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Synthesis of Organic−Inorganic Polymer Hybrids Controlled by Diels−Alder Reaction

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ABSTRACT: The homogeneity of the polymer hybrid was controlled by Diels−Alder reaction. The polymer hybrids were prepared from styrene copolymer bearing pendent furan moieties (20%) and tetraethoxysilane using maleimide silane coupling agent by a sol−gel process. Styrene copolymer was synthesized by free radical copolymerization of styrene with 4-furfuryloxymethylstyrene. IR spectroscopic data of the hybrid materials support the occurrence of Diels−Alder reaction between the pendent furan moieties of the styrene copolymer and the maleimide silane coupling agent. The thermal and morphological properties of the hybrid materials were investigated by DSC, TGA, and SEM. The retro-Diels−Alder reaction was observed in the DSC thermogram. The polymer hybrids showed higher solvent resistance property at the boiling point of THF, but because of the retro-Diels−Alder reaction, the organic polymer in the polymer hybrid obtained was extracted with DMF at 130 °C.

Introduction

Hybrid materials and nanocomposites have been attracting a great deal of attention because of their high performances. Various kinds of "organic−inorganic polymer hybrids" which are nanocomposites of organic polymer and silica gel have been investigated.[1−7] Generally, the polymer hybrids have high performances especially in the field of thermal stability, mechanical property, and so on. Most of the polymer hybrids are prepared by the sol−gel method. The sol−gel reaction is the method to prepare the silica gel at low temperature, and this reaction involves the hydrolysis of Si−OR groups to Si−OH groups and the condensation of the Si−OH groups into −Si−O−Si− linkages.[8] The polymer hybrids are prepared by the sol−gel reaction in the presence of organic polymer.

In our previous research, various interactions such as covalent bonding interaction, hydrogen bonding interaction, and aromatic interaction between organic polymers and silica matrix were utilized for nano-ordered combination of the two moieties. For example, poly(*N*-vinylpyrrolidone), poly(2-methyl-2-oxazoline), and poly(*N*,*N*-dimethylacrylamide) were hybridized with silica gel utilizing hydrogen bonding interaction. Polystyrene−silica hybrids utilizing $\pi-\pi$ interaction and ionic interaction were also reported.[9,10] Besides, the stimulus-responsive polymer hybrids have been investigated. Stimulus-responsive materials are attracting attention in many fields. Previously, photochromic polymer hybrids and reversible IPN polymer hybrids were prepared in our group.[11,12] In those polymer hybrids, the isomerization or cross-linking reaction of the organic functional groups proceeded in the homogeneous polymer hybrid. However, the control of the homogeneity of the polymer hybrids by stimuli has not been studied yet. In this paper, homogeneity control of the polymer hybrid by a stimulus was investigated.

As mentioned above, nano-ordered structures of organic polymers and silica matrix depend on the interactions between two components, such as covalent bonding interaction, hydrogen bonding interaction, and aromatic interaction. Thus, the importance to control the homogeneity by various stimuli is the control of compatibility between organic polymer and silica matrix. When the photodimerization of cinnamoyl groups was applied to the cross-linkage, homogeneity control of the polymer hybrid by UV irradiation could be accomplished.[13]

Scheme 1. Diels−Alder Reaction and Retro-Diels−Alder Reaction of Maleimide and Furan

This article describes the thermal homogeneity control of the polymer hybrids by utilizing the Diels−Alder (DA) reaction of maleimide and furan moieties. The DA reaction generally involves the coupling of diene and dienophile, and the DA reaction between maleimide groups and furan groups proceeds at ambient temperature and the retro-DA (RDA) reaction takes place on heating. Many applications of DA chemistry such as the polymer synthesis[14−18] and cross-linking[12,19−22] have been studied. Here, the coupling by the DA reaction was applied to the cross-linkage between organic polymer and silica matrix. Furthermore, the characterization and the thermal properties of the polymer hybrids obtained are also reported.

Experimental Section

Materials. Tetraethoxysilane (TEOS) was distilled and stored under a N_2 atmosphere. Acetone was dried and distilled over $MgSO_4$ under a N_2 atmosphere. Hexane was dried over $CaCl_2$ and distilled under a N_2 atmosphere. Styrene monomer and 1,4-dioxane were purified by distillation under vacuum. 2,2-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. *N*-Methylolmaleimide was synthesized as reported.[23] Poly(styrene-*co*-4-furfuryloxymethylstyrene) (PS-F) was also synthesized as reported.[14] Maleimide-modified alkoxysilane (M-TEOS) was synthesized by the following method. Other reagents were used as supplied.

