

## Synthesis of Graft Copolymer from Polysilsesquioxane Initiated by Photoiniferter

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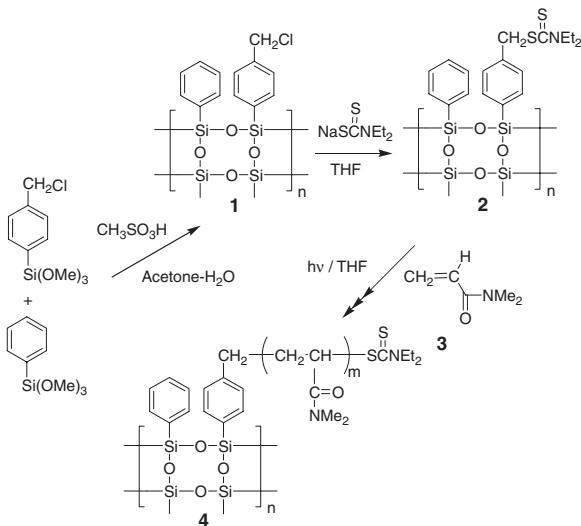
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From the polysilsesquioxane having phenyl groups and diethyldithiocarbamate groups served as the photoiniferter, the graft derivative (**4**) was obtained by the polymerization with *N,N*-dimethylacrylamide under UV irradiation without gelation. The effects of the grafting on physical properties were shown in the measurements of thermal stability and contact angle of **4**.

The investigations concerning the functional polysilsesquioxanes have been exploited to provide the new candidates for useful organic–inorganic hybrid materials.<sup>1</sup> In the investigations, the polysilsesquioxanes modified with various organic functional groups demonstrate the interesting properties in electrical, optical, mechanical, and chemical applications.<sup>2</sup> Very recently, several techniques of living radical polymerization are shown to be effective for the introduction of polymeric components into a variety of polysiloxane structures.<sup>3</sup> The facts promise that the application of the processes to the polysilsesquioxane having multi-initiation sites creates various new and interesting hybrid materials. Namely, the processes should enable the ready graft polymerization on polysilsesquioxane, in which the molecular weight, specie, and composition of side chains are controlled. In this report, the graft polymerization by the use of diethyldithiocarbamate groups on polysilsesquioxane under UV irradiation was examined. The previous works have presented that dithiocarbamate group is an effective photoiniferter.<sup>4</sup>

As shown in Scheme, the polysilsesquioxane having phenyl and chloromethylphenyl groups (**1**) was prepared from the tri-



Scheme 1.

methoxysilanes containing chloromethylphenyl group and phenyl group, respectively, by co-condensation under acidic conditions.<sup>5</sup> The polysilsesquioxane **1** containing both phenyl and chloromethylphenyl groups was isolated as a solid insoluble in hexane and easy to handle. The introduction of diethyldithiocarbamate groups was achieved efficiently by the reaction of chloromethylphenyl groups in **1** and sodium diethyldithiocarbamate conducted at room temperature in THF. The contents of the organic groups in **1** and **2** were determined from the <sup>1</sup>H NMR spectral data measured with hexamethyldisiloxane as an internal standard.<sup>6</sup> The estimated contents of phenyl and diethyldithiocarbamate groups in **2** were 3.94 and 2.23 mmol equiv./g. This molar ratio, 1.8/1, was almost same to that of phenyl group/chloromethylphenyl group, 1.9/1, in **1**. The number-average molecular weight ( $M_n$ ) and the polydispersity ( $M_w/M_n$ ) of **2** estimated by GPC analysis (polystyrene standards) were 2000 and 1.30, respectively.

As the monomer for grafting, *N,N*-dimethylacrylamide (**3**), known to form the hydrophilic polymer, was employed.<sup>7</sup> The photopolymerization of **2** with **3** was conducted to examine the relationships between  $M_n$ ,  $M_w/M_n$ , and monomer conversion.<sup>8</sup> After polymerization for a given time, the mixture was evaporated and the residue was employed for the analyses of <sup>1</sup>H NMR and GPC. As shown in Figure 1, the  $M_n$  of **4** increased almost linearly and the polydispersities were in the narrow range from 1.44 to 1.56 until the conversion of ca. 80%. The  $M_n$  of **4** after 3 h polymerization was estimated to be 3200 by GPC data, while the calculated one at 100% conversion was 3800. In the <sup>1</sup>H NMR spectrum of **4**, the ratio of the initiating site/the monomer unit was estimated to be 1/4.5, when the initial feed ratio of diethyldithiocarbamate group/**3** was adjusted to be 1/4. These results were interpreted by that the controlled radical polymerization essentially proceeded on **2**, although the monomer **3** could not be consumed quantitatively in the period showing the linear

