

Effect of Silane Coupling Agent on Swelling Behaviors and Mechanical Properties of Thermosensitive Hybrid Gels

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ABSTRACT: A series of organic–inorganic hybrid thermosensitive gels with three different structures were prepared from *N*-isopropylacrylamide (NIPAAm), and *N*, *N*'-methylenebisacrylamide (NMBA) and tetraethoxysilane (TEOS) [*N*-IPN]; NIPAAm, 3-(trimethoxysilyl) propyl methacrylate (TMSPMA) as coupling agent and TEOS [NT-IPN]; and NIPAAm, TMSPMA, and TEOS [NT-semi-IPN] by emulsion polymerization and sol–gel reaction in this study. The effect of different gel structures and coupling agent on the swelling behavior, mechanical properties, and morphologies of the present gels was investigated. Results showed that the properties of the gels would be affected by the gel networks such as IPN or semi-IPN and with or without existence of TMSPMA as the bridge chain between networks. The

NT-semi-IPN gel had higher swelling ratio and faster diffusion rate because poly(NIPAAm) moiety in the semi-IPN gels was not restricted by NMBA network. However, the IPN gels such as *N*-IPN and NT-IPN had good mechanical properties and lower swelling ratio, but had a poor thermosensitivity due to the addition of coupling agent, TMSPMA, into the gel system that resulted in denser link between organic and inorganic components. The morphology showed that IPN gels had partial aggregation (siloxane domain) and showed some denser phases. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2025–2034, 2009

Key words: hydrogels; networks; polysiloxanes; stimuli-sensitive polymers; structure–property relations

INTRODUCTION

Hydrogel is a crosslinked hydrophilic polymeric network that is not soluble in water but swells. Some hydrogels are sensitive to environmental stimuli and have response to these stimuli such as temperature, pH, solvent composition, light, and ion strength.^{1–7} Because of the nature of stimuli-sensitive hydrogels, they can be applied as separation membranes, biosensors, artificial muscles, chemical valves, and drug delivery devices.⁸ Poly(*N*-isopropylacrylamide) [poly(NIPAAm)] hydrogels are well known to show thermally reversible swelling–deswelling behavior around 32°C in aqueous solutions with respect to a critical gel transition temperature (CGTT). Poly(NIPAAm) hydrogel in aqueous solution exhibits a rapid and reversible hydration–dehydration change in response to small temperature changes around its lower critical solution temperature (LCST).⁹ Many

studies have been focused on the field of controlled drug delivery,¹⁰ regulation of the activity of enzymes,^{11,12} and thermocontrolled chromatography.⁴ Kurihara and coworkers had been reported that the preparation of the hydrogel membranes by graft copolymerization of NIPAAm on poly(vinyl alcohol) (PVA-g-NIPAAm) and their temperature dependence of the permeation through the PVA-g-NIPAAm membranes.^{13,14}

A new class of materials, inorganic–organic hybrid sol–gel, has attracted much attention in the field of material science. Incorporation of organic polymers into inorganic glass matrices via covalent bonding is particularly interesting because the new hybrid materials will have a controllable combination of properties of both organic polymers and inorganic glasses.¹⁵ The swelling and adsorption behavior of poly(NIPAAm)-SO₂ hybrid gels derived from copolymerization of NIPAAm and 3-methacryloxypropyl trimethoxysilane (MPTMOS) were investigated by Kurihara et al.¹⁶ Their results showed that the phase transition temperature of the hybrid gel was decreased with increasing of the amount of MPTMOS content. In our previous study, three series of thermosensitive copolymeric hydrogels were prepared from MPTMOS, 2-methacryloyloxyethoxy

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TABLE I
Feed Compositions and Yield and Equilibrium Swelling Ratio for the Hybrid Gels (in mol %)

Sample	NIPAAm	TMSPMA	NMBA	TEOS	Yield (%)	SR (g/g)
NT-IPN	95	5	3	5	87.90	4.77
NT-semi-IPN	95	5	0	5	78.14	8.35
N-IPN	100	0	3	5	86.31	7.04

trimethylsilane (METMS), and methacryloyloxy trimethylsilane (MTMS), and *N*-isopropylacrylamide (NIPAAm) by solution polymerization. The effect of the structures and amounts of silane monomers on the swelling ratio, physical properties, and drug-released behaviors were studied.¹⁷ Results showed that the more the silane monomers in copolymeric hydrogels, the lower the swelling ratios of the gels due to the hydrophobicity of silane group. The gel strength and the polymer–water interaction were related to the structure of the silane monomer in the copolymeric gels. In addition, two series of NIPAAm-siloxane copolymeric hydrogels were prepared from NIPAAm and 3-(trimethoxysilyl) propyl methacrylate (TMSPMA) and 3-acrylamidopropyl trimethoxysilane (APTMO). Their swelling behaviors, mechanical properties, and drug release behavior were investigated.¹⁸ Liu and coworkers¹⁹ prepared a series of IPN gels composed of NIPAAm and porous silica and served these gels as thermosensitive drug delivery system. A sustainable positive thermoresponsive drug release profile is obtained in their research, and the overall release rate can be adjusted by changing the composition of the nanogel. By modulating the water content in feed from 95 to 55 wt %, the pore dimensions changed from 30 to 8 nm, and the drug release were affected and controlled by pore dimensions. The main concept for IPN gels in Liu's work is using the interaction of the channels formed by silica network and the thermoresponse of PNIPAAm. The type of IPN gel in Liu's work can be demonstrated as the *N*-IPN gel in our study, that is, there is no silane coupling agent between organic and inorganic component. The shrinkage of PNIPAAm network would not get affected by any covalent bonding but siloxane network.

