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^{1}H HRMAS NMR Study on Phase Transition of Poly(*N*-isopropylacrylamide) Gels with and without Grafted Comb-Type Chains

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ABSTRACT: Phase transition occurring in three different types of poly(*N*-isopropylacrylamide) gels—normal cross-linked gel, comb-type grafted gel, and comb-type grafted gel with styrene-modified comb chains—has been investigated by variable-temperature measurements of ^{1}H NMR spectra and spin−spin relaxation time. Three different gels exhibit distinct collapse behaviors in response to increasing temperature. For the normal gel, remarkable network shrinking occurs in a relatively narrow temperature range from 32 to 35 °C. For the styrene-modified comb-type gel, overall chain shrinkage appears in a very broad temperature range from 22 to 35 °C in which the styrene-modified comb chains shrink at lower temperatures (22−32 °C) than the backbone networks (32−35 °C). In the comb-type gel without styrene modification, however, the backbone networks shrink first (at 32−35 °C) on heating, followed by collapsing of comb chains (at 35−36 °C). During shrinkage of backbone networks the comb chains are expulsed from the main gel networks which is revealed by abnormal T_2 increase of comb chains. T_2 measurements also reveal that the styrene-modified comb-type gel in the equilibrium swelling state has more rigid network structure than both conventional gel and comb-type gel without styrene modification.

Introduction

Gels that undergo volume change in response to environmental stimuli such as temperature,[1] pH,[2,3] and ionic strength,[4,5] are known as intelligent gels. Poly(*N*-isopropylacrylamide) (PNIPAM) gel, with a charming lower critical solution temperature (LCST), has fascinated researchers for decades and has been investigated for many applications, for example, drug delivery systems, selective separation, enzyme, and biosensor.[6−10]

Since the normal PNIPAM gel exhibits very slow kinetics of swelling and shrinking, Yoshida et al. grafted comb-type PNIPAM chains to the gel networks to improve the response dynamics, and they found that the comb-type grafted PNIPAM gel showed drastic acceleration of shrinking kinetics compared to the normal PNIPAM gel.[1] The mechanism for the rapid collapse of comb-type PNIPAM gel has also been investigated by several methods such as fluorescence and small-angle X-ray scattering (SAXS).[11−15] Both fluorescence and SAXS measurements reveal the formation of the microphase-separated structure during the shrinking process due to temperature jump from a temperature lower than LCST to a temperature higher than LCST. It is proposed that after temperature jumping the freely mobile comb chains collapse first, and the collapsed comb chains create the hydrophobic cores and increase the void volume within the gel which enhance the hydrophobic aggregation of the networks and provide a pathway of water molecules. However, in previous studies, little attention has been paid to investigate the equilibrium shrinkage behaviors of the normal comb-type grafted PNIPAM gel during the thermotropic phase transition. Moreover, although the normal comb-type grafted gel has shown rapid deswelling, the shrinking kinetics of styrene-modified type grafted gel is not discussed.

In this study, three types of PNIPAM gels—normal cross-linked gel (NG), comb-type grafted gel (GG), and comb-type grafted gel with styrene-modified comb chains (GG-st)—were prepared by the inverse suspension polymerization technique.[16] The grafted chains with styrene modification were synthesized by free radical copolymerization of styrene and *N*-isopropylacrylamide (NIPAM) monomer. Originally, the styrene monomers were introduced into comb side chains as a label or probe to separately monitor the shrinking behavior of comb side chains during the phase transition. But we have found that the appearance of such hydrophobic styrene monomers dramatically changes the shrinking behavior of comb-type grafted gel; even the styrene monomer content is very low, say, e.g. 0.54 styrene units per comb side chain. In this paper we have investigated the thermotropic phase transition of three types of gels, using ^{1}H HRMAS (high-resolution magnetic-angle spinning) spectra and spin−spin relaxation measurements, with a nano-NMR MAS probe. As we know, NMR methods provide useful information about the structure, molecular motion, and interaction of gel at the atom level.[17−24] Particularly, the HRMAS spectrum has a better line-narrowing effect and a better high resolution at the rate of 1k to 3k Hz, providing a good method to study the property of hydrogels.

