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Selected Paper

Synthesis of Organic–Inorganic Polymer Hybrids Utilizing Amphiphilic Solvent as a Compatibilizer

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Transparent organic–inorganic polymer hybrids with various organic polymers (polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC) and poly(acrylic acid) (PAA)) that are soluble in amphiphilic solvents such as *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMAc), could be easily synthesized by the sol–gel reaction of tetramethoxysilane (TMOS) in an amphiphilic solvent. It is because DMF and DMAc form strong hydrogen bonds with the silanol groups of the silica gel and have a high compatibility with organic polymers. DMF and DMAc play a role as compatibilizers between the organic polymer and silica gel. The hydrogen bonding interaction was confirmed by FT-IR spectra. The compatibility of the organic polymer with the amphiphilic solvent was explained by the solubility of the polymer in an amphiphilic solvent. The thermal stability of the polymer hybrids obtained was increased compared to that of bulk polymer by post-treatment. The homogeneity of the obtained polymer hybrids was confirmed by SEM and nitrogen porosimetry studies.

Organic–inorganic polymer nanocomposites, which are the hybridization of an organic polymer and inorganic material on a nano scale, have attracted tremendous attention because of the combined distinct properties of the organic polymer and inorganic material within a single molecular material.[1–5] The properties of the organic polymer include high flexibility, versatility in design of functionality, and film-forming properties. Inorganic compounds provide the potential for marvelous tensile strength, gas barrier property,[6] and high thermal and mechanical stability. Furthermore, nano-scale hybrid materials offer different chemical and physical properties such as flame resistance, high transparency,[7] and excellent solvent resistance-properties[8] which were different from those of bulk materials. In particular, transparency is one of the most striking features of the hybrid materials. Scattering loss is avoided because of the dispersion of components on the order of nanometers.

One of the useful methods for preparing polymer hybrids has been through the use of a low-temperature sol–gel polymerization route wherein a metal alkoxide precursor undergoes hydrolysis and condensation reactions to form an inorganic material.[9] Also, the reaction is performed in a low-viscosity solution that allows a high uniformity if the organic parts are dissolved in the initial solution. However, in order to prevent the phase separation of the organic polymer and inorganic material, it is necessary to introduce some interactions between the organic and inorganic phases. One of the normal methods is using covalent bonds between the organic polymer and silica gel.[10–12] We have prepared transparent polymer hybrids using physical interactions such as hydrogen bonding[13,14] or aromatic[15,16] or ionic interactions[17] between the organic polymer and silica gel. In addition, the other preparation method of transparent polymer hybrids was utilizing a compatibilizer between the organic polymer and silica gel. Recently, we reported that a new concept of "compatibilizer" between organic polymers and silica gel was applied to obtain transparent polymer hybrids by utilizing cyclodextrin as a compatibilizer.[18]

In this study, organic–inorganic polymer hybrids were prepared using an amphiphilic solvent as a compatibilizer (Scheme 1). *N*,*N*-Dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMAc) were used as an amphiphilic solvent. Generally, DMF and DMAc were not often used as a sol–gel solvent because their boiling points were too high to evaporate at room temperature. Therefore, low boiling point solvents such as methanol, acetone, and tetrahydrofuran (THF) were mainly used. But, to our surprise, the highly transparent polymer hybrids with the organic polymers that had poor interactions with the silica gel could be obtained by using DMF and DMAc as a sol–gel solvent. From these observations, we thought that DMF and DMAc played a role as compatibilizers between the organic polymer and silica gel, as shown in Scheme 1.

DMF and DMAc can dissolve several organic commodity polymers such as polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), and poly(acrylic acid) (PAA) indicating that DMF and DMAc have a high compatibility with these organic polymers. Furthermore, the amide groups of DMF and DMAc can form the strong hydrogen bonds with silanol moieties resulting from the hydrolysis and condensation of the alkoxysilane. This expectation is supported by the formation of the strong hydrogen bonds between the amide groups of poly(2-methyl-2-oxazoline) (POZO), a polymeric analog of DMAc, and the silanol moieties of the alkoxysilane for the transparent POZO/silica hybrids (Scheme 1a).[13,14] As shown in Scheme 1b, DMF and DMAc play a role as a compatibilizer between the organic polymer