Hydrogels are attractive and potential material. Combining with inorganic matrix or interface can be applied in applications such as protein microchips. Although most of hybrid materials were focused on application by combining hydrophobic organic compound and silica. Moreover, researches of organic–inorganic hybrid hydrogels were few and focused on oil phase system. However, there's no research about effects of interactions between organic and inorganic components on gel properties. Therefore, preparation of organic–inorganic hybrid hydrogels with different gel structures and effects of combina-

tion and interaction between organic and inorganic components on swelling and mechanical properties of hybrid hydrogels were investigated. Hence, in this study, four different structures of hybrid hydrogels were prepared: NT-IPN, NT-semi-IPN, *N*-IPN, and *N*-semi-IPN. For IPN and semi-IPN hydrogels, the interpenetration situations of organic and inorganic networks modulated by adding organic crosslinker, NMBA, were compared and discussed. For NT and N hydrogels, the effect of silane coupling agent, TMSPMA, were discussed. By modulating the gel structures, the effect of interaction and combination between organic and inorganic components on gel properties can be investigated.

EXPERIMENTAL

Materials

N-isopropylacrylamide (NIPAAm) (TCI, Tokyo, Japan) was recrystallized in *n*-hexane before use. 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA) as coupling agent obtained from ACROS (Geel, Belgium) and *N, N, N', N'*-tetramethylethylene diamine (TEMED) as an accelerator obtained from Fluka Chemical Co. (Buchs, Switzerland) were used as received. *N, N'*-methylenebisacrylamide (NMBA) as a crosslinking agent and ammonium persulfate (APS) as an initiator were purchased from Wako Pure Chemical Co. Ltd. (Osaka, Japan). Tetraethoxysilane (TEOS) was purchased from Showa Chemical Inc. (Tokyo, Japan). Sodium lauryl sulfate (SLS) was purchased from Nippon Shiyaku Kogyo (Osaka, Japan).

Preparation of organic–inorganic hybrid thermosensitive gels

Three series of hybrid gels were prepared by NIPAAm (95 mol %) /TMSPMA (5 mol %) or NIPAAm (100 mol %), TEOS (5 mol %), and NMBA (3 mol %). The feed compositions are listed in Table I. Typically, NIPAAm, TMSPMA, TEOS, and 0.2 mol % SLS as emulsifier were dissolved in 10 mL of deionized water, and then the preemulsification by ultrasonication was carried out (TP690, ELMA Co.) until the solution reached to homogeneous phase. Then, 3 mol % NMBA and 0.5 mol % APS based on total monomer concentration, as crosslinker and initiator, respectively, were added into the afore-

mentioned solution. Finally, 0.2 mol % TEMED was added as an accelerator. The mixture was immediately injected into the space between two glass plates. The gelation was carried out at 25°C for 2 days. After the gelation was completed, the gel membrane was cut into disks and immersed in 1M HCl(aq) for 2 days to proceed the sol-gel reaction. Then, the gels were immersed in excess deionized water to remove unreacted monomers and HCl. After the afore-mentioned process, the swollen gels were freeze dried.

Instrumental analysis

Gel structures of hybrid gels were analyzed by solid state NMR (Varian 400 MHz Solid State Nuclear Magnetic Resonance Spectrometer) and IR spectroscopy (Perkin-Elmer FTIR Spectrum System GX).

Composition evaluation by TGA analysis

The composition of the gel was analyzed by the TGA method using the residual content of SiO₂ under air atmosphere from 200 to 800°C at a heating rate of 40°C/min by the thermogravimetric analyzer, Pyris 1 TGA, Perkin-Elmer. Experimental molar ratios were demonstrated from the concept of mass balance and calculated by the equation we derived as follows:

$$\frac{\text{Si weight}}{\text{Gel weight}} = \text{Si wt \% (fit the results of TGA)} \quad (1)$$

Set molar ratio of NIPAAm = y , TMSPMA = $100 - y$

$$\text{Gel weight} = \left[a \times \frac{y}{95} + b \times \frac{100 - y}{5} + c + d \right] \times \text{yield} \quad (2)$$

$$\text{Si weight} = a \times \frac{100 - y}{5} \times \frac{29}{248.35} + d \times \frac{29}{208.33} \quad (3)$$

a = weight of feed of NIPAAm.
 b = weight of feed of TMSPMA.
 c = weight of feed of NMBA.
 d = weight of feed of TEOS.

