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Fluorescence study on the mechanism of rapid shrinking of grafted poly(*N*-isopropylacrylamide) gels and semi-IPN gels

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Abstract

In order to clarify in nanometer scale the mechanism of rapid shrinking of grafted poly(*N*-isopropylacrylamide) (PNIPAM) hydrogels during temperature jump from room temperature to 40 °C, temperature dependences of dansyl fluorescence were studied for the rapid-shrinking grafted PNIPAM gels in which dansyl groups are attached to graft chains or network main chains. Gradual decrease in dansyl fluorescence peak wavelength, λ_f, with the increase in temperature between 17 and 32 °C for grafted chains in the grafted PNIPAM gel from 540 to 500 nm showed the occurrence of coil-globule transition of graft chains during this temperature range. However, λ_f of network main chains showed abrupt decrease at 30–34 °C from 540 to 510 nm reproducing the macroscopic volume phase transition of PNIPAM gels. The coil-globule transition and further aggregation of graft chains enhance the formation of heterogeneous structure during the temperature jump, providing water-expelling channels at the surface skin layer of the collapsed PNIPAM gel. The possible importance of large-scale heterogeneity with a much larger size than the mesh size of network on the rapid-shrinking is suggested, because this type of large-scale heterogeneity can be introduced by the network formation in the presence of linear macromonomer. A post-crosslinked semi-IPN gel also showed rapid shrinking and gradual decrease in λ_f for the linear polymer chains inside.

Keywords: Dansyl fluorescence; Grafted PNIPAM hydrogel; Semi-IPN gel

1. Introduction

Some polymer gels are very sensitive to environmental conditions such as temperature, solvent composition, pH, and others. Because of the change in the environmental conditions, in some cases volume phase transitions of polymer gels take place [1,2]. A poly(*N*-isopropylacrylamide) (PNIPAM) gel known as a thermosensitive hydrogel undergoes abrupt shrinking in volume at 32 °C in water [3] and has been widely investigated both fundamentally and for biomedical, pharmaceutical, and other applications, but the shrinking process takes usually long time (sometimes it takes a week) depending on the size of the gels [4]. The formation of high-polymer-density skin layer on the surface of the shrinking gel was supposed to suppress the expulsion of water from inside out, leading to a marked decrease in shrinking rate [5]. This slow shrinking prevented wider application of PNIAM gels and was an important topic to be solved. In 1995 comb-type graft chains were introduced into PNIPAM network by Yoshida et al. [6], realizing a rapid shrinking of the polymer hydrogel in about 20 min in response to temperature change from 10 to 40 °C. Since then, improvements of response rates by the control of network structure have been reported by introducing semi-interpenetrating polymer network (semi-IPN) [7], controlling crosslink density of the gel [8,9], preparing a gel under pressure [10,11], and by introducing the macroporosity into the gel [12]. In the case of rapid shrinking of the grafted PNIPAM gels, the grafted side chains were suggested to create hydrophobic regions, aiding the expulsion of water from the network during collapse [6]. The decrease in lower critical solution temperature (LCST) of the main chains due to the

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hydrophobic aggregation of grafted chains was also suggested [13,14]. However, details of the mechanism of rapid shrinking were still unknown and to be elucidated based on submicron- and nanometer-scale measurements.

Fluorescence techniques such as steady-state fluorescence spectroscopy, lifetime measurements, and steady-state as well as transient fluorescence anisotropy measurements give nano-scale insider look in polymer systems [15–17], and have been applied to polymer gels for studying network structure [18,19], volume phase transition [20–22], deuterium isotope effects [23], and so on. A typical fluorescent probe, *N*,*N*-(dimethylamino)naphthalenesulfonamide (dansyl) group, was used for the studies of PNIPAM gels in reentrant-type mixed aqueous solutions [21,23] and in water [22]. The fluorescence spectroscopy of dansyl derivatives has been studied extensively. Dansyl fluorescence is relatively insensitive to quenching by oxygen, and its absorption maximum (350 nm) is essentially independent of the medium. The wavelength of maximum emission, λ_f, in contrast, exhibits a strong and well-defined dependence on the polarity and/or viscosity of the probe nanoenvironment. In polar, nonviscous solvents it shows green fluorescence ($\lambda_f = 560$ nm in water), but it shows marked blue shift and becomes blue in nonpolar or viscous solvents [24]. Thus, we can easily distinguish the polarity and hydrophobicity of nanoenvironment of the sites where the dansyl groups are chemically incorporated. One of the big advantages of using fluorescence probes for the study of gels is that we can measure the hydrophobicity of nanoenvironment, local mobility, and anisotropy of the chromophore at the site where exactly the probe is attached or located. So, we intended to use fluorescence technique for making clear the mechanism of rapid shrinking of grafted PNIPAM gels together with its study with scanning microscopic light scattering [25]. A fluorescence study on grafted PNIPAM gels was reported recently [22], however, no clear difference in hydrophobicity was observed between dansyl labels attached to graft chains and network main chains. It is not clear in the paper [22] that their grafted PNIPAM gels really showed such a rapid shrinking as reported by Yoshida et al. [6].

