patterns were averaged circularly and corrected for the scattering from air and the dark current of the detector. A dumbbell-shaped specimen was placed between the crossheads of the tensile test unit with a load cell. The tensile unit was then mounted on the synchrotron beam line. The 2D data were transformed into one-dimensional (1D) analytical data by integration and averaged in a defined direction using Eq. (6-2):

$$I_{\phi_s < \phi < \phi_e}(2\theta) = \frac{1}{(\phi_e - \phi_s)P} \int_{\phi_s}^{\phi_e} \frac{I(2\theta, \phi)}{\cos^3 2\theta} d\phi \quad (6-2)$$

where ϕ is the angle clockwise from the direction of the meridian (Figure 6-2) and θ denotes the Bragg angle. Furthermore, P , which denotes the polarization factor, was assumed to be 1, and ϕ_s and ϕ_e were assumed to be $(\phi + 5)^\circ$ and $(\phi - 5)^\circ$, respectively.

II-6-2-3. Curing procedure for the epoxy resins

DGEDHMS, DGE(C2-MS-C2), and DGE(C3-MS-C3) were cured with stoichiometric amounts of DDEt or m-PD. To prepare the networks, a molten mixture of the LCE and a curing agent was transferred to an oven and cured under predefined conditions. To prepare the LC networks, the oven temperature was kept as low as possible, so that no crystals were formed in the reaction system. When the composition of DGE(C3-MS-C3) and m-PD was cured at a temperature lower than 60 °C, crystals that could be oligomers of DGE(C3-MS-C3) and m-PD were initially generated in the cured system. Therefore, this composition was cured at 60 °C to avoid crystal generation during the initial stage, and then cured at a lower temperature in the following curing stage.

The curing conditions employed were as follows.

DDEt cured system

DGEDHMS/DDEt: 110 °C for 2.5 h + 160 °C for 0.5 h

DGE(C2-MS-C2)/DDEt: 90 °C for 3.5 h + 170 °C for 0.3 h

m-PD cured system

DGEDHMS/m-PD: 110 °C for 2.5 h + 160 °C for 0.5 h

DGE(C2-MS-C2)/m-PD: 80 °C for 4 h + 120 °C for 1 h

DGE(C3-MS-C3)/m-PD: 60 °C for 2 h + 50 °C for 2 h + 40 °C for 20 h + 120 °C for 1.0 h

II-6-2-4. Structure of the LC network

The LC networks generated from the DGEDHMS/DDEt, DGE(C2-MS-C2)/DDEt, DGEDHMS/m-PD, DGE(C2-MS-C2)/m-PD, and DGE(C3-MS-C3)/m-PD systems were analyzed using a dynamic viscoelasticity measuring device, polarized light optical microscopy (POM), and XRD, and then characterized by tensile tests, as discussed in Chapters 2 and 5. All the above LC networks were considered to consist of major nematic-like structures and minor smectic-like structures, as shown in Figure 6-3. Because the d-spacings calculated from the results of the XRD measurement for DGEDHMS/DDEt and DGE(C2-MS-C2)/DDEt were approximately half the length of a repeating unit composed of one epoxy resin and one curing agent, a layered structure in which both methylstilbene units and diphenylethylene units exist in the same layer was suggested for the DGEDHMS/DDEt and DGE(C2-MS-C2)/DDEt systems (Figure 6-3(a)).² On the other hand, a layered structure composed of one unit of epoxy resin and one unit of m-PD was proposed for the DGEDHMS/m-PD, DGE(C2-MS-C2)/m-PD, and DGE(C3-MS-C3)/m-PD systems (Figure 6-3(b), Chapter 5).

Figure 6-3. Schematic illustration of the LC networks with spacers.

II-6-3. RESULTS AND DISCUSSION

II-6-3-1. DDEt cured system

The stress-strain curve and 2D SAX diffraction pattern for the LC network of DGEDHMS cured with DDEt is shown in Figure 6-4. A sharp image was not observed because a neatly layered structure was not generated owing to the absence of spacers, as discussed in previous papers.^{1,2} Although the image was not clear enough to evaluate quantitatively, it suggested that the smectic-like structure did not change remarkably during the tensile test (Figure 6-4). On the other hand, the LC network of DGE(C2-MS-C2) showed yielding and high strain, which is consistent with the evaluation result according to the ISO 527-2 standard^{1,2} (Figure 6-5). A uniform round image was initially observed, and then with increasing strain the image showed a long horizontally elliptic shape; furthermore, the image faded with increasing strain.

