

Synthesis and Molecular Structure Analysis of Nano-Sized Methacryl-Grafted Polysiloxane Resin for Fabrication of Nano Hybrid Materials

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ABSTRACT: The molecular structures of methacryl-grafted polysiloxane resins from 3-(trimethoxysilyl)propyl methacrylate (MPTS) and diphenylsilanediol (DPSD) were determined by theoretical computation and experimental measurement. The molecular structures obtained from theoretical computation coincided well with those from experimental measurement, and we found that the structural changes in the resins could be controlled by precursor compositions. While molecular weights and polysiloxane chain lengths of the resins increase with DPSD contents, their molecular sizes do not vary significantly. In the present study, molecular sizes and shapes of the resins with various compositions are hypothesized theoretically and proven experimentally. © 2005 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 43: 827–836, 2005

Keywords: nano hybrid resin; Raman spectroscopy; quantum chemistry; neutron scattering

INTRODUCTION

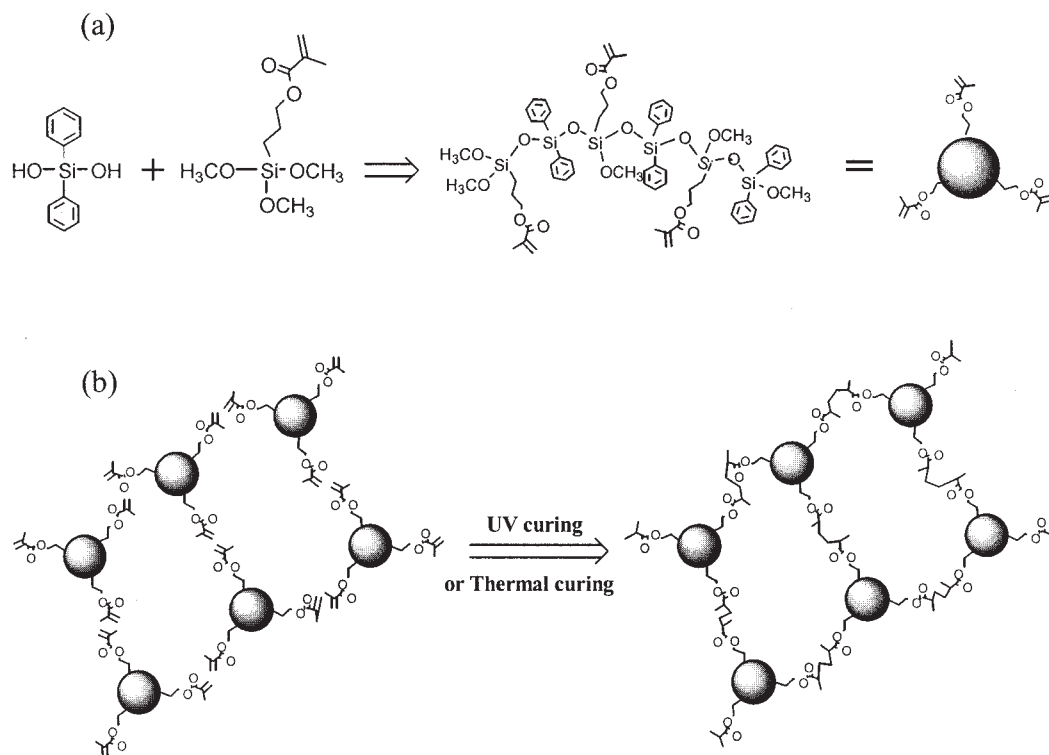
Organic-inorganic nano hybrid materials (OINHM) have received considerable attention in the composite materials field due to their exhibiting both inorganic and organic properties.^{1–9} An important aspect of the fabrication of OINHM is the distribution of the inorganic and organic components homogeneously at the nano-scale, since improvement and reproducibility of OINHM properties can be achieved through precise control of component size and distribution.^{10–18} In this regard, the employment of nano-sized, organically-grafted polysiloxane resin as a structuring

unit is particularly suited to the fabrication of OINHM.^{19–21} Bulk or thick coating films of OINHM with an homogeneous distribution of inorganic and organic components can be easily made from this nano-sized resin since they are obtained by simple polymerization of the functional organic groups in the resin. Thus, by a suitable selection of precursor molecules and optimization of processing parameters, many nano-sized, organically-grafted polysiloxane resins have been synthesized for the fabrication of OINHM.^{5,11–14,19–21}