Measurement of swelling ratio

The preweighed dried gels (W_d) were immersed in deionized water at constant temperature until swelling equilibrium was attained. The gel was removed from the water bath, tapped with delicate task wipers to remove excess surface water, and weighed as the wet weight of the gel (W_w). The swelling ratio (Q) was calculated from the eq. (4):

$$Q = (W_w - W_d)/W_d \quad (4)$$

Dynamic swelling

The swelling ratio was obtained by weighing the initial and swollen gels at various time intervals. The amount of water absorbed, W_t , was reported as a function of time, and the equilibrium sorption at infinitely long time was designated as W_∞ . To obtain a quantitative understanding of the nature of the sorption kinetic in the hybrid gels, the initial swelling data were fitted to exponential heuristic eq. (5) for $M_t/M_\infty \leq 0.6$.^{20,21}

$$\frac{M_t}{M_\infty} = kt^n \quad (5)$$

where M_t is the amount of water sorbed at a given time, M_∞ is the equilibrium sorption at infinitely long time, k is a characteristic constant of the gel, and n is the characteristic exponent of the mode transport of the penetrate. Values of n and k were calculated from the slopes and intercepts of the plot of $\log M_t/M_\infty$ against $\log t$, respectively. Diffusion coefficient (D) was calculated from the eq. (6) for $M_t/M_\infty \leq 0.8$.²²

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \times \left(\frac{D \times t}{L^2} \right)^{1/2} \quad (6)$$

where t is the time, and L is the initial thickness of the dried gel. The penetration velocity (v) of solvent in each gel was determined by weight gain method as described by Peppas and coworkers.^{23,24} The penetration velocity was calculated from the slope of the initial portion of the water uptake curve by eq. (7) as follows:

$$v = \frac{1}{2\rho_w A} \cdot \frac{dw}{dt} \quad (7)$$

where dw/dt is the slope of the weight gain versus time curve, ρ_w is the density of water, and A is the area of one face of the disc, and factor 2 accounts for the fact that penetration takes place through both sides.

Mechanical properties measurement

The mechanical strengths of these gels were measured by uniaxial compression experiment with universal tester (LLOYD, LRX; J. J. Lloyd, Poole, UK). The shear modulus was calculated from eq. (8):^{25,26}

$$\tau = F/A = G(\lambda - \lambda^{-2}) \quad (8)$$

where τ is the compression stress, F is the compression load, A is the cross-sectional area of swollen gels, and λ is the compression strain (L/L_0) (L_0 is the initial thickness of wet gel, and L is the thickness of wet gel after compression). At low strain, a plot of

shear stress versus $-(\lambda - \lambda^{-2})$ would yield a straight line whose slope is shear modulus (G). The effective crosslink density (ρ) can then be calculated from shear modulus and polymer volume fraction (v_2) as follows:

$$\rho = G/v_2^{1/3}RT \quad (9)$$

where R is the gas constant, and T is the absolute temperature.

Morphologies of hybrid gels

Samples were equilibrated in deionized water for 1 day, and then the swollen gels were freeze-dried for 2 days. The gels were immersed in liquid nitrogen and fractured. The fractured specimens were examined for morphological details by using scanning electron micrograph (SEM) (Joel JSM5600, Tokyo, Japan) with an acceleration voltage of 15.0 kV. The specimens were coated with a gold metal layer to provide proper surface conduction.

RESULTS AND DISCUSSION

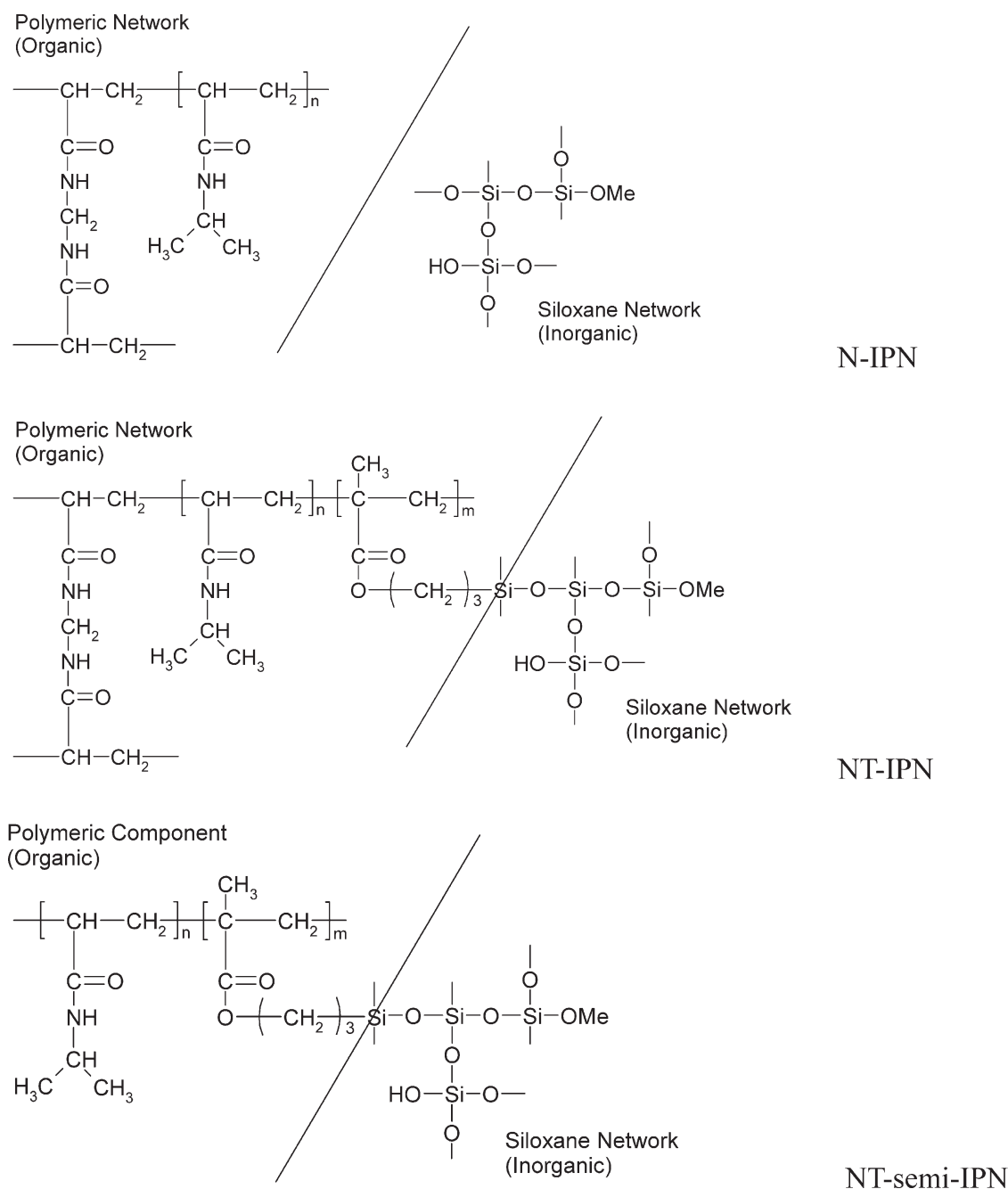
Preparation of organic–inorganic hybrid gels

