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Synthesis of Photosensitive Organic−Inorganic Polymer Hybrids by Utilizing Caged Photoactivatable Alkoxysilane

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ABSTRACT: Photosensitive polymer hybrids with poly(acrylic acid) (PAA) could be obtained by using caged (photosensitive protecting group modified) alkoxysilane (NVOC-U-PTEOS). Transparent polymer hybrids were prepared with UV irradiation, while the obtained materials were turbid without UV irradiation. This can be attributed to the strong ionic interaction between carboxylic acid groups of PAA and amino groups generated from NVOC-U-PTEOS by photoirradiation. The ionic interaction in polymer hybrids was confirmed utilizing FT-IR and ^{1}H NMR, and the transparency of the polymer hybrids was evaluated by SEM.

Introduction

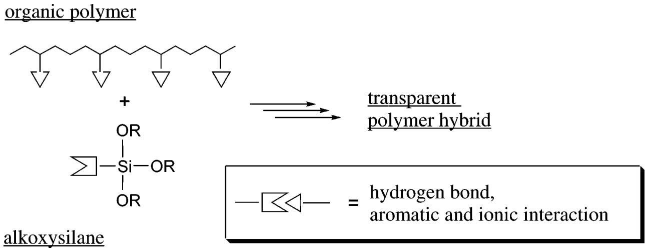
A combination of different type of materials (organic, inorganic, and metallic) is an important and evolutionary way to achieve the desired properties which cannot be accomplished with single materials. Especially, nanosize level composite materials show unique chemical and physical properties which are different from microsize level composites.[1−6] Organic−inorganic polymer hybrids, in which organic polymers are dispersed in inorganic matrix at a nanometer or molecular level, have attracted tremendous attention and been widely investigated because of unique properties of the polymer hybrids resulting from nanometer level composite such as high gas-barrier property,[7] excellent solvent resistance,[8] flame resistance, and high transparency.[9] The transparency of the nanocomposite materials is the most characteristic property due to the dispersion of components on the order of nanometers, which is far less than the wavelength of visible light and even near-ultraviolet light, and as a result, the scattering loss is avoided.

The most popular, practical approach for preparing organic−inorganic polymer hybrids is utilizing sol−gel reaction.[10] The advantage of sol−gel reaction is its mild processing characteristics. The process involves the hydrolysis of metal alkoxide, followed by a condensation reaction with solvent evaporation to produce metal oxides. A silicon alkoxide such as tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) was widely used to obtain silica gel by far.

Organic−inorganic polymer hybrids are easily prepared by the sol−gel reaction of alkoxysilanes in the presence of organic polymer. However, the appearance of the obtained polymer hybrid is usually turbid by only mixing organic polymer and alkoxysilane in the solvent because the aggregation of organic polymer in silica gel matrix would take place during the preparation of polymer hybrids. To obtain transparent polymer hybrids, it is necessary to introduce covalent bond[11−13] or physical interaction between organic polymer and silica gel.

In our group, novel organic−inorganic polymer hybrids could be created by utilizing physical interactions such as hydrogen bond,[14−16] aromatic,[17,18] and ionic interactions[19] between organic polymer and silica gel (Scheme 1). For example, the hydrogen bond interaction between residual silanol groups from sol−gel reaction and organic polymer having strong hydrogen-accepting groups such as poly(2-methyl-2-oxazoline) (POZO), poly(*N*-vinylpyrrolidone) (PVP), and poly(dimethylacrylamide) (PDMAAm) results in the molecular dispersion in silica gel matrix.

Scheme 1



In this research, we pay attention to the transparency changes of the polymer hybrids depending on the interactions between organic polymer and silica gel. The controlling of the transparency of the polymer hybrids can be achieved by creating the interaction between organic polymer and silica utilizing stimuli (photo, thermal, oxidation−reduction, and so on), while the appearance of the polymer hybrids is phase separated without stimuli. The concept of caged compounds is introduced during the preparation of polymer hybrids to obtain photosensitive polymer hybrids in this article. Caged compounds are biologically active molecules or ions, which are modified chemically with photosensitive protecting groups. In other words, caged compounds are nonactive usually and can be activated upon photoirradiation. Therefore, caged compounds are mainly applied in the field of biochemistry and drug delivery system.[20−22] Nitrobenzyl groups were widely used as a photocaged compound. In the present study, photosensitive polymer hybrids could be prepared by utilizing caged (photosensitive protecting groups modified) alkoxysilane. The idea is shown in Scheme 2.

In path I, the polymer hybrids with caged alkoxysilane were prepared without photoirradiation. In this case, the obtained polymer hybrid was phase separated due to weak interaction between organic polymer and silica gel resulting from “nonactive” caged alkoxysilane.