Diphenylsilanediol (DPSD) contains silanol groups, which can react with alkoxy groups in organo alkoxy silane, and 3-(trimethoxysilyl)propyl methacrylate (MPTS) contains a polymerizable methacryl group. Thus, methacryl-grafted polysiloxane resin can be synthesized via a con-

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Scheme 1. Fabrication of methacryl-polysiloxane nano hybrid materials: (a) synthesis of nano-sized, methacryl-grafted polysiloxane resin from MPTS and DPSD; and (b) fabrication of methacryl-polysiloxane nano hybrid materials from the resin.

condensation reaction between the silanol group of DPSD and the methoxy group of MPTS. Methacryl-polysiloxane nano hybrid materials can then be obtained by a polymerization reaction between methacryl groups in the resin. These reactions are illustrated in Scheme 1.⁵

Recently, these methacryl-polysiloxane nano hybrid materials have been investigated for electronic and optical applications because of their many advantages, including: low optical absorption caused by low silanol contents, low dielectric constants, good adhesion behaviors on various substrates, high dielectric strength, high thermal stability, and excellent photo-patternability.^{5,11–14} However, most of the related research centers on the properties of methacryl-polysiloxane nano hybrid materials, while the molecular structure of methacryl-grafted polysiloxane resin remains unclear. The polysiloxane chain length and the molecular size and shape of the resin can influence rheological and polymerization behavior of the resin, which directly impacts on the mechanical, optical, and electrical properties of the methacryl-polysiloxane nano hybrid materials. In this sense, to improve and control the

properties of methacryl-polysiloxane nano hybrid materials more precisely, it is important to understand the molecular structure of methacryl-grafted polysiloxane resin.

The present study is the first to investigate the molecular structure of the methacryl-grafted polysiloxane resins from DPSD and MPTS. Formations of polysiloxane in the resins were confirmed using ²⁹Si-NMR spectroscopy. Molecular weights and structures of the resins were estimated by gel permeation chromatography (GPC) and Raman spectroscopy. Radius of gyration (R_g) and molecular sizes of the resins were theoretically computed from quantum chemistry using the Gaussian03 package, and experimentally measured by small-angle neutron scattering (SANS). The study also found that the molecular structure of the resin could be controlled by varying the composition ratio of the precursors, DPSD and MPTS.

EXPERIMENTAL

Materials and synthesis

3-(Trimethoxysilyl)Propyl methacrylate (MPTS, Aldrich) and diphenylsilanediol (DPSD, TCI)

Table 1. Formulation of Methacryl-Grafted Polysiloxane Resin

Notation	MPTS	DPSD	Ba(OH) ₂ · H ₂ O	mol % of DPSD
MD 33	18.4g	8.0g	0.02g	33.3
MD 41	16.1g	10.0 g	0.02g	41.7
MD 50	13.8g	12.0 g	0.02g	50
MD 55	12.4g	13.2 g	0.02g	55

were used as precursor molecules without further purification, and barium hydroxide monohydrate (Ba(OH)₂·H₂O, Aldrich) was used as a catalyst to promote a condensation reaction between the two. MPTS and Ba(OH)₂·H₂O were mixed at 80°C, and DPSD was added to the mixture continuously for two hours to prevent self-condensation of DPSD and phase separation. The solution was kept at 80°C for a further two hours to progress the reaction. After that, methanol, a by-product of the condensation reaction, was removed by vacuum heating. The solution was cooled to room temperature and filtered through 0.45 μm-size Teflon filter to remove Ba(OH)₂·H₂O, leaving the methacryl-grafted polysiloxane resin as a clear solution. The formulations and notations of the methacryl-grafted polysiloxane resins in this study are shown in Table 1.