To investigate the effect of different gel structures and silane coupling agent TMSPPMA on the properties of thermosensitive hybrid gels, a series of NIPAAm hybrid gels with different structures were prepared, that is, *N*-IPN, *N*-semi-IPN, NT-IPN, NT-semi-IPN. The main differences between these gels are (1) whether the combination between organic and inorganic components to be the Si–O–Si covalent bonding through vinyl silane coupling agent or (2) just the interpenetration of networks and entanglement of polymers and (3) whether the addition of NMBA to form two different gels, i.e., interpenetrating or semiinterpenetrating. The effect of structures on thermosensitivity of NIPAAm gels was also discussed. On the other hand, the *N*-semi-IPN gel cannot form because the NIPAAm component cannot form water-insoluble crosslinking networks without adding crosslinker NMBA but just form NIPAAm polymer or oligomer, and the covalent Si–O–Si bonding cannot be generated with the inorganic siloxane networks in the absence of silane coupling agent, TMSPPMA.

The definition of hybrid material is quite broad and different classifications have been proposed on the basis of their structural properties and interactions. A classification that is generally accepted has been proposed by Sanchez and Ribot,²⁷ who divided the organic–inorganic hybrid materials in two main classes. In the first group, “class I,” is included the organic–inorganic hybrid materials whose interactions between the organic and inorganic parts are

mainly regulated through hydrogen bonding, van der Waals forces. In the second group of organic–inorganic hybrid materials, the organic and inorganic components are strongly linked through chemical bonds, such as covalent or ionic bonds, to form the “class II” of hybrids. It is important to observe more closely some of the organic–inorganic hybrid materials included in class II. Hybrids of this class are generally prepared employing organically modified alkoxides which contain one or more covalent bonds that are not cleaved during the sol–gel process. These alkoxides can be divided in two types: alkoxides bearing polymerizable organic functional groups, such as epoxides, methacrylates, or alkoxides whose organic groups are only modifying the inorganic network. This is very similar to that of inorganic glasses, where alkali ions act as network modifiers. Another special class of nanostructured organic–inorganic hybrid materials is obtained by sol–gel polycondensation of bridging silsesquioxane precursors, whose general formula is $(RO)_3\text{—Si—R—Si—(OR)}_3$.^{28,29}

The structures of the designed hybrid gels are shown in Scheme 1. NT-IPN gel is an interpenetrating polymer network composed of organic network that was formed by NMBA and inorganic siloxane network that was formed by sol–gel process of TEOS. These two networks were interconnected by covalent bonding through sol–gel process of coupling agent, vinyl silane monomer TMSPPMA; NT-semi-IPN gel is a semiinterpenetrating polymer network composed of linear poly(NIPAAm) and inorganic siloxane network, the linear polymer, and siloxane network were interconnected through coupling agent, TMSPPMA. *N*-IPN gel is an interpenetrating polymer network composed of organic poly(NIPAAm) network and inorganic siloxane network, and there existed no covalent bonding between two networks. From a structural point of view, types of network and existence of interconnection between networks would affect the properties of the gels. Based on this reason, the effect of existence of silane coupling agent and types of interpenetration on the properties of these three types of gels are investigated. For the definition of IPN, two or more polymeric networks were formed by independent polymerization, and the networks were not necessary independent to each other. Networks can be combined by additional reaction with crosslinker or coupling agent to form covalent bonding between two networks. A polymer is formed through any conventional polymerization process and then swollen by or dissolved in a monomer of a different type. A second polymerization takes place and forms the second polymeric component in the presence of the first. During the second polymerization, entropy of mixing is lost as the molecules increase



Scheme 1 Structures of the hybrid gels.

in size, and phase separation generally occurs, which resulted in the two-phase morphology common to IPNs.³⁰ In this research, different IPN structures modulated by silane coupling agent to combine two independent networks would affect the miscibility and resulted in different mechanical properties which was described in this article.

