

# Rheological Properties of Poly(ethylene glycol)/Poly(*N*-isopropylacrylamide-*co*-2-acrylamido-2-methylpropanesulphonic acid) Semi-Interpenetrating Networks

Chi Zhang, Allan J. Easteal

Department of Chemistry, The University of Auckland, Auckland, New Zealand

Received 29 March 2008; accepted 30 March 2008

DOI 10.1002/app.28481

Published online 2 June 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** For the increasing demands of multifunctional materials in applications such as drug delivery system, a pH- and temperature-responsive polyelectrolyte copolymer gel system was studied using rheometry. Rheological properties, determined by plate–plate rheometry in oscillatory shear, of hydrogels formed by free radical initiated copolymerization of *N*-isopropylacrylamide (NIPA) and 2-acrylamido-2-methylpropanesulphonic acid (AMPS) in the presence of methylene bisacrylamide (MBAA) as crosslinker are compared with the properties of semi-interpenetrating network (SIPN) polyelectrolyte gels made by incorporation of poly(ethylene glycol) with molar mass 6000 g mol<sup>-1</sup> (PEG6000). Based on our systematic studies for this PEG/SIPN system, the effects of initiator and crosslinker concentration, relative proportions of comonomer units in

the main chains, PEG6000 content and temperature on viscoelastic properties, unusual high storage moduli at small strain for the SIPN were discussed. The SIPN gel with characteristics of PEG molecules as well as pH and temperature responsiveness from AMPS and NIPA units has potential application in drug delivery system design. Ice-like rheological behavior of the PEG/AMPS-NIPA SIPN gels at low temperature was first time reported and water remains homogeneous without phase separation in PEG/AMPS-NIPA SIPN hydrogels at low temperature may be considered as an ideal candidate for water storage material. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3578–3589, 2008

**Key words:** rheology; semi-interpenetrating network; hydrogels; PEG; AMPS; viscoelastic properties

## INTRODUCTION

The polyelectrolyte hydrogels have been extensively studied in recent years because of their fundamental importance<sup>1</sup> and potential applications in drug carriers,<sup>2,3</sup> water absorbent materials,<sup>4,5</sup> sensing,<sup>6,7</sup> tissue engineering<sup>8</sup> and biomaterials.<sup>9</sup> By virtue of a lower critical solution temperature (LCST) above 30°C,<sup>10</sup> the water soluble *N*-isopropylacrylamide (NIPA) units in chains normally act as a thermoresponsive vector<sup>11</sup> and 2-acrylamido-2-methyl-1-propanesulphonic acid (AMPS) unit is a relatively strong acid and ionic<sup>12</sup> brings in pH sensitivity in functional material design. The advantage of combining AMPS with NIPA is obvious where NIPA homopolymer with temperature responding has no pH sensitivity and AMPS homopolymer with pH but without temperature responsiveness. Incorporation of polyethylene glycol (PEG) in the gel increases the potential for hydrogen bond formation, because the lone pair electrons of oxygen in the repeat unit (CH<sub>2</sub>CH<sub>2</sub>O) of PEG serve as hydrogen bond acceptors<sup>13</sup> whereas

ethyl groups have hydrophobic nature<sup>14</sup> increasing compatibility to many hydrophobic systems. PEG itself is a stable polymer which is a linker molecule for peptide or proteins.<sup>15,16</sup> PEG can be used as plasticizer for rigid polymers for decreasing glass transition temperature.<sup>13</sup> Attempts to combine the useful functions to one polymer system have been paid increasing attentions.<sup>17–20</sup> And in thermodynamics, complete miscibility in a mixture of two polymers such as PEG6000 with AMPS-NIPA crosslinked network requires that the free energy of mixing is negative<sup>21,22</sup> and a negative heat of mixing is usually required because of the long polymer chains the entropy of mixing two polymers is small. Consequently, strong interactions are needed to produce a negative heat of mixing.<sup>21</sup> It is obviously that blending polymers in forms of the interpenetrating networks (IPNs) or semi-interpenetrating system (SIPNs) is able to make polymer mixture more thermodynamically stable because IPNs or SIPNs increase entanglements and physical interactions, i.e. hydrogen bonding, ion–ion in a crosslinked structure.

