

Thermoresponsive Organic–Inorganic Polymer Hybrids from Poly(*N*-isopropylacrylamide)

Yusuke IMAI, Naoki YOSHIDA, Kensuke NAKA, and Yoshiki CHUJO†

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606–8501, Japan

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ABSTRACT: Thermoresponsive organic–inorganic polymer hybrids were prepared from *N*-isopropylacrylamide (NIPA), methylenebisacrylamide (BIS), and tetramethoxysilane (TMOS) by the *in situ* polymerization method. The obtained PNIPA/silica polymer hybrids were examined by porosimetry, swelling degree measurement, and DSC. Samples with BIS content (the mass of BIS per the total mass of the organic component) larger than 1/100 showed excellent solvent-resistant property due to their interpenetrating polymer network (IPN) structure. The polymer hybrids swelled in water, and the swelling degree decreased continuously with raising temperature. This behavior was related to an endothermic peak of DSC analysis of the swollen hybrid, which corresponded to the dissociation of the hydrophobic interaction of PNIPA chain.

KEY WORDS Organic–Inorganic Polymer Hybrids / *In Situ* Polymerization Method / Interpenetrating Polymer Networks / *N*-Isopropylacrylamide / Tetramethoxysilane / Swelling Property / Thermoresponsive /

Molecular composites of organic and inorganic compounds have been of great interest as a novel class of materials.^{1–3} They potentially serve and surpass the parent materials in properties. The sol–gel technique of alkoxy silanes have been found to be the most convenient means for the preparation of these composite materials. It consists of hydrolysis of the alkoxy silanes and subsequent polycondensation of silanols, and finally a three-dimensional siloxane network can be formed at ambient temperature. During the process, organic materials can co-exist and be incorporated into silica gel. A noteworthy feature of the sol–gel reaction is the presence of unreacted silanol groups after the gelation. It allows us to utilize hydrogen bonding interaction to obtain molecular composite materials of organic polymers and silica gel (organic–inorganic polymer hybrids).^{4,5} Organic polymers having amide groups in their repeating unit such as poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone), and poly(*N,N*-dimethylacrylamide) have been incorporated in silica gel homogeneously at the molecular level by adding them into a sol–gel reaction mixture at an initial stage. The formation of hydrogen bond between silanol groups and amide groups was confirmed from FT-IR study. Recently another method for the preparation of the polymer hybrids has been developed.^{6–8} Radical copolymerization of organic monomers and the sol–gel reaction of alkoxy silanes were carried out simultaneously *in situ*. One of the advantages of this “*in situ* polymerization method” is that by employing multi-functional organic monomers with mono-functional ones, three-dimensional organic gel can be formed in the polymer hybrids. The resulting materials are so-called interpenetrating polymer networks (IPNs) of organic gel and inorganic silica gel, and one can expect high thermal, mechanical, and solvent-resistant properties.

Many researchers have showed particular interests in polymeric materials which change their physical or chemical properties reversibly in response to a certain external stimuli (light, heat, pH, and so on) from both

scientific and practical points of view. We have demonstrated photoresponsive organic–inorganic polymer hybrids prepared from side-chain functionalized organic polymers. Photoresponsive organic–inorganic polymer hybrids were prepared from azobenzene-modified poly(2-methyl-2-oxazoline) and reversible *trans-cis* isomerization of azobenzene was investigated kinetically.^{9,10} Photochromic polymer hybrids were prepared from spiropyran-modified poly(*N,N*-dimethylacrylamide).¹¹ Photodimerization of coumarin groups was utilized to form IPN structure reversibly in the polymer hybrids.¹² The solvent-resistant property was found to be improved by the formation of IPN structure.

In this study we would like to present another kind of polymer hybrids which respond to a variation of temperature. Poly(*N*-isopropylacrylamide) (PNIPA) was employed as a thermoresponsive organic polymer.^{13–26} PNIPA has a lower critical solution temperature (LCST) in water and its gel in water undergoes a volume phase transition from swollen to shrunken states at T_c ($\approx 34^\circ\text{C}$) when the temperature is raised.^{14–18} This is attributed to the hydrophobic interaction between PNIPA and water molecules. There are some examples of PNIPA/silica composite materials. Porous glass grafted with PNIPA altered pore size with temperature owing to thermoresponsive coil-globule conformation change of PNIPA chain.^{27,28} PNIPA has also been grafted or adsorbed on silica surface to modify their surface properties from hydrophilic to hydrophobic in response to temperature.^{29–31} And molecular composite of PNIPA and silica gel *via* sol–gel method has been reported by Kurihara *et al.*³² In their system, PNIPA domain and silica gel were linked through covalent bond. Here we describe the preparation of PNIPA/silica polymer hybrids, where PNIPA (gel) and silica gel are combined without covalent bonding between them. As PNIPA contains amide group in the repeating units, we can expect the hydrogen bonding interaction between PNIPA and silica. Moreover, NIPA is radically polymerizable monomer, both the traditional and the *in situ* polymerization methods can be applied. The swelling property to water and thermoresponsive behavior were also