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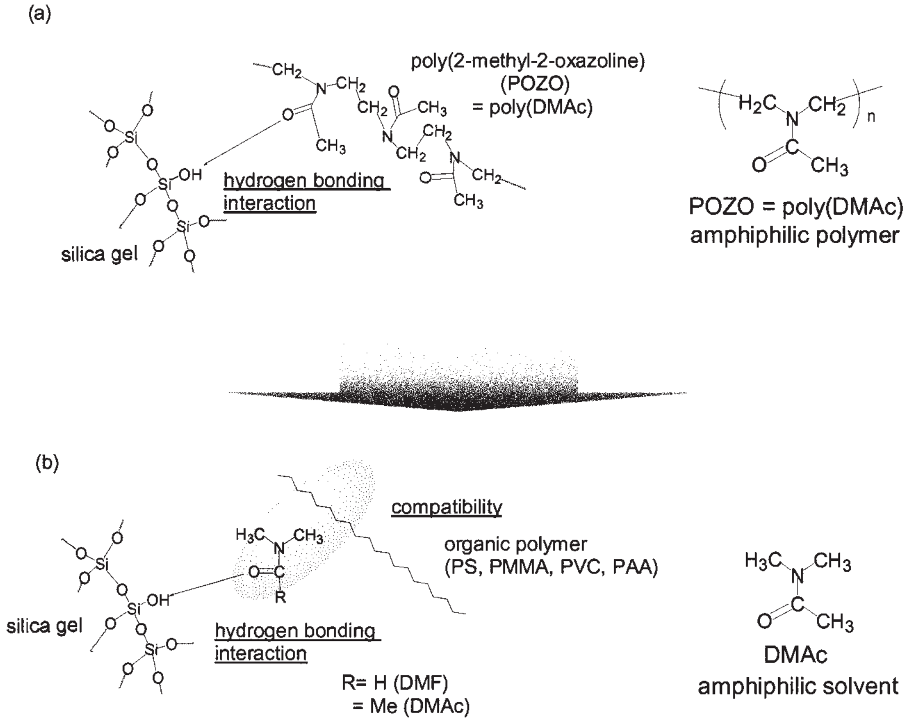


Scheme 1.

and silica gel. That might be the reason why transparent and homogeneous polymer hybrids could be obtained in DMF or DMAc, even if the organic polymers with no hydrogen bonding accepting groups such as PS, PMMA, PVC, and PAA interacted poorly with the silica gel. Therefore, the polymer hybrids with those polymers bring about a phase separation in other solvents such as THF and toluene. It is interesting that DMF and DMAc are used not only as a sol–gel solvent but also as a compatibilizer during the preparation of polymer hybrids. DMF and DMAc may remain in the polymer hybrid as a compatibilizer because of their high boiling points (boiling points of DMF and DMAc are 153.0 °C and 166.1 °C, respectively). Nevertheless, DMF and DMAc can be completely removed by post-treatment via extraction and annealing of polymer hybrids. It is important to note that this preparation method is very simple, novel, and widely applied to a large variety of organic polymers having poor affinity with silica gel.

Experimental

Materials. Polystyrene (PS, DP = 1000–1400 and DP = 7000–7500) was purchased from Nakarai Tesque Inc. Poly(acrylic acid) (PAA) of average molecular weight 5000 was obtained from Wako Pure Chemical Industries, Ltd. Poly(vinyl chloride) (PVC, $M_n = 22000$, $M_w/M_n = 1.95$), poly(vinylidene fluoride) (PVdF, $M_n = 71000$, $M_w/M_n = 2.53$) and polyacrylonitrile (PAN, $T_g = 85$ °C, $T_m = 317$ °C) was obtained from Aldrich. Tetramethoxysilane (TMOS) was distilled and stored under nitrogen. *N*,*N*-Dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMAc) were dried and distilled over magnesium sulfate under reduced pressure and stored under nitrogen. Tetrahydrofuran (THF) was dried and distilled over sodium under nitrogen. The other solvents and reagents were used as supplied.

Measurements. The ^{1}H NMR spectra were recorded on a 270 MHz JEOL JNM-GX270 NMR spectrometer. The FT-IR spectra were obtained using a Perkin Elmer 1600 infrared spectrometer. Thermogravimetric analysis (TGA) was performed using a TG/DTA6200, SEIKO Instruments, Inc., with a heating rate of 10 °C min^{-1} in air. Scanning electron microscopy (SEM) measurements were conducted using a JEOL JNM-5310/LV system. Nitrogen absorption porosimetry was conducted with a BEL JAPAN INC.

Synthesis of Organic–Inorganic Polymer Hybrids. An organic polymer was dissolved in the solvent with prescribed amounts of TMOS and HCl_{aq}. The resulting mixture was stirred in a sealed bottle for 5 h before allowing the solvent to evaporate at 60 °C. To prevent the evaporation of TMOS, the preparation of polymer hybrids was carried out in a bottle covered with an aluminum foil having a few pinholes. The resulting samples were dried in a vacuum oven at 80 °C to remove solvents.