Characterization and instrumentation

²⁹Si-NMR spectra were recorded using a Bruker FT 500MHz instrument from 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 30mg/L. Pulse delays were 30s, the sample temperature was 300K, and TMS was used as a reference. Raman Spectra were measured with a 488nm Ar-Kr ion laser (Coherent Innova 70 series, Laser Innovations, Moorpark, CA) and double-grating monochromator (U-1000, Jovin Yvon, Inc., Edison, NJ). Gel permeation chromatograms (GPC) were obtained using a Polymer Laboratories PL-GPC220, equipped with RI detector and two PL gel columns (10 μm, mixed-B). The system was calibrated using polystyrene standards. The resins were diluted to 0.1 wt % concentrations in THF as an eluent, and the flow rate was 1.0 mL/min at 30°C. 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 5.08 Å with a wavelength spread (FWHM) of 12%, and detector-sample distance of 3 m. The scattering vector ranged between 0.04 Å⁻¹ and 0.25 Å⁻¹. The resins were diluted to 10 wt % concentrations in acetone-d₆ to obtain good contrast between the resins and the solvent. All geometry parameters of the resin molecules were obtained through a full optimization at the self-consistent density functional B3LYP level of theory, with the STO-3G Pople basis sets. All calculations were performed using the Gaussian03 package.

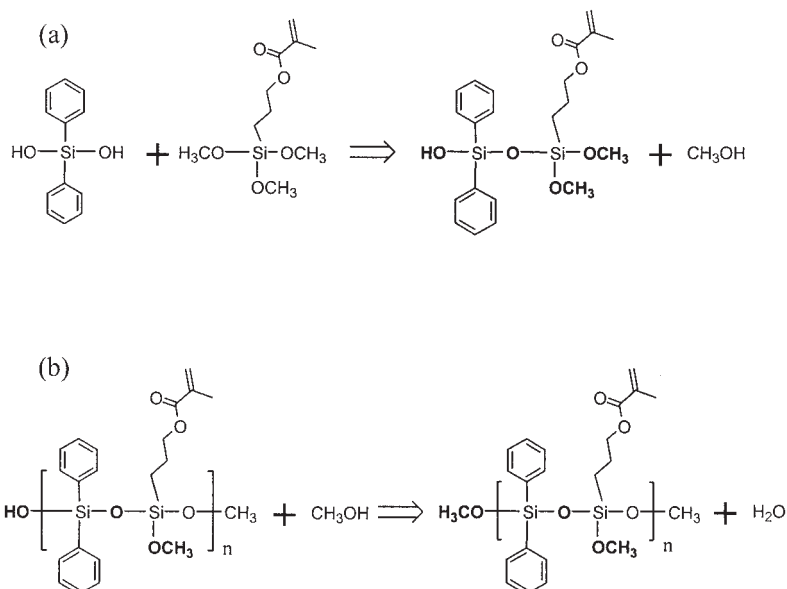
RESULTS AND DISCUSSION

Formation of polysiloxane

Siloxane bonds can be formed by condensation reaction between the silanol group of DPSD and the methoxy group of MPTS. As this condensation reaction proceeds, methacryl-grafted polysiloxane resin is formed. The condensation reaction is terminated by the reaction of silanol groups (in the oligomeric resin) with methanols. These reactions are briefly illustrated in Scheme 2.

Formation of resins, with various compositions, from the condensation reaction between the two precursors was confirmed by ²⁹Si-NMR spectroscopy (Fig. 1). The notations of Si atoms in NMR spectroscopy are as follows: Dⁿ and Tⁿ represent Si from DPSD and MPTS, respectively. The superscript, n, denotes the number of siloxane bonds of the Si atom. The chemical shifts of Si according to its bond states are shown in Table 2.^{5,22-24}

A small amount of the D⁰ species, diphenyldimethoxysilane (-29 ppm), which can be produced by the reaction between DPSD and methanol, was left in the resins of all compositions. This indicates that the condensation reaction between the two precursor molecules proceeds almost to completion, and that the methacryl-grafted polysiloxane resins have been successfully synthesized. The MD 55 composition is the only one in which a small amount of DPSD (-34 ppm) remains in the resin. As the DPSD content increases, the molecular size of the resin becomes larger due to the further condensation reaction, and the methoxy groups in the resins are sterically blocked by more methacryl and phenyl groups. As a result, the silanol groups of DPSD cannot react completely



Scheme 2. Condensation and reverse reaction: (a) condensation reaction between MPTS and DPSD; and (b) reaction between silanol group and methanol.

with methoxy groups and DPSD remains in the resin.

