Headline Articles

Synthesis of IPN Polymer Hybrids by In-Situ Radical Polymerization Method and Their High Resistivity to Solvent Extraction

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Two different types of polymer hybrids having an interpenetrating polymer network (IPN) of the organic gel and silica gel were prepared by the in-situ polymerization method. One type is the IPN polymer hybrids of poly(*N*,*N*′-dimethylacrylamide) gel and silica gel that were prepared by simultaneous polymerization of *N*,*N*′-dimethylacrylamide and *N*,*N*′-methylenebisacrylamide in a methanol solution of tetramethoxysilane (TMOS). The other type is IPN polymer hybrids of polystyrene gel and silica gel that were prepared by the polymerization of styrene monomer in the presence of divinylbenzene and TMOS. Radical polymerization of these organic monomers proceeded effectively in the sol–gel reaction mixture of TMOS, resulting in homogeneous glassy materials. The formation of IPN structure was confirmed by the solvent extraction. The loss of organic elements could be prevented in both cases by the incorporation of cross-linking points in the organic network. The homogeneity of these IPN polymer hybrids were supported by nitrogen porosimetry measurements. The results demonstrated that the porous silicas obtained from the polymer hybrids had high surface areas and large pore volumes and exhibited a sharp distribution of pore size below 2 nm in both types of IPN polymer hybrids. These results indicate a molecular-level integration of the organic gel and silica gel in the IPN polymer hybrids.

Increasing attention has been paid to hybrids of organic polymers and inorganic materials because they provide various functionalities and improved mechanical properties.[1—4] For the preparation of these hybrid materials, especially hybrids with silica gel, the sol-gel technique for alkoxysilanes is often used because of its simplicity and low reaction temperature. The sol-gel reaction comprises hydrolysis and subsequent condensation reaction of alkoxysilanes.[5—9] We have reported the synthesis of polymer hybrids utilizing hydrogen bonding interactions between silanol groups of silica matrix and polar functional groups of organic polymers such as amide groups and urethane groups. Poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone) or poly(*N*,*N*′-dimethylacrylamide) were incorporated homogeneously by utilizing this interaction.[1,10—14]

It is also very important for industrial application to prepare polymer hybrids having solvent-proof property. As is often observed in the case of polymer hybrids prepared by the above method, the loss of organic segments by solvent extraction might be a problem in hybrid materials. Utilization of silane coupling agents is one solution to this problem.[15] Organic segments are covalently bonded to the silica matrix, preventing extraction with solvents. Another possible way to solve the problem is the formation of a so-called interpenetrating polymer network (IPN) structure. The resistivity to solvent extraction would be anticipated if the organic network forms cross-linking points in silica gel matrix. There is, however, a critical problem for the synthesis of the solvent-proof polymer hybrids having IPN structure because a cross-linked organic polymer itself is insoluble in common organic solvents. Therefore, the usual preparative method that requires dissolution of an objective organic polymer in a solution of sol-gel reaction of alkoxysilanes seems unsuitable.

On the other hand, we have recently reported the synthesis of poly(*N*,*N*′-dimethylacrylamide) (PDMAAm) and silica gel polymer hybrids by utilizing the in-situ radical polymerization of vinyl monomers of *N*,*N*′-dimethylacrylamide (DMAAm) in a sol-gel reaction mixture as another synthetic route for the preparation of polymer hybrids.[16] By choosing the appropriate condition, i.e. contents of an acid catalyst and the stirring time before initiation of the radical reaction that would govern the degree of gelation of silica gel at an initiation point of radical reaction, a nano-level dispersion of the organic polymer and silica gel was successfully accomplished. It was found that the homogeneity of the polymer hybrids was much improved by the increase of the acid content and the prolonged stirring time that resulted in the further cross-linking of silica gel. In addition, we have also succeeded in the preparation of polystyrene and silica gel polymer hybrids by utilizing this synthetic method. Styrene monomer was radically polymerized by azobisisobutyronitrile (AIBN) in the sol-gel reaction mixture of tetramethoxysilane (TMOS). In this polymer hybrid, a nano-meter level homogeneous dispersion of the organic phase and inorganic phase was confirmed even though no specific interaction existed between these two phases.[17)] These results indicate that entrapment of growing organic polymer species inside the growing silica gel would prevent the aggregation of the organic polymer even when the polymer itself has poor affinity with silica gel.

In this paper we describe the synthesis of IPN polymer hybrids using the in-situ polymerization method in the presence of cross-linking agents. By introduction of a cross-linking agent to the above system, it was expected that the polymerization and cross-linking reaction of organic species would proceed simultaneously while the sol-gel reaction of alkoxysilanes would afford a rigid silica gel network that would entrap the in-situ formed organic gel. This might expectedly allow the homogeneous dispersion of organic phase and inorganic phase, even though the organic gel has poor solubility in the solvent. Initially, we report the preparation of IPN polymer hybrids between PDMAAm gel and silica gel and then the IPN polymer hybrids of polystyrene gel and silica gel. Evaluation of IPN structure of these polymer hybrids was carried out by the solvent extraction and the homogeneity was confirmed by nitrogen porosimetry study.