Synthesis of 3-(Triethoxysilyl)propylcarbamic Acid Maleimidemethyl Ester (M-TEOS). The maleimide-modified alkoxysilane, M-TEOS, was synthesized by addition reaction of alcohol and isocyanate. *N*-Methylolmaleimide (0.5

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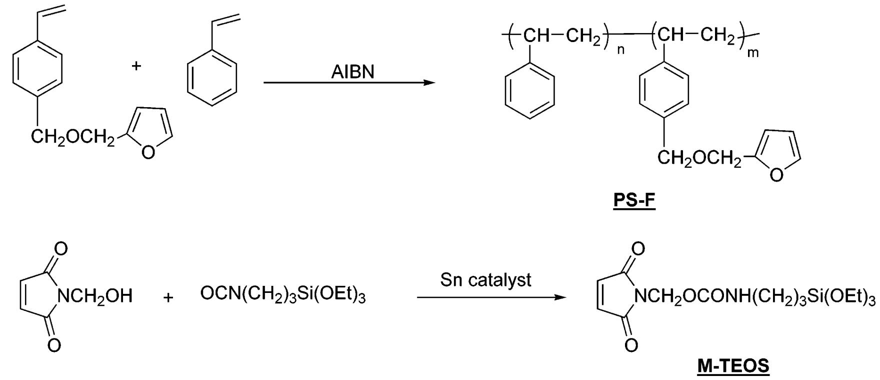
Scheme 2. Synthesis of PS-F and M-TEOS



Scheme 3. Synthesis of Polymer Hybrids Utilizing DA Reaction

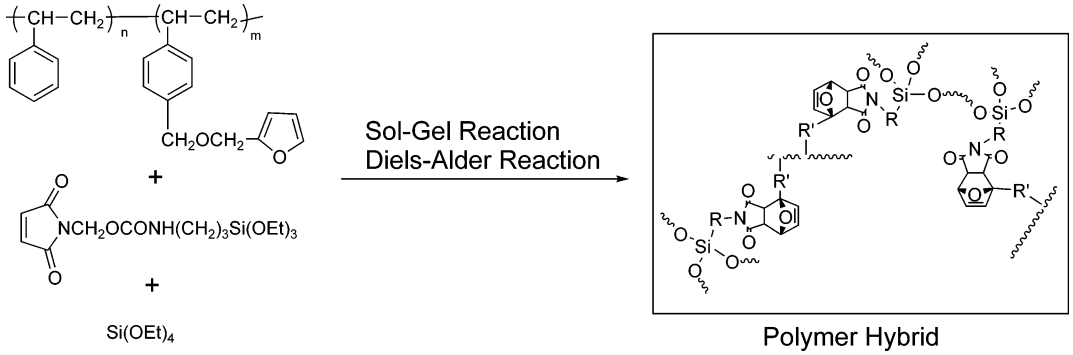


Table 1. Preparation of DA Polymer Hybrids

run	PS-F (g)	M-TEOS (g)	TEOS (mL)	1,4-dioxane (mL)	0.1 M HCl_{aq} (mL)	temp (°C)	appearance
1	0.05		0.1	1	0.036	60	turbid
2	0.05	0.025	0.1	1	0.036	60	transparent
3	0.05	0.025	0.1	1	0.036	rt	turbid
4	0.05	0.025	0.1	1	0.036	90	transparent

g, 3.94 mmol) and 3-isocyanatopropyltriethoxysilane (0.73 mL, 7.87 mL) were dissolved in 10 mL of acetone. The resulting solution was refluxed overnight followed by an addition of 3 drops of tin catalyst (di-*n*-butyltin dilaurate). The solvent was evaporated, and the liquid obtained was washed with 20 mL of hexane three times. Propylcarbamic acid maleimidemethyl ester, the maleimide model compound, was synthesized by the same manner from *N*-methylolmaleimide and propyl isocyanate.

Preparation of Polymer Hybrids. Polymer hybrids were synthesized by utilizing the sol–gel reaction of TEOS in the presence of PS-F and M-TEOS. PS-F, TEOS, and M-TEOS were dissolved in 1,4-dioxane in a sealed bottle. To the solution, acid catalyst (0.1 M HCl_{aq}) was added. After 1 h stirring, the seal of the bottle was removed and the solvent was allowed to evaporate. The glassy polymer hybrid films were obtained after 24 h. The obtained films were subjected to further analyses after drying at 60 °C for 2 days.