Considering the steric effect of the bulky organic group and the stoichiometry between the silanol groups of DPSD and the methoxy groups of MPTS, when the DPSD content is 50 mol % or less, the shape of the polysiloxane resin is more likely to be linear or cyclic. On the other hand, in the MD 55 composition, the polysiloxane in the resin is favored to be branched due to the stoichi-

ometry. Thus, the number of siloxane bonds of silicon from MPTS should be 1 or 2 in the resins of composition MD 41 and MD 50. However, T^3 species exist and increase with DPSD content in these compositions. One of the plausible explanations for the formation of T^3 is the hydrolysis and condensation mechanism.⁵ Water produced by the reaction between the silanol group and methanol can react with T^2 to give T^2 -OH, and then T^3 can be formed by a condensation reaction between

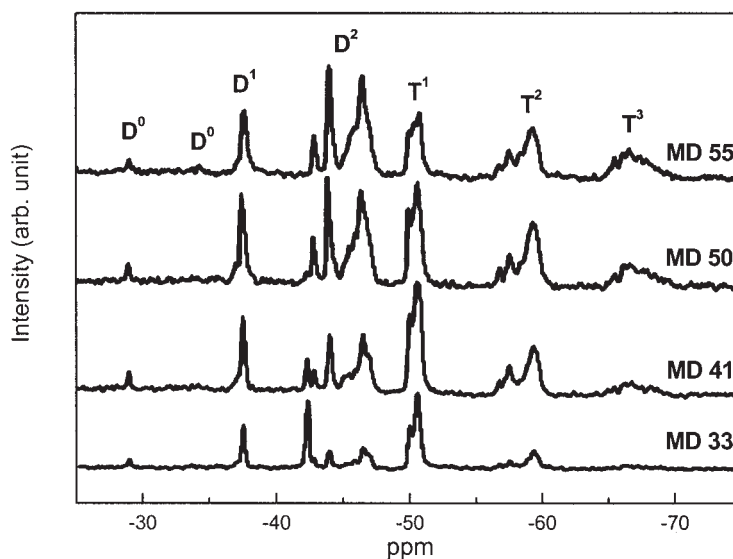


Figure 1. ^{29}Si -NMR spectra of resins of varying composition.

Table 2. Chemical Shifts of Silicon According to its Bond States^{5, 22–24}

Species	Chemical shifts
D ⁰ (diphenyldimethoxysilane)	– 29 ppm
D ⁰ (diphenylsilanediol)	– 34 ppm
D ¹	– 36 ≈ – 38 ppm
D ²	– 42 ≈ – 47 ppm
T ¹	– 49 ≈ – 51 ppm
T ²	– 57 ≈ – 61 ppm
T ³	– 65 ≈ – 69 ppm

T²-OH and MPTS. Another possible cause for T³ formation is a siloxane bond exchange.^{17,25} In polysiloxane resins, Si-OMe and Si-O-Si bonds are randomly distributed at the equilibrium of redistribution reached by heating. In this regard, T³ species can be formed by Si-OMe and Si-O-Si bond exchanges during the synthesis. Nonetheless, we can expect that the polysiloxanes in the resins of these compositions are mainly linear or cyclic, since these T³ species are much smaller than T¹ and T² species.

Raman spectroscopy was employed to confirm whether the polysiloxanes in the resin are linear or cyclic. Raman spectra of resins of varying composition are shown in Figure 2. 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 refer-

ence. It has already been reported that the three-membered ring of polysiloxane was observed around 606 cm⁻¹, and the broad bands from multi-membered polysiloxane rings appeared under 500 cm⁻¹ in Raman spectra.^{26,27} As shown in Figure 2, the resins have three-membered rings of polysiloxane. However, compared with HPCTS (which contains many more phenyl groups than the resins), the amount of polysiloxane ring in the resins is very small. Also, it has already been reported that the yield of cyclic polysiloxane is low in the presence of the basic catalyst.²⁸ Therefore, we can verify that the main parts of the polysiloxanes in the resins are linear.