*In situ* copolymerization of AMPS and NIPA comonomers and crosslinking the propagating copolymer chains with *N,N'*-methylene-bisacrylamide (MBAA) were initiated by ammonium persulphate in the presence of PEG6000 molecules. The *in situ*

Correspondence to: C. Zhang (z.chi@auckland.ac.nz).

copolymerization/crosslinking resulted in a semi-interpenetrating copolymer network. The poly(ethylene glycol)/crosslinked poly(*N*-isopropylacrylamide-*co*-2-acrylamido-2-methyl-1-propanesulphonic acid) [PEG/poly(NIPA-*co*-AMPS)] semi-interpenetrating network (SIPN) has interesting properties,<sup>12,23</sup> and as a water-swollen gel potential applications as a drug encapsulation/controlled release system will be present in another paper of our studies. For the SIPN changes in experimental variables such as mole ratio of AMPS to NIPA, wt % PEG, crosslinker concentration and the solvent content, result in changes in the kinetics of gel formation,<sup>23,24</sup> morphology<sup>12</sup> and physicomechanical properties. In the swollen state, the interactions between the hydrophilic network of the gels and solvent water, as well as long-range Coulombic interactions, significantly affect the physical and mechanical properties of the gels<sup>12,25</sup>. A study on NIPA-AMPS copolymer gels (with  $\leq 10$  mol % AMPS) swollen in PEG aqueous solution showed<sup>26</sup> that NIPA segments in the copolymer network have strong interactions with PEG molecules. A recent thermal analysis study<sup>12</sup> has shown that PEG has strong interactions with AMPS-NIPA copolymer network in the dried state.

The initial goal of the study using rheometry was to determine the gelation temperature in association with time and gel composition in our previous work.<sup>23</sup> Further we studied the other properties of the SIPN gels<sup>12</sup> including more investigations of rheological properties which led to the present work. The present article focuses on the rheological properties of PEG/poly(NIPA-*co*-AMPS) SIPNs in the context of (a) the relationship between microstructure of the gels and experimental variables of gel formation, (b) the influence of water and PEG on the mechanical properties of the gels formed, particularly at low temperatures, (c) the shift of phase transition temperatures (LCST) in relation to SIPN composition, and (d) the elasticity of the SIPNs. The discussion of low temperature rheological property of SIPN hydrogels comparing to water in present paper draws attention first time to interactions between network of solid water (ice) to elastic copolymer network. The phase stability of PEG/AMPS-NIPA SIPN hydrogels at low temperature indicated in rheological experimental may be considered as an ideal candidate for water storage material.

## EXPERIMENTAL

### Materials

Poly(ethylene glycol) with average molecular weight about  $6000 \text{ g mol}^{-1}$  was supplied by BDH Chemicals (Poole, England). NIPA (from Acros Organics) and 2-acrylamido-2-methylpropane sulfonic acid (Merck-

Schuchardt, Hohenbrunn, Germany) were both synthesis grade ( $>99\%$ ) materials. *N,N'*-methylene-bisacrylamide (Sigma-Aldrich, St. Louis, MO), used as crosslinker, was electrophoresis reagent grade material. Ammonium persulphate (Ajax Chemicals, Auburn, NSW, Australia) used as free radical initiator was  $> 98\%$  pure. All of these chemicals were used without further purification.

### Preparation of gels

Pregel solutions and gels were made similarly to published papers elsewhere<sup>12,23</sup> with varying AMPS/NIPA, MBAA and APS mol % in the absence or presence of PEG6000. Because it is to compare relative quantity for comonomers, crosslinker and wt % of PEG6000 in the gels, a constant total weight of AMPS and NIPA (with varying relative mol % ratio between comonomers AMPS and NIPA) to constant PEG weight is required in most gel preparations. A typical gel disc was made described hereafter: A 1.6-mL aliquot of pregel solution was transferred to a PTFE cylindrical vessel with internal diameter 26 mm. The vessel was closed with a PTFE lid and heated at  $70^\circ\text{C}$  in a water bath for 2 h to form gel. The vessel was then rapidly transferred to an ice/water bath and kept at  $0^\circ\text{C}$  for about 10 min, then allowed to stand at ambient temperature for 1 h. The gel sample was removed from the vessel and transferred to the rheometer. Densities of dehydrated gels were measured using the flotation method, with cyclohexane ( $\rho = 0.778 \text{ g cm}^{-3}$ ) and tetrachloromethane ( $\rho = 1.60 \text{ g cm}^{-3}$ ) at 293.2 K as flotation liquids.