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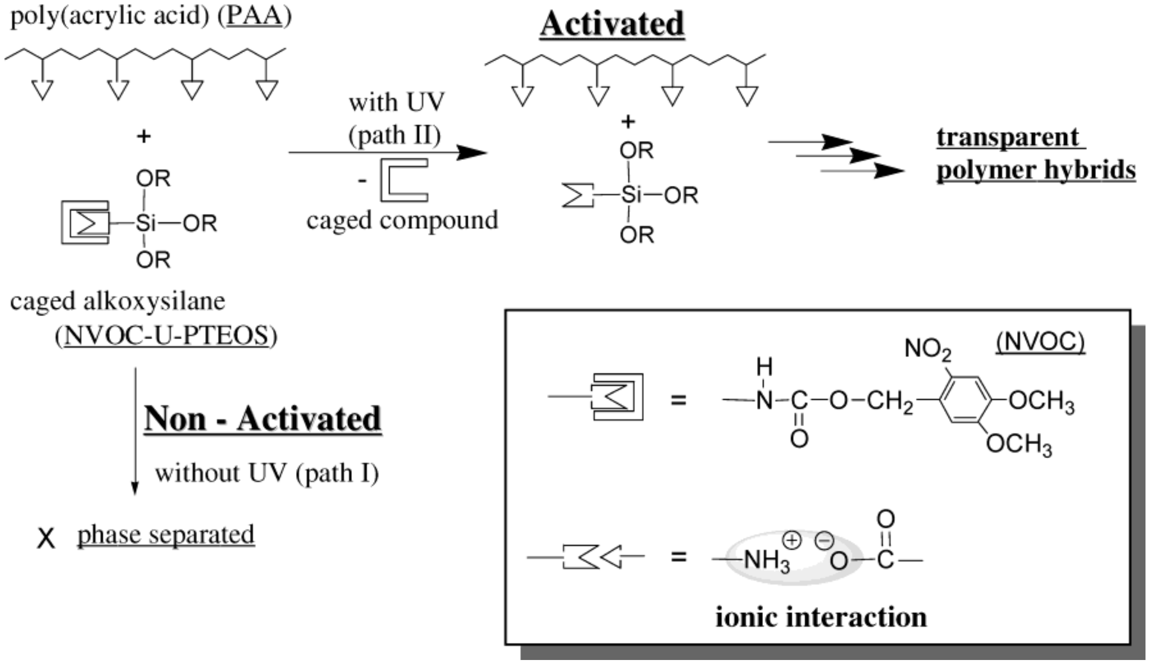
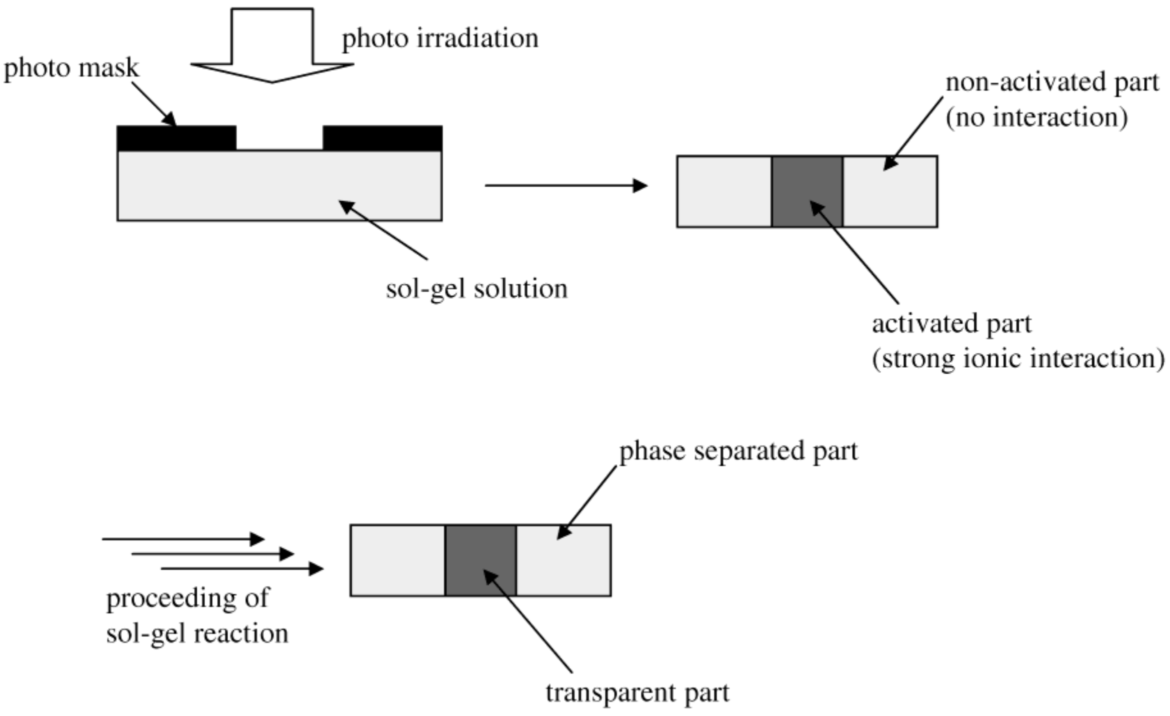
Scheme 2



