

Synthesis and Characterization of Nano-Sized Epoxy Oligosiloxanes for Fabrication of Transparent Nano Hybrid Materials

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ABSTRACT: Nano-sized epoxy oligosiloxanes (EO) were prepared by condensation reaction between 3-glycidoxypropyltrimethoxysilane (GPTS) and Diphenylsilandiol (DPSD). Through a composition change of GPTS and DPSD, EO of various structure and sizes were obtained. The molecular structure and size of EO synthesized were investigated by experimental measurements. Regardless of their composition, molecular structure of EO was linear or branch. The amount of species of high molecular weight and their molecular size increased with addition of DPSD. We confirmed that epoxy groups of EO were thermally cured using a thermal initiator and curing agent. Finally, we fabricated transparent epoxy-based hybrimer films by thermal curing of EO resins. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 47: 756–763, 2009

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INTRODUCTION

Inorganic-organic nano hybrid materials (hybrimer) fabricated by sol-gel process have received considerable attention because they can exhibit both inorganic and organic properties.^{1–6} When hybrimer is fabricated, the distribution of inorganic and organic component must be homogeneous to obtain their uniform properties. Therefore, precise control of the component size and distribution in hybrimer is important. From this point of view, the use of nano-sized organo-oligosiloxane which is synthesized by simple sol-gel reaction of organo-silanes as an inorganic structure unit is suitable for the fabrication of hybrimer.^{7–11} Bulk or thick coating films of hybrimer with a homogeneous distribution of inorganic and organic com-

ponents can be fabricated by the polymerization of the organo-oligosiloxanes. Thus, synthesis of the fully condensed organo-oligosiloxane is significant to optimize the characteristics of hybrimer in ideal hybrid nano-structure. Some nano-sized oligosiloxanes have been investigated for the fabrication of hybrimer through the option of proper precursors and the control of process conditions.^{7–12}

Epoxy-based hybrimer using the sol-gel reaction of 3-glycidoxypropyltrimethoxysilane (GPTS) have been widely studied for many applications such as nano-imprinting, protective coatings and waveguide.^{13–17} However, the formation of nano-sized epoxy-oligosiloxane (EO) by the sol-gel reaction has not been investigated into details. The molecular weight and size as well as the shape of EO have an effect on rheological and polymerization behavior of EO, which influence on the mechanical, optical, and electrical properties of the fabricated epoxy-based hybrimer. Thus, to improve and control properties of epoxy-based

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Table 1. Formulation of the Resins of Nano-Sized Epoxy Oligosiloxanes

Samples	GPTS	DPSD	Ba(OH) ₂ ·H ₂ O	Mol % of DPSD
GD50	11.82 g (0.05 mol)	10.81 g (0.05 mol)	0.04 g	50
GD60	11.82 g (0.05 mol)	16.23 g (0.075 mol)	0.05 g	60

hybrimer, it is essential to optimize the reaction condition of the precursors for synthesizing fully condensed EO and to acquire the information on the size and structure of it.

In this article, we synthesized EO by direct condensation reaction of diphenylsilandiol (DPSD) and 3-glycidoxypropyltrimethoxysilane (GPTS) using nonhydrolytic sol-gel reaction. Siloxane formation, structure, distribution and size of species in EO were confirmed by experimental measurements. Also we verified the thermal curing behavior of epoxy groups in EO. Then, transparent epoxy-based hybrimer samples were prepared by thermal curing of EO resins. Finally we measured transmission spectrum of the transparent epoxy-based hybrimer samples.