We present here a comparative study of dansyl fluorescence labeled to graft chains or main chains of grafted PNIPAM gels undergoing rapid shrinking with that of dansyl groups labeled to main chains of normal PNIPAM gel which does not shrink rapidly. Fluorescence of dansyl labels on network or linear polymer chains in semi-IPN-type PNIPAM gels produced in different orders in network and linear-polymer preparation gave clear consistent results with the fact that rapid shrinking occurs only with the post-crosslinked semi-IPN gel. Some discussion is given on the mechanism of rapid shrinking of the grafted PNIPAM gels in water in response to temperature jump from 25 to 40 °C and the importance of two types of heterogeneous structure of the polymer gels.

2. Experimental

2.1. Sample preparation

2.1.1. Fluorescent-labeled monomer

Dansylaminoethylacrylamide (DAEAM, Fig. 1) was prepared by the procedure reported by Shea et al. [19]. The solution of dansyl chloride (1.87 g, 6.93 mmol) in THF (75 ml) was drop-wise added to the solution of ethylenediamine (4.63 ml, 69.3 mmol) in THF (300 ml) at 273 K. The solution was stirred at 273 K for 3 h, and 10 ml of 1 N KOH solution was added. The THF was evaporated, and the aqueous layer was extracted with CH_2Cl_2 (4×100 ml). The organic layer was dried using $MgSO_4$ and evaporated. The residue was recrystallized from benzene/hexane (5/1, v/v) solution. Dansylethylenediamine was obtained (1.41 g, 69.4% yield). To a solution of dansylethylenediamine (0.50 g, 1.70 mmol) in THF (25 ml) at room temperature was added acryloyl chloride (0.146 ml, 1.80 mmol) and triethylamine (0.25 ml, 1.80 mmol). The solution was stirred at room temperature for overnight. The salts were then filtered and washed with THF. After the solvent was

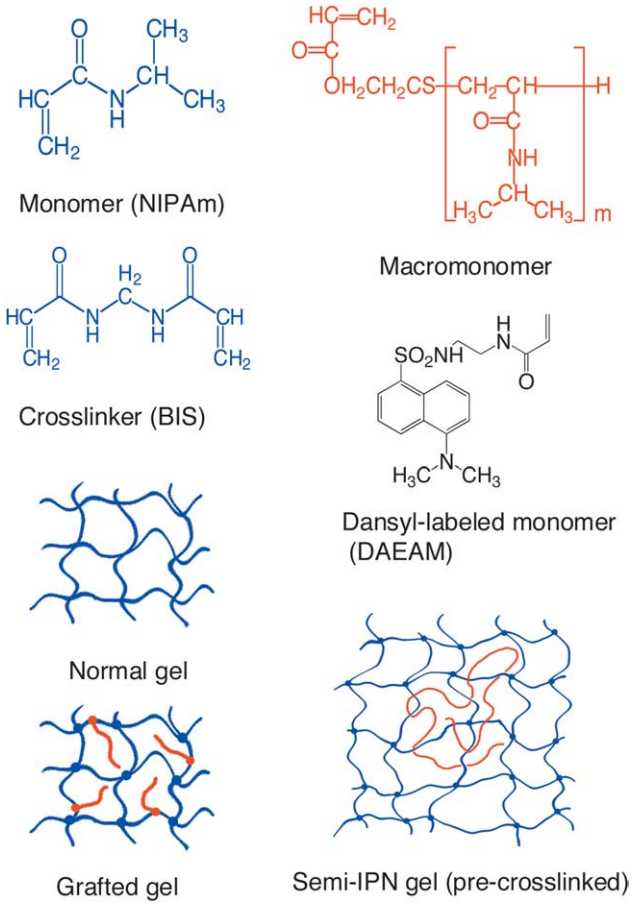

Fig. 1. Chemical structures of the monomer, macromonomer, crosslinker, and fluorescent-labeled monomer used in the present study. Schematic structures of the grafted PNIPAM gel, normal gel and semi-IPN gel (pre-crosslinked) are also given.

evaporated under reduced pressure, water and CH_2Cl_2 were added. The organic layer was dried using anhydrous sodium sulfate and evaporated under reduced pressure. The residue was chromatographed on silica with CH_2Cl_2/diethyl ether (4/1, v/v) as an eluent to provide DAEAM (0.53 g, 94.8% yield). The ^{1}H NMR spectra of the products (dansylethylenediamine and DAEAM) were identical to the results reported by Shea et al. [19].