Molecular weight and molecular structure

Molecular weight change in the methacryl-grafted polysiloxane resins was investigated by GPC. Figure 3 shows GPC curves of the resins with various compositions. Three small peaks around 180, 250, and 430 appear in the curves. To identify these peaks, molecular weights of both diphenyldimethoxysilane (Fluka) and MPTS were measured under the same experimental conditions. We found that the peaks around 180 and 250 corresponded to diphenyldimethoxysilane and MPTS, respectively, suggesting that the peak at approximately 430 corresponds to the dimeric species produced from the condensation reaction between DPSD and MPTS. The amount of these

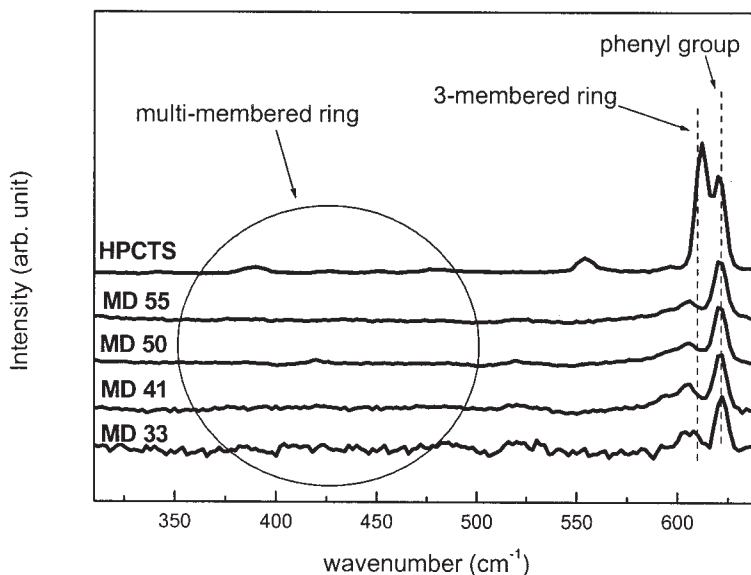


Figure 2. Raman spectra of resins of varying composition, and of hexaphenylcyclotrisiloxane.

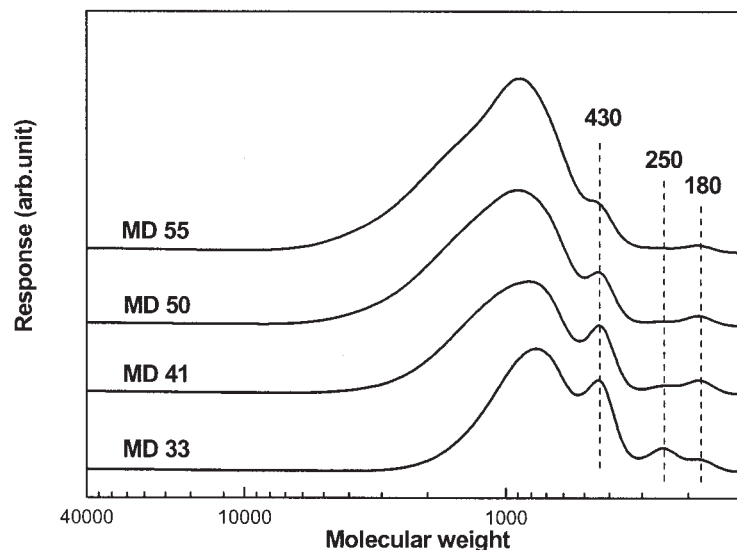


Figure 3. GPC curves of resins of varying composition.

dimeric species decreases with increasing DPSD content due to the continuing condensation reaction.

From these GPC curves, the weight average molecular weight (M_w) of the resins can be calculated, and the corresponding molecular structures of the resins can be estimated. M_w of the resins changes from 770 to 1290 as the DPSD content is increased, suggesting that the main molecular structure of the resins can be expected to be tetramer, pentamer, and hexamer, since the molecular weights of the precursors are around 200. The M_w values and estimated molecular structures of the resins are shown in Table 3.