EXPERIMENTAL

Synthesis of Epoxy Oligosiloxane Resins

Nano-sized epoxy oligosiloxanes (EO) were synthesized using 3-glycidoxypropyltrimethoxysilane (GPTS, 98%, Aldrich) and diphenylsilandiol (DPSD, Gelest) as precursors. Barium hydroxide monohydrate (Ba(OH)₂·H₂O, 98%, Aldrich) was used as a catalyst to promote a condensation reaction between the two precursors. We mixed GPTS with Ba(OH)₂·H₂O at 80 °C under N₂ purging, and added DPSD in the solution during 2 h to avoid self-condensation of DPSD. We kept the solution under same condition for 2 h for an additional reaction. Subsequently, we used vacuum heating to remove the methanol, which was a byproduct of the condensation. The solution was then cooled to room temperature and filtered through a 0.45- μ m diameter Teflon filter to remove Ba(OH)₂·H₂O. Eventually, the resins of EO were obtained in the form of a clear solution. The formulations and notations of the resins of EO in this article are shown in Table 1.

Characterization of Epoxy Oligosiloxane Resins

To confirm formation of siloxanes in EO, ²⁹Si and ¹H nuclear magnetic resonance (NMR) spectra

were measured from a Bruker FT 500MHz instrument using a sample consisting of 30 vol % of the resin in chloroform-d. Chromium(III) acetylacetonate as a relaxation agent of silicon was added at a concentration of 30 mg L⁻¹. Structure and distribution of EO were measured by Raman spectroscopy and matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-TOF MS). Raman spectra were recorded using a Bruker RFS 100 Raman-spectrometer (Bruker Analytische Messtechnik GmbH, Karlsruhe, D), equipped with an Nd:YAG Laser (1064 nm) as the excitation source and a liquid-nitrogen-cooled, high sensitivity Ge-detector. The spectra were measured in sample holders of glass tube with a laser power of 300 mW (100 scans per spectrum) and a resolution of 2 cm⁻¹. The spectra of matrix assisted laser desorption and ionization-time of flight mass spectroscopy (MALDI-TOF MS) were obtained with a Voyager-DE STR 4700 proteomics analyzer (PerSeptive Biosystems, Framingham, MA) equipped with a nitrogen laser using a wavelength of 337 nm and a pulse width of 3 ns. The sample preparations for MALDI-TOF MS were as follows. The 2,5-dihydroxybenzoic acid (DHB, Aldrich) matrix solution was prepared by dissolving 20 mg in 1 mL of acetone. The matrix and resins of EO were mixed in a 4:1 volume ratio. Solution droplet of the matrix-sample mixture were deposited on the sample plate target and allowed to dry at room temperature. The size of synthesized EO was determined by using small-angle neutron scattering (SANS). Particularly, the nano-size of EO with wide distribution of the molecular weights was characterized from radius of gyration (R_g) quantized by Guinier plot of SANS. Small angle neutron scattering (SANS) experiments were performed in the SANS instrument at the HANARO Reactor at the Korea Atomic Energy Research Institute (KAERI). The experimental set-up included a wavelength of 4.31 Å with a wavelength spread (FWHM) of 12%, and detector-sample distance of 2 m. The scattering vector ranged between 0.25 and 0.4 Å⁻¹. The resins were diluted to 10 wt % concentrations in acetone-d₆ to obtain good contrast between the resins

and the solvent. Differential scanning calorimetry (DSC, NETZSCH) measurements were performed under nitrogen atmosphere at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ to confirm thermal curing behavior of epoxy groups in EO.