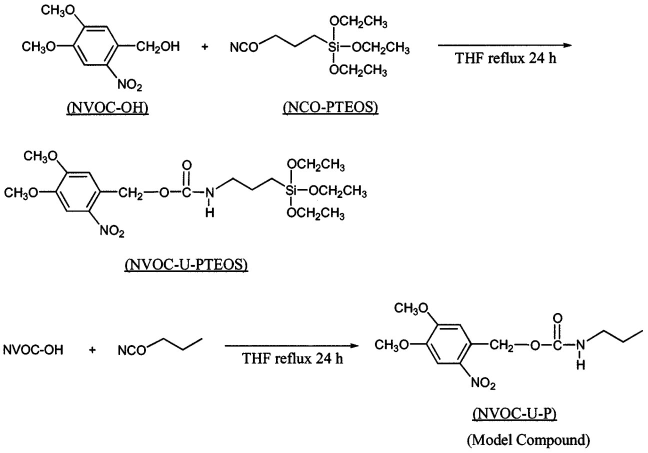
Scheme 3



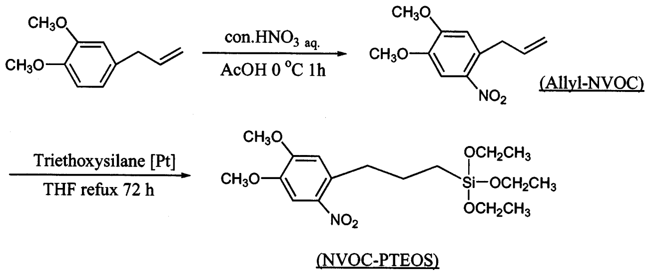
The organic polymer aggregated in the silica gel matrix. On the other hand, transparent polymer hybrids could be obtained with photoirradiation during preparing polymer hybrids (path II). It is because “nonactive” caged alkoxysilane was changed to nonprotected “active” alkoxysilane with photoirradiation by removing cage groups and the strong interaction formed between organic polymer and silica gel from nonprotected alkoxysilane. That is the reason why organic polymer can be dispersed in a silica gel matrix at the nanometer level, and the obtained polymer hybrid is transparent with photoirradiation. In this study, ionic interaction between carboxylic acid groups of poly(acrylic acid) (PAA) and amine groups of 3-(aminopropyl)triethoxysilane (APTEOS) and the caged compound of 6-nitroveratryloxycarbonyl (NVOC) group were used. It is interesting to note that the control of the transparency of the polymer hybrids can be easily achieved by utilizing the concept of the caged compounds. As shown in Scheme 3, photoresist like polymer hybrids could be prepared using this preparation method.

The photoirradiated parts are activated and bring about transparent, while the other parts without photoirradiation (utilizing photomask) are nonactivated and become phase separation as a result. To our best knowledge, it is little known that the transparency of the polymer hybrids can be controlled by utilizing photoirradiation. The properties of the obtained polymer

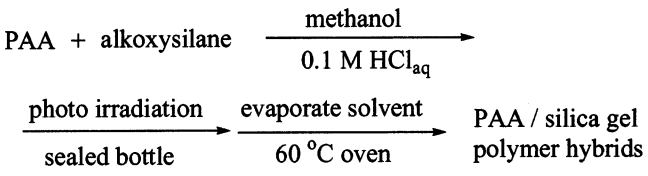
Scheme 4



Scheme 5



Scheme 6



hybrids dramatically depended on the miscibility between organic polymer and silica phase. The dispersion of organic polymer in silica gel matrix could be easily controlled by the time of the UV irradiation in this approach. Therefore, the polymer hybrid having desired properties resulting from the miscibility between organic polymer and silica gel could be obtained using this photosensitivity. Therefore,the transparent parts preparing with photoirradiation should show the high mechanical and thermal properties compared to phase separation parts due to nanometer level miscibility between organic polymer and silica gel. It is the first report that the biochemical idea of caged compounds is utilized in the field of nanocomposite materials science. This photosensitive polymer hybrid can be accomplished by not using covalent bond but using physical interaction because it is easy to create physical interaction between organic polymer and silica by photoirradiation compared with the formation of covalent bonds.

Experimental Section

Materials. Poly(acrylic acid) (PAA) of average molecular weight 25 000 was obtained from Wako Pure Chemical Industries, Ltd. Tetraethoxysilane (TEOS) was distilled and stored under nitrogen. Tetrahydrofuran (THF) was dried and distilled over sodium under nitrogen. Methanol was dried with magnesium methoxide and distilled under a nitrogen atmosphere. Hexane was dried and distilled over MgSO$_4$ 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. Thermogravimetric analysis (TGA) was performed using a TG/DTA6200, Seiko Instruments, Inc., with heating rate of 10 °C min^{-1} in air. Scanning electron microscopy (SEM) measurements were conducted using a JEOL JNM-5310/LV system. Absorption spectra were obtained on a Jasco V-530 spectrometer. The FT-IR spectra were obtained using a Perkin-Elmer 1600 infrared spectrometer.

Synthesis of 6-Nitroveratryloxycarbonyl (NVOC) Group Modified Alkoxysilane via Urethane Functional Group (NVOC-U-PTEOS) (Scheme 4). To 20 mL of THF were added 1.00 g (4.68 mmol) of 6-nitroveratryloxycarbonyl alcohol (NVOC-OH), 2.00 mL (2.00 g, 8.07 mmol; about 2 equiv to NVOC-OH) of isocyanatopropyltriethoxysilane (NCO-PTEOS), and 0.03 mL of di-*n*-butyltin dilaulate (used as a catalyst to proceed urethane formation[23,24] between alcohol and isocyanate group), and the mixture was refluxed overnight under a nitrogen atmosphere. After evaporation of THF, the crude product was washed using hexane three times under nitrogen. The solubility of NVOC-OH was very poor in hexane compared with that of NCO-PTEOS. Therefore, excess molar amounts of NCO-PTEOS could be easily removed by washing with hexane. The compound NVOC-U-PTEOS was obtained as a light pink solid in a quantitative yield. ^{1}H NMR (CDCl$_3$): δ 7.68 (s, 1H), 7.00 (s, 1H), 5.51 (m, 2H), 5.16 (br, 1H), 4.02–3.90 (m, 6H), 3.85–3.76 (m, 6H), 3.25 (t, 2H), 1.67 (m, 2H), 1.23 (m, 9H), 0.67 (t, 2H).