Experimental Section

Materials. *N*-Isopropylacrylamide (NIPAM; J&K Chemical Ltd.) was recrystallized from the mixture of toluene and *n*-hexane. *N*,*N*′-Methylenebis(acrylamide) (BIS; Acros Organics), ammonium persulfate (APS; Degussa-AJ(Shanghai) Initiators Co. Ltd.), 2-hydroxyethanethiol (HESH; Beyotime Institute of Biotechnology), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED; Acros Organics), tetrahydrofuran (THF; Sinopharm Chemical Reagent Co. Ltd.), styrene (St; Sinopharm Chemical Reagent Co. Ltd.), acryloyl chloride (Sinopharm Chemical Reagent Co. Ltd.), and sorbitan monooleate (Span80; Sinopharm Chemical Reagent Co. Ltd.) were all used as received.

Preparation of Gel. NIPAM polymer with a terminal hydroxyl end group was prepared by radical telomerization of NIPAM monomer using HESH as a chain transfer agent. NIPAM macromonomer was synthesized by the esterification of acryloyl

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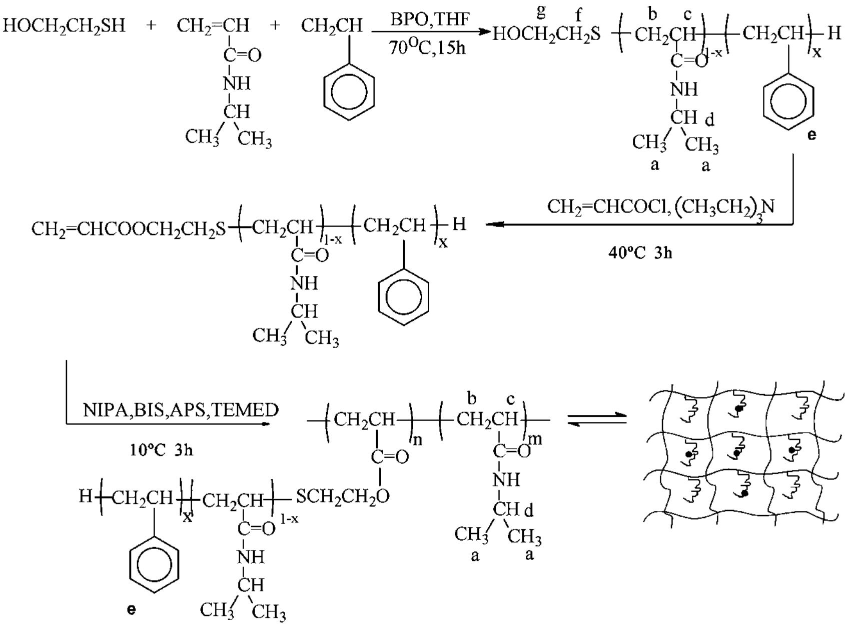
Scheme 1. Preparation of GG-st Gel[a]



[a] The closed circle (●) represents styrene unit.

Table 1. Preparation and Characterization of Two Hydroxyl Polymer Chains with and without Styrene Modification

	NIPAM (g)	St (μL)	HESH (μL)	BPO (g)	THF (mL)	M_n[a]
hydroxyl polymer-st (g)	5.5676	30	68	0.0202	20	5631
hydroxyl polymer (g)	5.5675		68	0.0202	20	3992

[a] Measured in NMR spectra.

Table 2. Feed Compositions for Preparation of NG, GG, and GG-st Gels

sample	NG	CG	GG-st
NIPA macromonomer-st (g)			0.2000
NIPA macromonomer (g)		0.2000	
NIPAM (g)	0.6000	0.6000	0.6000
BIS (g)	0.0060	0.0060	0.0060
APS (g)	0.0127	0.0127	0.0127
TEDEM (μL)	40	40	40
Span80/cyclohexene (1:2 in vol) (mL)	20	20	20
H_2O (mL)	4	4	4

chloride with hydroxyl NIPAM polymer. GG-st gel was prepared by inverse suspension polymerization using cyclohexane as the continuous phase and Span80 as the nonionic polymeric surfactant.[16] Acetone was added into the reactant to separate the gel and oil phase, and then the gel was washed several times with methanol and water. GG and NG gels were prepared in a similar manner.

The preparation of GG-st gel is shown in Scheme 1, and the feed compositions of monomer and other chemical materials are listed in Table 1 and Table 2.