Fabrication and Characterization of Transparent Epoxy-Based Hybrimer Films

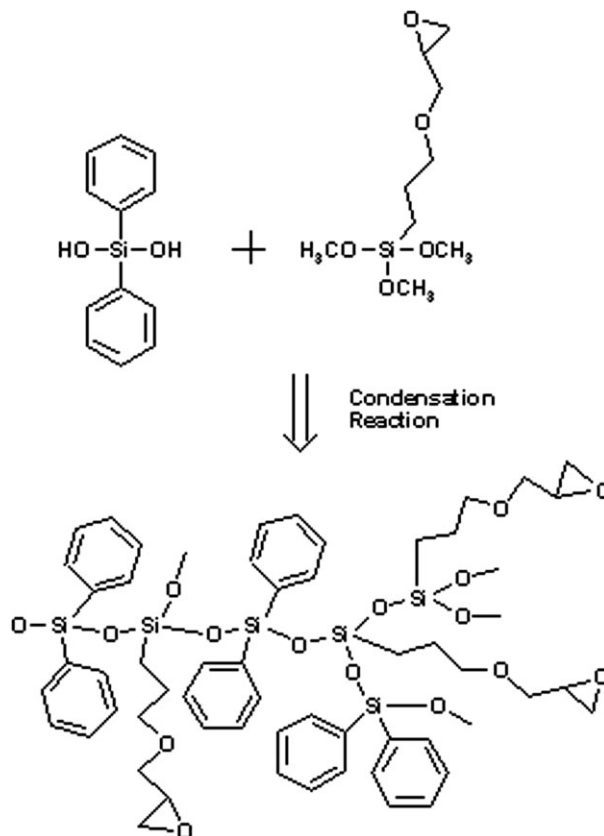
Transparent epoxy-based hybrimer films was prepared from EO resins, curing agent and catalyst. Methyl hexa-hydrophthalic anhydride (MHHPA, Aldrich) was added to EO as a curing agent to EO. The ratio between epoxys in EO and anhydride was 1:1. Benzyltrimethylammonium chloride (BDMA, 98%, Aldrich) was mixed as a catalyst. The amount of BDMA was fixed at 1 mol % in anhydride. Then EO resins, MHHPA and catalyst were mixed for 3 h at room temperature. The mixed resins were de-gased under vacuum condition to remove oxygen. Through these procedures, we obtained homogeneous and thermally curable EO resins. These resins were bar-coated on a quartz substrate. And then they were thermally cured at $175\text{ }^{\circ}\text{C}$ for 12 h under N_2 condition. Heating rate was $5\text{ }^{\circ}\text{C min}^{-1}$. After these procedures, we obtained the transparent epoxy-based hybrimer films. The transmission spectrum of transparent epoxy-based hybrimer films prepared by thermal curing of EO resins was obtained in the wavelength between 300 and 800 nm using an ultraviolet-visible-near infrared (UV/VIS/NIR) spectrophotometer (Shimadzu, UV3101PC).

RESULTS AND DISCUSSION

Formation of Epoxy Oligosiloxanes

DPSD and GPTS were used as precursors for EO. Siloxane bond of EO can be formed by a condensation reaction between silanol groups of DPSD and methoxy groups of GPTS. The condensation reaction is completed by the reaction of silanol groups in EO with methanols. This reaction scheme is depicted in Scheme 1.

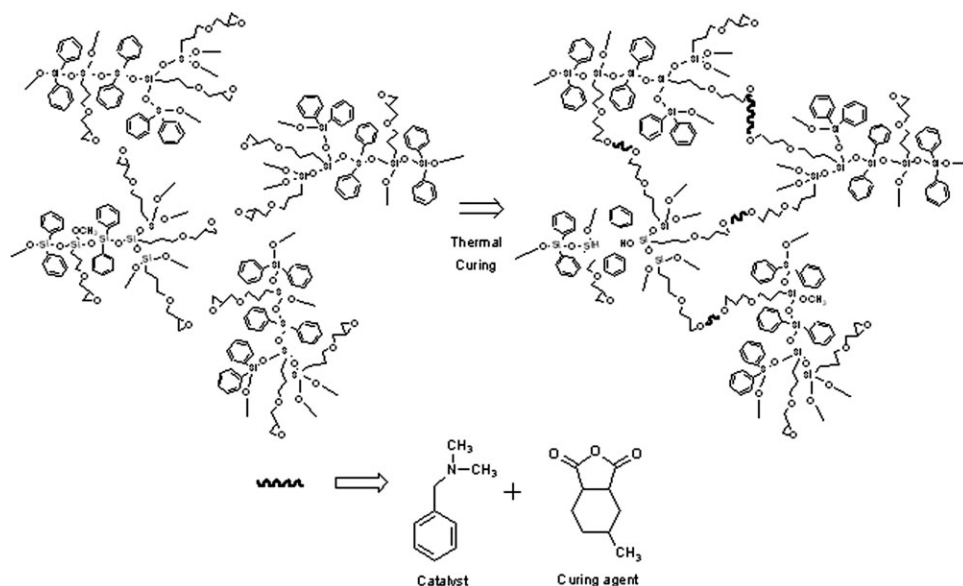
GPTS owns a polymerizable epoxy group. Generally, the epoxy ring opening is easily occurred under basic catalyst over $60\text{ }^{\circ}\text{C}$. However, the use of $\text{Ba}(\text{OH})_2\cdot\text{H}_2\text{O}$ as a basic catalyst and process temperature of $80\text{ }^{\circ}\text{C}$ had no effect on epoxy ring opening in this experiment. Due to the preservation of epoxy ring, hybrimer can be fabricated by cross-linking of thermally curable EO resins. In