Post-Treatment of Polymer Hybrids to Remove Remaining DMF. After drying in a vacuum oven at 80 °C, DMF still remained in the polymer hybrids. The remaining DMF in the polymer hybrids could be completely dried using two post-treatments. One is solvent extraction with methanol using a Soxhlet's extractor for 10 days, since DMF is widely miscible with methanol. The other is annealing of polymer hybrids at 150 °C for 24 h.

Nitrogen Adsorption Porosimetry. The powder of polymer hybrids was heated at 600 °C in an ambient atmosphere for 24 h to remove organic components. The sample was dried at 150 °C for 2 h at reduced pressure under a nitrogen atmosphere before porosimetry measurements. The surface area was calculated with the Brunauer–Emmett–Teller (BET) equation[19] in the range of 0.05 to 0.30 (p/p_0) and the pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method.[20]

Results and Discussion

Synthesis of Organic–Inorganic Polymer Hybrids. Organic–inorganic polymer hybrids were prepared utilizing am-

Table 1. Synthesis of Organic–Inorganic Polymer Hybrids Utilizing Amphiphilic Solvents[a)]

Run	PS	TMOS	HCl_{aq}	Solvent	Appearance	Ceramic yield/wt %	
	mg	mg	mL	mL		Calcd.	Obsd.
1	**50**	200	0.1 M 0.03	DMF 5	**transparent**	61.5	51.7
2	**25**	200	0.1 M 0.03	DMF 5	**transparent**	76.2	59.9
3	**80**	200	0.1 M 0.03	DMF 5	**transparent**	50.0	41.9
4	**250**	200	0.1 M 0.03	DMF 15	**transparent**	24.2	22.3
5	50	200	**1 M 0.03**	DMF 5	phase separated	—	—
6	50	200	**0.1 M 0.06**	DMF 5	phase separated	—	—
7	50	200	**0.1 M 1.00**	DMF 5	phase separated	—	—

a) Stirring time 5 h, evaporate solvent at 60 °C.

Table 2. Effect of Solvents on Homogeneity[a)]

Run	PS	TMOS	HCl_{aq}	Solvent	Appearance	Ceramic yield/wt %	
	mg	mg	mL	mL		Calcd.	Obsd.
1	50	200	0.1 M 0.03	**DMF 5**	**transparent**	61.5	51.7
8	50	200	0.1 M 0.03	**DMAc 5**	**transparent**	61.5	45.6
9	50	200	0.1 M 0.03	**THF 5**	phase separated	—	—
10	50	200	0.1 M 0.03	**Toluene 5**	phase separated	—	—

a) Stirring time 5 h, evaporate solvent at 60 °C.

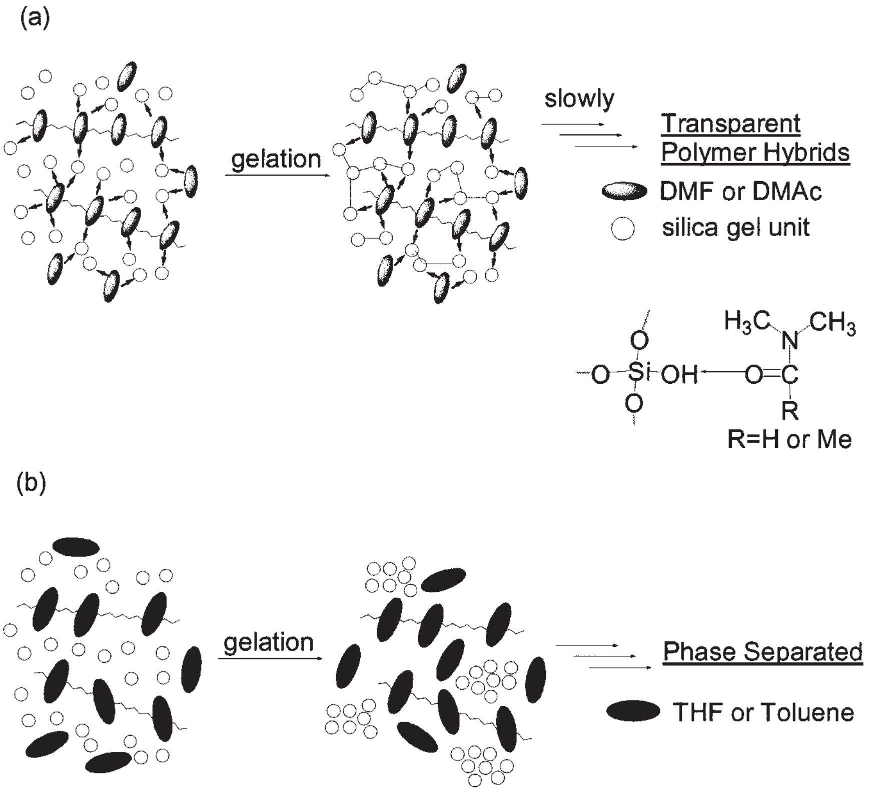
phiphilic solvents such as DMF and DMAc. DMF and DMAc not only have excellent compatibility with various organic polymers such as PS, PMMA, PVC, and PAA, but also form strong hydrogen bonds with silanol groups resulting from hydrolysis of TMOS. It means that DMF and DMAc play a role as a compatibilizer between the organic polymer and silica gel as shown in Scheme 1. At first, PS/silica hybrids were prepared in DMF and DMAc. The affinity of PS with silica gel was too weak to obtain a transparent PS/silica hybrid. Thus, to obtain a transparent PS/silica hybrid, it was necessary to modify the aromatic interaction between PS and silica gel resulting from phenyltrimethoxysilane.[15,16] In the present research, we tried to prepare a transparent PS/silica hybrid using DMF and DMAc as compatibilizers. The solubility of PS in DMF is so high that DMF should have excellent compatibility with PS. The results are shown in Table 1.