Swelling Experiments. Gels were placed respectively in glass tubes (i.d. = 5 mm) filled with D_2O, the temperature of which was controlled at 22 °C. One week later, the glass tubes were centrifuged at 1K rpm, and the upper-layer liquid was wiped off by filter paper. The equilibrium swelling degree of the gel, m/m_0, was obtained by measuring the weight of the gel (m) and the weight of dry gel (m_0).

NMR Experiment. ^{1}H HRMAS NMR spectra of swollen gels were recorded on a liquid-state Varian INOVA-600 spectrometer equipped with a dual nanoprobe. All samples were spun at 2.4 kHz in a 4 mm rotor. The 90° radio-frequency (RF) pulse length was 4.8 μs. For the variable-temperature ^{1}H MAS spectrum measurement, sample was heated in 1 or 2 °C increment, and the NMR spectrum was recorded after a 30 min dwell time, using a small angle excitation (30°) and a long recovery time 35 s so as to observe the quantitative variation of water signal (HOD $T_1 \sim 4.5-16$ s from 22 to 40 °C in three gels). No obvious loss of HOD proton signal was observed during the variable-temperature experiment. All other NMR experiments were made using a 90° excitation pulse and a recovery time of 10 s, which is much longer than the proton T_1 ($\sim$1 s) of polymer. Spin−spin (T_2) relaxation curves were measured by the Carr−Parcell−Meiboom−Gill (CPMG)[25,26] pulse sequence. All samples were first swollen in D_2O solution (0.1 g/mL) using TSP as an internal NMR standard and then sealed in NMR rotor after it reached the equilibrium swollen state.

Results and Discussion

Structure. The ^{1}H NMR spectrum of hydroxyl polymer-st chain and the ^{1}H HRMAS NMR spectrum of GG-st gel in D_2O at 22 °C are shown in parts A and B of Figure 1, respectively. The assignments of the ^{1}H lines refer to the indices in Scheme 1. In Figure 1A, the four stronger peaks are methyl protons of the *N*-isopropyl group (a), methylene protons (b), methyne proton (c), and lone proton of the *N*-isopropyl group (d). The peaks at 3.7 ppm (f) and 2.7 ppm (g) belong to the chain transfer agent, while the peaks between 7.4 and 7.2 ppm (e) are ascribed to the phenyl protons of styrene units (Figure 1A). In Figure 1B, we can also observe the phenyl protons peak between 7.4 and 7.2 ppm, indicating that the comb chains were indeed grafted onto the gel networks. The peaks labeled by asterisk (*) in Figure 1B are the spinning sidebands of water and methyl protons.

Because one comb-type polymer chain has only one end group of chain transfer agent, we can calculate the number-average molecular weights (M_n) of hydroxyl polymer chains and the average number (n) of styrene structure unit per hydroxyl polymer chain from the areas of the relative peaks (d, e, and f) in Figure 1A. The resultant values are $M_n \approx (5.6 \pm 0.3) \times 10^3$ ($\sim$48 NIPAM structure units per comb-type chain) and $n = 0.54 \pm 0.06$. Furthermore, utilizing the above values of M_n and n together with the areas of peaks d and e in Figure 1B, we

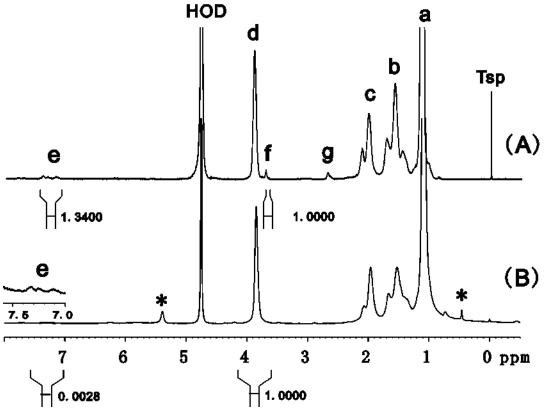


Figure 1. NMR spectra of hydroxyl polymer-st chains (A) and GG-st gel (B) in an equilibrium swollen state in D_2O at 22 °C in the Varian INOVA-600.