Structural analysis

The structures of hybrid gels were investigated by solid state NMR and IR spectra. Figure 1 shows the

solid state ¹³C NMR spectra of the hybrid gels. NIPAAm monomer was the main component of the hybrid gels and the content of NIPAAm was up to 95 mol %, resulted in three similar spectra shown in Figure 1. Considering the intensity of each signal of these hybrid gels shown in Table II, it was found that the intensity of each signal of N-IPN gel was higher than that of the other hybrid gels. Because of no inner standard during measurement, the intensities of the peaks cannot be used to quantify the content of NIPAAm and different compositions between these gels. In addition, structures of

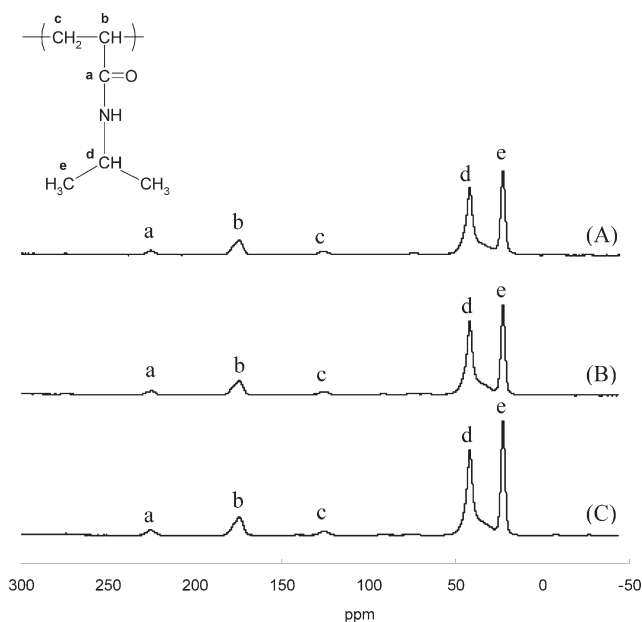


Figure 1 CP/MAS ^{13}C NMR spectra of hybrid gels. (A) NT-IPN gel; (B) NT-semi-IPN gel; and (C) N-IPN gel.

organic-inorganic hybrid materials such as modified silica or glass can be determined by ^{29}Si NMR, but the silicone contents in the hybrid gels were too low to be detected. Hence, the composition of the gel was analyzed by the TGA method using the residual content of SiO_2 under air atmosphere at 800°C . The results listed in Table III indicated that the theoretical and experimental values of the molar ratio of NIPAAm/TMSPMA are not approximate especially for NT-IPN gel. The reasons were explained as followed. Although the theoretical molar ratios of NIPAAm/TMSPMA in NT-IPN and NT-semi-IPN gels are 95/5, the experimental values obtained by TGA analysis were quite different to the theoretical values, especially for NT-IPN gels which had higher NIPAAm content than the NT-semi-IPN gels. This result may due to the loss of TEOS sols or gels that were not combined with TMSPMA and caused lower ratio of silane in the gels. From the results, the NIPAAm content in NT-semi-IPN gels were lower than NT-IPN gels. This is because partial poly(NIPAAm) did not combined with inorganic siloxane networks composed of TEOS via coupling agent

TMSPMA after gelation, some linear poly(NIPAAm)s were dissolved in water solution and lost from gel matrix in the process of washing (to remove unreacted monomer) or swelling, and resulted in lower NIPAAm content in the TGA analysis of NT-semi-IPN gels. The loss of NIPAAm polymer was just caused a more approximate value to the theoretical value. The lower yield of NT-semi-IPN gel helps to account for the loss of NIPAAm. To sum up, the TEOS component in the feed composition of the hybrid gels was easily lost from gel matrix and resulted in higher ratio of organic component. Organic part without addition of crosslinker NMBA, i.e., NT-semi-IPN, would cause loss of NIPAAm and made the organic-inorganic ratio of gels adjusted approximately to the theoretical values.

Figure 2 shows the IR spectra of three hybrid gels and their corresponding feed compositions. In the IR spectra, the stretching absorption peak occurred at 1615 cm^{-1} due to vinyl group of $\text{C}=\text{C}$ for spectra (A), (C), and (E), but that disappeared after they were polymerized to form gels, i.e., spectra (B), (D), and (F). The absorption peaks at 1028 cm^{-1} in spectra (A) and 1032 cm^{-1} in spectra (C) are corresponding to methoxysilane of TMSPMA and ethoxysilane of TEOS (both of these two peaks of methoxysilane and ethoxysilane are close to each other). Then alkoxy silane transferred to siloxane linkage that absorption peak occurred at $1100\text{--}1000\text{ cm}^{-1}$ after condensation by treatment with $\text{HCl}_{(\text{aq})}$. The absorption peak at 1018 cm^{-1} in spectra (E) is corresponding to ethoxysilane of TEOS and then transferred to siloxane linkage that absorption peak occurred at 1073 cm^{-1} in spectra (F) after condensation by treatment with $\text{HCl}_{(\text{aq})}$.³¹ The results showed that the sol-gel reaction was confirmed.