Synthesis of NVOC Propane via Urethane Functional Group (NVOC-U-P) (Model Compound) (Scheme 4). Under a nitrogen atmosphere, NVOC-OH (1.00 g, 4.69 mmol), propyl isocyanate (1.00 mL, 9.67 mmol), and 0.03 mL of di-*n*-butyltin dilaulate (catalyst) were dissolved in 15 mL of THF, and the mixture was refluxed overnight. After evaporation of THF, the crude product was purified by recrystallization in hexane three times. The light pink solid (NVOC-U-P) was obtained (1.29 g, 4.09 mmol, yield 87.2%). ^{1}H NMR (CDCl$_3$): δ 7.72 (s, 1H), 7.00 (s, 1H), 5.55 (s, 2H), 4, 86 (br, 1H), 4.02–3.93 (m, 6H), 3.19 (t, 2H), 1.57 (m, 2H), 0.94 (m, 3H).

Synthesis of NVOC Group Modified Alkoxysilane via Alkyl Group (NVOC-PTEOS) (Scheme 5). The compound of allyl-NVOC was prepared according to the detailed experimental procedure described in a previous literature.[25] The compound of NVOC-PTEOS was prepared by the hydrosilylation of allyl-NVOC with triethoxysilane using a platinum catalyst. Under a nitrogen atmosphere, 0.70 g (3.12 mmol) of allyl-NVOC, 1.50 mL (8.13 mmol) of triethoxysilane, and 0.03 mL of the platinum–divinyltetramethyldisiloxane complex (in xylene solution) were dissolved in 2 mL of THF solution, and the mixture was refluxed for 72 h. After evaporation of THF, the oily product was washed using hexane three times under nitrogen. The slightly black oily product was obtained (yield 12.6%). ^{1}H NMR (CDCl$_3$): 7.59 (s, 1H), 6.73 (s, 1H), 4.02–3.90 (m, 6H), 3.85–3.80 (m, 6H), 2.96 (t, 2H), 1.78 (m, 2H), 0.74 (t, 2H).

Preparation of Polymer Hybrids with Photoirradiation. The organic–inorganic polymer hybrids were prepared from PAA by utilizing the sol–gel reaction of various kinds of alkoxysilanes (Scheme 6). PAA and alkoxysilanes were dissolved in methanol, and a prescribed amount of aqueous hydrochloric acid was added as a catalyst for the sol–gel reaction. The mixture was stirred at 2 h in a sealed bottle with photoirradiation. As an ultraviolet source, a 450 W high-pressure mercury lump was used. Then, the mixture was placed in an open container with a paper towel and left in an oven at 60 °C to evaporate the solvent. The resulting samples were dried in a vacuum oven at 80 °C to remove the solvent completely.

Results and Discussion

Effect of APTEOS on Homogeneity of PAA/Silica Polymer Hybrids. The effect of APTEOS on the homogeneity of PAA/silica hybrids was investigated (Table 1). As illustrated in Figure 1, APTEOS, MeTEOS,

Table 1. Effect of APTEOS on Homogeneity of PAA/Silica Hybrids[a]

run	alkoxysilane	PAA/alkoxysilane (w/w)	appearance
1	APTEOS	4	transparent
2	MeTEOS	4	translucent
3	PhTEOS	4	turbid
4	TEOS	4	turbid

[a] Methanol 5 mL, HCl_{aq} (0.1 M) 0.2 mL, stirring time 2 h, evaporating methanol at 60 °C.

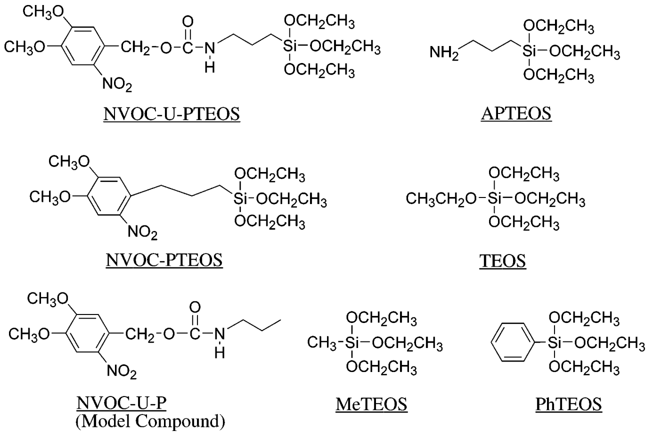
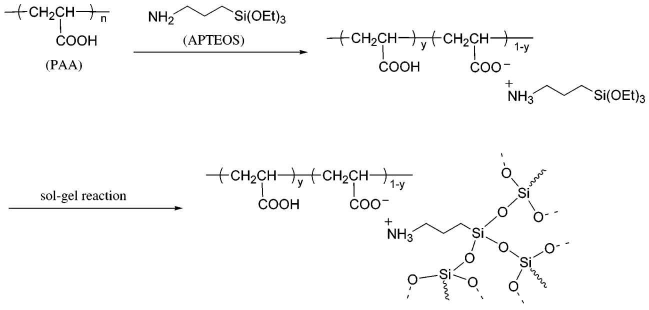


Figure 1. Alkoxysilanes for preparation of polymer hybrids and model compound.

Scheme 7



PhTEOS, and TEOS were used for the synthesis of PAA/silica hybrids.