† To whom correspondence should be addressed.

investigated.

EXPERIMENTAL

Materials

N-Isopropylacrylamide (NIPA) was recrystallized from *n*-hexane. *N,N'*-Methylenebisacrylamide (BIS) was recrystallized from ethanol. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Tetramethoxysilane (TMOS) was distilled and stored under nitrogen atmosphere. Methanol was dried with and distilled from magnesium methoxide, and stored under nitrogen atmosphere. Deionized sterile water (WAKO Pure Chemical Industries, Ltd.) and 0.1 M aqueous hydrochloric acid were used as received.

Measurements

¹H NMR spectra were recorded on a 270 MHz JEOL-JNM-GX270 NMR spectrometer. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC200, Seiko Instruments Inc. Thermogravimetric analysis (TGA) was performed on a Shimadzu TG-30, TGC-30 at the rate of 10°C min⁻¹ in air. Nitrogen adsorption porosimetry was conducted with BEL JAPAN INC., Nitrogen Adsorption Porosimetry.

Synthesis of PNIPA/Silica IPN Polymer Hybrids by In Situ Polymerization Method

A typical procedure is as follows. In a 50 ml sample tube, NIPA (1.8 g, 15.9 mmol), BIS (0.20 g, 1.3 mmol), TMOS (1.0 g) and AIBN (29 mg, 0.18 mmol) were dissolved in 10 ml of methanol. To the solution was added 0.25 ml of 0.1 M HCl_{aq}. The tube was sealed and the mixture was stirred at room temperature for 3 h. The cover of the tube was then changed to an aluminum foil with 5 pores (1 mm in diameter). The mixture was then heated at 60°C under nitrogen atmosphere for 1 week. Polymer hybrid was obtained as a transparent lump.

Solvent-Resistant Property of Polymer Hybrids

Polymer hybrids were ground in a mortar and the resulting powders were extracted with methanol by using Soxhlet apparatus for 1 week. The quantity of the organic component remaining in the polymer hybrids after extraction was evaluated from elemental analysis of nitrogen.

Swelling Property of Polymer Hybrids in Water

A piece of the polymer hybrid was swollen in deionized water until the weight of the swollen hybrid no longer changed. Swelling degree was defined as

$$\text{Swelling degree} = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \quad (1)$$

where W_{wet} is the weight of the swollen hybrid and W_{dry} is the weight of the dried hybrid.

Differential Scanning Calorimetry (DSC)

Polymer hybrid swollen in water was sealed in a seal-type aluminum pan, and DSC thermogram was recorded from 20°C to 60°C with the heating rate of 3°C min⁻¹.