The concentration and the amount of HCl_{aq} affected the transparency of the polymer hybrids. Transparent and homogeneous polymer hybrids could be obtained in a wide range by using a low concentration (0.1 M) and small amount of HCl_{aq} (0.03 mL) as a catalyst of the sol–gel reaction (Table 1, runs 1–4). On the other hand, in the case of high HCl concentration (1 M) (Table 1, run 5) or a large amount of HCl_{aq} (Table 1, runs 7 and 8) as the blank experiments of run 1, the obtained polymer hybrids brought about phase separation. The sol–gel reaction of the alkoxysilane was generally accelerated by using a high concentration or a large amount of HCl_{aq}. Consequently, the gelation of alkoxysilane took place faster. Thus, these results indicate that the sol–gel reaction of TMOS should proceed as slowly as possible to obtain transparent polymer hybrids. The reason is that the evaporation speed of DMF as a compatibilizer between PS and the silica gel was decreased by processing the sol–gel reaction slowly. The silanol groups from TMOS remained when the speed of the sol–gel reaction was slow. Therefore, DMF formed strong hydrogen bonds with the silanol groups was evaporated with difficulties. It was necessary that DMF as a compatibilizer be kept in the polymer hybrids system by controlling the sol–gel reaction of TMOS to obtain highly transparent polymer hybrids.

Effect of Solvents on the Homogeneity of Polymer Hybrids. The influence of solvents used in the sol–gel reaction on the homogeneity of polymer hybrids was examined. The employed solvents are DMF, DMAc, toluene, and THF. The polymer hybrids were prepared by dissolving PS and TMOS in a 1/4 ratio in these solvents. The results are shown in Table 2.

The appearance of polymer hybrids was phase-separated by using toluene or THF as the sol–gel solvent (Table 2, run 9 and run 10). In contrast, the polymer hybrids using DMF or DMAc as the solvent were transparent (Table 2, run 1 and run 8). All these solvents easily dissolved PS. But DMF and DMAc have a higher affinity with silica gel than THF and toluene because of the strong hydrogen bonds between the amide groups of DMF or DMAc and the silanol groups resulting from the hydrolysis of TMOS, which was confirmed by FT-IR spectra (discussed in the next section). Therefore, as illustrated in Scheme 2(a), DMF and DMAc played a role as a compatibilizer between PS and the silica gel, and the transparent polymer hybrids were obtained after the sol–gel reaction. On the other hand, in the case of using toluene or THF (Scheme 2(b)), those solvents that don't have much affinity with silanol groups, the results were phase-separated polymer hybrids.

FT-IR Spectra of Polymer Hybrids. The hydrogen bonding interaction between an amphiphilic solvent (DMF and DMAc) and silanol moieties was confirmed by FT-IR measurement. It was recognized that the stretching band of the amide carbonyl peaks of the amphiphilic solvent in the polymer hybrids was shifted to lower wavenumbers compared to that of bulk amphiphilic solvent due to the strong hydrogen bonding interaction.



Scheme 2.