As shown in Table 1, the obtained polymer hybrid using APTEOS was homogeneous and transparent (run 1). On the other hand, when MeTEOS was used as an alkoxysilane, the polymer hybrid brought about turbid (run 2). The same results were also observed with PhTEOS (run 3) and TEOS (run 4). These observations resulted from strong ionic interaction between carboxylic acid groups of PAA and amine groups of APTEOS.

As described in Scheme 7, the proton transfer should be performed from carboxylic acid groups to amino groups at the moment of addition of APTEOS to the solution of PAA. Then the ionic interaction between the caboxylate ion and the ammonium ion would be formed and link PAA and APTEOS by the ionic pairs. Therefore, the obtained polymer hybrid with APTEOS was transparent as a result.

Evidence of Ionic Interaction between PAA and APTEOS. The ionic interaction between PAA and APTEOS was confirmed by FT-IR spectra. It was recognized that the new C=O stretching band of carboxylate ion was observed due to the proton transfer from carboxylic acid groups to amine groups. The FT-IR spectra are shown in Figure 2.

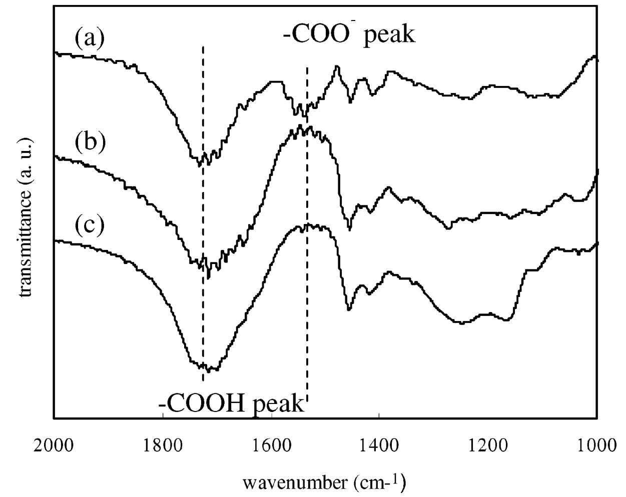


Figure 2. FT-IR spectra of the PAA/silica hybrid (a) using APTEOS (Table 1, run 1), (b) using MeTEOS (Table 1, run 2), and (c) PAA.

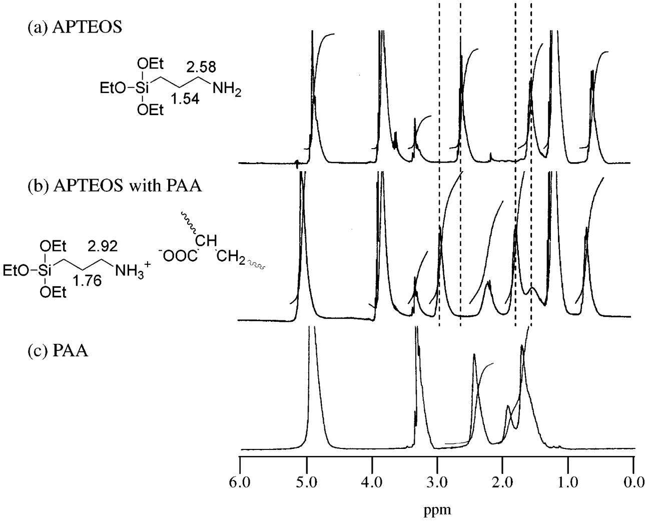


Figure 3. ^1H NMR spectra of (a) APTEOS, (b) APTEOS with the same molar ratio of PAA, and (c) PAA in CD_3OD.

In all samples were found the C=O stretching bands of carboxylic acid at 1700 cm^{-1}. In addition, the new peak appeared around 1550 cm^{-1} in the case of the transparent samples using APTEOS (Figure 2a) compared to the other phase-separated samples using MeTEOS (Figure 2b) and PAA (Figure 2c). This peak was assignable to the C=O stretching vibration of the carboxylate ion.[26] This result indicates the proton transfer from the carboxylic acid groups to amino groups and the formation of ionic bonds.

^1H NMR was also utilized to check the ionic interactions between carboxylic acid groups of PAA and amino groups of APTEOS. As shown in Figure 3a, alkyl peaks of APTEOS were observed at 2.58 and 1.54 ppm in CD_3OD. But these peaks were shifted to 2.92 and 1.76 ppm with the same molar ratio of PAA in CD_3OD (Figure 3b). It suggests that anime groups are changed to ammonium ion moieties because of the proton transfer from carboxylic acid groups to amine groups.[27]

Photocleavage Reaction of NVOC Caged Compound. The photocleavage reaction of the model compound (NVOC-U-P) in methanol was checked (Scheme 8). The change of UV absorption spectra during the photoirradiation is shown in Figure 4.