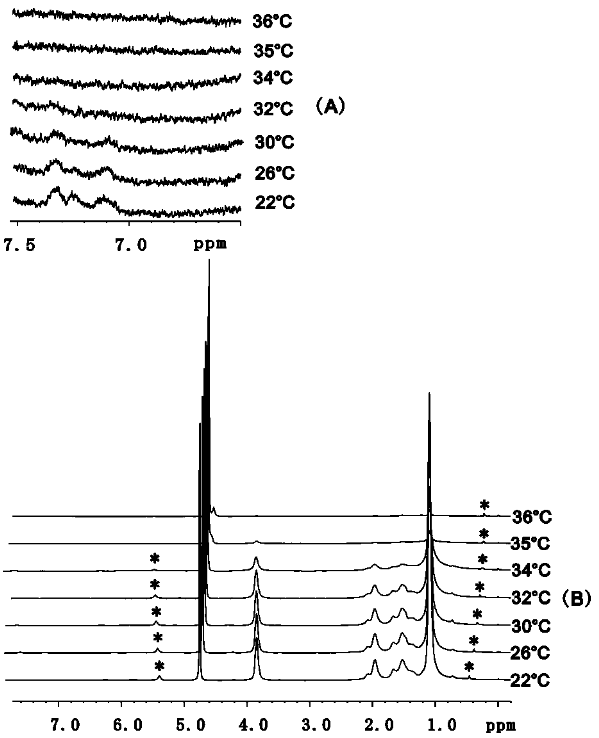


Figure 2. ^{1}H HRMAS NMR spectra of GG-st gel in D_2O at different temperatures: partially enlarged (256 times) spectra of phenyl protons of styrene units (A) and the whole spectra (B).

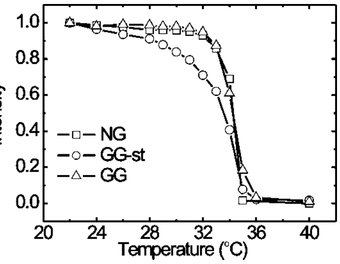


Figure 3. Peak intensity variations with temperature for lone proton of the *N*-isopropyl group in three types of gels.

estimate that about 25% NIPAM units are located in the comb-type polymer chains for the GG-st gel.

Swelling Property. The equilibrium swelling ratios in D_2O measured at 22 °C are 19 ± 2 for NG, 23 ± 2 for GG, and 23 ± 2 for GG-st. Two comb-type grafted gels GG and GG-st have the same equilibrium swelling ratio which is slightly higher than that of normal gel NG. The higher equilibrium swelling ratios found in two comb-type grafted gels can be ascribed to the higher hydration ability of the mobile grafted chains.[1,11]

Variable-Temperature ^{1}H HRMAS NMR. Figure 2 shows the ^{1}H HRMAS NMR spectra of GG-st gel obtained at different temperatures from 22 to 36 °C. All the spectra were obtained using the same instrumental parameters. It can be seen that with increasing temperature the ^{1}H peaks of NIPAM in GG-st gel (say, e.g., methyl protons and lone proton of the *N*-isopropyl group, methylene protons, and methyne proton) are diminished. A large and rapid decrease in peak intensity appears around 34 °C (also see Figure 3). Similar NMR results were also reported previously.[20,23] At 36 °C the above peaks become very small. This indicates that the collapse transition of backbone networks occurs around 34 °C because the observed proton signals of NIPAM units are mainly from backbone networks (75%). The losing of gel peaks at high temperatures can be understood: below the LCST the gel network is in a swollen state with high chain mobility, and the chain motion effectively averages out the ^{1}H dipole−dipole coupling, giving rise to the narrow resonances; above the LCST the gel network shrinks into the tight globule like a solid, and the ^{1}H dipole−dipole coupling becomes very strong which extremely broadens the ^{1}H peaks and thus causes losing of the gel signals. As shown in Figure 2A, however, the phenyl protons peak intensity of the styrene-modified comb chains decreases rapidly around 30 °C during heating, about 4 °C lower than the temperature at which rapid decrease in the ^{1}H peak intensity of backbone network occurs (see Figure 2B). At 32 °C, the phenyl protons peaks are almost unobservable, but the ^{1}H peaks of backbone network are still strong. The above results clearly illustrate that as temperature increases, the styrene-modified comb chains collapse first at a lower temperature (30 °C) and then backbone polymer networks collapse at a higher temperature (34 °C). The above result also shows that styrene monomer incorporation into comb chains dramatically lowers the collapse temperature of comb chains; even the styrene monomer content is very low (0.54 units per side chain).