Swelling kinetics

The swelling and deswelling kinetic profiles as a function of time for the hybrid gels containing 5 mol % of TEOS at 25 and 37°C were shown in Figure 3. From the results of the kinetic profiles, the gel without crosslinker NMBA, i.e., NT-semi-IPN, has a highest swelling ratio because the semi-IPN formed

TABLE II
Signals and Intensity of ^{13}C NMR Spectra of Hybrid Gels

Signal	NT-IPN		NT-semi-IPN		N-IPN	
	ppm	Intensity	ppm	Intensity	ppm	Intensity
a	225.53	6916.18	225.44	6615.56	225.53	9058.92
b	174.58	24919.24	174.58	24628.41	174.67	32795.10
c	126.27	5543.19	126.01	5490.33	125.59	6968.02
d	41.96	118162.60	41.96	130627.60	41.87	151837.10
e	22.85	153925.30	22.85	159387.40	22.85	203271.30

TABLE III
Wt % of SiO₂ and Si and Molar Ratio of NIPAAm/TMSPMA Obtained by TGA Test

Sample	SiO ₂ wt %	Si wt %	Theoretical Si wt %	Molar ratio of NIPAAm/TMSPMA	
				Theoretical	Experimental ^a
NT-IPN	3.3521	1.5936	2.1518	95/5	98.78/1.22
NT-semi-IPN	5.9075	2.8085	2.2281	95/5	95.20/4.80
N-IPN	2.1026	0.9996	1.1328	100/0	100/0

^a Experimental molar ratios were calculated as follows:

$$\frac{\text{Si weight}}{\text{Gel weight}} = \text{Si wt \% (fit the results of TGA).}$$

Set molar ratio of NIPAAm = y , TMSPMA = $100 - y$.

$$\text{Gel weight} = \left[a \times \frac{y}{95} + b \times \frac{100-y}{5} + c + d \right] \times \text{yield.}$$

$$\text{Si weight} = a \times \frac{100-y}{5} \times \frac{29}{248.35} + d \times \frac{29}{208.33}.$$

a = weight of feed of NIPAAm.

b = weight of feed of TMSPMA.

c = weight of feed of NMBA.

d = weight of feed of TEOS.

a looser gel structure, and the hydrophilic polymer would not be restricted by the networks. Comparing two IPN gels, NT-IPN and *N*-IPN, the former gel has lower swelling ratio because it contains hydrophobic silane coupling monomer and covalent bonding between two networks. Thermosensitivity for a thermosensitive gel was the ability to response the

stimuli of temperature. The more the difference of swelling ratios between swelling and deswelling of the gel referred to better thermosensitivity. The profiles of shrinking kinetics showed that the *N*-IPN gel has a better thermosensitivity and more obvious shrinkage because the inorganic siloxane network with covalent Si—O—Si bonding would not restrict the NIPAAm network. To discuss the thermoreversibility, swelling and deswelling experiments were taken for three cycles by modulation of temperature (25°C and 37°C). Figure 3 shows the thermoreversibility of the hybrid gels containing TEOS. The result showed that three types of the hybrid gels still exhibited good thermoreversibility after three swelling–deswelling cycles.

To investigate the diffusion model of the gel, the initial swelling data were fitted into the eqs. (2) and (3), the n , k , D values were calculated from these two equations. The results shown in Table IV indicate that the values of n for the gels NT-IPN, *N*-IPN, and NT-semi-IPN are 0.32, 0.27, and 0.46,

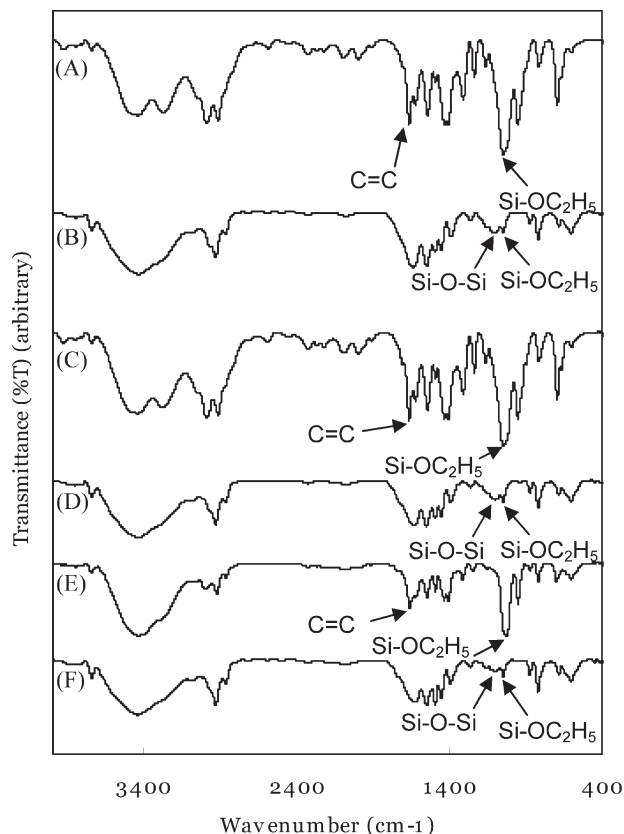


Figure 2 IR spectra of (A) NT-IPN feed; (B) NT-IPN gel; (C) NT-semi-IPN feed; (D) NT-semi-IPN gel; (E) *N*-IPN feed; and (F) *N*-IPN gel.

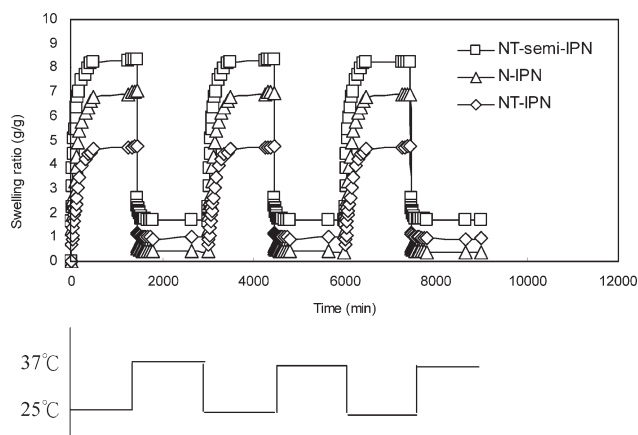


Figure 3 Thermoreversibility of the hybrid gels.