As previously mentioned, in the case of the MD 55 composition, we can expect that linear and branched shapes of polysiloxane coexist in the resin. A weak shoulder around 1600 in the GPC curve for the MD55 composition may be caused by the coexistence of these different structures and their differing molecular weights. However, if the molecular structure of the resin in this composition is estimated only by the M_w value obtained from the GPC experiment, it is close to hexamer, even though M_w is somewhat larger than that of hexamer.

In the MD 33 composition, tetramer consisted of three MPTSs and one DPSD. This can be inter-

Table 3. M_w , Estimated Molecular Structure, R_g , Polysiloxane Chain Length, and Molecular Size of the Resin of Varying Composition

Composition	GPC		Quantum chemistry			SANS		
	M_w	E. M. S.	R_g	P. C. L.	S.R.	R_g	S. S. R.	S. T. R. R.
MD 33	770	M-D-M-M (tetramer, M_w : 864)	0.57 nm	0.54 nm	1.98 nm	0.56 nm	1.45 nm	1.94 nm
MD 41	1000	M-D-M-D-M (pentamer, M_w : 1,048)	0.60 nm	0.68 nm	2.01 nm	0.63 nm	1.63 nm	2.18 nm
MD 50	1200	M-D-M-D-M-D (hexamer, M_w : 1,246)	0.66 nm	0.90 nm	2.01 nm	0.68 nm	1.76 nm	2.36 nm
MD 55	1290	M-D-M-D-M-D (hexamer, M_w : 1,246)	0.66 nm	0.90 nm	2.01 nm	0.77 nm	1.99 nm	2.66 nm

M : MPTS, D : DPSD, E. M. S. : estimated molecular structure, R_g : radius of gyration, P.C.L. : polysiloxane chain length of resin, S. R. : molecular size of resin, S. S. R. : molecular size of spherical resin, S. T. R. R. : molecular size of thin rod-like resin.

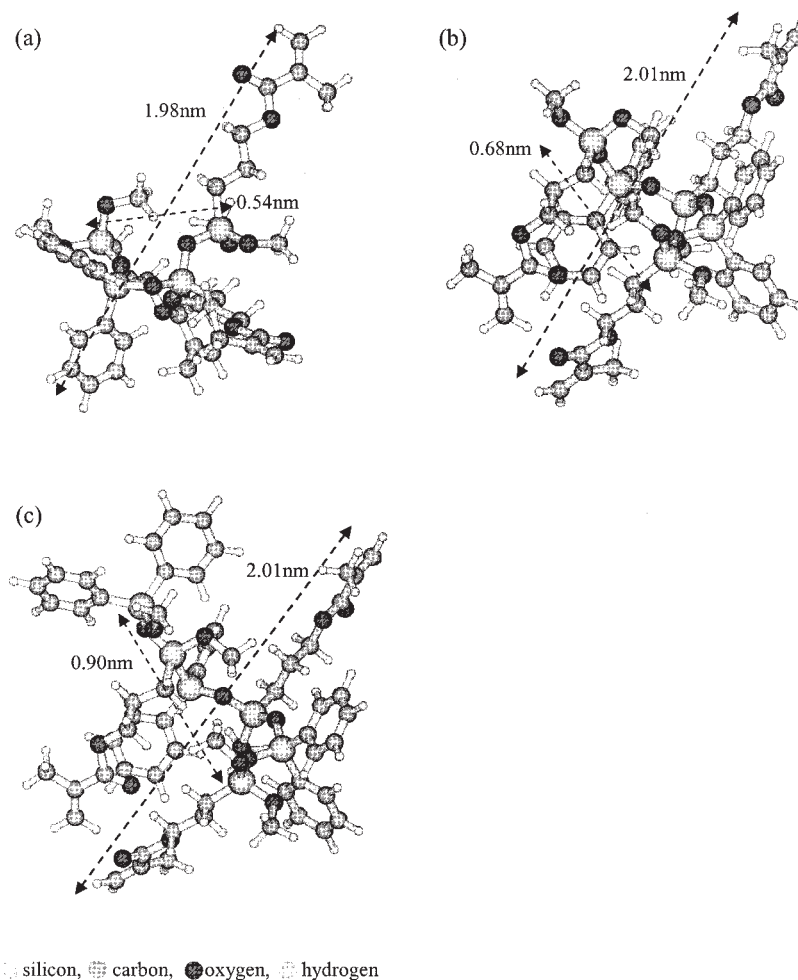


Figure 4. Molecular structures of methacryl-grafted polysiloxane resins from quantum chemistry, showing (a) tetramer structure, (b) pentamer structure, and (c) hexamer structure.

preted in a similar manner to the T³ species formation mechanism discussed previously.