To contrast the phase transition behaviors of three different gels, NG, GG, and GG-st, the relative peak intensities (integral areas) of lone CH for three gels were recorded and plotted as a function of temperature in Figure 3. Comparing the three curves in Figure 3, an obvious difference is easily found in the low-temperature regime below 32 °C. Below 32 °C, the ^{1}H intensity of GG-st gel drops significantly with increasing temperature, from 1 at 22 °C to 0.71 at 32 °C, whereas the ^{1}H intensity of GG and NG gels decreases only slightly. In the phase-transition temperature regime (from 32 to 35 °C), the ^{1}H intensity of lone CH for all three gels decreases rapidly with increasing temperature, indicating collapsing of backbone networks.[20,23] The heating-induced loss of lone CH ^{1}H intensity below 32 °C for the GG-st gel is attributed to the collapsing of the styrene-modified comb chains, considering the fact that the peak intensity of phenyl protons located at comb chains also decreases rapidly in the same temperature range. In Figure 3, It is also noticed that at 35 °C a relatively strong lone CH ^{1}H signal (0.18) is still observed in GG gel, compared to the NG and GG-st gels. This implies that some polymer segments in GG gel are still in the mobile coil state at 35 °C although main gel networks have collapsed. Here the observed signal at 35 °C in GG gel is assigned to the comb chains, which is verified by T_2 measurement (see next section). At 36 °C, this signal becomes very small, indicating occurrence of collapse transition of comb chains. The above results illustrate that for the GG gel the overall shrinking process occurs in a narrow temperature range from 32 to 36 °C, during which the backbone networks first collapse and then comb-type chains collapse on heating, which is contrary

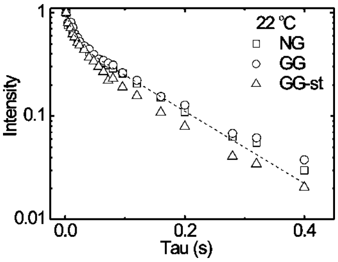


Figure 4. Decay curves of transverse magnetization of lone proton of the *N*-isopropyl group obtained at 22 °C for three different gels. Dashed line shows a biexponential fit for the experimental data (□) of the NG gel.

to the collapse process of GG-st gel. For the latter, the overall shrinking occurs in a very broad temperature range from 22 to 35 °C, during which the styrene-modified comb chains collapse first on heating, followed by collapsing of the backbone networks on further heating.

^{1}H Spin−Spin Relaxation Time. Figure 4 shows decay curves of transverse magnetization of lone proton of the *N*-isopropyl group measured at 22 °C for three different gels in equilibrium swollen state. All three decay curves are approximately biexponential. The decay curves of NG and GG gels are almost identical, with short $T_2 = 12-13$ ms and long $T_2 = 130-140$ ms. The overall magnetization decay of GG-st gel (with a short $T_2 = 11 \pm 2$ ms and a long $T_2 = 97 \pm 8$ ms) is obviously more rapid than that of NG and GG gels. These indicate that the GG-st gel networks in the equilibrium swelling state are less mobile or more rigid than NG and GG gels. Double-exponential T_2 relaxation was observed previously in polymer solution, and it was ascribed to the polymer−polymer and polymer−solvent interaction.[25] Double-exponential T_2 relaxation was also observed in polymer melts and chemically cross-linked gels and was attributed to the restricted and high mobile chain segments.[27,28] Following the previous interpretation,[27,28] the relaxation component with a short T_2 value observed here is ascribed to the restricted chain segments, e.g., the segments near the crunodes, and the component with a long T_2 value corresponds to the highly mobile segments.