Figure 6-4. Time-resolved SAX pattern of the LC network of DGEDHMS cured with DDEt during the tensile test.

Figure 6-5. Time-resolved SAX pattern of the LC network of DGE(C2-MS-C2) cured with DDEt during the tensile test.

Shiota et al.³ reported the results of the deformation experiments for smectic-like networks in the rubbery region, and demonstrated the smectic-like structures initially tilted with respect to the tensile direction showed smectic-C-like structure, whereas the smectic-like structures initially oriented parallel to the stress direction maintained a smectic-A-like structure. However, there is no specific angle that indicates a strong diffraction in the SAX images in Figure 6-4. Besides, an azimuthal scan of the smectic peak of DGE(C2-MS-C2)/DDEt was featureless except for a slightly stronger intensity at $\varphi = 90^\circ$ when the strain was higher than 10% (Figure 6-6). Therefore, we concluded that the smectic layer does not tilt but another specific phenomenon may occur in the LC DGE(C2-MS-C2)/DDEt network.

Figure 6-6. Azimuthal scan for the SAX diffraction of DGE(C2-MS-C2)/DDEt LC network.

Thus, the 2D data for DGE(C2-MS-C2)/DDEt were transformed into 1D data so that they could be evaluated quantitatively. The obtained SAX diffraction data were averaged sector-wise according to the predefined direction, ϕ . The obtained 1D SAX patterns for $\phi = 0^\circ$ and 90° are shown in Figure 6-7.

Figure 6-7. Time-resolved SAX pattern of DGE(C2-MS-C2) cured with DDEt for the direction of (a) $\phi = 0^\circ$ and (b) $\phi = 90^\circ$ during a tensile test.

The intensity maximum (I_m') and peak area (A) of the obtained data were corrected by transforming the thickness with the increase in the strain by assuming that

Poisson's ratio is 0.33 (Scheme 6-1).

Scheme 6-1. Correction scheme of diffraction data by transforming the thickness with the increase in the strain during a tensile test.

The analytical results from the SAX diffraction data are shown in Figure 6-8. Figure 6-8(a) shows the profile of Im for each direction. While an immediate decrease of Im with increasing strain was observed for $\phi = 0^\circ$, Im for $\phi = 90^\circ$ first increased to a strain of 4%, where a shift from the elastic deformation region to the plastic deformation region occurs, then decreased at higher strains. On the other hand, the full width at half maximum (FWHM) for $\phi = 90^\circ$ increased remarkably from a strain 5%. Therefore, the peak area under the $\phi = 0^\circ$ and $\phi = 90^\circ$ diffraction patterns, denoted as A_0 and A_{90} , respectively, were plotted against the strain (Figure 6-8(c)).

Figure 6-8. Analytical results of SAX diffraction patterns of DGE(C2-MS-C2) during the tensile test.

Figure 6-9. Magnified illustration of smectic-like structure.

Figure 6-8(c) shows that A_{90} increases to a strain of 4% then decreases at higher strains, whereas A_0 decreases throughout the tensile test. This result reveals that the smectic-like structure oriented along the tensile direction (Figure 6-9(a)) initially increases then decreases and the smectic-like structure orthogonal to the tensile direction (Figure 6-9(b)) starts to decrease as soon as an external stress was applied.

As a strain of 4% proved a critical point for structural changes of network chains, as discussed above, it should be noted that the network changes its deformation behavior from elastic deformation to plastic deformation at a strain of 4 or 5%. Therefore, we discuss the deformation mechanisms for the regions of strain lower than 4% and higher than 4%, and we refer to these regions as the “elastic deformation region” and “plastic deformation region”, respectively.

In the elastic deformation region, A_{90} increases and A_0 decreases with increasing strain (Figure 6-8(c)). The increase in A_{90} is almost equal to the decrease in A_0 . Therefore, we propose a smectic-like structure oriented along the tensile direction (Figure 6-10). At a strain of 0%, every smectic-like structure disperses randomly, and each smectic-like structure might change its orientation with respect to the tensile direction without causing significant structural changes. However, this behavior would not be consistent with the assumption that the molecular chains surrounding the smectic-like structures are drawn toward the stress direction (Figure 6-10). When the smectic-like structure rotates, as shown in Figure 6-10, the molecular chains constituting the smectic-like structure and the molecular chains outside the smectic-like structure would move in the opposite direction from each other. Because the molecular chains outside and inside the smectic-like structure are connected with each other through covalent bonds on the surface of the layered structure, this hypothesis would be

unlikely.