2.1.2. NIPAM macromonomer

A semitelechelic NIPAM macromonomer (Fig. 1) and semitelechelic dansyl-labeled NIPAM macromonomer were prepared by radical telomerization of NIPAM monomer using 2-hydroxyethanethiol (HESH) as a chain transfer agent and following esterification with acryloyl chloride. Semitelechelic PNIPAM with a terminal hydroxy end group was prepared by radical photo-polymerization of NIPAM (5.00 g) with HESH (0.08 g) as a chain-transfer agent and *N*,*N*′-azobisisobutylonitrile (AIBN) (7.32 mg) as a photosensitized initiator in 10 ml of distilled *N*,*N*′-dimethylformamide (DMF) under an ultrahigh-pressure Hg lamp irradiation. For the preparation of dansyl-labeled PNIPAM macromonomer, 0.01 g of DAEAM (0.06 mol% to NIPAM monomer) was added to the DMF solution for the copolymerization. The NIPAM macromonomer with or without dansyl groups on its chain was prepared by the esterification of terminal hydroxy group of corresponding semitelechelic PNIPAM (2.50 g) in THF (15 ml) for 2 h with a large excess of acryloyl chloride (0.12 ml) in the presence of triethylamine (0.21 ml). Details are similar to those given in Ref. [13]. The weight-average molecular weights, M_w of the NIPAM macromonomers with and without dansyl labels were determined to be 1.5×10^5 and 1.1×10^5, respectively, with a gel permeation chromatography using a TSK GMH_{HR}-M column and a JASCO RI-2031 detector.

2.1.3. Grafted PNIPAM gels with dansyl labels on main chains or graft chains

Dansyl-labeled grafted PNIPAM gels (Fig. 1) were prepared by radical copolymerization of NIPAM monomer, NIPAM macromonomer and *N*,*N*′-methylenebisacrylamide (BIS) as a crosslinker in the presence of ammonium persulfate (AP) as an initiator and tetramethylethylenediamine (TEMED) as an accelerator at 6 °C in water. The weight ratio of macromonomer to NIPAM was kept constant (30/70 w/w). Total concentration of NIPAM and macromonomer was 0.89 mol/L. For getting grafted PNIPAM gels dansyl-labeled on main chains (graft gel-m), 0.03 mol% of DAEAM to NIPAM monomer was supplied into the pregel solution. Dansyl-labeled NIPAM macromonomer was used for getting grafted PNIPAM gels dansyl-labeled on graft chains (graft gel-g). After filtration of the pregel solution containing NIPAM, macromonomer, and BIS in distilled water by using a membrane filter of 3.0 μm diameter, AP and TEMED were added to the solution under stirring in an ice bath under nitrogen atmosphere. The solution containing dipped glass tubes (0.8 or 2.8 mm in diameter and 25 mm in length) was kept at 6 °C for about 30 h. The cylindrical gels were taken off from the glass tubes, swollen in distilled water at 5 °C, and the residual monomer and macromonomer if any were removed by changing water several times. A dansyl-labeled normal PNIPAM gel without graft chains (normal gel-m) as a reference sample was prepared in a similar way but without using macromonomer. The preparation conditions of dansyl-labeled grafted PNIPAM gels are summarized in Table 1.