Figure 5 shows decay curves of transverse magnetization of lone proton of the *N*-isopropyl group for three gels at various temperatures from 22 to 34 °C (or 35 °C). It is found that in the low-temperature regime from 22 to 30 °C, which is far below the LCST temperature, the T_2 relaxation behavior of all three gels is still approximately double-exponential and only weakly temperature-dependent. But above 30 °C, overall T_2 decays of all three gels change markedly with temperature. Interestingly, the T_2 decay behavior of NG gel is obviously different from that of two comb-type gels. For the NG gel, the T_2 relaxation is still approximately biexponential above 30 °C, but T_2 values of both rapid and slow decay components decrease with increasing temperature, from $T_2 = 12 \pm 3$ ms (44%) at 30 °C to 4.8 ± 0.8 ms (53%) at 34 °C for rapid decay component and from $T_2 = 127 \pm 15$ ms at 30 °C to 66 ± 4 ms at 34 °C for slow decay component. These suggest that the shrinking of polymer segments occurs above 30 °C, which results in the decreased segmental mobility of gel networks and thus the decreased T_2 values. Here, it is worth pointing out that above 32 °C some polymer segments become a dense solidlike globule which cannot be detected both in CPMG experiment and in single-pulse NMR spectrum experiment. That is to say, the T_2 values measured above 32 °C correspond only to the rather mobile polymer segments (for example, at 34 °C they reflect the behavior of about one-half of lone protons of the *N*-isopropyl CH protons for GG gel, and at 35 °C they reflect the behavior of small fraction of these protons (see Figure 3)), while below 32 °C T_2 values reflect the behavior of virtually all *N*-isopropyl CH protons. For GG and GG-st gels, however, the T_2 relaxations are no longer biexponential above 32 °C. Instead, a well-resolved triexponential decay curve, which corresponds to the rather mobile uncollapsed structural units, is observed at 33 and 34 °C. The three T_2 values obtained at 33 °C are $T_2 \approx 4.5 \pm 0.7$, 29 ± 5, and 330 ± 40 ms for GG gel and $T_2 \approx 3.2 \pm 0.2$, 27 ± 3, and 240 ± 20 ms for GG-st gel. Note that the slowest decay of a few hundred milliseconds found at 33 and 34 °C in two comb-type gels is absent in the NG gel. We ascribe such a slow-decay component to the comb chains in GG and GG-st gels which have free ends and thus have higher mobility than backbone chains.

The most interesting feature seen in Figure 5 is that when temperature is increased from 33 to 34 °C, the T_2 values of two more rapid relaxation components for CH protons of the *N*-isopropyl groups in two comb-type gels still decrease substantially, but T_2 values of the slowest relaxation component increase abnormally (not decrease as expected). The CH_3 protons of the *N*-isopropyl groups also exhibit the similar abnormal T_2 behavior (the result is not shown here). The above results imply an increase in mobility of comb chains and a decrease in mobility of uncollapsed backbone segments at 34 °C, since the mobility of backbone chains is mainly associated with two shorter T_2 components and the mobility of comb chains is characterized by longest T_2 component. For the GG gel, the long-T_2 component at 34 °C occupies 9.3% of all three relaxation components, which is markedly larger than that of the GG-st gel (3.5%). When temperature is further elevated to 35 °C, the overall T_2 relaxation of the GG gel seems biexponential, with the short $T_2 = 8.9 \pm 0.9$ ms (57%) and the long $T_2 = 310 \pm 30$ ms (43%). The fraction of the slow relaxation component increases to 43% at 35 °C from 9.3% at 34 °C, suggesting that the observed signal at 35 °C is mainly from the comb chains. Above 35 °C, only very weak NMR signal can be observed, indicating collapsing of comb chains in GG gel. The above results demonstrate that backbone chains of GG gel collapse prior to the comb chains during heating.

We interpret this abnormal T_2 behavior as follows. As temperature is increased from 33 to 35 °C, some backbone segments of GG gel collapse and become undetectable, while others shrink to some extent which shortens T_2 of two more rapid relaxation components associated with main networks. During this process, some parts of the comb chains are structurally separated from (or protrude out of) the main gel networks due to their higher mobility and higher hydrated ability and thus become more hydrated at 34 °C than at 33 °C. As a result, the comb chains are freer and therefore have longer T_2 at 34 °C than at 33 °C (note that below 33 °C the T_2 relaxation behaviors of backbone and comb chains are indistinguishable). At 35 °C, the backbone networks shrink tightly (or collapse), and their NMR signal becomes unobservable. In this case, the observable signal is mainly contributed from the comb-type chains which are still in mobile coil state. Therefore, the long-T_2 component is expected to have larger fraction at 35 °C. The above interpretation is further supported by the result obtained in GG-st gel. For GG-st gel, the fraction of the long-T_2 component in GG-st is about 3.5% of the totally observed signal intensity at 34 °C, which is much smaller than the corresponding fraction value (9.5%) obtained in GG gel at same temperature. As aforementioned, per comb chain in GG-st gel contains on average about 0.54 styrene structure units and the styrene-modified comb chains collapse below 32 °C. At 34 °C, only those unmodified comb chains (occupying 46% of total comb chains) contribute to the long-T_2 relaxation. Thus, the fraction of the long-T_2 component in GG-st is expected to be ~46% smaller than that in GG. In a recent study of PNIPAM-grafted