Scheme 1. Synthesis of nano-sized epoxy oligosiloxane from GPTS and DPSD.

general, Lewis bases such as BDMA are used as anhydride accelerators. BDMA opens anhydride rings to form internal salts which then act as initiators of cure. The carboxylate ions generated by BDMA react with epoxy group of EO to make alkoxide esters. The resulting alkoxide esters react with further anhydride to form carboxylate anion function esters. Also these react with further epoxy group of EO. Finally, this alternating sequence leads to the formation of a polyester.¹⁸ Scheme 2 illustrates the expected structures and schematic synthetic route of thermally curable inorganic-organic hybrid materials from epoxy oligosiloxanes.

The formation of EO resins can be confirmed by ^{29}Si -NMR spectroscopy (Fig. 1a). D^n and T^n are the notation of Si from DPSD and GPTS, respectively. The superscript, n, represents the number of siloxane bonds of the Si atoms. A small amount of D^0 from diphenyldimethoxysilane (-29 ppm) produced by the reaction between DPSD and methanol remained in GD50, whereas the D^0 from diphenyldimethoxysilane (-29 ppm) did not



Scheme 2. Fabrication of thermally curable inorganic-organic hybrid materials using nano-sized epoxy oligosiloxanes.

exist in GD60. Regardless of their compositions, the D^0 peaks (-34 ppm) from unreacted DPSD were not shown. This indicates that the condensation reaction is completed and EO resins are successfully synthesized. Due to the increased amount of incorporated DPSD, the D^0 species of GD60 were completely removed and the T^1 species (-49 to -51 ppm) of GD60 were dramatically decreased. This is because the number of silanol groups of DPSD that can be reacted with methoxy groups of GPTS is increased. However, the D^1 (-36 to -38 ppm), T^1 and T^2 (-57 to -61 ppm) species in the resin of GD60 were still in existence due to the steric effect of phenyl group in DPSD and epoxy group in GPTS, even though the number of silanol group of DPSD was increased.^{7,19–21}

The degree of condensation (DOC) of GD50 and GD60 can be calculated using the following equation.²²

$$\text{DOC} = \frac{D^1 + 2D^2 + T^1 + 2T^2 + 3T^3}{2(D^0 + D^1 + D^2) + 3(T^0 + T^1 + T^2 + T^3)} \times 100$$

DOC increases from 73 to 90% with a change of DPSD contents. As a result of ^{29}Si -NMR spectroscopy, it is found that highly condensed EO with 90% of DOC could be obtained.

^1H -NMR spectra was measured to verify the preservation of the epoxy ring during the condensation reaction. Figure 1b shows ^1H -NMR spectra

of EO resins according to their compositions. The chemical shift of the H atoms at C atom directly bonded to the Si atom is 0.5 ppm. Also, the chemical shifts of epoxy ring are 2.5 and 2.7 ppm. The cleavage of the epoxy ring can be confirmed by comparison between the peak area of 0.5 ppm and the sum of peak area of 2.5 and 2.7 ppm since the same number of H atoms is involved in the two cases. There is no difference in the areas of the peaks for any of the compositions. It is implied that the EO were successfully synthesized without the cleavage of the epoxy rings.