Experimental

General Procedures: Thermogravimetric analyses (TGA) were measured on Shimadzu TG-30 and TGC-30 at the rate of 10 °C min^{-1} in air. Nitrogen absorption porosimetry was conducted with BEL Japan Inc.

Materials: All solvents and reagents were used as supplied except the following. Methanol (Wako Pure Chemical Industries, Ltd.) was distilled with sodium under nitrogen. Acetone (Nacalai Tesque, Inc.) was distilled with calcium hydride under nitrogen. *N,N'*-Dimethylacrylamide (DMAAm) (Kohjin Co., Ltd.) and tetramethoxysilane (TMOS) (Tokyo Kasei Kogyo Co., Ltd.) were distilled under nitrogen. *N,N'*-Methylenebisacrylamide (MBAAm) (Wako Pure Chemical Industries, Ltd.) and azobisisobutyronitrile (AIBN) (Wako Pure Chemical Industries, Ltd.) were recrystallized from ethanol. Styrene monomer (Wako Pure Chemical Industries, Ltd.) and divinylbenzene (DVB) were distilled under nitrogen.

Preparation of DMAAm Gel Polymer Hybrids: Prescribed amounts of DMAAm, MBAAm were dissolved in methanol (20 ml) in a 50 ml glass sample-flask, followed by addition of TMOS (2.0 g), AIBN (1.0 mol% of the vinyl monomers) and 0.1 M (1 M = 1 mol dm^{-3}) HCl (0.50 ml). The total amount of MBAAm and DMAAm was 2.0 g. After the mixture was stirred at room temperature for 5 h, the vessel was covered with a piece of aluminum-foil having a few pinholes and was heated at 60 °C in an oven in air for 2 weeks. The obtained dried gel was ground and subjected to further analyses.

Preparation of Polystyrene Gel Polymer Hybrids: Prescribed amounts of styrene and DVB were dissolved in 10 ml of acetone in a 50 ml glass sample-flask, followed by addition of TMOS (1.0 g), AIBN (1.0 mol% of the vinyl monomers) and 0.1 M HCl (0.24 ml). The total amount of MBAAm and DMAAm was 1.0 g. After the mixture was stirred at room temperature for 5 h, the vessel was covered with a piece of aluminum-foil having a few pinholes and was heated at 60 °C in an oven under N_2 for 1 week. The obtained dried gel was ground and subjected to further analyses.

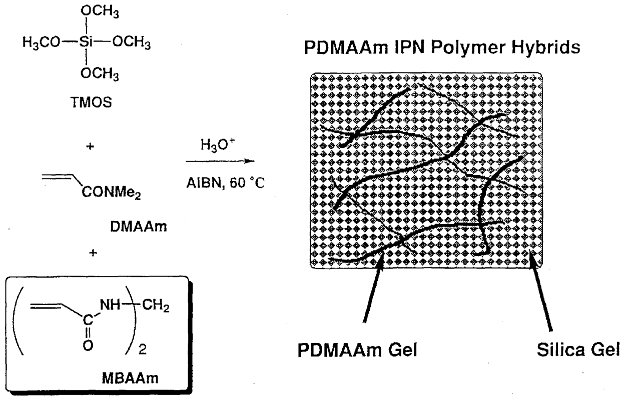
Soxhlet Extraction: The powdered hybrids were put in cellulose timbers (28 mm × 100 mm, Whatman Int., Ltd.) and extracted with methanol (for PDMAAm system) or $CHCl_3$ (for polystyrene gel system) for 7 d in a Soxhlet extraction apparatus. After the extraction, samples were dried in a vacuum oven.

Nitrogen Absorption Porosimetry: The powder of the hybrid was charred at 600 °C in air to remove organic parts. The sample was then dried at 200 °C for 2 h at reduced pressure under nitrogen atmosphere. Surface area was calculated with the Brunauer–Emmett–Teller (BET) equation[18)] 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.[19)]

Results and Discussion

Preparation of PDMAAm Gel and Silica Gel Polymer Hybrids. We designed PDMAAm gel and silica gel polymer hybrids to have a varying number of cross-linking points. Cross-linking points were introduced by the further addition of MBAAm to a reaction mixture of DMAAm and TMOS, which were the starting materials for the synthesis of "linear" poly(DMAAm) and silica gel polymer hybrids.[16)] As shown in Scheme 1, DMAAm and MBAAm were added into a methanol solution of TMOS. AIBN was employed as a radical polymerization initiator and 0.1 M HCl was used as a catalyst for the sol-gel reaction. The weight ratio of MBAAm to DMAAm was varied from 0 to 1.0 as is shown in Table 1 to control the number of cross-linking points. After being stirred for 5 h at room temperature, the mixture was heated in a vessel covered with aluminum-foil having a few pinholes at 60 °C in air to initiate the polymerization of the vinyl monomers. During this process, PDMAAm gel as well as silica gel was expected to grow simultaneously, resulting in glassy materials. No precipitation appeared during this process. The mixture was kept uniform. The obtained polymer hybrids were all transparent, which indicates the homogeneous dispersion of the organic and inorganic phase.