The UV absorbance of around 340 nm was decreased by photoirradiation, and the reaction was saturated

Table 2. Synthesis of UV-Sensitive Organic−Inorganic Polymer Hybrids Using Caged Alkoxysilane[a]

run	PAA (mg)	alkoxysilane (mg)	UV[b]	appearance	ceramic yield (wt %) calcd	ceramic yield (wt %) obsd[c]
1	100	APTEOS 25	−	transparent	6.03	4.57
5	100	NVOC-U-PTEOS 25	+	transparent	3.03	2.08
6	100	NVOC-U-PTEOS 25	−	translucent		
7	100	NVOC-PTEOS 25	+	phase separated		
8	100	NVOC-PTEOS 25	−	phase separated		
9	100	NVOC-U-P 10 + TEOS 25	+	phase separated		
10	100	NVOC-U-P 10 + TEOS 25	−	phase separated		

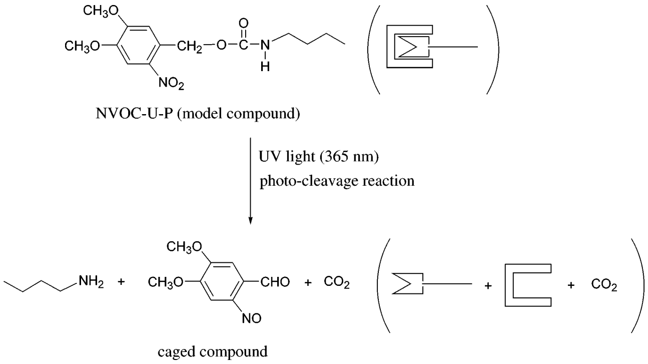
[a] Methanol 5 mL, HCl_{aq} (0.1 M) 0.2 mL, stirring time 2 h. [b] Irradiating time of UV ($\lambda = 365$ nm) 2 h. [c] Calculated from TGA.

Table 3. Synthesis of Photosensitive PAA/Silica Hybrids Using Caged Alkoxysilane[a]

run	PAA (mg)	NVOC-U-PTEOS (mg)	0.1 M HCl_{aq} (mL)	UV[b]	appearance	ceramic yield (wt %) calcd	ceramic yield (wt %) obsd[c]
5	100	25	0.2	+	transparent	3.24	2.08
6	100	25	0.2	−	turbid		
11	100	50	0.2	+	translucent		
12	100	50		+	transparent	5.46	3.26
13	100	50		−	phase separated		

[a] Methanol 5 mL, stirring time 2 h, evaporating methanol at 60 °C. [b] Irradiating time of UV ($\lambda = 365$ nm) 2 h. [c] Calculated from TGA.

Scheme 8



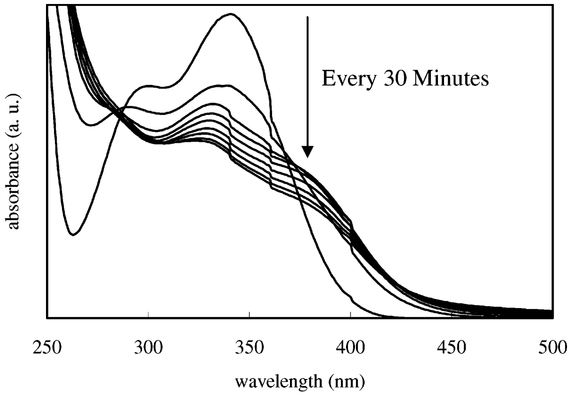
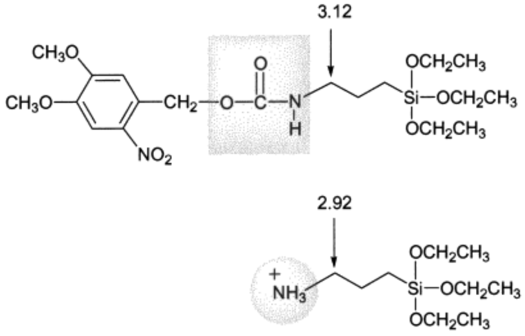


Figure 4. Change of UV absorption during irradiation of NVOC-U-P in methanol.

within 2 h. The photocleavage reaction of the model compound (NVOC-U-P) occurred readily in methanol. This result is consistent with the previous observations of the spectral changes during photoirradiation of accompanying NVOC-modified compounds.[24,25]

Synthesis of Photosensitive Polymer Hybrids Utilizing NVOC-Modified Alkoxysilane. Organic−inorganic polymer hybrids of PAA utilizing NVOC-modified alkoxysilane were prepared. NVOC-U-PTEOS, NVOC-PTEOS, and the mixture of TEOS and NVOC-U-P (model compound) were used for preparation of PAA/silica hybrids (Figure 1). The results are summarized in Table 2.

Scheme 9



The transparent polymer hybrid utilizing NVOC-U-PTEOS could be obtained with UV (run 5). In contrast, the polymer hybrid without UV was translucent (run 6). The interaction between “nonactive” NVOC-U-PTEOS and PAA was so weak that the obtained polymer hybrids were phase-separated. But, by photoirradiation, “nonactive” NVOC-U-PTEOS was converted to “active” APTEOS. Then the strong ionic interaction between ammonium ion resulted from APTEOS and carboxylate ion of PAA formed. Therefore, transparent polymer hybrids could be obtained in the case of the sample with photoirradiation. Furthermore, in the case of the sample using NVOC-PTEOS without UV, the obtained polymer hybrid was phase-separated (run 8). The obtained polymer hybrid using NVOC-PTEOS with photoirradiation also brought about phase separation (run 7). NVOC-PTEOS was inert and nonactivated by photoirradiation; thus, the obtained polymer hybrids were phase-separated even if the sample was photoirradiated. Both samples using NVOC-U-P and TEOS with UV (run 9) and without UV (run 10) were phase-separated. NVOC-U-P was changed to propylamine by photoirradiation and formed ionic interaction with carboxylic acid of PAA. But there is no interaction between PAA and silica because ionic interaction groups of ammonium ion could not connected with silica gel from TEOS.