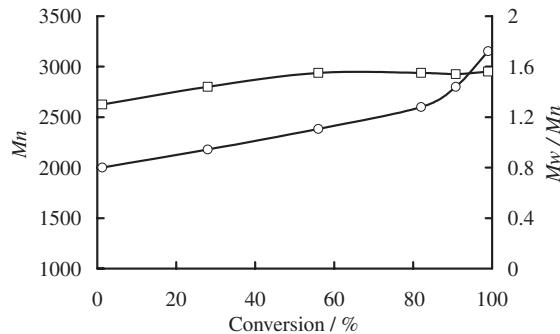
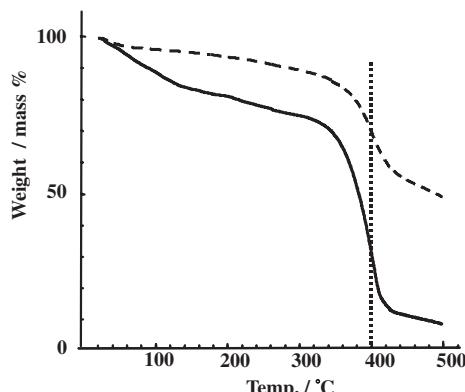


Figure 1. The dependence of  $M_n$  (○) and  $M_w/M_n$  (□) on the conversion of **3**.



**Figure 2.** TGA curves of **4** (---) and poly(*N,N*-dimethylacrylamide) obtained by free radical process (—).

relationship. The reason why the increase of  $M_n$  deviates from the straight line after the point of conversion of 80 % in Figure 1 have not been clarified yet. This seemed to indicate that coupling reaction or free radical polymerization proceeded in the later period. From the fact that the obvious formation of gel products by the radical coupling is not observed, the free radical polymerization is speculated to be a possible reason. This might be supported by the estimation that the content of diethylamino groups in **4** was 84 % of that in **2**.

The thermal behavior<sup>9</sup> and the contact angle of **4**,<sup>10</sup> prepared in a similar manner mentioned above, were examined to obtain the fundamental information concerning the effects of the grafting.<sup>11</sup> In TGA analyses, the thermal stability of **4** was examined in comparison with that of homopolymer of **3**, obtained by free radical polymerization.<sup>12</sup> As shown in Figure 2, the homopolymer and **4** began to decompose at ca. 50 °C. However, the weight loss of 40% was recorded on the homopolymer at 400 °C, whereas that was only 25% on **4**. From the results, the effects of the homopolymer, which might be formed through chain transfer step as mentioned above, could not be detected, even if there contained. One of the expected properties due to presence of the polymeric units of **3** was affinity to water. This was shown in the difference of contact angles of the starting polysilsesquioxane **2** and **4**. The contact angle was increased from 70° of **2** to 90° of **4**. Although the observed effect of the graft chains was less satisfactory, the increase of contact angle seemed to be more obvious with the increase of amount of *N,N*-dimethylacrylamide units.

Thus, the preparation of the graft polysilsesquioxane **4** by the use of photoiniferter was shown in this report. Such kind of graft polysilsesquioxanes is essentially soluble in usual organic solvents. This seems to be an important factor in the use as a functionalized organic–inorganic hybrid material and/or an additive.

## References and Notes

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- 5 The  $M_n$  and  $M_w/M_n$  of **1** were 2100 and 1.40, respectively. The contents of phenyl and chloromethylphenyl groups estimated by <sup>1</sup>H NMR spectral data were 3.25 and 1.71 mmol equiv./g, respectively.
- 6 In the estimation of contents of the functional groups by <sup>1</sup>H NMR spectral data, the signals at 3.65 and 3.96 ppm ( $-\text{N}-\text{CH}_2\text{CH}_3$ ), 4.43 ppm ( $-\text{C}_6\text{H}_4\text{CH}_2-$ ), and ca. 7.3 ppm ( $\text{C}_6\text{H}_5-$ ,  $-\text{C}_6\text{H}_4-$ ) were used.
- 7 For example: K. Haraguchi, R. Farnworth, A. Ohbayashi, and T. Takehisa, *Macromolecules*, **36**, 5732 (2003).
- 8 A mixture of **2** (0.11 g, 0.25 mmol equiv. of diethyldithiocarbamate unit) and **3** (0.11 g, 1.12 mmol) in THF (2 mL) was fed into a glass tube and sealed after three freeze-pump-draw cycles. Then, the mixture in the glass tube was irradiated at room temperature by using a RIKO RH400 UV lamp equipped with water jacket from a distance of 10 cm.
- 9 The thermal degradation test was conducted with 10 mg of the sample from room temperature to 800 °C, in which a heating rate was 10 °C min<sup>-1</sup> under nitrogen.
- 10 The solution of **2** or **4** in toluene was cast on polyethylene sheet and, then, removed toluene at 120 °C for 1 min in an oven. Static contact angles on **2** and **4** were measured with deionized water drops on the resulting sheet at room temperature.
- 11 The  $M_n$  and  $M_w/M_n$  of **4**, isolated as an insoluble part of diethyl ether, were 3100 and 1.58, respectively. The contents of the functional groups were estimated as follows: phenyl group = 1.95 mmol equiv./g, diethylamino group = 1.05 mmol equiv./g, and dimethylacrylamide unit = 4.55 mmol equiv./g.
- 12 The  $M_n$  and  $M_w/M_n$  of the poly(*N,N*-dimethylacrylamide) used as the sample compared with **4** were 13000 and 1.20, respectively.