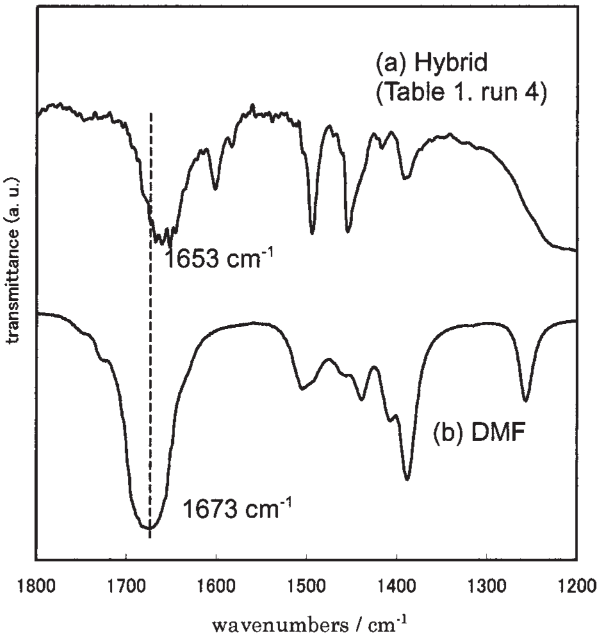


Fig. 1. FT-IR spectra of (a) PS/silica hybrid (Table 1, run 4), and (b) DMF.

As shown in Fig. 1, in the case of the sample after vacuum drying of the transparent polymer hybrids using DMF (Table 1, run 4) at 80 °C for 72 h, the amide carbonyl stretching band of DMF was observed (Fig. 1a). DMF was incorporated and remained in the polymer hybrids because of the strong hydrogen bonds with the silanol groups, while DMF was easily evaporated under vacuum drying conditions. This result means that DMF formed the strong hydrogen bonds with residual silanol groups. The amide carbonyl band of DMF in the polymer hybrids was shifted from 1673 cm^{-1} (bulk DMF, Fig. 1b) to 1653 cm^{-1}. In addition, poly(2-methyl-2-oxazoline) (POZO), a polymeric analog of DMAc, also formed strong hydrogen bonds with the silanol groups. The peak for the amide carbonyl stretching band of pristine POZO is originally positioned at 1634 cm^{-1} and shifted to 1622 cm^{-1} when POZO was dispersed into the silica gel matrix at the nanometer level.[13,14] From these observations, it was thought that the strong hydrogen bonds between DMF and the silanol groups formed in the polymer hybrids.

Furthermore, two post-treatments were performed to remove the remaining DMF in polymer hybrids completely: (i) DMF extraction with methanol for 10 days and (ii) annealing of polymer hybrids from 150 °C to 200 °C for 48 h. Using both methods, the remaining DMF in the polymer hybrids was almost removed. As shown in Fig. 2, the amide carbonyl band of DMF in polymer hybrids disappeared in both cases. The changes in thermal stability and transparency of the polymer hybrids by removing DMF are shown in the following sections.

Compatibility of Amphiphilic Solvent with Organic Polymer. This preparation method of polymer hybrids was applied for synthesizing polymer hybrids with the polymers having a high solubility in an amphiphilic solvent such as DMF and DMAc. PMMA, PVC, and PAA, which have excellent solubility in DMF, were used as organic polymers. The affinity of these polymers with silica gel was the same as that of PS, so that the polymer hybrids with these polymers were usually phase-separated.

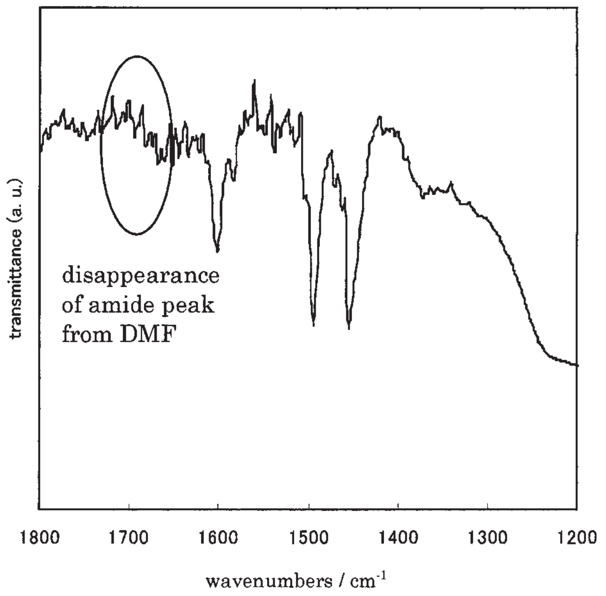


Fig. 2. FT-IR spectrum of PS/silica hybrid (Table 1, run 4) after post-treatment (using solvent extraction with methanol).