PAA/silica hybrids using NVOC-U-PTEOS was prepared in different PAA/silica ratios (Table 3). When the PAA/NVOC-U-PTEOS ratio was 4/1, transparent PAA/silica hybrids were obtained by photoirradiation (run 5). The appearance of the polymer hybrid was phase-

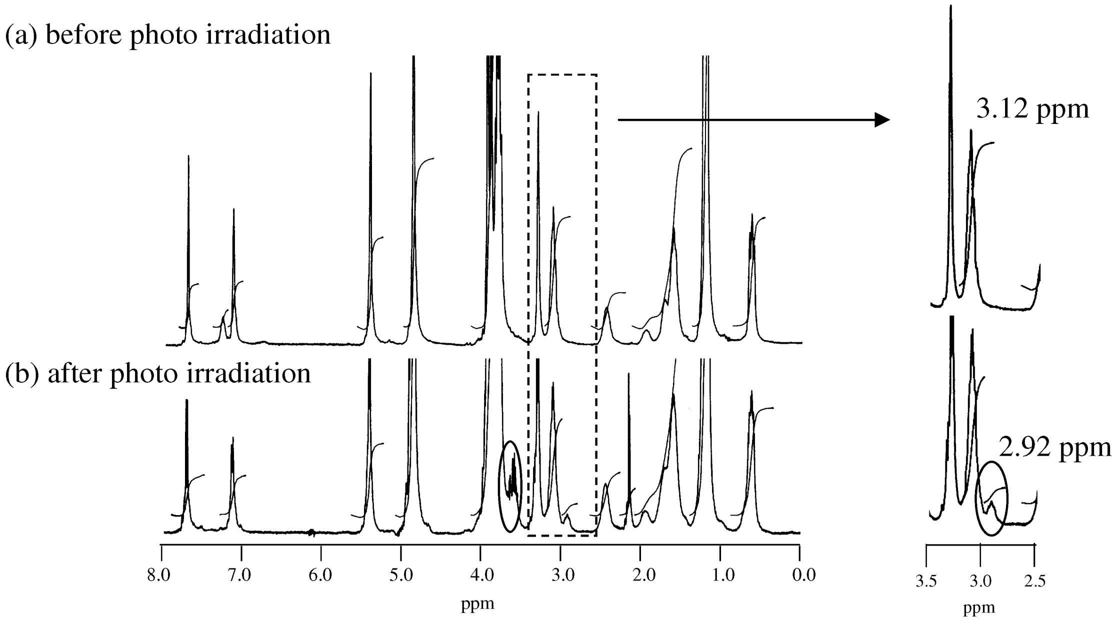


Figure 5. ^{1}H NMR spectra of NVOC-U-PTEOS with PAA (a) before photoirradiation and (b) after photoirradiation in CD_3OD.