Measurement. Scanning electron microscopy (SEM) measurements were conducted using a JEOL JSM-5600 system. The thermal behavior was examined with differential scanning calorimetry (DSC) under a nitrogen atmosphere. Fourier transform infrared (FT-IR) spectra were recorded on a Prekin Elmer 1600 infrared spectrometer. Thermogravimetric analysis (TGA) was performed on a SEIKO TG/DTA 6200 with a heating rate of 10 °C/min in air.

Results and Discussion

Preparation of Polymer Hybrids Controlled by DA Reaction. Furan-modified polystyrene (PS-F), maleimide-modified alkoxysilane (M-TEOS), and TEOS were used to prepare the polymer hybrid. PS-F was synthesized as reported,[14] and M-TEOS was synthesized by addition reaction of *N*-methylolmaleimide with isocyanatopropyltriethoxysilane (Scheme 2).

The organic–inorganic polymer hybrids were prepared by the sol–gel reaction of TEOS in the presence of PS-F and M-TEOS (Scheme 3). Generally, the homogeneity of the obtained polymer hybrids is affected by the preparation conditions.[9,24,25] The effect of the presence of M-TEOS was evaluated. The effect of the preparation temperature was also evaluated (Table 1).

In the absence of M-TEOS (run 1), only turbid materials were obtained while homogeneous polymer hybrids were obtained in the presence of M-TEOS (run 2). Figures 1 and 2 show the optical images and SEM images for the obtained polymer hybrids, respectively. In the case without M-TEOS, phase separation was clearly observed in Figures 1a and 2a, and the silica gel domain was larger than 5 μm. On the other hand, no phase separation was observed in Figures 1b and 2b. With M-TEOS, maleimide groups can be dispersed into silica matrix by sol–gel processes. In the presence of maleimide groups in the silica matrix, PS-F can be dispersed through the DA reaction between maleimide groups and furan groups. This dispersion might give homogeneous mixing of the silica gel and PS-F. No linkage between the silica matrix and PS-F can form without M-TEOS, and accordingly phase separation might be observed.

The effect of the temperature was examined in runs 2–4. At low temperature (run 3), a turbid composite was obtained while transparent hybrids were obtained at 60