Table 3. Synthesis of Organic–Inorganic Polymer Hybrids Utilizing DMF[a)]

Run	Polymer	TMOS	Appearance
	mg	mg	
1	**PS 50**	200	**transparent**
11	**PMMA 50**	200	**transparent**
12	**PVC 50**	200	**transparent**
13	**PAA 50**	200	**transparent**
14	**PVdF 50**	200	translucent
15	**PAN 50**	200	translucent

a) HCl_{aq} (0.1 M) 0.03 mL, DMF 5 mL, stirring time 5 h.

As shown in Table 3, the transparent and homogeneous polymer hybrids using PMMA, PVC and PAA could be obtained by controlling the concentration and the amount of HCl_{aq} catalyst (Table 3, runs 11–13). But the sample using PVdF and PAN brought about a translucent film regardless of the concentration and the amount of the catalyst because of the low solubility of these polymers in DMF (dissolved in a large amount of DMF by heating) (Table 3, run 14 and run 15). From these observations, it was easy to obtain transparent polymer hybrids using organic polymers having a high solubility with DMF such as PS, PMMA, PVC, and PAA. However, the transparent polymer hybrids with PVdF and PAN that have poor solubility with DMF could not be obtained. The compatibility between organic polymers (PS, PMMA, PVC and PAA) and the amphiphilic solvents such as DMF and DMAc was confirmed by the solubility of the organic polymer in these amphiphilic solvents.

Thermal Properties of Polymer Hybrids. The thermal stability of the polymer hybrids was examined by TGA measurement (Fig. 3). In the case of the sample before removing DMF completely, thermal stability was not increased a lot compared to PS (Figs. 3a and 3b). T_{10} of the polymer hybrid (a : before post-treatment) and PS (b) was 201.7 °C and 308.5 °C, respectively. In the polymer hybrids (a), weight loss around low temperature (100–200 °C) was observed. This means that the sol–gel reaction of the remaining silanol groups, which were stabilized with DMF by hydrogen bonds, still proceeded according to the evaporation of DMF by heating. However, the weight loss of the polymer hybrids at low temperature completely disappeared by removing DMF in the polymer hybrid using two post-treatments described previously (Fig. 3c). In the polymer hybrid after post-treatment (c), T_{10} of the polymer hybrid was 384.3 °C, indicating that the thermal stability of the polymer hybrid was markedly increased over that of PS (Figs. 3b and 3c).

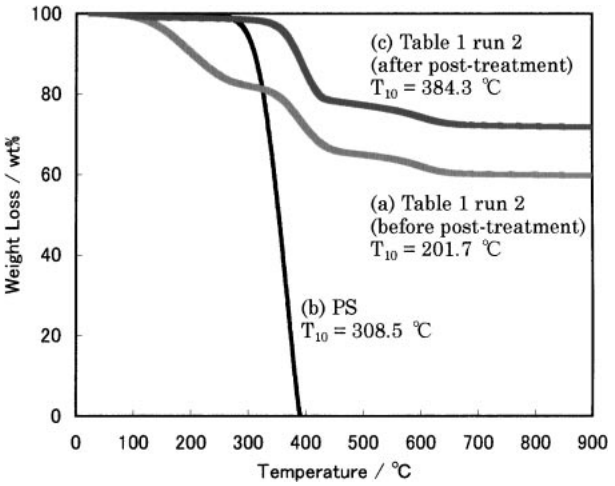


Fig. 3. TGA traces of (a) PS/silica hybrid (Table 1, run 2), (b) PS, and (c) PS/silica hybrid after post-treatment of annealing.

SEM Images of Polymer Hybrids. The dispersion between organic and inorganic phases was examined by SEM (Fig. 4). As shown in Fig. 4a, the sample with high HCl concentration (1 M) (Table 1, run 7) showed phase separation between the silica gel and organic polymer about 1500 magnifications. The white parts indicate silica. The surface of the sample was rough and micro-pores were observed. In the case of the sample with THF (Table 2, run 9), the size of the silica domain could be estimated to be around 5 µm (Fig. 4b). In the translucent sample with PVdF (Table 3, run 14), some domains were also observed (Fig. 4c). However, when the PS/silica hybrid was prepared in DMF (Table 1, run 1), some particles or domains disappeared completely (Fig. 4d). It is noted that silica is dispersed at the nanometer level. But the transparency of the polymer hybrids was changed by post-treatment. In the case of the sample in low silica ratio (Table 1, run 4), the appearance of the polymer hybrid changed from transparent to translucent using two post-treatments, and some white particles were observed around 300 nm by SEM (Fig. 4e). This observation shows the aggregation of the silica gel in the PS matrix. Under this condition, the matrix of polymer hybrids was linear PS. It is considered that the sol–gel reaction of some silanol moieties stabilized by hydrogen bonds with DMF may proceed and aggregate during the post-treatment. On the other hand, the transparency of the polymer hybrid in the high silica ratio (Table 1, run 2) did not change after removing DMF in the polymer hybrid (Fig. 4f).