2.1.4. Semi-IPN gels with dansyl-labeled linear polymer and dansyl-labeled network

Semi-interpenetrating network (semi-IPN) gels composed of PNIPAM chains were prepared in two different procedures, i.e. network formation before linear polymerization (pre-crosslinked semi-IPN, Fig. 1) and network formation in the presence of linear polymer (post-crosslinked semi-IPN). A normal network for the preparation of pre-crosslinked semi-IPN was formed by redox radical copolymerization of NIPAM monomer (1.58 g, 140 mmol) with BIS (26.6 mg, 1.73 mmol) in water (18.3 ml) by adding 140 μl of aqueous solution of AP (40 mg/ml) and 48 μl of TEMED. The resulting gel was taken off from glass tubes, swollen in distilled water, washed several times by changing water, and dried. Then, NIPAM monomer (12 g, 106 mmol) was photopolymerized in methanol (60 ml) in the presence of pre-swollen normal network, AIBN (45.4 mg, 0.276 mmol), and 2-aminoethanethiol (AESH, 0.29 g, 2.64 mmol) under UV irradiation for 6 h, leading to the pre-crosslinked semi-IPN PNIPAM gel. The introduction of dansyl probe to the network chains (pre-semi-IPN-m) or to the linear chains (pre-semi-IPN-l) was carried out by adding DAEAM (about 0.03 mol% to NIPAM monomer) in the corresponding polymerization step. For the preparation of post-crosslinked semi-IPN gels, a linear PNIPAM (0.634 g) prepared in advance by photopolymerization of NIPAM (13.4 g) with AIBN (19.9 mg) and AESH (0.128 g) in DMF (25 ml) was introduced into NIPAM (0.634 g) and BIS (10.6 mg) solution in water (7.33 ml). The addition of 56 μl of aqueous solution of AP (40 mg/ml) and 19.2 μl of TEMED into the solution provided a semi-IPN gel, which was taken off from a glass tube, swollen in distilled water, and washed several times by changing water. The introduction of dansyl probe to the network chains (post-semi-IPN) or to the linear chains (post-semi-IPN-l) was carried out by adding DAEAM (about 0.03 mol% to NIPAM monomer) in the corresponding polymerization step.

2.2. Size measurements and fluorescence measurements

The diameters of grafted PNIPAM gels, *L*, at equilibrium swollen states in a thermostat were measured with a cathetometer after standing the sample for 6 h before

Table 1
Preparation conditions of dansyl-labeled grafted and normal PNIPAM gels and reference gels without dansyl groups

Sample	NIPA (g)	DAEAM solution (ml)	Macromonomer (g)	Dansyl-labeled macromonomer (g)	BIS solution[a] (ml)	AP solution[b] (μl)	TEMED (μl)	Water (ml)
Graft gel-m	0.555	1.30[c]	0.238		0.60	70	24	7.27
Graft gel-g	0.555			0.238	0.60	70	24	8.56
Graft gel	0.277		0.119		0.28	35	12	4.30
Normal gel-m	1.19	0.95[d]			1.20	105	36	13.4
Normal gel	1.19				1.20	105	36	12.4

[a] 16.7 mg/ml in water.
[b] 40 mg/ml in water.
[c] 0.367 mg/ml in water.
[d] 1.76 mg/ml in water.

every measurement at a new temperature. The changes in gel sizes during a temperature jump from 25 to 40 °C were followed by a CCD camera and analyzed using a personal computer system. The fluorescence spectra of the dansyl-labeled grafted and semi-IPN PNIPAM gels as well as linear PNIPAM and DAEAM in water were measured by a Hitachi-850 fluorescence spectrophotometer. The temperature of the samples was adjusted by a circulator-type thermostat and measured with a Simaden SD20 digital thermometer. The excitation wavelength was fixed at 340 nm where the dansyl group exhibits big absorption.

3. Results and discussion

3.1. Rapid shrinking and fluorescence spectra of grafted PNIPAM gels

In order to ascertain the rapid shrinking of presently prepared grafted PNIPAM gels, volume changes after a temperature-jump from 25 to 40 °C were measured for the grafted and normal PNIPAM gels swollen in water. The volume change was calculated from the cube of diameter change of cylindrical samples. Fig. 2 shows that the present grafted PNIPAM gel shrinks very rapidly within 20 min after the temperature jump from 25 to 40 °C in a similar manner to the case reported in Ref. [6], while the normal gel without graft chains remains in 86% of the initial volume after 3 h. Pictures of the cylindrical samples by CCD camera after 3 and 60 min are also shown in Fig. 2(b).

Temperature dependences of equilibrium volumes compared to the volume of as-prepared state for grafted and normal PNIPAM gels are summarized in Fig. 3. The results for semi-IPN PNIPAM gels are also given in Fig. 3. Almost similar temperature dependence of the equilibrium volume was observed for both grafted and normal PNIPAM gels, which is consistent with the results in Ref. [6]. Both grafted and normal PINPAM gels reach the collapsed state at 34 °C. The results in Fig. 3 also ascertain that the introduction of dansyl labels onto main chains (gel-m) or graft chains (gel-g) of the PNIPAM gels gave no influence on the volume change phenomena of these gels.