Nitrogen Adsorption Porosimetry

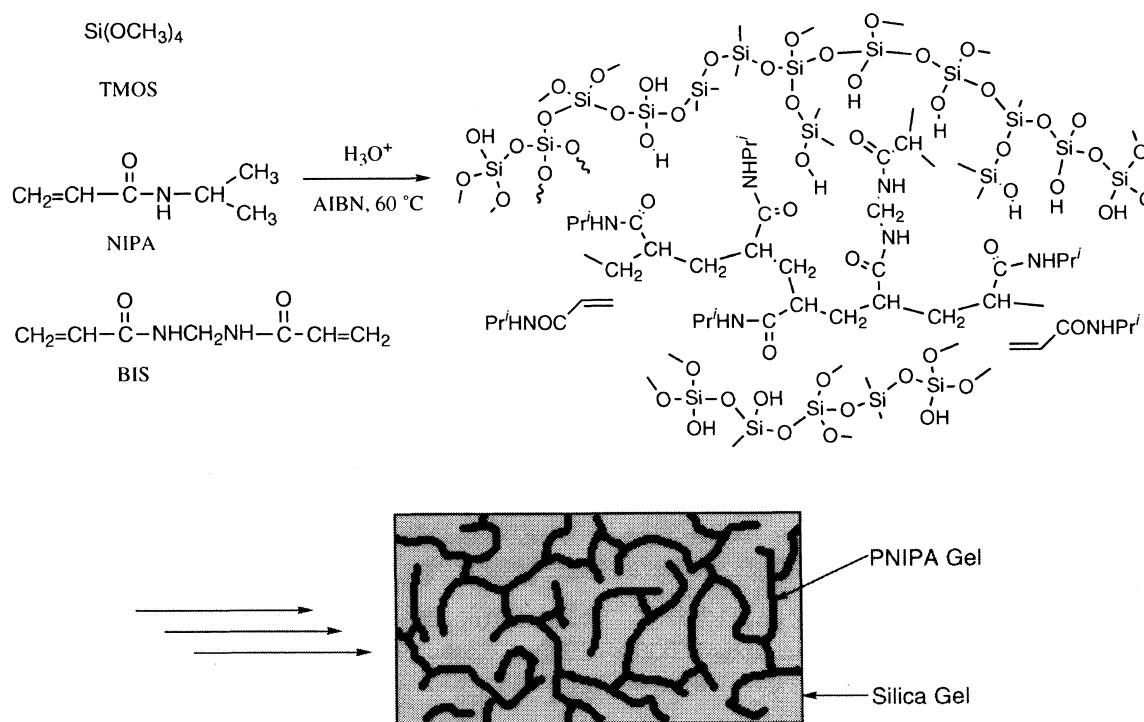
The ground polymer hybrid was calcined at 600°C for 24 h under ambient atmosphere to remove organic component. The resulting porous sample was then dried at 200°C for 2 h at reduced pressure under nitrogen atmosphere. Surface areas were calculated with the BET equation in the range of 0.05 to 0.30 (p/p_0) and the pore size distribution was calculated by BJH method from the desorption curve.

RESULTS AND DISCUSSION

Synthesis of PNIPA-Silica IPN Polymer Hybrids

Polymer hybrids of PNIPA and silica gel can be prepared by either the traditional and the *in situ* polymerization methods. As the objective of this study is the investigation of swelling property in water and thermoresponsive behavior of the hybrids, extraction of organic component into water must be suppressed. IPN polymer hybrids are one of the promising candidates. Therefore we mainly studied the preparation of PNIPA/silica polymer hybrids by the *in situ* method. NIPA, BIS, AIBN, and TMOS were dissolved in methanol and 0.1 M HCl_{aq} was added. Then the mixture was stirred at room temperature for 3 h to make the sol-gel reaction of TMOS take place to some extent. Next the mixture was heated at 60°C to initiate the radical copolymerization of NIPA and BIS (Scheme 1). It was observed that the reaction proceeded homogeneously and glassy transparent materials were obtained after removal of the solvent. The results of the preparation of PNIPA/silica gel polymer hybrids by the *in situ* method are summarized in Table I. Transparent and homogeneous polymer hybrids were obtained in most cases, except when the content of the crosslink agent BIS (defined as the mass of BIS per the total mass of the organic component) was too high (run 5). The feed ratio of the organic monomers to TMOS could also be varied between 2 and 1/2 without any influence on the homogeneity. The weight loss values calculated by TGA agreed well with the expected polymer contents in the polymer hybrids. This means that the sol-gel reaction of TMOS proceeded quantitatively. The conversion of the organic monomers to polymer was confirmed from the results of ¹H NMR spectra of extracts from the polymer hybrids with methanol. The olefin protons were not observed at all in low BIS content samples. Organic materials were hardly extracted at higher BIS content. These results suggest an effective conversion of the organic monomers in the sol-gel reaction mixture. Solvent-resistant properties of the hybrids are discussed separately in later section.

Preparation of polymer hybrids by the traditional method was also examined with preformed PNIPA and TMOS. However, transparent hybrids were obtained only when PNIPA/TMOS ratio was equal to or lower than 1/10. Higher polymer ratio resulted in inhomogeneous hybrids. Improvement of the homogeneity of the polymer hybrids by employing the *in situ* method was reported in the case of polystyrene/silica gel polymer hybrids.⁶ In addition, it is difficult to expect good solvent-resistant property for the traditional polymer hybrids because PNIPA is not crosslinked at all. There-



Scheme 1.