The conversion of DMAAm was confirmed by TGA. The TGA study of these polymer hybrids showed onset of decom-



Scheme 1.

Table 1. Synthesis of PDMAAm–Silica Gel IPN Polymer Hybrids[a]

Run	MBAAm/DMAAm	Polym. cont.[b]		
	wt/wt	Before (%)	After (%)	Weight loss[c] (%)
1	0	72	30	59
2	0.001	74	36	51
3	0.01	73	53	28
4	0.1	73	72	1.4
5	1	73	73	0

a) Each hybrid was prepared by adding DMAAm and MBAAm to a methanol (20 ml) solution of TMOS (2.0 g), 0.1 M HCl (0.05 ml) and AIBN (1.0 mol% of the organic monomers). The total amount of MBAAm and DMAAm was 2.0 g. The mixture was heated at 60 °C in air. b) The polymer contents in the hybrids were calculated by TGA before and after MeOH extraction. c) Weight loss was calculated as follows: Weight loss = {polym. cont. (before)−polym. cont. (after)} × 100/polym. cont. (before).

position only around 250 °C, which indicates complete conversion of the vinyl monomer.[17] If the monomer remained inside the polymer hybrids, the decomposition would start at a much lower temperature. This result indicates that the polymerization of DMAAm proceeded as effectively even in the presence of MBAAm as was observed in the in-situ polymerization reaction of only DMAAm.[17]

Resistivity to Solvent Extraction. For the elucidation of IPN structure of the polymer hybrids, we have carried out the solvent extraction experiment. It was expected that the extraction of the organic elements would be prevented if the cross-linking points were properly introduced in the organic network by the polymerization of MBAAm with DMAAm. The hybrids obtained were crushed into powder, which were then subjected to methanol extraction by Soxhlet apparatus for 1 week. This solvent was chosen because PDMAAm shows good solubility in the solvent and the solvent would intervene in the hydrogen bonding interaction between amide groups of PDMAAm and silanol groups of silica gel, which would ease the extraction of the organic polymer from the silica gel. Chloroform that can also dissolve the organic polymer has less polarity, thus it is a poor hydrogen bonding acceptor compared with MeOH. Therefore, this solvent is not suitable for the present purpose. The contents of organic polymer in the hybrids after methanol extraction were confirmed by TGA. The organic elements were completely eliminated from the polymer hybrids, leaving a residue of inorganic elements at 900 °C. Thus, the ceramic yield at 900 °C corresponds to the weight ratio of silica in polymer hybrids. As shown in Fig. 1, when MBAAm was not employed, therefore when the organic parts consisted of only linear chains, the ceramic yield of the polymer hybrid at 900 °C increased after methanol extraction compared with the ceramic yield before the extraction. The results indicate the decrease of the organic contents in the polymer hybrid after the extraction. The polymer contents were calculated by subtracting the ceramic yield at 900 °C from the total weight of the polymer hybrid. The values were 72 and 30% for the polymer hybrid before and after the extraction, respectively (Table 1). Almost 60% of PDMAAm was extracted without MBAAm. The results demonstrated the weakness of the polymer hybrids against exposure to solvents, as was expected for linear organic polymers.

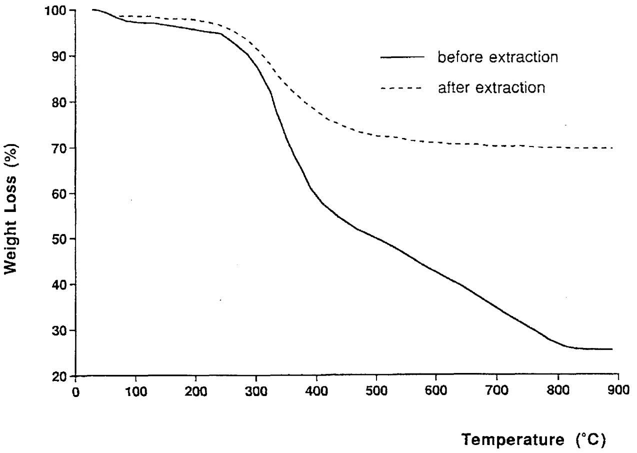


Fig. 1. TGA traces of PDMAAm–silica gel polymer hybrid (MBAAm/DMAAm = 0)—before and after MeOH extraction.