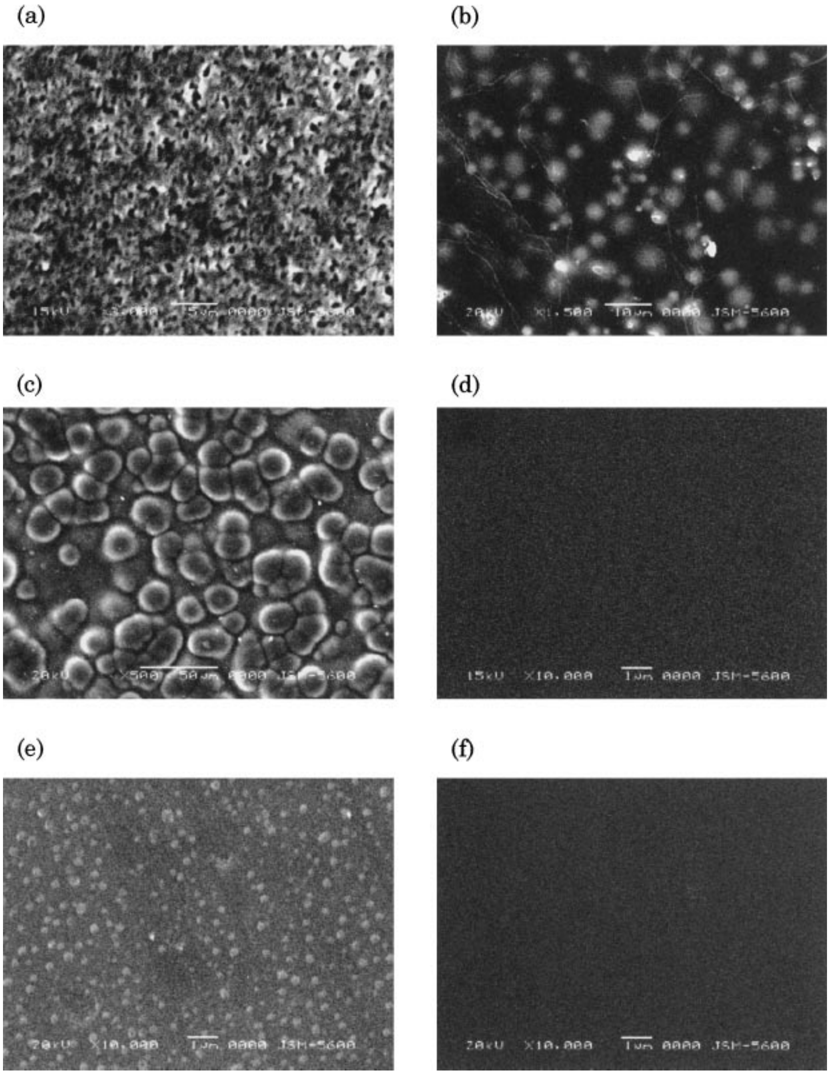
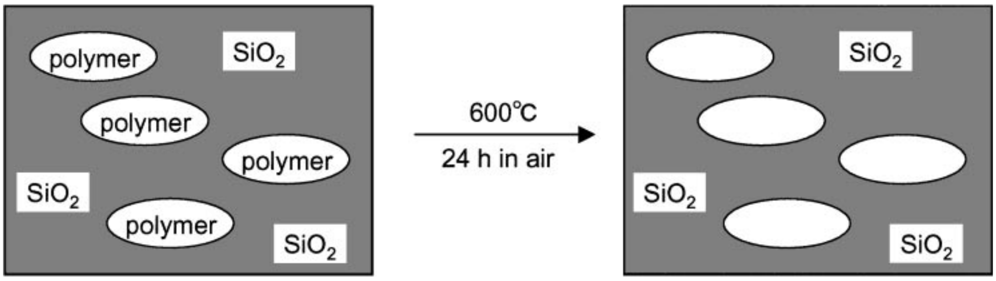


Fig. 4. SEM images of (a) PS/silica hybrid using large amounts of 0.1M HCl_{aq} (Table 1, run 7), (b) PS/silica hybrid using THF (Table 2, run 9), (c) PVdF/silica hybrid using DMF (Table 3, run 14), (d) PS/silica hybrid using DMF (Table 1, run 1), (e) PS/silica hybrid in low silica ratio (Table 1, run 4) after post-treatment (annealing) and (f) PS/silica hybrid in high silica ratio (Table 1, run 2) after post-treating of annealing.