Table I. PNIPA/Silica gel polymer hybrids by the *in situ* polymerization method^a

Run	TMOS ^b	BIS ^b	Appearance	Weight loss/wt% ^c	Unextracted polymer content/wt% ^d	Swelling degree in water
	NIPA + BIS	NIPA + BIS				
1	1	0	Transparent	68	25	—
2	1	1/1000	Transparent	68	25	—
3	1	1/100	Transparent	62	76	1.18
4	1	1/10	Transparent	63	96	1.19
5	1	1/2	Turbid	—	—	—
6	2	1/100	Transparent	53	82	0.39
7	2	1/10	Transparent	51	99	0.53
8	1/2	1/100	Transparent	86	85	12.54
9	1/2	1/10	Transparent	85	99	4.16

^a Condition: NIPA + BIS = 2.0 g; AIBN = 1 mol% to total organic monomers; methanol = 20 ml; 0.1 M HCl_{aq} = 2 eq to TMOS. ^b w/w. ^c Calculated by TGA. ^d Remained polymer content after extraction with methanol, calculated from the results of elemental analysis of nitrogen.

fore further investigation was carried out on the *in situ* method samples.

Size of organic domain was evaluated by nitrogen adsorption porosimetry of calcined hybrids (Figure 1). Pore size distribution was calculated by BJH method. A typical example is shown for run 6 in Figure 2. Pore size distribution had a maximum at 3.5 nm. This pore size seems somewhat larger than those of poly(2-methyl-2-oxazoline) (POZO)/silica or poly(*N*-vinylpyrrolidone) (PVP)/silica polymer hybrids,^{4,5} indicating the tendency of PNIPAs to aggregate due to the hydrophobicity of isopropyl groups. No larger pores, however, were observed. This suggests that PNIPAs gel and silica gel are combined in the order of nano-meter and the IPN structure is definitely formed.

As the amide groups of PNIPAs is secondary amide and can form hydrogen bonding by themselves, it was difficult to distinguish the formation of hydrogen bonding between amide groups and silanol groups by FT-IR. It can be said at least that the molecular composites of PNIPAs and silica having IPN structure were prepared

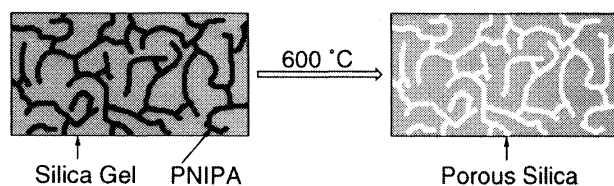


Figure 1. Formation of porous silica gel from a polymer hybrid.

by this method without utilizing covalent bonding between PNIPAs and silica.

Solvent-Resistant Property

Solvent-resistant property of the PNIPAs/silica IPN polymer hybrids was examined by Soxhlet extraction method using methanol. Contents of PNIPAs remained in the polymer hybrids were evaluated from the results of elemental analysis of nitrogen (Table I, 5th column). Most of PNIPAs was found to remain after extraction when BIS content was equal to or higher than 1/100, while larger part of the polymer was extracted with lower

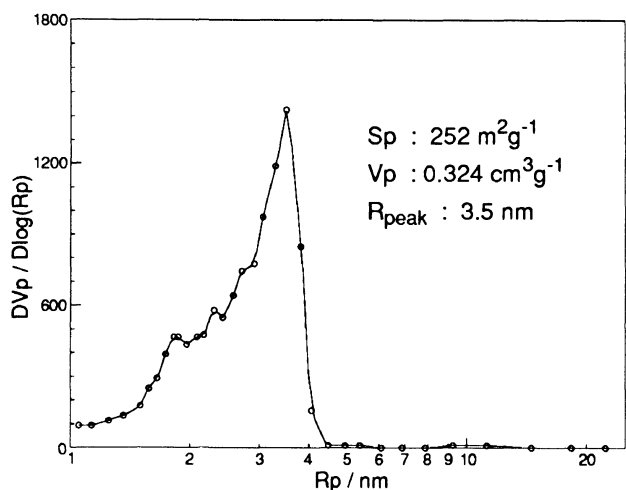


Figure 2. Pore size distribution of calcined PNIPA/silica polymer hybrid (run 6).