Temperature dependence of fluorescence spectra of dansyl labels introduced into the graft chains of grafted PNIPAM gel (grafted gel-g) are shown in Fig. 4. The fluorescence peak wavelength, λ_f, is 540 nm at 13.6 °C, decreases gradually from 17 °C with the increase in temperature and reaches around 510 nm at 33.4 °C. The temperature dependences of λ_f of dansyl fluorescence at the main chains (grafted gel-m) and the graft chains (grafted gel-g) of the grafted PNIPAM gel and that at the main chains of normal gel (normal gel-m), as well as λ_f of dansyl

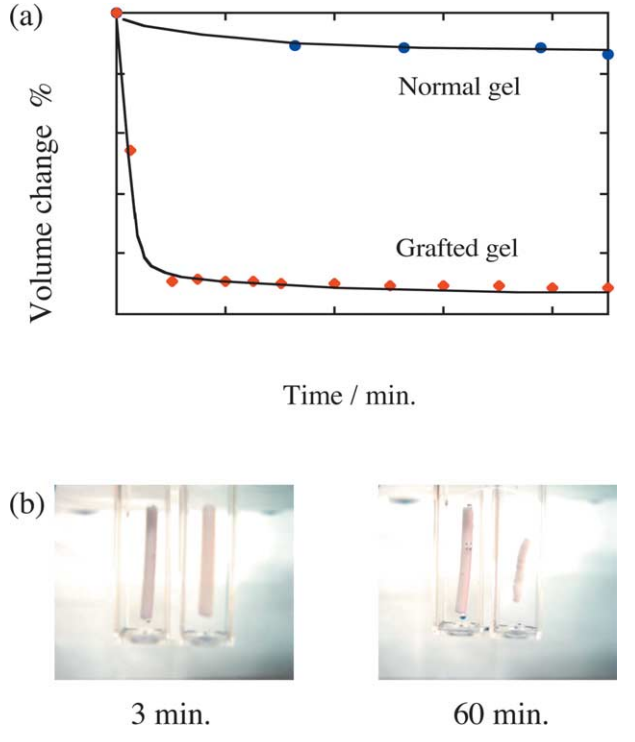

Fig. 2. Rapid shrinking of the grafted PNIPAM gel compared to the normal PNIPAM gel after a temperature jump from 25 to 40 °C. (a) Time course of volume change, (b) pictures of the cylindrical samples after 3 and 60 min of the temperature jump; left sample of each picture: normal gel, right sample of each picture: grafted gel.

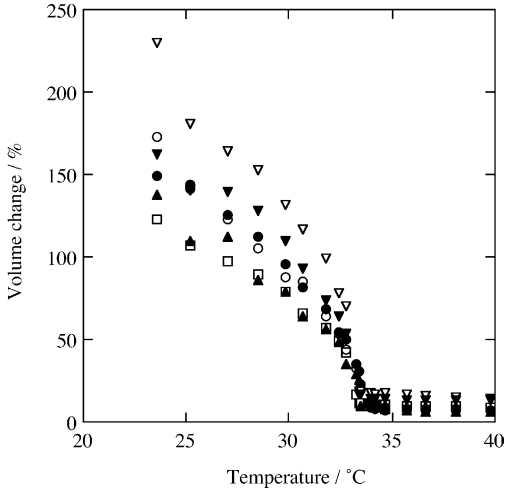

Fig. 3. Temperature dependences of equilibrium volume changes compared to the as-prepared state for grafted gel-m (○), grafted gel-g (●), normal gel-m (□), pre-crosslinked semi-IPN-m (▽), pre-crosslinked semi-IPN-l (▼), and post-crosslinked semi-IPN-l (▲).

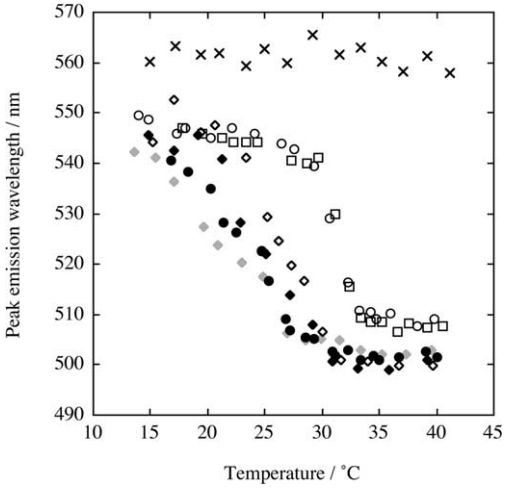

Fig. 5. Temperature dependence of peak wavelengths of dansyl fluorescence for grafted gel-m (○), graft gel-g (●), normal gel-m (□), linear PNIPAM with polymer concentrations of 7.45 w/v% (◉), 0.745 w/v% (◆), 0.075 w/v% (■), and DAEAM (×).