For the polymer hybrid prepared with 10 wt% of MBAAm, we carried out the same experiment. In contrast to the previous results, it was found that the ceramic yield hardly changed from before to after the extraction when 10 wt% of MBAAm was used, indicating that the organic contents in the polymer hybrids were retained even after the extraction

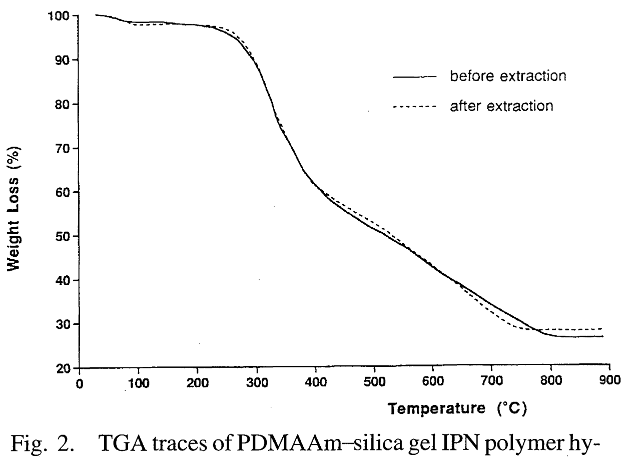


Fig. 2. TGA traces of PDMAAm–silica gel IPN polymer hybrid (MBAAm/DMAAm = 0.1)—before and after MeOH extraction.

(Fig. 2). The polymer contents before and after extraction were 73 and 72%, respectively. The loss of PDMAAm was only 1.4%. For other polymer hybrid systems with different MBAAm contents, the same experiments were conducted. The results are summarized in Table 1 and for clarity these numbers are plotted against MBAAm contents as shown in Fig. 3. These results clearly demonstrate the effect of the introduction of MBAAm on the solvent resistivity. Even with 1 wt% of MBAAm, the effect of cross-linking in the organic polymer network was apparent. With a further addition of MBAAm above 10 wt%, the resistivity to the solvent extraction was much improved and the loss of the organic elements was completely prevented. The polymerization of MBAAm and DMAAm was expected to proceed simultaneously to form an organic polymer gel with a uniform dispersion of cross-linking points in these polymer hybrids. If the polymerization of each segment occurred separately, then some part of the organic phase would comprise only linear chains and other parts would comprise a cross-linked network. In this case, the extraction of the linear part would occur even when MBAAm was introduced. However, the results of solvent extraction study showed the improved resistivity with an increase of MBAAm contents. Therefore, both organic elements were confirmed to be dispersed uniformly and the cross-linking points were expected to be introduced in a number controlled by the initial content of MBAAm. Judging from the complete prevention of the extraction, we expected that a percolation network of the organic polymer gel inside the silica gel was formed with more than 10 wt% of MBAAm.

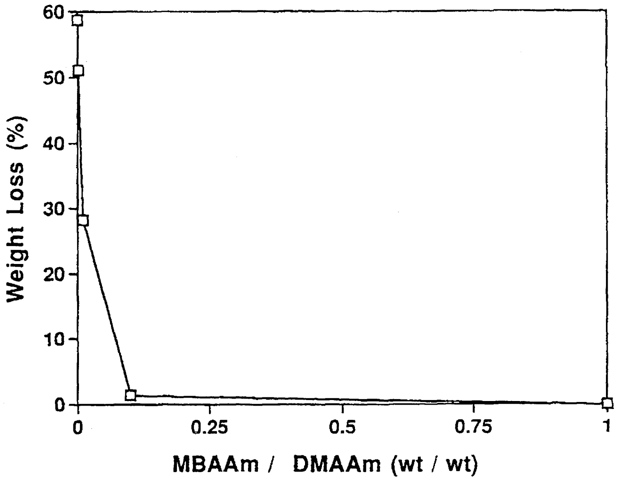
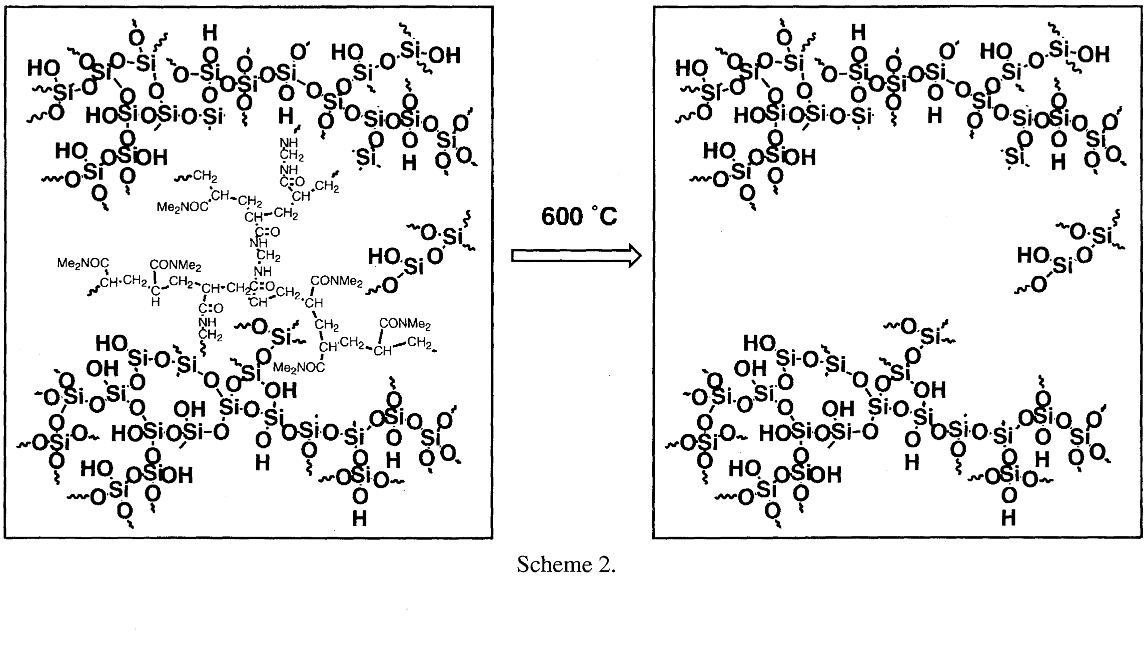