TABLE IV
n, k, D Values of the Hybrid Gels

Sample	<i>N</i>	<i>K</i> × 10 ²	<i>D</i> × 10 ⁴ (cm ² /s)	<i>v</i> × 10 ³ (cm/min)
NT-IPN	0.32	3.65	6.23	0.99
NT-semi-IPN	0.46	1.47	10.37	1.38
N-IPN	0.27	5.24	6.26	1.12

respectively. This result shows that the swelling transport mechanism for the hybrid gels all tend to belong to Fickian transport according to the distinction of transport mechanism mode proposed by Alfrey et al.³² The data shown in Table IV also indicate that the diffusion coefficients *D* for the gels increase in swelling ratio of the gels (i.e., NT-semi-IPN > N-IPN > NT-IPN). The penetration velocities calculated from eq. (4) for the present hybrid gels also increase as the same tendency as their diffusion coefficients.

Furthermore, a definition was given for swelling kinetics to get more swelling characteristics of the hybrid gels. The interval of the difference of swelling ratio [Δ SR (%)] was defined as the ratio of swelling ratio difference between two successional time point to swelling ratio difference between beginning and final point as following equation:

$$\Delta\text{SR} (\%) = \frac{\text{SR}_2 - \text{SR}_1}{\text{SR}_{\text{final}} - \text{SR}_0} \quad (10)$$

When the Δ SR (%) was below 1%, it was defined that the gel reached swelling equilibrium, and the time was defined as equilibrium time. The initial swelling rates and equilibrium swelling time for the hybrid gels were also calculated and shown in Table V. The results in Table V show that NT-IPN gel needs about 1260 min, N-IPN gel needs 1380 min, and NT-semi-IPN gel needs only 480 min to reach equilibrium swelling. The initial swelling rate for the gels increasing in the order of NT-semi-IPN > N-IPN > NT-IPN indicates that NT-semi-IPN gel has highest initial swelling rate and NT-IPN has lowest initial swelling rate. From earlier results, the NT-IPN and N-IPN gels need more time to reach equilibrium swelling than NT-semi-IPN gel. This result explicitly showed that the gel with IPN structure show denser

TABLE V
Equilibrium Time and Initial Swelling Ratio for the Hybrid Gels

Sample	Eq. time (min)	Initial swelling rate (g H ₂ O/min)
NT-IPN	1260	0.0317
NT-semi-IPN	480	0.0849
N-IPN	1380	0.0464

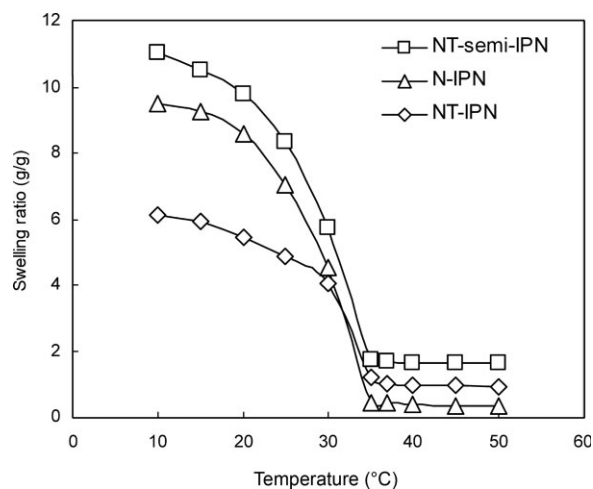


Figure 4 The equilibrium-swelling ratio of the hybrid gels in different temperatures.

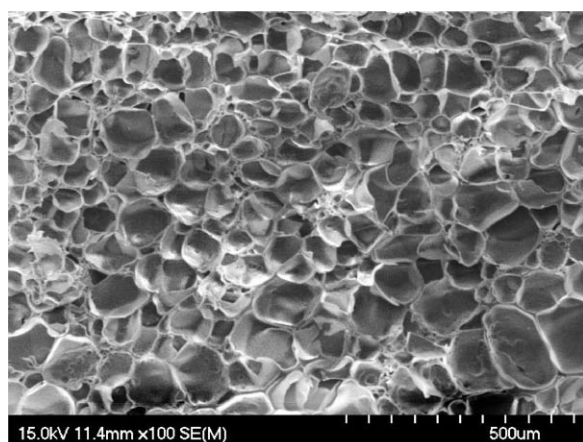
structure that resulted in lowering water penetrating rate into the gel and decreasing diffusion coefficient of water into the gel. Hence, these two gels need more time to reach equilibrium.