fluorescence of linear PNIPAM and DAEAM are summarized in Fig. 5. The λ_f for normal gel-m stays above 540 nm at temperatures below 30 °C showing the hydrophilic nanoenvironment of PNIPAM network chains in the swollen state at these temperatures. The λ_f abruptly decreases at 30 °C and

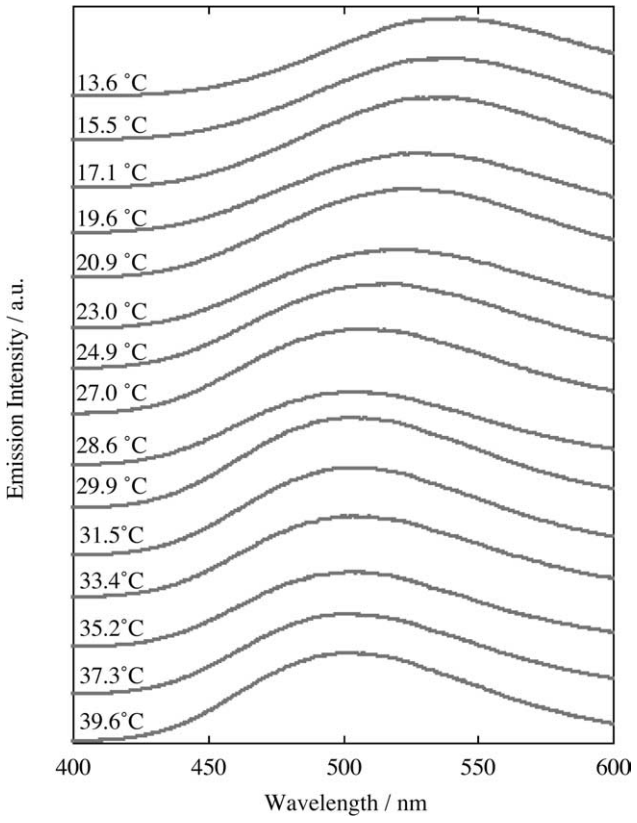

Fig. 4. Temperature dependence of fluorescence spectra of dansyl labels introduced into graft chains of the rapid-shrinking-type grafted PNIPAM gel (grafted gel-g) in water. Excitation wavelength: 340 nm. Temperatures are shown beside the curves.

becomes 510 nm at 34 °C, which corresponds to well-known macroscopic volume phase transition of PNIPAM gels in water. The value of 510 nm reflects the hydrophobic nanoenvironment of network main chains in the collapsed PNIPAM gel. The λ_f for main chains of the grafted gel (grafted gel-m) completely overlaps with λ_f for the normal gel-m, suggesting that nanoenvironment of network chains of the grafted gel has completely the same temperature dependence as that of network chains in normal gels. However, λ_f for graft chains of the grafted PNIPAM gel (graft gel-g in Fig. 5) decreases gradually with the increase in temperature from 17 to 34 °C as already mentioned above. This shows that the graft chains behave quite differently from the main chains of the grafted gel in regard to temperature change in water and suggests that coil-globule transition of a PNIPAM linear chain may occur at a lower temperature than the volume phase transition temperature (32 °C) of PNIPAM gels. In order to ascertain this point, λ_f for the dansyl-labeled linear PNIPAM was measured and are shown in Fig. 5. The λ_f begins to decrease gradually at 17 °C from 540 nm (hydrophilic) and reaches to 502 nm (hydrophobic) around 32 °C for the polymer solution of 7.45 wt% in water. The onset temperature of the decrease in λ_f corresponding to the onset of coil-globule transition shifts to higher side with the decrease in polymer concentration. It is noteworthy that the present observation of the onset of coil-globule transition of linear PNIPAM in water at temperatures even below 20 °C was realized for the first time by using dansyl fluorescence as a fluorescent label, because dansyl groups can detect the hydrophobicity around them in nanometer scale but usual cloud point measurements (32–33 °C) [26] detect the aggregation of PNIPAM chains in submicron scale.