Fig. 3. Loss of the organic phase from PDMAAm–silica gel IPN polymer hybrids by MeOH extraction.

Nitrogen Porosimetry Study of Porous Silica Obtained from the Polymer Hybrids. The homogeneity of IPN polymer hybrids could be preliminarily estimated by optical observation. Since the refractive indices of organic and inorganic parts have different values for the organic and inorganic phase, the composites would become opaque when the domain of each component is larger than the wavelength of visible rays. As shown in Table 1, the obtained polymer hybrids were all transparent. Therefore the size of the organic domain was expected to be less than a few hundred nanometers.

The homogeneity of IPN polymer hybrids was confirmed more precisely by a nitrogen porosimetry method. The organic segments were removed from the polymer hybrids by charring them at 600 °C for 24 h without shrinkage of silica gel (Scheme 2).[13,20] It was confirmed by our previous study that the pore size in these porous silica corresponds to the domain size of organic polymers in the original polymer hybrids. Therefore, it is possible to verify the dispersity of organic polymers in the hybrids by measuring the pores size, pore volume and surface area.[13]

Surface areas and pore volumes of porous silicas that were obtained from the polymer hybrids with 0.1 and 1.0 wt% of MBAAm were calculated by applying the BET method on the absorption side of isotherm curve obtained from nitrogen porosimetry study on the porous silicas.[21] As shown in



Scheme 2.

Table 2. Pore Volume and Surface Area of Porous Silica[a]

Run	MBAAm	Pore volume[b]	Surface area[b]	Pore diameter[c]
	/DMAAm	ml g^{-1}	m^2 g^{-1}	nm (desorption)
1	0.1	78	337	1.8
2	1.0	79	343	1.7
3[d]	0	84	365	1.9

a) The porous silicas were obtained by charring the IPN polymer hybrids at 600 °C for 24 h. b) Calculated by the BET method. c) Calculated by the BJH method from the desorption curve. d) From previous result.[16]

Table 2, it was found that the porous silicas had high surface area and large pore volume even when the weight ratio of MBAAm to DMAAm was 1.0. Both silicas showed almost the same values for the pore volume and surface area. The values were 78 ml g^{-1} for the pore volume and 340 m^2 g^{-1} for the surface area. These values were almost the same as those of porous silica obtained from linear DMAAm polymer hybrids prepared by the in-situ polymerization method of DMAAm, which showed 84 ml g^{-1} and 365 m^2 g^{-1} for pore volume and surface area, respectively.[16]

The pore size was calculated by the BJH method from the desorption isotherm curve from which the radius of the pore (R_p) was estimated assuming a cylindrical pore.[21] The results are illustrated in Fig. 4 and Table 2. The porous silicas obtained from the polymer hybrids with 0.1 and 1.0 wt% of MBAAm both exhibited sharp distributions at 1.8 nm. Again, these values were almost the same as those of porous silica obtained from linear DMAAm polymer hybrids.

The high surface area and the large pore volume indicate that the introduction and cross-linking of PDMAAm chain in the polymer hybrid system did not cause any aggregation of the organic phase, even when the organic gel has a poor solubility in the solvent. The sharp distribution of pore size below 2 nm also supports a nano-level dispersion of PDMAAm gel inside silica gel at a nanometer scale. Judging from the value of the pore size, we conclude that chains of organic and inorganic phase are interweaved and formed homogeneous one phase rather than micro-phase separated state, as is often observed in organic polymer blend systems. It is thus expected that the PDMAAm gel and the silica gel formed interpenetrating polymer networks.