Figure 6-10. Schematic illustration based on the assumption that the smectic-like structures in DGE(C2-MS-C2)/DDEt rotate in the elastic deformation region.

Thus, the behavior of the molecular chains in the elastic deformation region is explained as follows. It is noted that the d-spacing decreases from an initial value of 18.2 Å for each direction to 18.1 Å for $\varphi = 90^\circ$ at a strain of 4% and then decreases further throughout the tensile test (Figure 6-8(d)). In addition, the 2D SAX image shows a relatively stronger diffraction for $\varphi = 90^\circ$ at strains higher than 30% (Figure 6-5). This result is consistent with the azimuthal scan that shows a slightly stronger peak at $\varphi = 90^\circ$ at a strain of 30% (Figure 6-6). Therefore, it is conceivable that the smectic-like structures would be deformed by shear stress in the elastic deformation region (Figure 6-11). The molecular chains in the smectic-like structure do not change direction but shift along the long axis of the molecular chains, thus the surface of the smectic-like structure would change orientation to the stress direction. In other words, the layered structure would change from a smectic-A-like to a smectic-C-like structure. This hypothesis would account for the increased A_{90} values in the elastic deformation region.

Figure 6-11. Schematic illustration (II) for the structural change of the smectic-like structure in DGE(C2-MS-C2)/DDEt in the elastic deformation region during the tensile test.

In the direction of $\varphi = 0^\circ$, the suggested behavior of the molecular chains in the layered structure in the elastic deformation region is illustrated in Figure 6-12 in conjunction with the behavior in the direction of $\varphi = 0^\circ$ in the plastic deformation region. The initial d-spacing value of 18.2 Å for each direction increases to 18.4 Å for $\varphi = 0^\circ$ at a strain of 4% (Figure 6-8(d)). These changes in the d-spacing could be attributed to conformational change of the flexible units. In Chapter 3 we investigated the thermal behavior of the LC network of DGE(C2-MS-C2)/DDEt and found that the smectic structures have an expanded conformation at room temperature. Smectic-like structures oriented orthogonal to the tensile direction could become immediately disordered because each molecular chain constituting the smectic-like structure is individually strained through the covalent bond because the expanded conformation of the flexible section with expanded conformation does not have a large enough margin to absorb any displacement. This behavior would occur even in the plastic deformation region (Figure 6-12).

Figure 6-12. Structural changes of the smectic-like structures of DGE(C2-MS-C2)/DDEt during the tensile test.

In the plastic deformation region, the layered structure oriented orthogonal to the stress direction becomes considerably disordered, as indicated by the decreased A_{90} values in the plastic deformation region (Figure 6-8(c)). It should be also noted that the d-spacing for $\varphi = 90^\circ$ shows a constant and large decrease from 18.1 Å at a strain of 4% to 16.2 Å at a strain of 40%, whereas the d-spacing for $\varphi = 0^\circ$ reaches a plateau of 19 Å at a strain of 35% (Figure 6-8(d)). In the smectic-like structure oriented along the tensile direction, the flexible section that has previously adopted an expanded conformation would be entangled, to some extent, by compressive stress. However, there might not be sufficient space to receive and secure the entangling flexible units. As a result, the flexible units might become inserted in and expand the hard segments, which contain an α -methylstilbene group and DDEt unit, to disorder the layered structure (Figure 6-12). The layered structure originally oriented orthogonal to the stress direction would be disordered at a significantly lower strain, thus the average d-spacing would become smaller monotonously with increasing strain. On the other hand, layered structures with larger tilting angles to the stress direction would adopt the diffraction angle of $\varphi = 90^\circ$, leading to the increase in FWHM for $\varphi = 90^\circ$ (Figure 6-8(b)).

It is reported that in the deformation experiment carried out in the rubbery region,³ the molecular chains in the layered structure have enough mobility to tilt with respect to the layered plane to maintain the molecular alignment. However, the stress applied in this study was more than 40 MPa in the plastic deformation region, whereas the stress applied in the previous study was 8 MPa. The large stress in the glassy state during the

tensile test resulted in molecular chains in the layered planes that were unable to tilt and maintain the alignment of the molecular chains, which caused catastrophic disintegration of the layered structure.