Effect of temperature on swelling ratios for hybrid gels

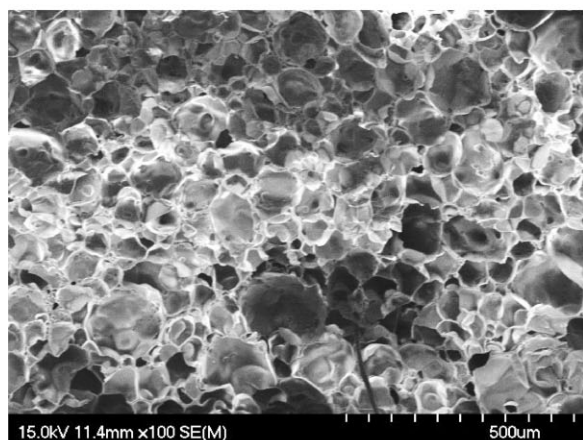
Figure 4 shows the equilibrium swelling ratios of the hybrid gels in various temperatures. The results indicate that the gels containing coupling silane agent get bad thermosensitivity for its hydrophobicity and denser structure. The N-IPN gel has a sharper decrease curve than NT-IPN gel and NT-semi-IPN gel near the CGTT. This behavior can be explained by the difference of gel structure of IPN and semi-IPN. The gel with semi-IPN structure has looser structure and consequently higher swelling ratio, and the gels with IPN structures have tighter network and resulted in lower swelling ratios. The CGTT of three types of hybrid gels were about 33°C and not affected by incorporation of hydrophobic monomer TMSPPMA. The reason is that the gel is hydrophilic and form hydrogen bonding with water molecules at temperature lower than CGTT, but the gel transform to hydrophobic because the heat supply the energy to break the hydrogen bonding at temperature higher than CGTT. The incorporation of

TABLE VI
Gel Moduli and Crosslinking Densities for the Hybrid Gels

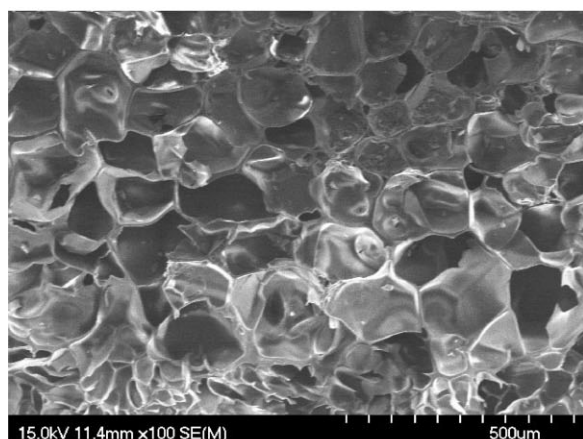
Sample	Avg. <i>G</i> (kPa)	Avg. ρ_x (mol/cm ³) × 10 ⁶
NT-IPN	596.29	11.36
NT-semi-IPN	196.04	3.75
N-IPN	187.25	3.42



(a)



(b)



(c)

Figure 5 Scanning electron micrograph (SEM) of cross section of the hybrid gels. (a) NT-IPN gel, (b) NT-semi-IPN gel, and (c) *N*-IPN gel.

hydrophobic TMSPMA monomer would not affect the CGTT because the hydrogen bonding does not exist between TMSPMA and water molecules even at the temperature lower than CGTT, therefore the hydrophobic TMSPMA would not affect the CGTT

but reduce the overall swelling ratio of the hybrid gels.

Mechanical properties

The mechanical properties of the hybrid gels are listed in Table VI. The moduli G and effective ρ_x for the present gels were calculated from eqs. (5) and (6). The results in Table VI indicate that NT-IPN has highest gel strength and crosslinking density. This is because NT-IPN gel was composed of two crosslinking networks, which were interconnected with covalent bonding, and the combination of two networks by silane coupling agent also made the NT-IPN networks more miscible. Moreover, inorganic silane component also contributed to gel structure and resulted in higher gel strength. NT-semi-IPN gel was composed of only one network and linear polymers, its mechanical strength and crosslinking density were relatively low. Comparing *N*-IPN with NT-semi-IPN, although *N*-IPN has two networks, there is no covalently bonding between these two networks. Hence, *N*-IPN showed lower gel strength and crosslinking density than NT-semi-IPN.

Morphologies of the hybrid gels

The microphotographs of the cross-sectional morphology of the hybrid gels are shown in Figure 5. Comparing these macroscopic gel structures, *N*-IPN gel [Fig. 5(c)] shows a looser structure and bigger pore size than the gels containing vinyl silane monomer. This is because the TMSPMA coupling agent can interconnect the organic and inorganic networks to form more compact structure. Comparing NT-IPN and NT-semi-IPN gels, semitype IPN [Fig. 5(b)] exhibits more irregular and looser structure than fully IPN gel [Fig. 5(a)].

CONCLUSIONS

A series of organic–inorganic hybrid gels with interpenetrating or semiinterpenetrating structures were prepared by changing the addition of crosslinker NMBA and coupling silane monomer. The vinyl silane monomer plays the key role of bridge between organic and inorganic networks. By free-radical polymerization and sol–gel reaction, organic and inorganic networks not only interpenetrated but also interconnected with covalent bonding. The existence of covalent bonding established via vinyl silane monomer would affect the swelling characteristics and mechanical properties of these hybrid gels. Considering two kinds of interpenetrating polymer networks, NT-IPN and *N*-IPN, the former contained vinyl silane monomer and resulted in denser structure, more compact mechanical strength, lower

swelling ratio, and smaller swelling volume. Comparing interpenetrating polymer network (NT-IPN) and semiinterpenetrating polymer network (NT-semi-IPN), organic part of the later gel would not be restricted by crosslinking structure and showed higher swelling ratio and swelling volume but lower mechanical strength. The content of Si and molar ratio of NIPAAm/TMSPMA for each hybrid gel were also evaluated.

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