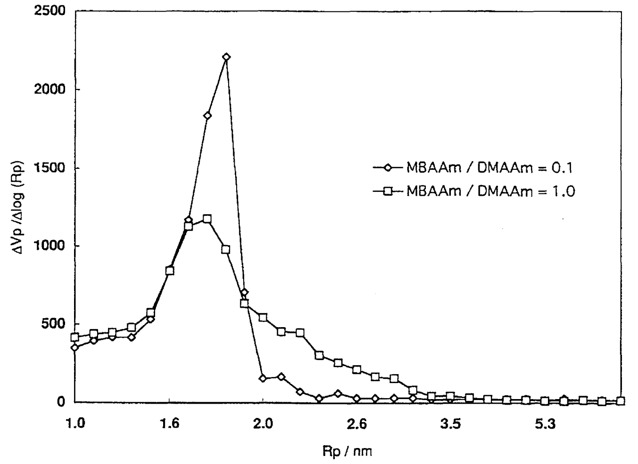
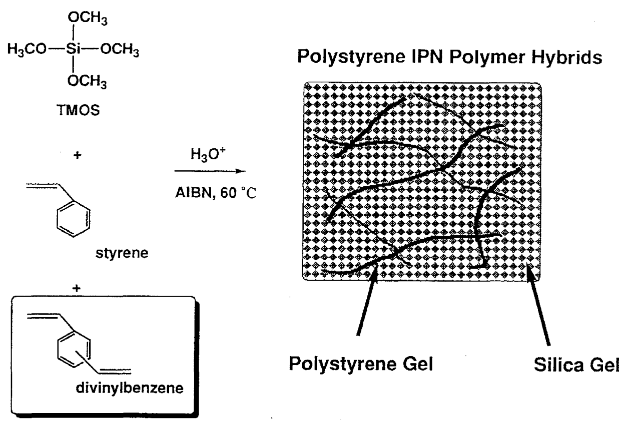


Fig. 4. Pore size distribution plots of porous silicas obtained from PDMAAm–silica gel IPN polymer hybrids.

Preparation of Polystyrene Gel and Silica Gel Polymer Hybrids. We have shown above the efficiency of the in-situ polymerization method for the preparation of PDMAAm gel and silica gel polymer hybrids having IPN structure. The organic polymer possesses amide groups that can act as acceptors of hydrogen bonding interaction with the residual silanol groups. Therefore, the above results were quite interesting but not unexpected considering the effectiveness of the hydrogen bonding interaction to form homogeneous polymer hybrids starting from various organic polymers. As mentioned in the introduction, we have also applied the in-situ polymerization method for the homogeneous formation of polystyrene and silica gel polymer hybrids starting from styrene monomer that does not possess hydrogen bonding accepting groups.[17] Here we investigated the preparation of homogeneous polystyrene gel and silica gel polymer hybrids having IPN structure by this in-situ polymerization method. It was a synthetic challenge to obtain homogeneous IPN type polymer hybrids of polystyrene gel and silica gel. The absence of good hydrogen-accepting groups as well as the introduction of cross-linking points that would reduce the solubility was expected to cause severe difficulty in the manifestation of homogeneity compared with PDMAAm system.

IPN polymer hybrids of polystyrene gel and silica gel were prepared by the same method as used for PDMAAm gel (Scheme 3). DVB was used as the origin of cross-linking points. Styrene and DVB were mixed with TMOS in ace-



Scheme 3.

tone. The weight ratio of DVB and styrene was varied from 0 to 0.2 in order to control the density of cross-linking points (Table 3). The sol-gel reaction of TMOS was catalyzed by 0.1 M HCl. The radical polymerization of vinyl monomers was initiated by AIBN. The mixture was stirred at room temperature for 5 h and subsequently heated at 60 °C under nitrogen for 1 week in a vessel with an aluminum foil cover having a few pinholes. The reaction in the air prevented the polymerization of styrene due to the presence of oxygen in this case. The mixture was kept uniform during the heating process and no precipitation appeared, resulting in transparent glassy materials.

TGA study for the obtained polymer hybrids showed onset of the polymer decomposition around 350 °C, at which temperature we assumed the complete consumption of the monomer (Fig. 5).[17] Weight loss at around 100 °C corresponds to residual solvent. $CHCl_3$ was used for extraction of the organic phase with Soxhlet apparatus. In this polymer hybrids system, we again observed significant effects of DVB on the resistivity to solvent extraction. As shown in Fig. 6, the loss of polystyrene gel occurred when the polymer hybrid was prepared without DVB. In this case, 64% of polystyrene was extracted from the polymer hybrid (Table 3). The amount of polymers extracted by the solvent was plotted against the initial content of DVB in Fig. 6. With the incorporation of 5 wt% of DVB to the system, the resistivity to the solvent was much improved. In this case, the loss of organic phase was suppressed to 20%. With further addition of DVB to 10 wt% to styrene monomer, the resistivity was further improved. The loss was just 6%. Coincidentally we have obtained the same value in the amount of cross-linking agent that would prevent the extraction of the organic polymers in the system of PDMAAm gel and polystyrene gel. Mol% of MBAAm was 6.4 and that of DVB was 8. In both cases, further addition of the cross-linking agent did not cause further improvement in the resistivity. Therefore, it was expected that the percolation of organic gel (one linked network) occurred with this amount of the cross-linking agents. The dispersion of cross-linking points among the organic network was also expected to be homogeneous in this polystyrene gel, as was observed in the polymer hybrids of PDMAAm gel and silica gel.