We believe that disintegration of the layered structure would increase the dissipation energy and contribute to larger fracture energies in the LC DGE(C2-MS-C2)/DDEt network. Therefore, it is expected that a network in which layered structures are the dominant structure would exhibit greater toughness.

II-6-3-2. m-PD cured system

We investigated how the network structure influences the behavior of the layered structures during a tensile test. The stress-strain curve and 2D SAX diffraction pattern for the LC network of DGEDHMS, DGE(C2-MS-C2), and DGE(C3-MS-C3) cured with m-PD are shown in Figures 6-13 – 6-15. The LC network of DGEDHMS/m-PD showed a clearer image than the LC network of DGEDHMS/DDEt. The initial round diffraction image broadened with increasing strain, but the test specimen was broken before the image showed any remarkable change of shape (Figure 6-13).

The initial uniform round image of the LC network of DGE(C2-MS-C2)/m-PD became a long horizontally elliptic shape and the image faded with increasing strain, similar to the behavior observed in the DDEt cured system (Figure 6-13). The image of the LC network of DGE(C3-MS-C3)/m-PD also became a long horizontally elliptic shape as the strain increased; however, the image did not fade so remarkably (Figure 6-14). Although a rather strong diffraction is observed in the direction of $\varphi = 0$ and 90° in 2D image (Figure 6-15), the azimuthal scan employed for the SAX of LC DGE(C2-MS-C2)/m-PD showed that the peak area only become larger in the $\varphi = 90^\circ$ direction (Figure 6-16).

Figure 6-13. Time-resolved SAX pattern of the LC network of DGEDHMS cured with m-PD during the tensile test.

Figure 6-14. Time-resolved SAX pattern of the LC network of DGE(C2-MS-C2) cured with m-PD during the tensile test.

Figure 6-15. Time-resolved SAX pattern of the LC network of DGE(C3-MS-C3) cured with m-PD during the tensile test.

Diffraction data was collected in the q range from 2.0 to 4.0 [$\text{\AA}^{-1}$]

Figure 6-16. Azimuthal scan for the SAX diffraction of DGE(C3-MS-C3)/m-PD LC network.

The 2D images of the LC networks of the DGEDHMS/m-PD, DGE(C2-MS-C2)/m-PD, and DGE(C2-MS-C2)/m-PD systems were transferred to 1D data for each direction ($\phi = 0^\circ$ and 90°) using the same scheme as the DDEt cured system; the profiles of the peak area and d-spacing against the strain are shown in Figures 6-17–6-19. Figure 6-17(a) shows the profile of the peak area for the LC network of DGEDHMS/m-PD. In the elastic deformation region of less than 4% strain, a constant decrease of A_0 and increase of A_{90} were observed with increasing strain. An increase and decrease of the d-spacing for the $\phi = 0^\circ$ and 90° directions, respectively, were observed. The same phenomena were also observed in the LC DGE(C2-MS-C2)/DDEt network (Figure 6-8(c)). Therefore, the behavior discussed for

the LC DGE(C2-MS-C2)/DDEt network in the elastic deformation region would also be expected for DGEDHMS/m-PD in the elastic deformation region.

Figure 6-17. Peak area and d-spacing profile from the SAX diffraction patterns of the LC DGEDHMS/m-PD network during the tensile test.

Figure 6-18. Peak area and d-spacing profile from the SAX diffraction patterns of the LC DGE(C2-MS-C2)/m-PD network during the tensile test.

Figure 6-19. Peak area and d-spacing profile from the SAX diffraction pattern of the LC DGE(C3-MS-C3)/m-PD network during the tensile test.

However, the specimen broke before a significant decrease of A_{90} or d-spacing was observed. This occurred because there are no flexible spacers that could disorder the alignment of the stacked mesogenic groups in higher deformation region in the LC DGE(C2-MS-C2)/DDEt network.