Molecular Weight and Molecular Structure of Epoxy Oligosiloxane

We confirmed the structure of EO in the resin using Raman spectroscopy and MALDI-TOF mass spectroscopy. In Figure 2, Raman spectroscopy is represented according to the composition of the resins. All spectra were normalized by the intensity of the peak from the phenyl group at 1000 cm^{-1} . Hexaphenylcyclotrisiloxane (HPCTS, Aldrich) was used as a reference. There are no bands in any of the spectra that indicates the formation of cyclic siloxane rings or cage structures.^{23–25}

To support the result of Raman spectroscopy, we measured MALDI-TOF mass spectroscopy and assigned each peak for MALDI-TOF mass spectra to calculated molecular weights from two precursors (Fig. 3). The calculation of molecular weights

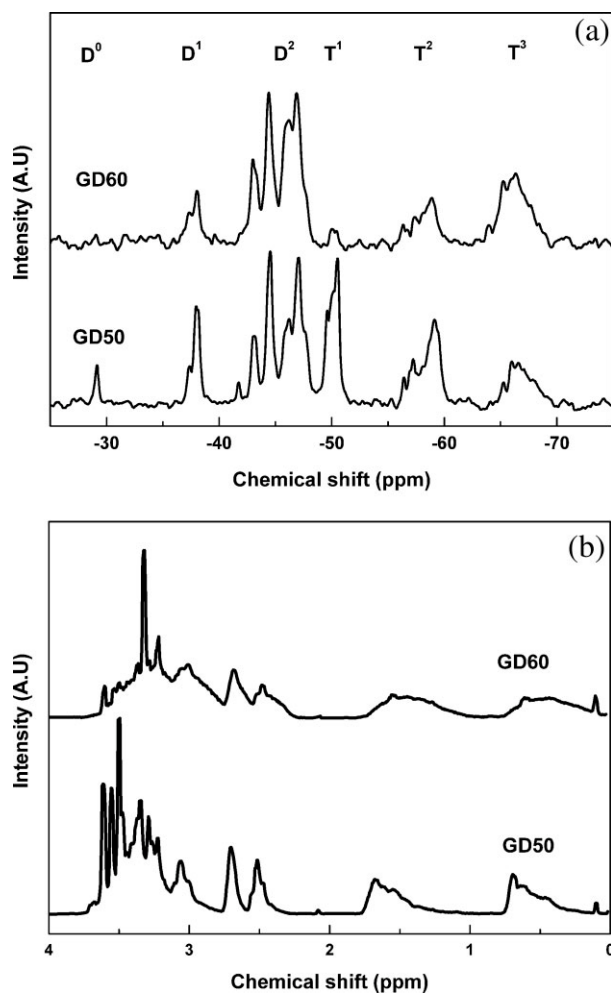


Figure 1. (a) ^{29}Si -NMR spectra of nano-sized epoxy oligosiloxane resins (b) ^1H -NMR spectra of nano-sized epoxy oligosiloxane resins according to their compositions.

was performed considering the structure of EO confirmed Raman spectroscopy.

The calculated molecular weights and the practical molecular weights of each peak from MALDI-TOF mass spectroscopy were found to be consistent (Table 2). Depending on Raman spectroscopy and MALDI-TOF mass spectroscopy, we verified that the structures of EO are linear or branch.

We calculated each peak area of MALDI-TOF mass spectra to find out main molecular species of EO (Fig. 4). Molecular species in GD50 were composed of 10 species from trimers to dodecamers, and four species from trimers to hexamers in GD50 had a majority. In the case of GD60, their molecular species consisted of 12 species from trimers to tetradecamers. Also, four species from