As to the mechnism of rapid shrinking of the grafted PNIPAM gel, it is clear from Fig. 5 that the graft chains

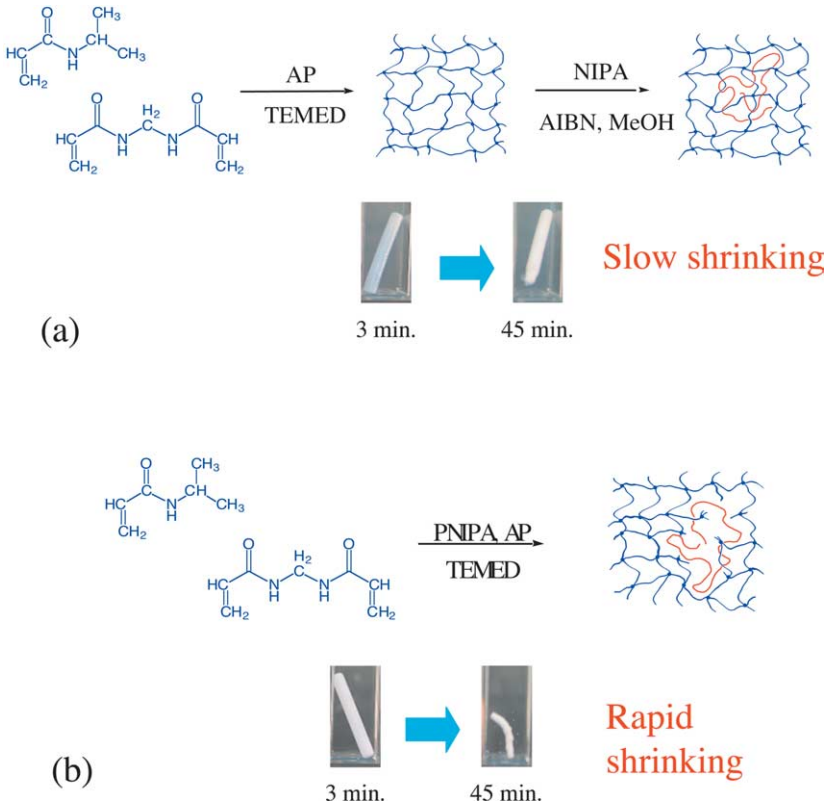

Fig. 6. Preparation procedures of (a) pre-crosslinked and (b) post-crosslinked semi-IPN gels and resulting differences in network structure. Pictures show difference in the shrinking behavior after the temperature jump.

become globule and begin to aggregate even at temperatures between 20 and 30 °C, while network chains are still hydrated and in coil state in this temperature range. Resulting heterogeneous structure would be magnified during the temperature jump to the macroscopic collapsed state, and hence, the formation of water-expelling channels from inside out at the surface of the collapsed PNIPAM gel can be facilitated. This would be a qualitative explanation of the mechanism of rapid shrinking of the grafted PNIPAM gels. However, as to the scale of heterogeneity, it is still open to discussion whether the heterogeneity within the mesh size of network caused by the globule formation of the graft chain is effective to the formation of water-expelling channels or the heterogeneity of a size much larger than the average mesh size of network is needed for the formation of water-expelling channels. Dynamic light scattering study using a home-made scanning microscopic light scattering (SMILS) apparatus [27] has revealed that the relaxation time distribution of the grafted gels consists of two distinct modes; the faster one is a cooperative diffusion mode usually observed in the swollen gels, and the slower one is an anomalously slow mode which may be related to the rapid shrinking and the heterogeneity of the network with a size much larger than the mesh size [25]. This suggested us to study the dansyl-labeled fluorescence of semi-IPN PNIPAM gels prepared in two different procedures, which is presented in next section.

3.2. Rapid shrinking and fluorescence spectra of semi-IPN PNIPAM gels

Schematic network structures of pre-crosslinked and post-crosslinked semi-IPN PNIPAM gels and their shrinking behaviors after a temperature jump from 25 to 40 °C in water are shown in Fig. 6. In pre-crosslinked semi-IPN gels, the network structure is supposed to be similar to the structure in normal gels and the linear polymer formed in the presence of swollen network behaves like a reptile chain entangling with network chains. In this semi-IPN gel the shrinking after the temperature jump did not proceed rapidly but proceeded slowly like in the normal gel. In post-crosslinked semi-IPN gels, the network is supposedly formed more easily at the sites where polymer molecules are absent and the heterogeneity with a larger size than the mesh size of usual network would be accordingly introduced. In this post-crosslinked semi-IPN gel, rapid shrinking was observed as is shown in Fig. 6(b).