Figure 6-18(a) shows the profile of the peak area for the LC network of DGE(C2-MS-C2)/m-PD. In the elastic deformation region, an increase in A_{90} and decrease in A_0 are observed, similar to the trends observed for the LC DGE(C2-MS-C2)/DDEt network. However, unlike DGE(C2-MS-C2)/DDEt, the A_{90} values of DGE(C2-MS-C2)/m-PD did not decrease significantly in the plastic deformation region, although the d-spacing for $\varphi = 90^\circ$ showed a considerable decrease from 25 Å to 21 Å (Figure 6-18(b)). We consider the layered structure generated in DGE(C2-MS-C2)/m-PD to have a larger margin than that of DGE(C2-MS-C2)/DDEt because the layered structure of DGE(C2-MS-C2)/m-PD has a flexible section composed of two units of spacer, one phenylene moiety, and two units of hydroxyl-propylene units (Figure 6-3(b)). The flexible section in the layered structure of DGE(C2-MS-C2)/m-PD is much longer than that of DGE(C2-MS-C2)/DDEt because the flexible section of DGE(C2-MS-C2)/DDEt is composed of one unit of the spacer and a hydroxyl-propylene unit (Figure 6-3(a)). This phenomena is more remarkable for the LC network of DGE(C3-MS-C3)/m-PD (Figure 6-19). The A_{90} values of DGE(C3-MS-C3)/m-PD increased to a strain of 30%, and then did not decrease significantly before breaking. The suggested structural changes in the layered structure of DGE(C3-MS-C3)/m-PD are illustrated in Figure 6-20. The layered structure oriented along the elongation direction increases by the same mechanism as discussed above for the LC network of the DGE(C2-MS-C2)/DDEt system, i.e., the smectic-like structure tilts at small angle with respect to the tensile direction is deformed by shear stress during the tensile test. For example, in a smectic-like structure that is tilted at 12° , the molecular chains do not change direction but shift along their long axis, thus the direction of the layers in the smectic-like structure changes toward the stress direction. As shown in Figure 6-19(b), the d-spacing at a strain of 10% for $\varphi = 90^\circ$ is 27.4 Å. Provided that the molecular length of the repeating units (28 Å) does not change, the direction of the layers agrees with the tensile direction at a strain of 10% (Figure 6-20). The changes in the smectic-like peaks in the SAX patterns for $\varphi = 0^\circ$ and 90° are shown in Figure 6-21. The intensities of these peaks were not corrected based on the transforming thickness. The $\varphi = 90^\circ$ peak shifted toward larger q vales, which indicates, that the d-spacing of the layered structure along the tensile direction decreased with increasing strain (Figure 6-21(a)). Furthermore, it should be noted that the layered structure with the original q vale almost disappeared at a strain of 20%. Thus, it is likely that the d-spacing of the layered structure oriented along the tensile direction became

smaller as the strain increased. The d-spacing could become somewhat smaller through compression in the orthogonal direction as the strain increases because the layers contain sufficient flexible sections. This would also contribute to the increase of the peak area for $\phi = 90^\circ$. However, at a strain of 35%, a slight decrease of A_{90} was observed. Thus, the smectic-like structure, which was originally oriented to the stress direction might become disordered at a relatively lower strain than the smectic-C-like structure that was generated during the tensile test.

In the elastic deformation region of DGE(C3-MS-C3)/m-PD, A_0 did not decrease unlike in other networks. We believe the DGE(C3-MS-C3)/m-PD layered structure oriented orthogonal to the elongation direction is not immediately disordered (Figure 6-19(a), Figure 6-21(b)) because the molecular chains between the crosslinking points include longer flexible units than those in the other layered structures.

Figure 6-20. Structural changes of the smectic-like structure of DGE(C3-MS-C3)/m-PD during the tensile test.

Figure 6-21. Change in the SAX pattern of the DGE(C3-MS-C3)/m-PD network during the tensile test.

We confirmed whether the characteristic behavior of the smectic-like structures discussed above influenced the WAX patterns. Figure 6-22 shows the azimuthal scan of the WAX diffraction of the DGE(C3-MS-C3)/m-PD LC network. If the discussion above is correct, the peak of the smectic-C-like structure, in which the molecular chains tilt at 28° with respect to the tensile direction, should reflect at 343° at a strain of 40%. However, no peak reflected by the smectic peak during the tensile test was observed. This result indicates that the fraction volume of the smectic-like structure in the LC network generated in this study is not sufficient to be reflected in WAX measurements.