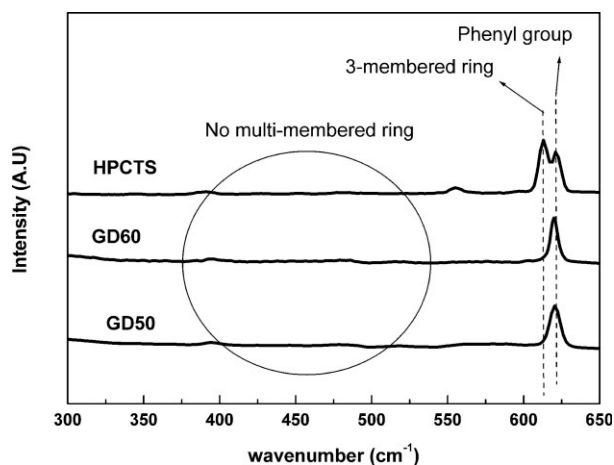


Figure 2. Raman spectra of nano-sized epoxy oligosiloxane resins according to their compositions. HPCTS (3-membered ring) was used as a reference substance for cyclic ring structured oligosiloxanes.

tetramers to heptamers were found to be the main molecular structures. With these results, it was confirmed that the increased amount of incorporated DPSD leads the formation of molecular species with high molecular weights.

Radius of Gyration (R_g) and Molecular Sizes of Epoxy Oligosiloxane

The radius of gyration (R_g) and molecular size of EO can be measured experimentally by SANS

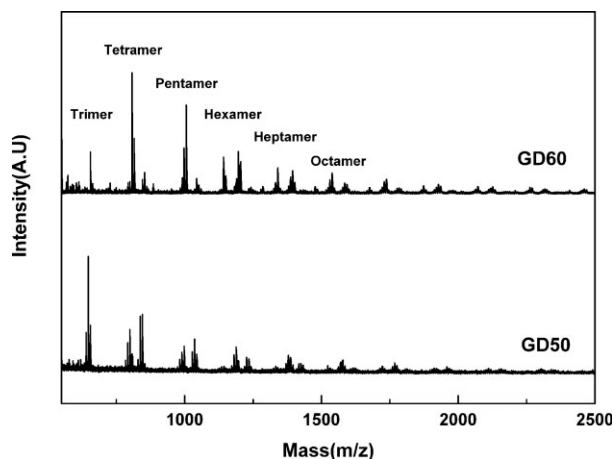


Figure 3. MALDI-TOF mass spectra of nano-sized epoxy oligosiloxane resins according to their compositions. Peaks corresponding to trimer, tetramer, pentamer, hexamer, heptamer, and octamer are represented.

Table 2. Comparisons Between the Practical Molecular Weights from the MALDI-TOF Mass Spectra and Calculated Molecular Weights from Molecular Weights of GPTS and DPSD

	Trimer	Tetramer	Pentamer	Hexamer	Heptamer	Octamer
Calculated m/z	616–640	806–838	996–1036	1186–1234	1377–1433	1567–1631
Practical m/z	639–666	791–869	981–1063	1181–1253	1379–1436	1576–1635

which is a very useful technique to characterize nano-sized materials.

The scattering intensity ($I(Q)$) is represented by the following equation according to the Guinier Law.²⁶

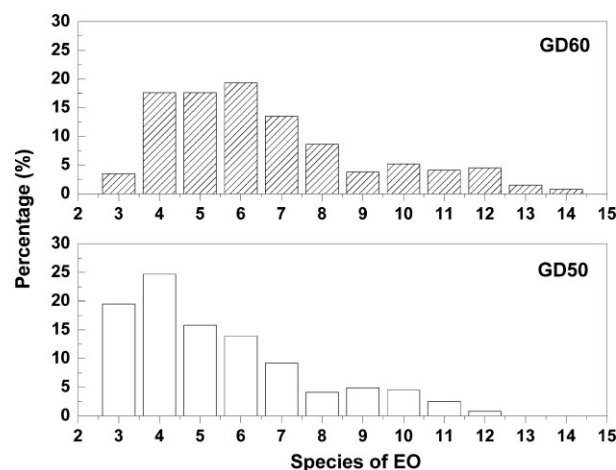
$$I(Q) = \rho_0^2 v^2 \exp\left(-\frac{1}{3} Q^2 R_g^2\right)$$

$I(Q)$ is the scattering intensity, Q is the scattering vector, ρ_0 is the scattering length density of the resin, v is the molar volume of the resin, and R_g is the radius of gyration of the resin.