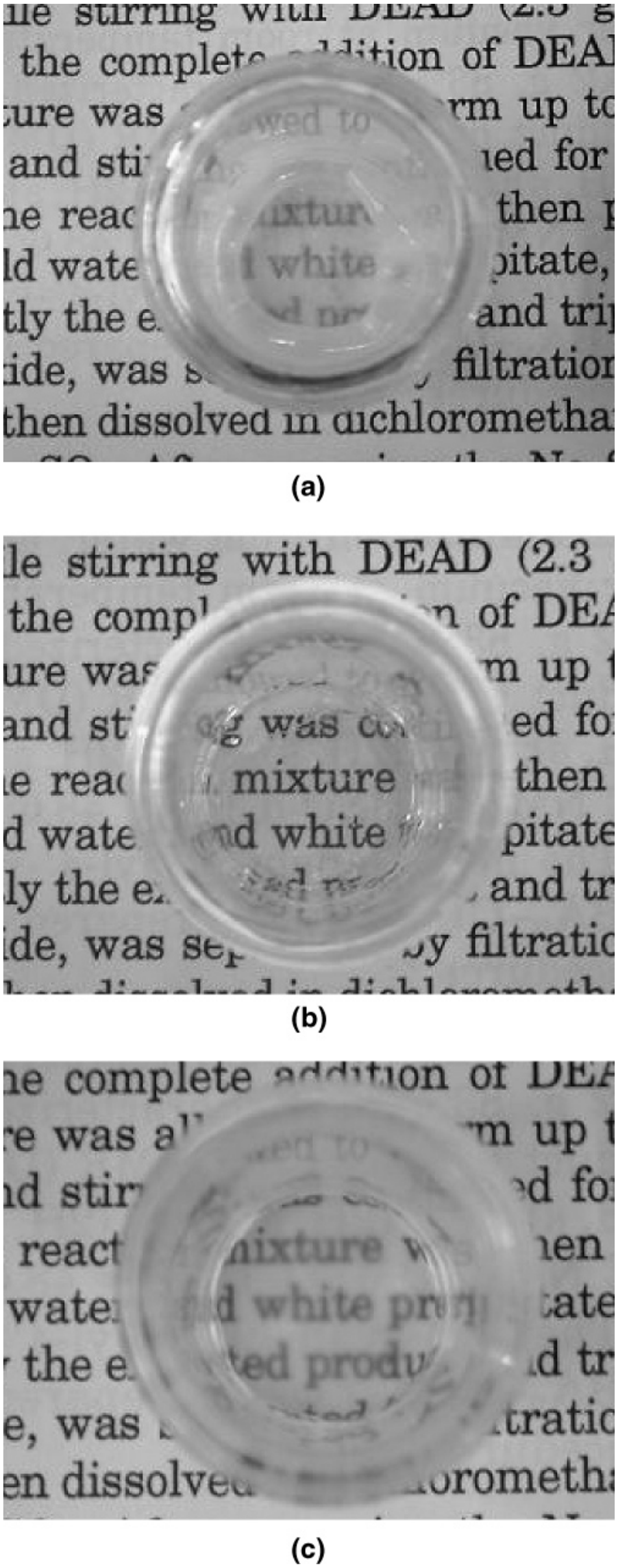


Figure 1. Optical images of transparent DA polymer hybrid and turbid composite: (a) prepared without M-TEOS; (b) prepared with M-TEOS at 60 °C; (c) prepared with M-TEOS at room temperature.

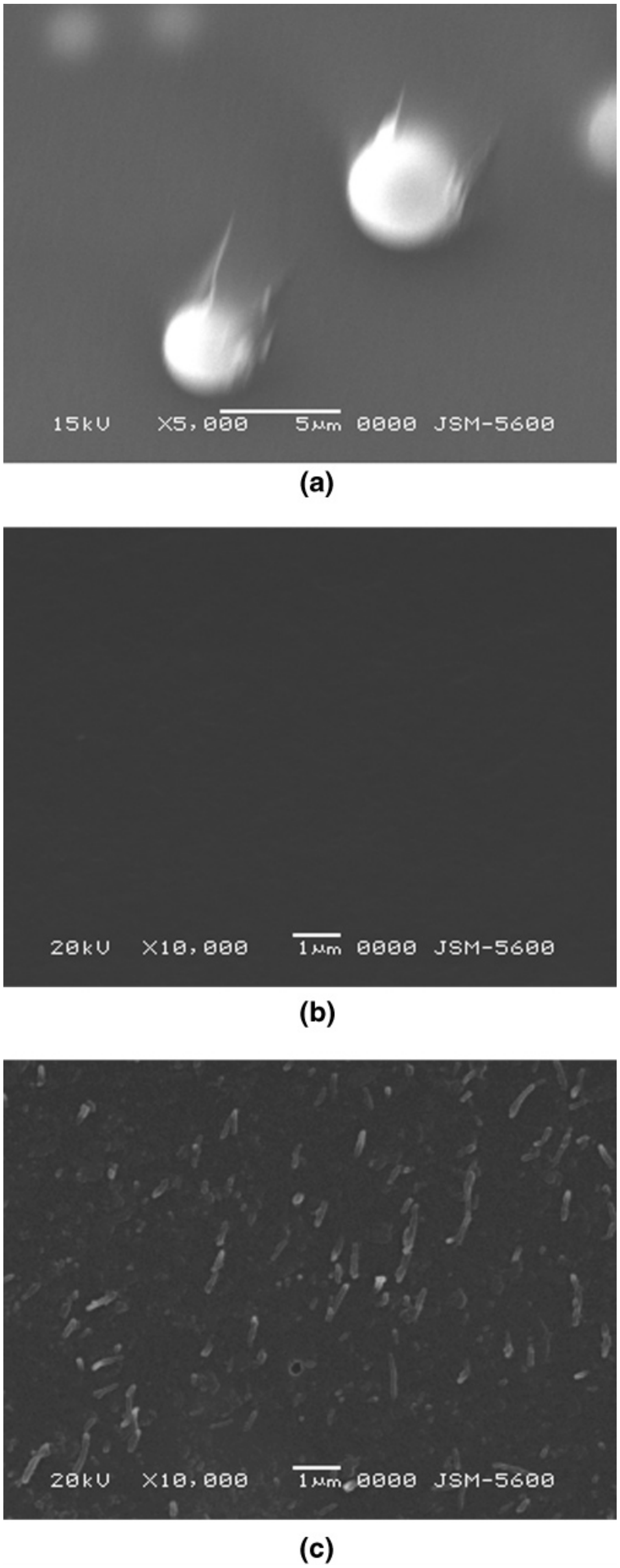


Figure 2. SEM images of transparent DA polymer hybrid and turbid composite: (a) prepared without M-TEOS; (b) prepared with M-TEOS at 60 °C; (c) prepared with M-TEOS at room temperature.