Radius of gyrations (R_g) and molecular sizes

The R_g and molecular size values of the resins whose molecular structures were estimated from GPC were calculated theoretically. The real R_gs and molecular sizes of the resins were measured experimentally to confirm that the molecular structure of the resin from GPC is similar to its actual molecular structure.

The R_g and molecular size values of the resin estimated from GPC can be calculated theoretically from quantum chemistry. The exact coordinates of silicon, carbon, oxygen, and hydrogen atoms in the estimated molecular structure at the lowest energy state can be solved in the Cartesian

coordinate system using the Gaussian03 package²⁹ (Fig. 4.).

The center of mass of the resin can be calculated from the coordinates of atoms, and the R_g values of the resins can be computed theoretically by eq (1).³⁰

$$R_g^2 = \frac{\sum_j b_j^2 r_j^2}{\sum_j b_j^2} \tag{1}$$

where b_j is the scattering length of the jth atom and r_j is the displacement of the jth atom from the center of mass.

The polysiloxane chain lengths and molecular sizes of the resin can also be calculated from

quantum chemistry, as shown in Figure 4. Table 3 shows R_g , polysiloxane chain length, and molecular size of the resins as obtained from quantum chemistry. The polysiloxane chain length of the resin changes from 0.54nm to 0.90nm with increasing DPSD content. On the other hand, the molecular size of the resin does not vary significantly with DPSD content. In the tetramer structure, the distance between the hydrogen at the end of the methacryl group and the phenyl group is the farthest. In the pentamer and hexamer structures, the distances between hydrogens at the end of opposite methacryl groups are the largest. All of these distances are around 2nm regardless of their molecular structures, as shown in Figure 4.

The real R_g and molecular size of the resin can be measured experimentally by SANS, which is a very useful technique for characterizing nano-sized materials. By comparing the value of R_g determined by quantum chemistry with those from SANS, it is possible to prove that the estimated molecular structure of the resin from GPC measurement is similar to its real molecular structure.

In SANS, the scattering intensity ($I(Q)$) is defined (eq (2)) by the Guinier Law.³⁰ R_g can be estimated from a linear plot of $\ln(I(Q))$ against Q^2 in the Guinier region.

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

$I(Q)$ 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.

Figures 5a and b show the results of SANS and the corresponding Guinier plots for the data in Figure 5a, respectively. As shown in Figure 5b, the gradients of the Guinier plots negatively increase with DPSD content, indicating that the molecular size of the resin becomes larger.

The real molecular size of the resins can be estimated from R_g by eq (3) or eq (4), depending on their shapes.³⁰

$$\text{Spherical shape} \quad R_s = \sqrt{\frac{5}{3}} R_g \quad (3)$$

$$\text{Thin rod-like shape} \quad R_T = \sqrt{12} R_g \quad (4)$$

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 radius of gyration.

When the resin has a spherical shape, the molecular size is smallest. On the other hand, when the resin has a thin-rod structure, the molecular size of the resin is largest. Thus, it can be expected that the real molecular size of the resin is in the range $2R_s$ and R_T . The R_g and molecular size values of the resins measured from the SANS experiment are shown in Table 3.

When the DPSD content is 50 mol % or less, the results from quantum chemistry and GPC are in good agreement with those from SANS, as shown in Table 3. Therefore, it is confirmed that the main molecular structures of the resins in these compositions change from linear tetramer to hexamer with increasing DPSD content.

However, in the MD 55 composition, the theoretical computation results differ from those measured by SANS. In this composition, it can be expected that linear and branched shapes of the polysiloxane molecule coexist, as previously mentioned. In the GPC experiment, the molecular weight of the resin that has a branched shape is measured as lower than its actual molecular weight. Thus, the real average molecular weight of the resin in this composition will be larger than the value of 1290 measured from the GPC experiment. However, the R_g and molecular size of the resin were calculated on the assumption that the resin is a hexamer, although the real average molecular weight of the resin will be higher than that of a hexamer. As a result, the R_g value for the MD 55 sample as measured by SANS is larger than that from theoretical computation.