The R_g of GD50 and GD60 were calculated by the following equation from Guinier plots (scattered intensity ($I(Q)$) vs. Q^2) in the Guinier region ($0.1 < R_g \times Q < 1$).²⁶

$$\ln(I(Q)) = A - \frac{1}{3} Q^2 R_g^2$$

The results of SANS are shown in Figure 5. Figure 5a represents an experimental SANS data of the resins. Figure 5b shows Guinier plots from Figure 5a. Figure 5b represents that the increase of DPSD contents in the resin negatively increases the gradient of the Guinier plots. It


Figure 4. Portion of molecular species in nano-sized epoxy oligosiloxane resins according to their compositions.

means that the molecular size of EO in the resin becomes larger.

The calculation of the real molecular size was performed by two equations according to their shapes.²⁶

$$\text{Sphere shape } R_g = \sqrt{\frac{3}{5}} R_s$$

$$\text{Rod like shape } R_g = \frac{1}{\sqrt{12}} R_T$$

R_s is the radius of the spherical resin, R_T is the length of the thin rod-like resin, and R_g is the

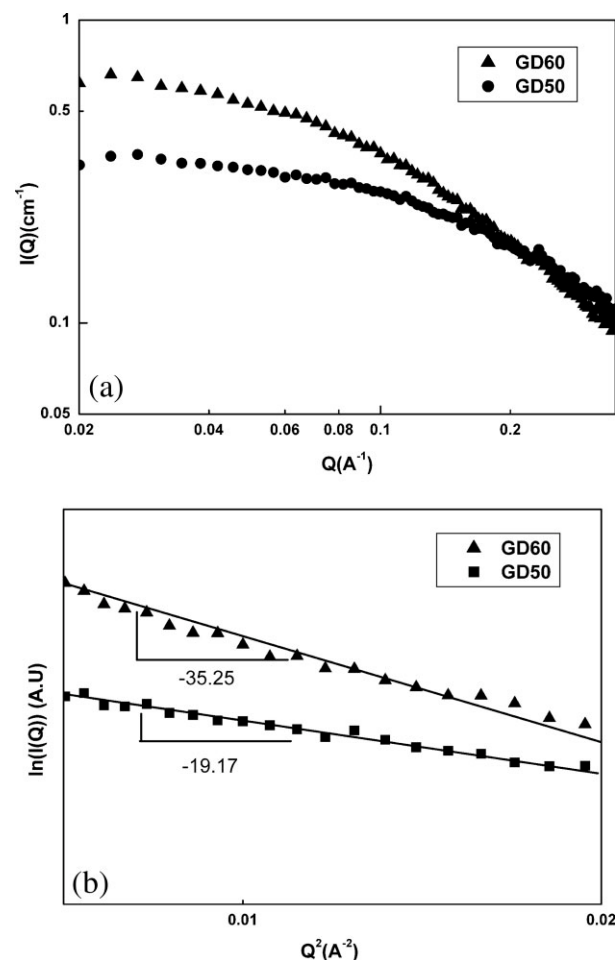

Figure 5. The results of SANS experiment of nano-sized epoxy oligosiloxane of varying compositions (a) experimental SANS data (b) Guinier plots ($\ln(I(Q))$) vs. Q^2) of SANS data.