and 90 °C. Figures 1c and 2c show turbid films resulting from phase separation. This phase separation might be explained as follows. In solutions of PS-F, M-TEOS, TEOS, and acid catalyst, both sol−gel and DA reactions occur simultaneously. The homogeneity of the obtained material is affected by the rate of these two reactions. The sol−gel reaction at room temperature is slower than at 60 or 90 °C. At room temperature, the DA reaction between maleimide groups and furan groups might be much faster than gelation of the alkoxysilanes. Then

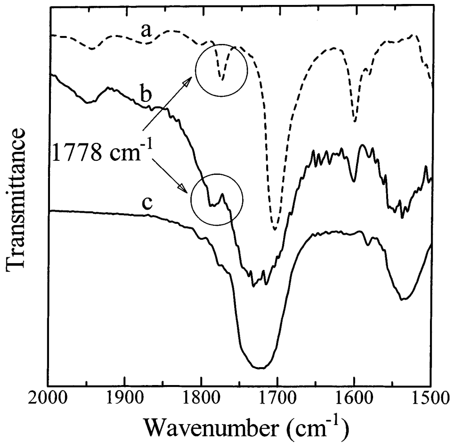


Figure 3. IR spectra of DA polymer hybrid, DA adduct, and M-TEOS. (a) DA adduct of PS-F and maleimide. (b) The polymer hybrid prepared with M-TEOS at 60 °C. (c) M-TEOS.

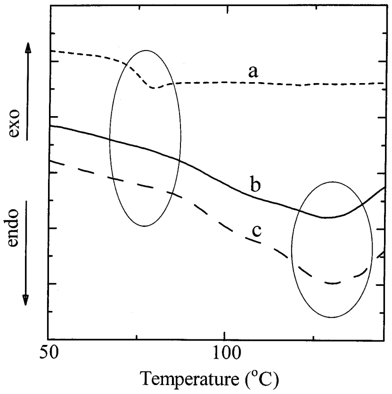


Figure 4. DSC thermograms of PS-F and DA polymer hybrid. (a) PS-F. (b) DA adduct of PS-F and *N*-maleimidemethylpropylcarbamate. (c) The polymer hybrid prepared with M-TEOS at 60 °C.

the PS-F is surrounded by the M-TEOS, and the intramolecular sol−gel reaction might take place. In the cases of runs 2 and 4, simultaneous DA reaction and gelation of alkoxysilanes which disperse maleimide groups into silica matrix might be carried out. This uniform dispersion of maleimide groups prevents aggregation of organic polymer by the DA reaction at various points in the polymer chain.

IR Spectra of the Obtained Polymer Hybrid. The DA reaction in the polymer hybrid was confirmed by FT-IR. Figure 3 shows the IR spectra of M-TEOS, PS-F reacted with maleimide, and that of the homogeneous polymer hybrid. In the case of M-TEOS (Figure 3c), only one $\nu_{C=O}$ band around 1725 cm^{-1} was observed. On the other hand, in parts a and b of Figure 3, which show the DA adduct of PS-F and maleimide and the polymer hybrid prepared with M-TEOS at 60 °C, respectively, a new peak at 1778 cm^{-1} specific to DA adducts was observed in both spectra.[14] These results indicate that the DA reaction took place during the preparation of the polymer hybrids. The DA adduct could form the cross-links between the organic polymer and silica gel. This might lead to the homogeneous mixing of silica gel and PS-F.

Thermal Properties of DA Polymer Hybrids. Figure 4 shows the DSC traces of PS-F, DA, polymer hybrid and the model compound. The model compound was prepared from PS-F and propylcarbamic acid maleimidemethyl ester. In Figure 4a, the glass transition temperature (T_g) of PS-F was clearly observed around 75 °C. With addition of propylcarbamic acid maleimidemethyl ester (Figure 4b), the T_g of the PS-F disappears, and a new endothermic peak appears, which is specific for the RDA reaction around 130 °C.[22] In the case of the polymer hybrid (Figure 4c), no T_g was observed and the RDA peak was observed. Judging from this result, the DA reaction in the polymer hybrid was confirmed.