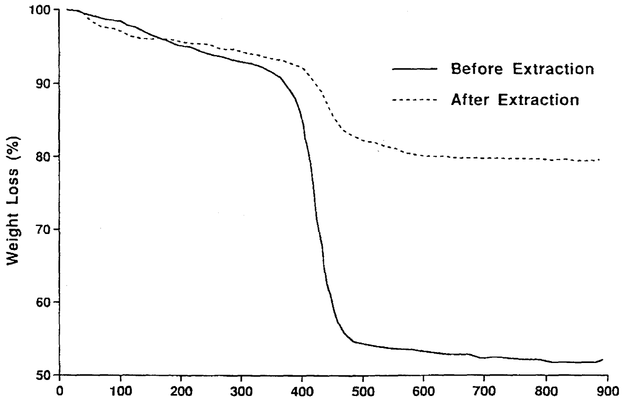


Fig. 5. TGA traces of polystyrene–silica gel polymer hybrid (DVB/styrene = 0)—before and after $CHCl_3$ extraction.

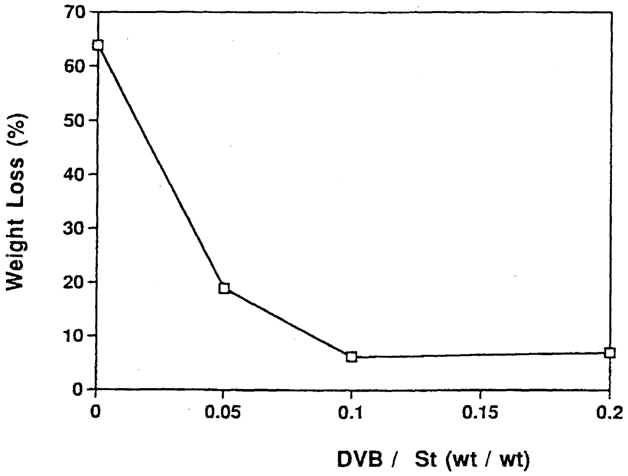


Fig. 6. Loss of the organic phase from polystyrene–silica gel IPN polymer hybrids by $CHCl_3$ extraction.

Evaluation of the Homogeneity of the Polystyrene Gel Polymer Hybrids. As shown in Table 3 the obtained polymer hybrids were all transparent, indicating the homogeneous dispersion of the organic domain in silica matrix. The homogeneity of the polymer hybrids was further evaluated quantitatively by the nitrogen porosimetry of porous silica obtained from polymer hybrids. As shown in Table 4,

Table 3. Synthesis of Polystyrene IPN Polymer Hybrids[a)]

Run	DVB/styrene	Homogeneity[b)]	Polym. cont.[c)]		
	wt/wt		Before (%)	After (%)	Weight loss[e)] (%)
1	0	Transparent	48	17	64
2	0.05	Transparent	50	40	19
3	0.1	Transparent	53	50	6.2
4	0.2	Transparent	56	52	7.0

a) Each hybrid was prepared by adding styrene and DVB to a acetone (10 ml) solution of TMOS (1.0 g), 0.1 M HCl (0.24 ml) and AIBN (1.0 mol% of the organic monomers). The total amount of DVB and styrene was 1.0 g. The mixture was heated at 60 °C under nitrogen. b) Homogeneity was observed optically. c) The polymer contents in the hybrids were calculated by TGA. d) Weight loss of the organic part was calculated as follows: Weight loss = {polym. cont. (before)−polym. cont. (after)} × 100/polym. cont. (before).

Table 4. Pore Volume and Surface Area of Porous Silica[a)]

Run	DVB/styrene	Pore volume[b)] ml g^{-1}	Surface area[b)] m^2 g^{-1}	Pore diameter[c)] nm (desorption)
1	0	64	277	1.8
2	0.1	65	282	1.9
3	0.2	68	295	2.6

a) The porous silicas were obtained by charring the polymer hybrids at 600 °C for 24 h.
b) Calculated by the BET method. c) Calculated by the BJH method from desorption curve.

it was found that the porous silica obtained from those polymer hybrids had high surface area and pore volume. In the case of polymer hybrid prepared with 10 wt%, pore volume was 64 ml g^{-1} and surface area was 280 m^2 g^{-1}. Even with a further addition of DVB, these values did not change much. And these values were almost the same as those of porous silica obtained from the linear polystyrene polymer hybrid. Therefore it was expected that the organic phase was dispersed uniformly in these polymer hybrids even when cross-linking points were introduced in the organic network. If an aggregation of the organic segment occurred, the porous silica would have much smaller values for surface area and pore volume. The pore size calculated by BJH method also demonstrated the homogeneity of the polymer hybrids, as shown in Fig. 7 and Table 4. Although the pore size is larger than that of porous silica obtained from the polymer hybrid of linear polystyrene and silica gel, the pore size distribution plot for the porous silica obtained from the polymer hybrids prepared with 10 and 20 wt% of DVB exhibited peaks at 1.9 and 2.7 nm, respectively. As the pore of the silica obtained from polymer hybrids corresponds to the domain size of the organic segment, it seems reasonable to say that polystyrene gel was dispersed at a nanometer-level in the polymer hybrids.

The homogeneity of these polymer hybrids could be attributed to confinement of organic network within silica gel matrix. Polymerization of styrene was expected to proceed in the solution containing sol of polysiloxane that was under continuing cross-linking reaction to form silica gel. Therefore, by the time the inorganic gel was formed, polystyrene gel was incorporated into the rigid silica gel cage that would prevent the phase separation of the organic phase and inorganic phase, regardless of the poor affinity of the styrene unit to silica gel and the insolubility of the organic network.