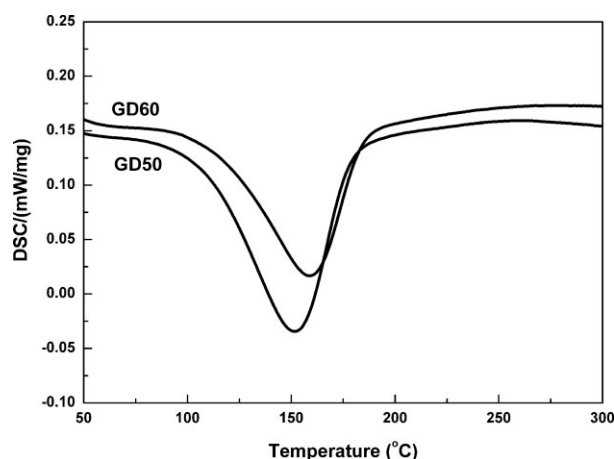
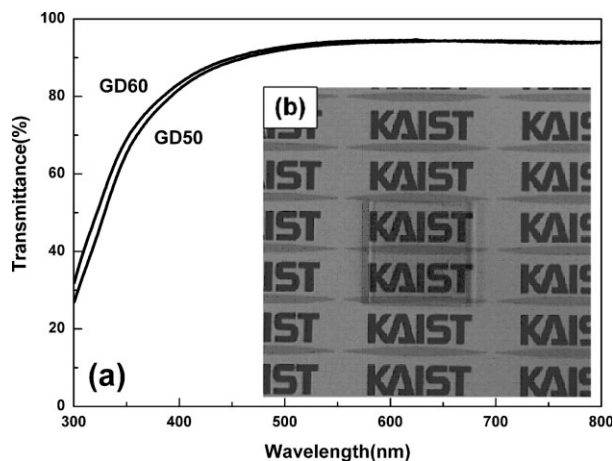
Table 3. The Radius of Gyration (R_g), Diameter of Sphere Shape ($2R_s$) and Length of Rod-Like Shape (R_T) from SANS

Samples	R_g	$2R_s$	R_T
GD50	0.76 nm	1.96 nm	2.63 nm
GD60	1.03 nm	2.66 nm	3.56 nm

radius of gyration. The calculated $2R_s$, R_T , and R_g are summarized in Table 3. The structures of EO in the resin are linear or branch and the molecular sizes of a sphere shape are smaller than that of a rod like shape. Therefore, real molecular sizes were expected to be between $2R_s$ and R_T .

Curing Behavior of Epoxy Oligosiloxane

MHHPA and BDMA used in our experiment make the epoxy curing through formation of polyester.¹⁸ The thermal curing of epoxy groups in the resins was confirmed by DSC for fabrication of homogeneous thermally curable inorganic-organic hybrid material. We observed the cure exothermic peak of GD50 between 110 and 179 °C with the peak maxima at 152 °C. In the case of GD60, the cure exothermic peak was shown between 115 and 185 °C with the peak maxima at 159 °C (Fig. 6). Exothermic energy of GD50 and GD60 for the thermal curing was -106.5 and -85.7 J g⁻¹, respectively. The exothermic energy of GD50 is higher than that of GD60 for the thermal curing because more epoxy groups per unit mass in GD50 resin existed. Through these DSC curves,

**Figure 6.** DSC of nano-sized epoxy oligosiloxane resins depending on their compositions.**Figure 7.** (a) UV-Vis spectra of transparent epoxy-based hybrimer films from GD50 and GD60 (b) transparent epoxy-based hybrimer films on quartz substrate.

curing behaviors of EO in GD50 and GD60 are confirmed.

Optical Transmittance of Transparent Epoxy-Based Hybrimer Films

Optical transmission spectra were measured to confirm the possibility of optical application such as LED encapsulant. Figure 7 shows the optical transmission spectra and photograph of transparent epoxy-based hybrimer films prepared by bar coating on a quartz substrate. Transparent epoxy-based hybrimer films are colorless. The thickness of transparent epoxy-based hybrimer films were around 400 μ m. They have high transmittance of 90% at 450 nm without reference to compositions of EO.

CONCLUSIONS

The nano-sized epoxy oligosiloxane resins with a various composition were successfully synthesized by a single step condensation reaction from DPSD and GPTS. The epoxy oligosiloxane had mainly linear or branch structure. Due to the increased amount of incorporated DPSD, species of molecular structures with high molecular weights increased. The size of EO was between 2 and 4 nm depending on their compositions, but not on their molecular structures. Also, we confirmed that EO resins have the thermally curable properties. Using the EO resins, transparent epoxy-based hybrimer films with high transmittance at 450 nm were fabricated.

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