CONCLUSIONS

Nano-sized methacryl-grafted polysiloxane resins of various compositions were successfully synthesized from MPTS and DPSD, and their molecular structures were determined by theoretical computation and from experimental measurement. It was found that the yields of cyclic polysiloxanes were very low in all compositions. When the DPSD contents were 50 mol % or less, the main molecular structure of the resin changed from a linear tetramer to a hexamer structure with increasing DPSD content, while the polysiloxane chain length in the resin increased from 0.54nms to 0.90nms. The molecular sizes of the resins were all around 2nms, regardless of molecular structure. On the other hand, when the DPSD contents

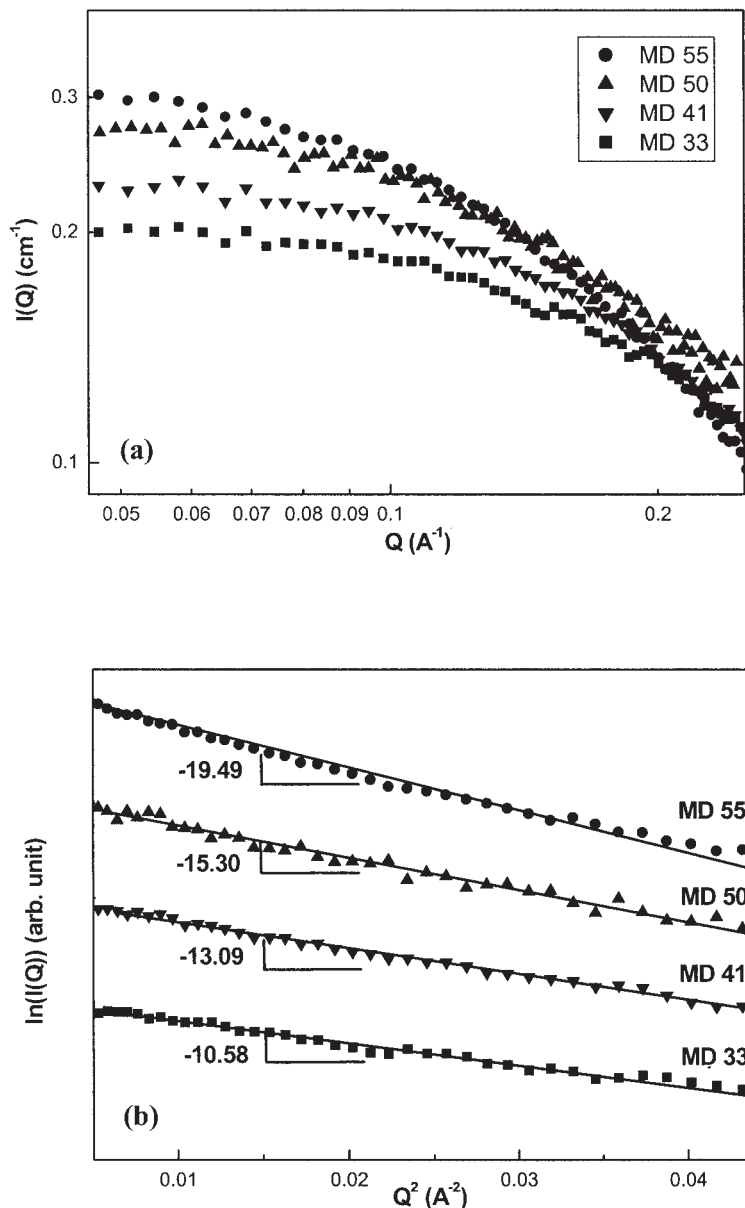


Figure 5. Results of SANS experiment of resins of varying composition: (a) experimental SANS data of the resins; (b) corresponding Guinier plots for the data in (a).

were more than 50 mol %, branched polysiloxane resins with expected molecular sizes beyond 2nm were synthesized.

Using these resins, it is possible to fabricate organic-inorganic nano hybrid materials whose structures are homogeneously nano-sized polysiloxane dispersed in a polymer matrix.

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