### Rheological experiments

Rheological properties of the hydrogels in oscillatory shear were carried out using a Paar Physica model UDS 200 rheometer (Paar Physica, Germany) with 25 mm diameter plate-plate measuring system. Amplitude sweeps were performed on all samples prior to frequency sweeps to establish the linear viscoelastic (LVE) regime,<sup>27,28</sup> and to determine the deformation stability or critical strains ( $\gamma_c$ ) for the gels.<sup>29</sup> Frequency sweeps were performed on samples within the LVE regime, usually at very low strain ( $\leq 1\%$ ) to give equilibrium moduli ( $G'_e$ ) when  $G'$  was independent of frequency or frequency near zero. Step-stress (creep and recovery) experimental were performed to measure the transient response of a gel to a given constant shear stress. For temperature sweep experiments, the heating rate was about  $7^\circ\text{C}$  per minute within a range from ambient to  $100^\circ\text{C}$  (occasionally, temperature sweeping from 0 to  $110^\circ\text{C}$ ). The reproducibility was verified for each experiment. All gel samples were trimmed after mounting that the area of the gel discs matched the plate area.

**TABLE I**  
**Effect of Initiator Concentration on Mean Values of**  
**Triplicate Determinations of  $G'_e$  and  $M_c$  at 20°C for SIPN**  
**Gels from Frequency Sweep**

[APS]/mol L <sup>-1</sup>	$G'_e$ /kPa	$M_c$ /kg mol <sup>-1</sup>
0.001	2.4	1.2
0.01	1.8	1.6
0.05	2.1	1.3
0.10	2.0	1.4

Gel composition: equimolar proportions of AMPS and NIPA, and 45.5 wt % PEG with 0.016 mol L<sup>-1</sup> MBAA. Data obtained from angular frequency sweep from 0.628 to 314 s<sup>-1</sup>, at 20°C.

Most experiments were carried out at 20°C except for the temperature sweep experiments with low strains <2%, and at angular frequencies no more than 314 s<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Initiator effects

At very low frequency or when the modulus is independent of frequency, the crosslinked network has an equilibrium storage modulus,  $G'_e$ , that is an intrinsic property of the gel defined by<sup>30</sup>

$$G'_e = G'(\omega \rightarrow 0) = G(t \rightarrow \infty) \quad (1)$$

Equation 2 allows the calculation of the number average molecular weight between crosslink junctions,  $M_c$ , which is inversely proportional to the crosslink density and equilibrium storage modulus, to be calculated<sup>22,31</sup>

$$G'_e = \rho RT/M_c \quad (2)$$

where  $\rho$ ,  $R$  and  $T$  are density, gas constant and temperature, respectively. Values of  $G'_e$  and  $M_c$  for gels made using varying initiator concentrations are given in Table I; density data for the gels are given in the Appendix. Table I shows the effects of initiator concentration on equilibrium storage and  $M_c$  of the SIPN gels. It shows that the crosslink density is, as expected, almost independent (to within the uncertainty of determination) of initiator concentration. This result is consistent with results of a kinetic study that gel network formation through incorporation of MBAA in the copolymer chains occurs in the early stages of chain growth.<sup>24</sup> It was believed that the initiator concentration affects on chain length rather than significantly on crosslinking density.

### Crosslinker effects

The concentration of crosslinker was varied to assess the effects of crosslink density on gel properties. As

a covalent bonded network, crosslinker concentration is vital to construct a stable 3D network of a gel. Figure 1 shows frequency dependency of PEG/poly (AMPS-*co*-NIPA) systems made with varying crosslinker concentrations. At zero crosslinker concentration, Figure 1(a) shows  $G' < G''$  and large variations in  $G'$  and  $G''$  in the frequency range as expected for a typical viscous liquid or noncrosslinked polymer system.<sup>31,32</sup> At a very small concentration (0.016 mol L<sup>-1</sup>) of crosslinker  $G'$  becomes larger than  $G''$  which are characteristics of solid-like system,<sup>31</sup> the gel behaves predominantly as a solid-like [shown in Fig. 1(b-d)] at the frequency of measurement) which indicates the formation of a network. The gels with higher concentration of crosslinker shown in Figure 1(b-d) perform similarly as solid-like gels but the higher concentration of crosslinker results in higher  $G'$  values. The above findings are significant because in absence of crosslinker the copolymerization initiated by APS in the presence of PEG, as shown in Figure 1(a), did not form a network and a covalent bonded gel. A minimum requirement of crosslinker concentration for constructing a covalent bonded network of copolymer was not studied. However, it was sure that at [MBAA]  $\geq$  0.016 mol L<sup>-1</sup> the covalent bonded network has been formed as shown in Figure 1(b-d). It is vital that  $G' > G''$  is the feature of crosslinking and gel formation at frequency sweep.