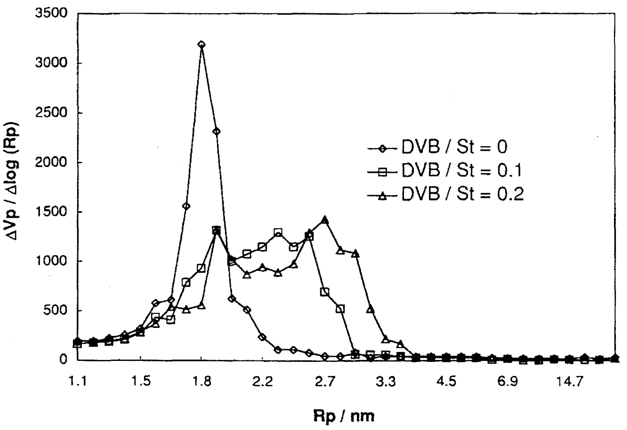


Fig. 7. Pore size distribution plots of porous silicas obtained from polystyrene–silica gel IPN polymer hybrids.

Conclusion. Here we demonstrated two extreme cases: one with an organic polymer having excellent affinity toward silica gel and the other with an organic polymer without any interaction with the inorganic part. It has been confirmed that homogeneous IPN-type polymer hybrids of PDMAAm gel and silica gel could be prepared by the in-situ polymerization method. PDMAAm network was found to be dispersed at a molecular level in the hybrids. The in-situ polymerization method was also found to be applicable to polystyrene gel having no hydrogen bonding acceptors. The IPN polymer hybrids were also homogeneous and the organic phase was confirmed to be dispersed at a nano-meter level. Introduction of cross-linking points in these systems proceeded effectively, forming an organic gel with uniform dispersion of the cross-linking points in either case. Especially from the latter case, it was speculated that the physical entrapment of the organic phase is more critical in this in-situ polymerization method rather than the interaction between two phases. Considering the insolubility of PDMAAm gel and polystyrene gel in the common organic solvents, the present method seems to be the most suitable for the preparation of homogeneous IPN polymer hybrids with high resistivity to solvents.

References

1) Y. Chujo, *Polym. Mater. Sci. Eng.*, **74**, 65 (1996).
2) B. M. Novak, *Adv. Mater.*, **5**, 422 (1993).
3) U. Schubert, N. Husing, and A. Lorenz, *Chem. Mater.*, **7**, 2010 (1995).
4) J. Wen and G. L. Wilkes, *Chem. Mater.*, **8(8)**, 1667 (1996).
5) H. Schmidt, H. Scholze, and A. Kaiser, *J. Non-Cryst. Solids*, **63**, 1 (1984).
6) C. J. Brinker, K. D. Keefer, D. W. Schaefer, R. A. Assink, B. D. Kay, and C. S. Ashley, *J. Non-Cryst. Solids*, **63**, 45 (1984).
7) F. Orgaz and H. Rawson, *J. Non-Cryst. Solids*, **82**, 57 (1986).
8) C. J. Brinker and G. W. Scherer, *J. Non-Cryst. Solids*, **70**, 301 (1985).
9) C. J. Brinker and G. W. Scherer, "Sol-Gel Science," Harcourt Brace & Co., Boston (1990).
10) Y. Chujo, E. Ihara, S. Kure, N. Suzuki, and T. Saegusa, *Makromol. Chem., Macromol. Symp.*, **42/43**, 303 (1991).
11) Y. Chujo and T. Saegusa, *Adv. Polym. Sci.*, **100**, 11 (1992).
12) Y. Chujo, E. Ihara, S. Kure, and T. Saegusa, *Macromolecules*, **26**, 5681 (1993).

13) Y. Chujo, H. Matsuki, S. Kure, T. Saegusa, and T. Yazawa, *J. Chem. Soc., Chem. Commun.*, **1994**, 635.

14) Y. Chujo, "Organic/Inorganic Polymer Hybrids," CRC Press, Boca Raton, New York, London, and Tokyo (1996), Vol. 6, p. 4793.

15) J. L. W. Nell, G. L. Wilkes, and D. K. Mohanty, *J. Appl. Polym. Sci.*, **40**, 1177 (1990).

16) R. Tamaki, K. Naka, and Y. Chujo, *Polym. J.*, **30**, 60 (1998).

17) R. Tamaki, K. Naka, and Y. Chujo, *Polym. Bull.*, **39**, 303 (1997).

18) S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

19) E. P. Barrett, L. G. Joyner, and P. P. Halenda, *J. Am. Chem. Soc.*, **73**, 373 (1951).

20) D. A. Loy and K. J. Shea, *Chem. Rev.*, **95**, 1431 (1995).

21) S. J. Gregg and K. S. W. Sing, "Adsoption, Surface Area and Porosity," 2nd ed, New York (1982).