Temperature dependence of peak wavelength of dansyl fluorescence, λ_f, at the network chains (semi-IPN-m) and linear chain (semi-IPN-l) of the pre-crosslinked and post-crosslinked semi-IPN PNIPAM gels as well as λ_f for the grafted and normal PNIPAM gels are summarized in Fig. 7. The λ_f for the network in post-crosslinked semi-IPN gel (post-crosslinked semi-IPN-m) completely overlaps with λ_f for the normal gel and λ_f for the main chains of the grafted

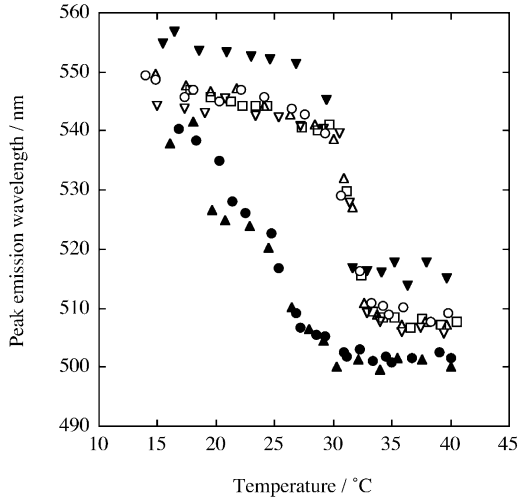

Fig. 7. Temperature dependence of peak wavelengths of dansyl fluorescence for grafted gel-m (○), graft gel-g (●), normal gel-m (□), pre-crosslinked semi-IPN-m (▽), pre-crosslinked semi-IPN-l (▼), post-crosslinked semi-IPN-m (△), post-crosslinked semi-IPN-l (▲).

gel, while λ_f for the linear PNIPAM in post-crosslinked semi-IPN gel (post-crosslinked semi-IPN-l) decreases gradually with increasing temperature from 20 to 30 °C in a similar manner to λ_f for the graft chains in the rapid shrinking grafted gel (graft gel-g). Thus, the coil-globule transition of linear PNIPAM chains at temperatures between 20 and 30 °C and the formation of large-scale heterogeneity in the network would be the reason of rapid shrinking after the temperature jump in the post-crosslinked semi-IPN PNIPAM gel. The λ_f for the network in pre-crosslinked semi-IPNgel (pre-crosslinked semi-IPN-m) again completely overlaps with λ_f for the main chains of normal and grafted gels. However, the λ_f for the linear PNIPAM in pre-crosslinked semi-IPN gel (pre-crosslinked semi-IPN-l) showed more hydrophilic values (550–555 nm) at 15–30 °C and abruptly decreased at 30 °C to hydrophobic 515 nm. The results may be explained by the multiply entangled structure of a linear PNIPAM polymer with network PNIPAM chains as is suggested in Fig. 6(a). This multiple entanglement would prevent the occurrence of coil-globule transition of the linear PNIPAM chain at temperatures below 30 °C. The results for pre-crosslinked semi-IPN-l are consistent to the fact that this pre-crosslinked semi-IPN gel did not show the rapid shrinking after the temperature jump.

In conclusion to the present section, the temperature dependences of dansyl fluorescence labeled to network or linear chains of post-crosslinked and pre-crosslinked semi-IPN PNIPAM gels support the above-proposed mechanism of rapid shrinking of the grafted PNIPAM gels, i.e. globule formation and aggregation of graft chains at temperatures between 20 and 30 °C leading to the formation of heterogeneous structure. As to the scale of heterogeneity, the possibility that the formation of water-expelling channels should be related to the large-scale heterogeneity of network structure shown in Fig. 6(b) cannot be neglected. This idea is based on the possibility of formation of the large-scale heterogeneous structure with a size much larger than the mesh size of the network also in the rapid-shrinking grafted PNIPAM gels due to the presence of macromonomer molecules during the network formation. The elucidation of this large-scale heterogeneous structure in rapidly-shrinking grafted PNIPAM gels will be a further topic using a scanning microscopic light scattering.

4. Conclusion

We studied the temperature dependences of dansyl fluorescence labeled to main chains or graft chains of rapid-shrinking grafted PNIPAM gels as well as those for a normal gel and semi-IPN gels. Gradual decrease in λ_f with increasing temperature for graft chains in grafted PNIPAM gel between 17 and 32 °C from 540 to 500 nm showed the occurrence of coil-globule transition of graft chains during this temperature range, while λ_f of main chains in network showed abrupt decrease at 30–34 °C reproducing the temperature dependence of macroscopic volume phase transition of PNIPAM gels. The results of fluorescence study clarified that the coil-globule transition and further aggregation of graft chains enhance the formation of heterogeneous structure during the temperature jump from 25 to 40 °C and facilitate the formation of water-expelling channels at the surface skin layer of the collapsed PNIPAM gel. The possibility of formation of large-scale heterogeneous structure of network in grafted PINPAM gels and its effects on the rapid shrinking were also suggested.

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