The data in Table II show the dependence of  $G'_e$  and  $M_c$  on crosslinker concentration. For [MBAA]  $\geq$  0.063 mol L<sup>-1</sup>, the value of  $M_c$  can be compared with that (2.2–13.4 kg mol<sup>-1</sup> at 20°C)<sup>33</sup> for typical vulcanized natural rubbers, indicating a relatively rigid gel.

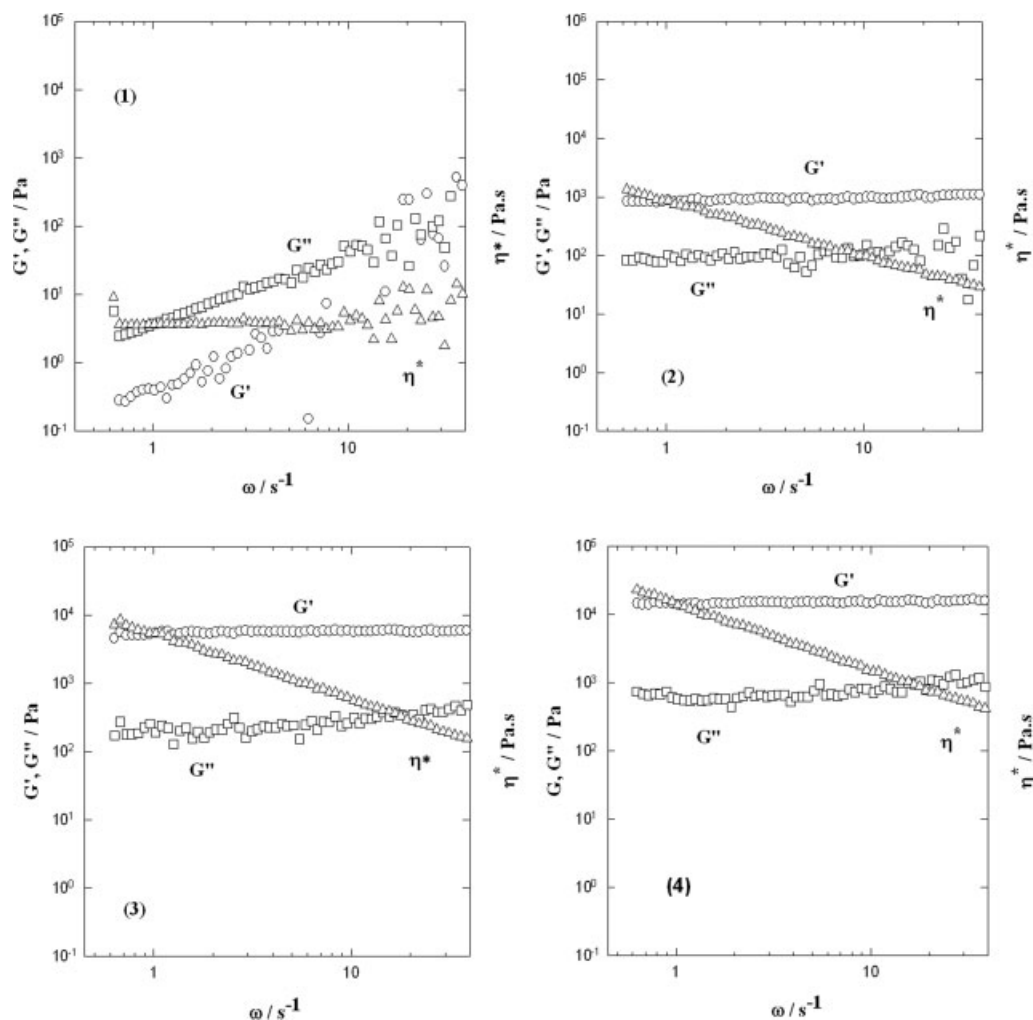
### Main chain composition effects

The dependence of viscoelastic properties of gels on copolymer main chain composition is investigated in oscillatory shear at increasing frequency with low strain.