Figure 22. Azimuthal scan for the WAX diffraction of DGE(C3-MS-C3)/m-PDLC network

II-6-4. CONCLUSIONS

The behavior of the smectic-like structures in the glassy state during tensile tests was investigated for networks with and without spacers. Whereas the SAX diffraction patterns of the networks without spacers did not show distinct features before breaking, the SAX diffraction patterns of the spacer-introduced networks indicated a change from the initial sequentially ordered structure to a disordered structure with increasing strain. The smectic-like structures oriented orthogonal to the tensile direction started to decrease when external stress was applied in the elastic deformation region. On the other hand, the smectic-like structures oriented along the tensile direction tended to increase in the elastic deformation region. The smectic-like structures oriented orthogonal to the tensile direction continued to decrease in the plastic deformation region. In the smectic-like structure oriented along the tensile direction, the layered structure consisting of the less flexible section decreased remarkably, whereas the layered structure consisting of the more flexible section was maintained or increased in the plastic deformation region. These phenomena were understood from the aspect of the behavior of the network chains.

II-6-5. ACKNOWLEDGEMENT

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II-6-6. REFERENCES

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CONCLUDING REMARKS

This research was carried out with the following objectives; the synthesis and characterization of liquid crystalline epoxy resin with low melting points, then to understand the thermal and mechanical behavior of the network chains.

Each Chapter is summarized below;

In Part I, the novel liquid crystalline epoxy resin with flexible spacers of carbon number two, DGE(C2-MS-C2), was synthesized and characterized. Then the cured properties of DGE(C2-MS-C2) were investigated.

Chapter 1

A novel liquid crystalline epoxy resin with flexible spacers of carbon number two outside α -methylstilbene moiety, DGE(C2-MS-C2), was synthesized. DGE(C2-MS-C2) has a low melting point of 72°C, which is much lower than the melting point, 128°C, of the diglycidylether of 4,4'-dihydroxy- α -methylstilbene (DGEDHMS).

LC network of DGE(C2-MS-C2)/DDEt had a more sequentially layered structure than LC network of DGEDHMS/DDEt. Both of LC and ISO network of DGE(C2-MS-C2) showed larger fracture energy on a tensile test than corresponding network of DGEDHMS. Furthermore, regardless of whether spacer is introduced or not, LC network showed larger fracture energy than Iso network.

Chapter 2

The behavior of molecular chains of LC and Iso networks during tensile tests in a glass region was understood. It was found that the LC network of DGE(C2-MS-C2)/DDEt was more highly orientated than the isotropic (Iso) network formed from the same resin composition. The dissipation energy, which would be generated during the reorientation process of the network chains in a glass region, is proposed as the source of the high fracture toughness of the DGE(C2-MS-C2)/DDEt network during the tensile test.

Chapter 3

The thermal behavior of molecular chains in the LC and Iso network of DGE(C2-MS-C2)/DDEt system was understood. It was proposed that the local mode motion of the methylstilbene moiety (denoted as α' relaxation) undergoes at slightly higher temperature than T_g which attributed to the micro-Brownian motion of flexible section except for the methylstilbene moiety.

Concerning the LC network of DGE(C2-MS-C2)/DDEt, the consideration was attempted for each of smectic-like structure and nematic-like structure. The smectic-like layer is maintained to 250 °C. It is considered that the nematic-like structure and Iso network of DGE(C2-MS-C2)/DDEt exhibit α and α' relaxation, and the nematic-like structure maintain the oriented structure above T_g but disordered at around 200 °C.

Chapter 4

It was found that the ISO network of DGE(C2-MS-C2)/DDEt performed much higher adhesive strength than the LC network of DGE(C2-MS-C2)/DDEt, LC and ISO network of DGEDHMS/DDEt. It was also understood that low internal stress is the main reason of the high adhesive strength of ISO network of DGE(C2-MS-C2)/DDEt. Relaxation behavior which occurred at around $T_g-30^\circ\text{C}$ in the Iso network of DGE(C2-MS-C2)/DDEt was proposed as the reason of the low internal stress.

In Part II, the influence of spacer structures of flexible spacers outside of mesogenic moieties on the cured and uncured properties of LCE was investigated.

Chapter 5

It was found that as the mesogenic epoxy resins have longer spacers, the MPs of the epoxy resins become lower. Lower MP of the mesogenic epoxy resin makes it possible to cure at lower temperature then provided more sequentially ordered structure.