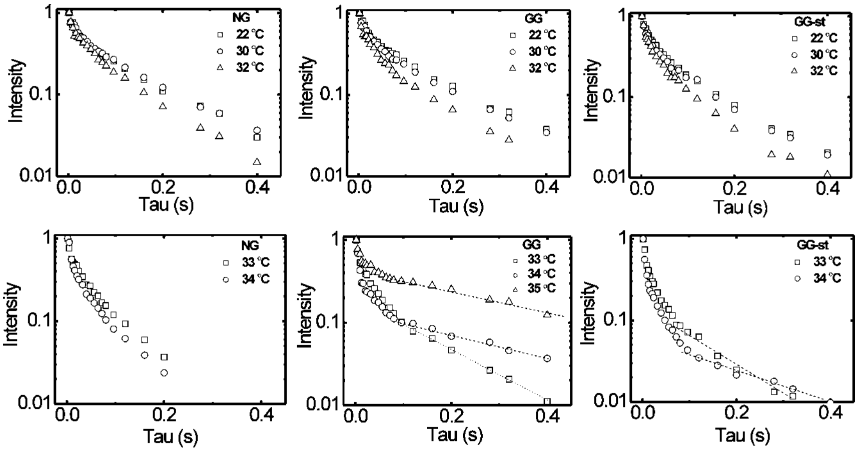


Figure 5. Decay curves of transverse magnetization for the lone proton of the *N*-isopropyl group in NG, GG, and GG-st gels at different temperatures. The dashed lines were drawn for indicating the longest T_2 relaxation component.

interfaces on the fused quartz, it was found that side-chain CH groups interact with water below the LCST, while they become dehydrated at water/PNIPAM interfaces above the LCST, which causes the reconstructing of main chains.[29]

The structural separation or expulsion of comb chains from the main gel networks in the phase transition regime not only prevents the temporal formation of the hard skin layers on gel particles during heating but also provides a pathway for internal water and therefore accelerates the deswelling dynamics of hydrogels. Finally, it should be pointed out that the equilibrium shrinking process described above is different from the temperature-jump-induced collapse where the freely mobile characteristics of grafted chains are expected to show the rapid dehydration to make tightly packed globules with temperature, followed by the subsequent hydrophobic intermolecular aggregation of dehydrated graft chains.[11−14]

Conclusion

In the present study, we prepared three types of poly(*N*-isopropylacrylamide) gels: NG, GG, and GG-st. The equilibrium shrinkage behaviors during the thermotropic phase transition in these three hydrogels have been characterized and compared by variable-temperature measurements of ^{1}H NMR spectra and spin−spin relaxation times. It is found that the styrene monomer incorporation into comb chains dramatically lowers the collapse temperature of comb chains, even the styrene monomer content is very low (0.54 units per side chain). T_2 measurements reveal that the GG-st gel in the equilibrium swelling state has more rigid network structure than both NG and GG gel. For the NG gel, remarkable network shrinking occurs in a relatively narrow temperature range from 32 to 35 °C. For GG-st gel, overall chain shrinkage appears in a very broad temperature range from 22 to 35 °C where the styrene-modified comb chains shrink at lower temperatures (22−32 °C) than the backbone networks (32−35 °C). In the comb-type gel without styrene modification, however, the backbone networks shrink first (at 32−35 °C) on heating, followed by collapsing of comb chains (at 35−36 °C). During the shrinkage of backbone networks form 32 to 34 °C, T_2 of comb chains without styrene modification increases abnormally, suggesting the expulsion of the mobile comb chains from the backbone networks.

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