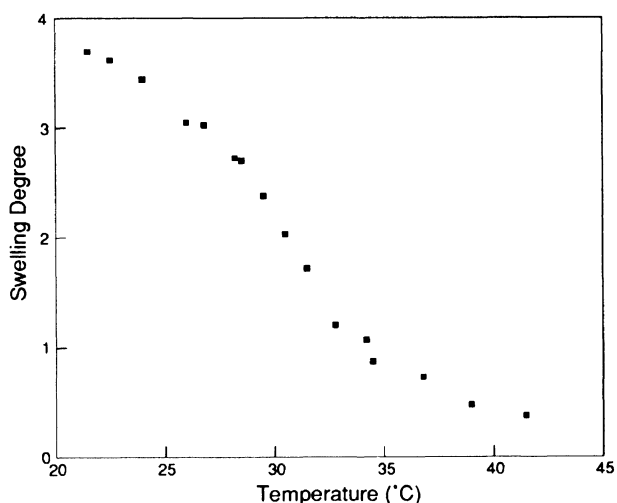


Figure 3. Temperature dependence of the swelling degree of PNIPA/silica IPN polymer hybrids (run 9).

crosslink densities (runs 1 and 2). Therefore BIS content equal to or higher than 1/100 is necessary to have enough solvent-resistant property to investigate the swelling property in water and thermoresponsive behavior of the hybrids.

Thermoresponsive Swelling Behavior to Water

Swelling degrees of the hybrids in water at temperature lower than 20°C are also summarized in Table I. A piece of the polymer hybrid of about 2 mm thick and 5 mm in diameter was swollen in deionized water until the weight of the swollen hybrid no longer changed. Equilibrium of the swelling was achieved within 2 days. The highest swelling degree (defined in eq 1) was obtained in run 8 to be 12.54, and the swelling degree was found to decrease with increasing BIS content (run 9). The swelling degrees also decreased with lower organic content, but these hybrids still absorbed water of almost same weight with themselves in runs 3 and 4. It seems that the BIS content did not affect the swelling degrees of these hybrids. Organic-inorganic ratio was found to be a decisive factor in these low organic content samples.

Temperature dependence of the swelling degree is

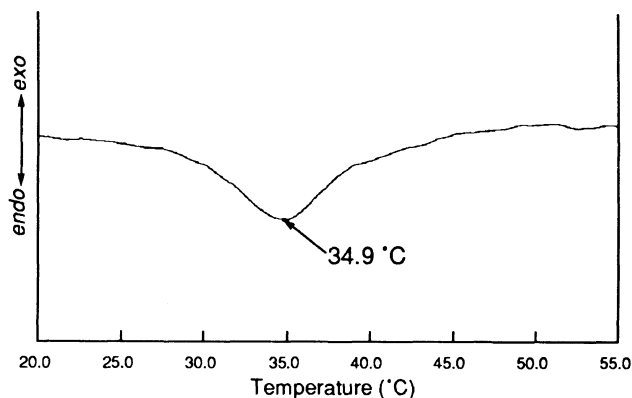


Figure 4. DSC thermogram of PNIPA/silica IPN polymer hybrids swollen in water (run 9).

demonstrated for run 9 in Figure 3. The swelling degree was measured after immersing the samples in water until equilibrium was achieved at various temperatures. The swelling degree decreased continuously with raising temperature. Figure 4 shows the DSC thermogram of PNIPA/silica hybrid (run 9) swollen in water. A clear endotherm was resolved, and the maximum endothermic point at 34.9°C was chosen as the phase-transition temperature. This temperature is almost the same with the value observed for PNIPA gel.^{15,19} This endothermic peak corresponds to the dissociation of the hydrophobic interaction,^{15,16} and the temperature dependence of the swelling is closely related to this.

CONCLUSIONS

PNIPA/silica IPN polymer hybrids were prepared by the *in situ* polymerization method and analyzed by porosimetry, swelling degree measurement, and DSC. Organic-inorganic ratio and BIS content could be varied without any influence on the homogeneity of the polymer hybrids. Solvent-resistant property was examined by the Soxhlet extraction method using methanol. BIS content higher than 1/100 was enough to prevent the extraction of PNIPA. PNIPA/silica polymer hybrids were swollen in water. The swelling degree was found to depend on organic-inorganic ratio and BIS content. It was found that the swelling degree decreased continuously with raising temperature. This behavior could be related to the dissociation of the hydrophobic interaction of PNIPA chain, which was obvious from the result of DSC thermogram of the swollen hybrid. Mechanical properties of these PNIPA/silica gel polymer hybrids are of interest and will be studied.

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