The behavior of network chain in the tensile test was analyzed by time-resolved WAX. As the result, it was proposed that the plastic deformation of LC network with spacers is composed of deformation of flexible section and the direction change of α -methylstilbene group, and that the dissipation energy which would be generated by the direction change is the main source of the large fracture energy of the LC network of DGE(C2-MS-C2)

Chapter 6

The behaviors of the smectic-like structures in the glassy state during tensile test were investigated for the LC networks with and without spacers.

It was found that the spacer-introduced type networks exhibit characteristic behaviors.

Concerning layered structure orthogonal direction to the tensile direction, the regularity of the layered structure decreases with increasing strain. On the other hand,

concerning layered structure along the tensile direction, the regularity of the layered structure which is consisted of less flexible section increases in the elastic deformation region and then decreases in the plastic deformation region. The regularity of the layered structure which is consisted of considerable amount of flexible sections increases gradually in the plastic deformation region.

These phenomena were understood from the aspect of the behavior of network chains.

In conclusion, the most significant findings were shortly summarized. These provide the novel networks including

- 1) Novel LC epoxy resins with low melting points were cured in the moderate temperature range to provide highly ordered networks.
- 2) The LC network generated from the LC epoxy resins performed though property, and the Iso network generated from the LC epoxy resins performed the large adhesive strength.
- 3) Direction change of the mesogenic moieties in the tensile test provides the large dissipation energies, which contributes to the large fracture toughness.
- 4) Layered structures consisted of less flexible section disordered considerably in the plastic deformation region in the tensile test.

LIST OF PUBLICATIONS

«Dissertations»

Chapter 1

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

H. Yamamoto, A. Fujita, M. Harada, M. Ochi

Mol. Cryst. Liq. Cryst., 2014, 588, 41-50.

Chapter 2

“Toughening Mechanism of Liquid Crystalline Epoxy Resin with Spacers Outside the Mesogenic Group”

H. Yamamoto, N. Sakamoto, A. Fujita, M. Harada, M. Ochi

Mol. Cryst. Liq. Cryst., In Press.

Chapter 4

“Physical and bonding properties of mesogenic epoxy resin with low melting point”

H. Yamamoto, N. Sakamoto, A. Fujita, M. Harada¹, M. Ochi, 2015, 51, *Special*

Issue on WCARP-V, The Journal of the Adhesion Society of Japan, in press.

«Patents»

Japan patents

1) JP 2014-122337

2) JP 2014-127495 (application number)

«Presentation in Symposium»

1) “Synthesis and characterization of liquid crystalline epoxy resin with spacer outside of mesogen unit”

62nd *The Society of Polymer Science, Japan*, Annual Meeting Preprints, p653 (2013)

2) “Synthesis and characterization of low melting point mesogenic epoxy resin”

The 51st Annual Symposium on Adhesion, The Adhesion Society of Japan Preprints,

p49 (2013)

- 3) "Synthesis and characterization of liquid crystalline epoxy resin with spacer outside of mesogen unit"
62nd Symposium on Macromolecules, The Society of Polymer Science, Japan, Preprints, p5285 (2013)
- 4) "Synthesis and characterization of low melting point mesogenic epoxy resin"
63rd The Network Polymer Symposium Japan, Proceeding of the Network Polymer Symposium Japan, p5 (2013)
- 5) "Novel Liquid Crystalline Epoxy Resin with Low Clearing Temperature"
37th Annual Meeting Abstracts, Adhesion Society, USA (2014)
- 6) "Influence of spacer structure on physical properties for cured and uncured spacer-introduced liquid crystalline epoxy resin"
63rd The Society of Polymer Science, Japan, Annual Meeting Preprints, p1072 (2014)
- 7) "Synthesis and characterization of low melting point mesogenic epoxy resin"
63rd The Society of Polymer Science, Japan, Annual Meeting Preprints, p1537 (2014)
- 8) "Influence of spacer structure on physical properties for cured and uncured spacer-introduced liquid crystalline epoxy resins"
The 5th World Congress on Adhesion and Related Phenomena (WCARP-V) Abstracts, p198 (2014)
- 9) "Physical and bonding properties of mesogenic epoxy resin with low melting point"
The 5th World Congress on Adhesion and Related Phenomena (WCARP-V) Abstracts, p242 (2014)
- 10) "Thermal and mechanical properties of low melting point mesogenic epoxy resin"
64th The Network Polymer Symposium Japan, Proceeding of the Network Polymer Symposium Japan, p41 (2014)

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Hisanao YAMAMOTO