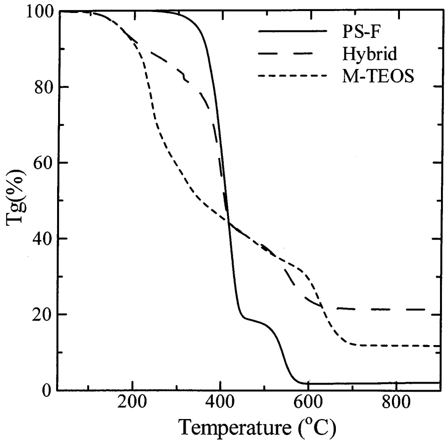


Figure 5. TGA thermograms of M-TEOS, PS-F, and DA polymer hybrid.

The inorganic content and the thermal stability of the polymer hybrids obtained were investigated by TGA. Figure 5 shows the TGA traces of PS-F, M-TEOS, and the polymer hybrid. The observed inorganic component in the polymer hybrid was 22 wt %, much lower than the calculated value of 34 wt %. This may be due to the residual silanol groups or unreacted alkoxy groups that remain in the polymer hybrid, and the mass loss at lower temperature (100−200 °C) might indicate further condensation reactions. However, the existence of inorganic moieties in the polymer hybrid was confirmed.

Generally, the thermal stability of the polymer hybrid is higher compared with that of the pure polymer. It is assumed that the rigid silica matrix surrounds the organic polymer by molecular level hybridization. Unfortunately, in the present study, the thermal stability of the polymer hybrid was lower than that of the PS-F. This decrease in thermal stability can be explained by the thermal instability of M-TEOS. As shown in Figure 5, M-TEOS decomposes even at 200 °C. This lower thermal stability likely causes the decrease in stability of the DA polymer hybrid.

Figure 6 shows the TGA traces of the polymer hybrid before and after solvent extraction. Generally, the linear polymer in the polymer hybrid, prepared by physical interaction, can be easily extracted with the good solvent. Solvent extraction was carried out by THF reflux for 24 h and by DMF at 130 °C for 72 h. Both are good solvents for PS-F. TGA of the samples dried under vacuum at 60 °C for 2 days shows mass loss curves after THF extraction that are almost the same as before extraction. This result suggests that PS-F and silica gel covalently bond by DA reaction, and the solvent-resistant properties of the polymer hybrid increase. On the other hand, after DMF extraction at 130 °C, the inorganic content increased. In the mass loss curve of the sample after DMF extraction, the curve at low temperature (∼350 °C) was almost the same as that before extraction. But the mass loss around 400 °C was smaller than that before extraction. The mass loss

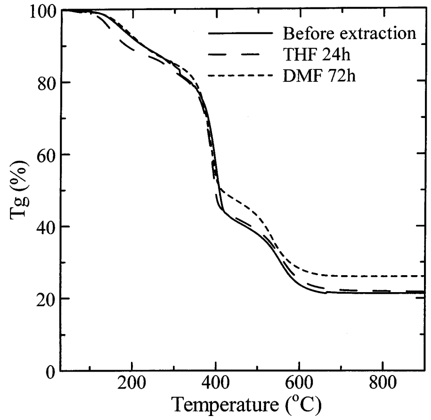


Figure 6. TGA thermograms of DA polymer hybrid before and after solvent extraction.

around this temperature was derived from decomposition of PS-F. This result suggests that during extraction at 130 °C RDA reactions might occur, breaking the cross-links between PS-F and silica matrix permitting PS-F extraction.

Conclusions

In this study, the homogeneity of organic−inorganic polymer hybrids was controlled by the reaction temperature. The homogeneity was affected by both the rate of gelation of alkoxysilanes and that of the DA reaction between furan group and maleimide group. At appropriate temperatures, PS-F and silica gel are mixed homogeneously by cross-linking between the organic polymer and silica matrix through DA adducts. On the other hand, only phase-separated composites were obtained at inappropriate temperatures or in the absence of cross-linker.

The obtained polymer hybrid showed high solvent resistance at the boiling point of THF because the PS-F was bonded with silica matrix covalently. Interestingly, PS-F could be extracted by DMF at 130 °C because of the cleavage of the DA adduct by RDA reaction. This thermal extraction control can be derived from the reversible character of DA and RDA reactions.

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