Scheme 3.

The physical entrapment of PS by the silica cage deterred the polymer aggregation even if the sol–gel reaction of the remaining silanol groups was proceeded during the removal of the remaining DMF in the polymer hybrids.

Pore Size Distribution of Porous Silica Obtained from Organic–Inorganic Polymer Hybrids. The homogeneity of the polymer hybrids was quantitatively evaluated on the nano-scale by nitrogen absorption porosimetry and SEM studies. The nitrogen porosimetry method was a very useful technique to investigate the dispersity of the organic polymer in the polymer hybrids. The calcination of the polymer hybrids at 600 °C for 24 h removed the organic elements effectively, which resulted in the formation of porous silica (Scheme 3).

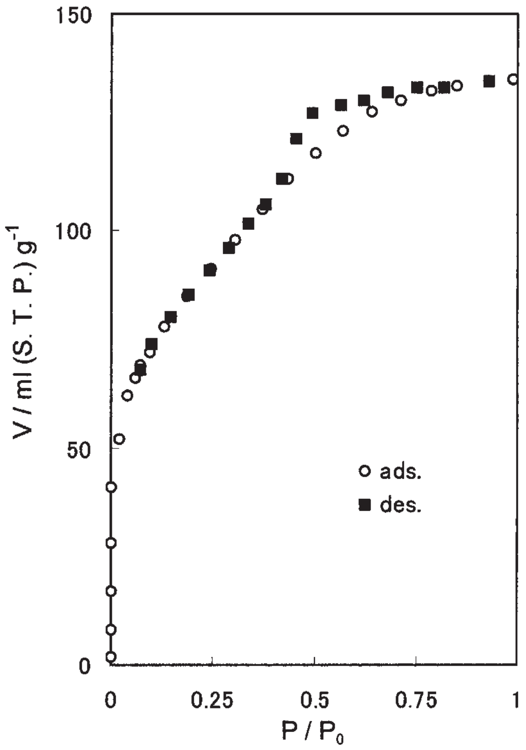


Fig. 5. Adsorption isotherm curve of the porous silica from PS/silica hybrid (Table 1, run 1).

The silica gel matrix is so rigid that it would not be affected at this temperature. The size of the remaining pores was found to correspond well to the size of the domain of the organic polymer. The PS/silica hybrids in DMF (Table 1, run 1) were calcinated and the resulting porous silica was measured by nitrogen porosimetry study. The absorption isotherm curves obtained from the nitrogen porosimetry study are shown in Fig. 5.

Porous silica from the polymer hybrids showed a type Ⅳ curve, which indicated the presence of nano-pores. The surface area was calculated from the BET method. The porous silica obtained from the transparent polymer hybrids had quite a large pore volume (70.0 mL/g) and surface area (304.4 m^2/g). The pore size distribution of the porous silica from the polymer hybrid was also calculated by the BJH method (Fig. 6). The sharp pore size distribution was peaked at 1.7 nm. These results are similar to the porous silica obtained from the polymer hybrids with POZO.[14] This indicates nano-level dispersion of the organic polymer in the polymer hybrids.

Conclusions

Transparent and homogeneous polymer hybrids were obtained in amphiphilic solvents such as DMF and DMAc. DMF and DMAc were used as a compatibilizer between the organic polymer and silica gel because DMF and DMAc formed strong hydrogen bonds with the silanol moieties and showed a high compatibility with the organic polymer. Hybridization of various DMF or DMAc soluble polymers can be potentially used to enlarge the pathways for new organic–inorganic polymer hybrids with silica by this preparation methodology.

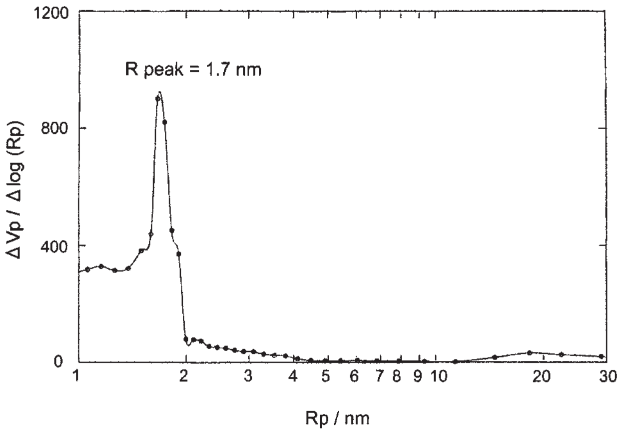


Fig. 6. Pore size distribution plots of porous silica obtained from PS/silica hybrid (Table 1, run 1).

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