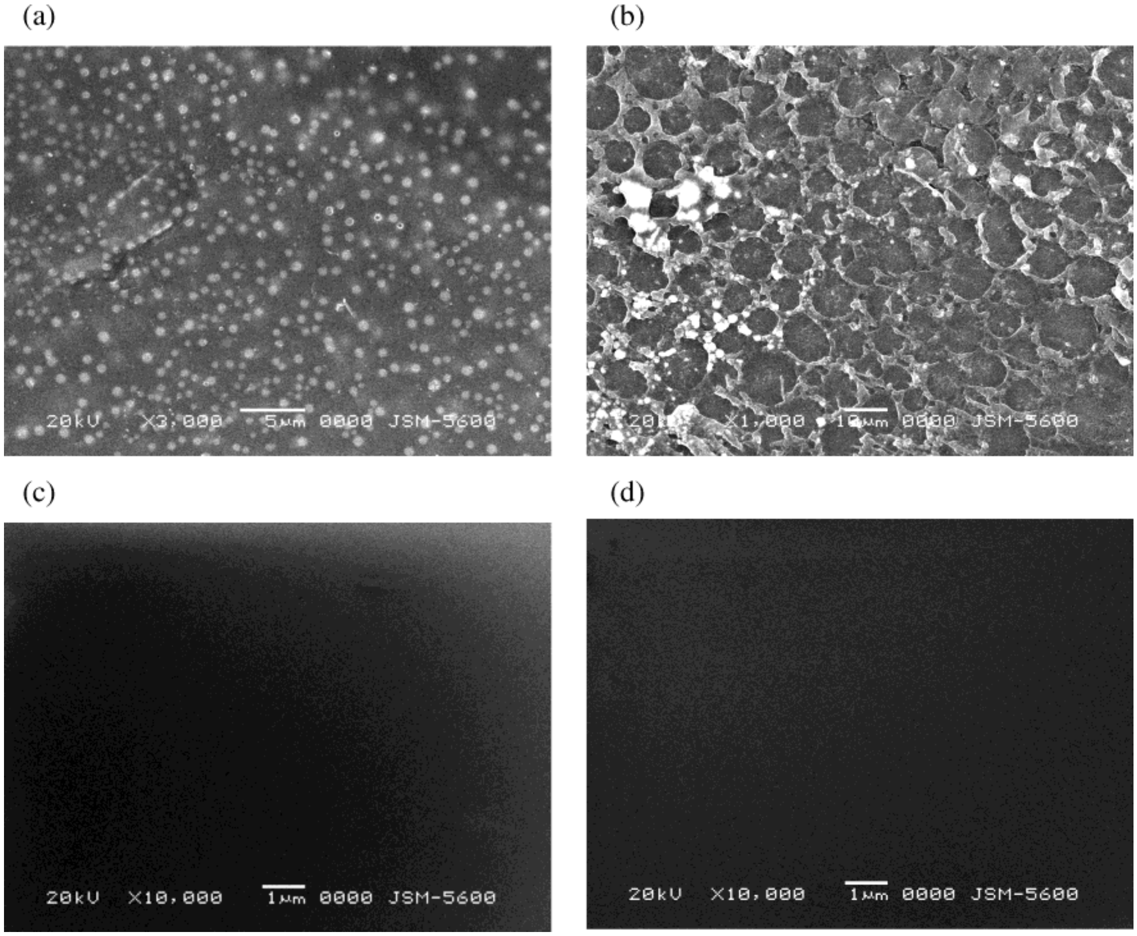


Figure 6. SEM images of polymer hybrids of PAA (a) using TEOS (Table 1, run 4), (b) using NVOC-U-PTEOS without photoirradiation (Table 2, run 6), (c) using APTEOS (Table 1, run 1), and (d) using NVOC-U-PTEOS with photoirradiation (Table 2, run 5).

separated with photoirradiation when the PAA/NVOC-U-PTEOS ratio was 2/1 (run 11). On the other hand, the sample without aqueous HCl (run 12), transparent and homogeneous polymer hybrid could be obtained with photoirradiation. It is thought that the ionic interaction was so weak in aqueous solution compared to methanol that transparent polymer hybrids could not be obtained by using aqueous hydrochloric acid. The strength of the ionic interaction could be attributed to the different dielectric constant of the solvent. Water has a much higher dielectric constant than methanol; thus, water can solvate ionic pairs via strong electronic interaction and should hinder the formation of the ionic interaction between PAA and APTEOS. The same trend was observed in the polymer hybrid using sulfonic acid groups of poly(styrenesulfonic acid) (PSSA) and amine moieties of APTEOS.[19]

As shown in Scheme 3, photoresist like polymer hybrids could be prepared using this preparation method. In the case of the sol state (liquid phase) of the polymer hybrids, the patterning using this approach is difficult because of the strong migration tendency. But, the sol state of the hybrid became the gel state according to the proceeding of the sol−gel reaction of alkoxysilane. In the gel stage, the migration tendency should be inhibited and the photoresist like polymer hybrids should be obtained. It is considered that the controlling of the UV irradiation timing and time can accomplish the preparation of the photoresist hybrid in this approach. This work is now under investigation.

Evidence of Ionic Interaction between PAA and NVOC-U-PTEOS after Photoirradiation. The ionic interaction between carboxylic acid groups of PAA and amine groups resulted from nonprotected NVOC-U-PTEOS by photoirradiation could be checked by FT-IR and ^{1}H NMR measurements as well as previously described ionic interaction between PAA and APTEOS. Unfortunately, it was difficult to observe the shift of C═O groups due to overlap with the band from phenyl groups around 1590 cm^{-1}. Therefore, ^{1}H NMR was utilized to examine the ionic interaction between carboxylic acid groups of PAA and amine groups of NVOC-U-PTEOS after photoirradiation.

As shown in Figure 5b, the proton peak of the methoxy groups of NVOC moieties, which were observed around 3.8−4.0 ppm, was shifted to about 3.6 ppm after UV irradiation. The shift resulted from the photocleavage. This observation was similar to the case of previously reported.[30] Furthermore, the new peak around 2.92 ppm was observed after photoirradiation in the sample of PAA/NVOC-U-PTEOS (1/1) in CD_3OD compared to Figure 5a (the same sample before photoirradiation). This peak consisted of the alkyl peak of the sample of the PAA/APTEOS in CD_3OD (Figure 3b). This result indicates the ionic interaction between amine groups generated from NVOC-U-PTEOS with photoirradiation and carboxylic acid groups of PAA. The efficiency of the formation of the ionic interaction was about 15%, which was calculated by the integration of the peak at 2.92 ppm. The percentage was slightly small, but it should be enough to obtain the transparent polymer hybrid because ionic interaction was stronger than the other kinds of physical interaction such as hydrogen bond and aromatic interaction.

SEM Images of Polymer Hybrids. The miscibility of organic and inorganic phase was confirmed by SEM (Figure 6). As shown in Figure 6a, the sample with TEOS (Table 1, run 4) showed phase separation between organic polymer and silica gel at about 3000 magnifications. The white parts indicate silica particles. The white particles about 1 μm could be clearly observed. The turbid polymer hybrids using NVOC-U-PTEOS without photoirradiation (Table 2, run 6) also showed honeycomb-like phase separation at 1000 magnifications (Figure 6b). However, in the case of the transparent PAA/silica hybrid using APTEOS (Table 1, run 1), aggregations of silica were not observed even at about 10 000 magnifications (Figure 6c). In the transparent sample using NVOC-U-PTEOS with photoirradiation (Table 2, run 5), some particles or aggregation at 10 000 magnifications were also not found (Figure 6d). These results suggest that silica is dispersed at the nanometer level in the hybrid materials.

Conclusions

The transparency of polymer hybrids utilizing caged alkoxysilane (NVOC-U-PTEOS) could be controlled by photoirradiation because caged alkoxysilane was changed to nonprotected alkoxysilane by utilizing photoirradiation and the ionic interaction formed between carboxylic acid groups of PAA and amine groups of nonprotected alkoxysilane. This strong ionic interaction could be confirmed by FT-IR and ^{1}H NMR spectra. The resist-like polymer hybrids could be obtained utilizing this idea. This novel photosensitive polymer hybrid using the biochemical concept of the caged compound is the first example and gives beneficial clues in the field of materials science.

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