Plots of log  $G'$  against log  $\omega$  linearly extrapolated to 0.01 s<sup>-1</sup> angular frequency [eq. (3)] are shown in Figure 2.

$$\log G' = A + B \log \omega \quad (3)$$

The best-fit values of equilibrium storage modulus  $G'_e$  and coefficient values from eq. (3) are given in Table III, respectively. The finding that  $G'_e$  for the SIPN gels is substantially larger than for the corresponding copolymer gels. The equilibrium storage modulus  $G'_e$  reflects the nature of a gel in the original state of the gel network without interference from external forces or stimuli such as shear force, compression, solvents, etc. The higher  $G'_e$  for SIPN



**Figure 1** Frequency dependence of storage and loss moduli and complex viscosity for PEG/poly(AMPS-*co*-NIPA) SIPN system with equimolar proportion of AMPS and NIPA, 41.8 wt% PEG6000 and varying crosslinker concentration (a) 0; (b) 0.016; (c) 0.063; (d) 0.126 mol L<sup>-1</sup>, respectively. Frequency sweep at 1% strain at 20°C. The feature of loss modulus  $G''$  higher than storage modulus  $G'$  in frequency sweep in Figure 1(a) indicated for a typical viscous liquid or noncrosslinked polymer system. All data presented in Figure 1 were logarithm values.

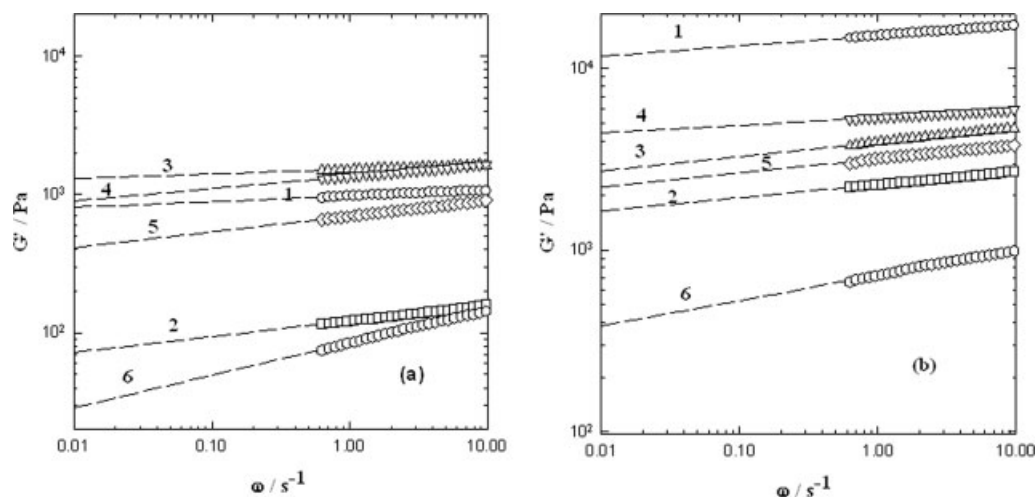
gel than that for copolymer gel indicates that stronger interactions including H-bonding (between a proton donor, such as  $-\text{NHCO}-$  groups in NIPA, and a proton acceptor such as  $(-\text{OCH}_2\text{CH}_2-)$  groups in PEG) and hydrophobic interactions (isopropyl groups of NIPA and ethylene group of the

**TABLE II**  
 $G'_e$  and  $M_c$  Data as a Function of Crosslinker Concentration for SIPN System with 50 mol % of AMPS and 41.8 wt % PEG

[MBAA]/mol L <sup>-1</sup>	$G'_e$ /kPa	$M_c$ /kg mol <sup>-1</sup>
0.016	0.84	3.4
0.063	5.1	5.5
0.126	14	1.9

$G'_e$  obtained from the  $G'$  almost independent of  $\omega$  where angular frequency approaching to 0 s<sup>-1</sup> at 20°C.

PEG chain) may contribute to strengthen of the SIPN gels which is consistent with the known ability of PEG to form strong intermolecular interactions with water<sup>34</sup> and with NIPA segments in NIPA-AMPS copolymer network,<sup>12,26</sup> Table III also indicates a significant copolymer composition effect. Qiu et al.<sup>35</sup> disclosed that the LCST increases with increasing hydrophilic AA content for poly(*N*-isopropylacrylamide-*co*-acrylic acid) (PNIPA-*co*-AA) copolymer at a given chain length in a dilute water solution and PNIPA-*co*-AA formed stable nanoparticles even at  $5 \times 10^{-4}$  g mL<sup>-1</sup>. PNIPA-*co*-AMPS or its PEG (non-ionic polymer) SIPNs should behave similar to PNIPA-*co*-AA in this sense. The unusual high values of equilibrium storage moduli of the hydrogels at 0% mol AMPS in Table III might be because of highest NIPA concentration that caused larger particle aggregation of PNIPA chains<sup>35</sup> at 20°C and those



**Figure 2** Storage modulus as a function of angular frequency at small strain for (a) copolymer gels; (b) SIPN gels with 50 wt % PEG crosslinked with MBAA at  $0.016 \text{ mol L}^{-1}$ , respectively. Broken lines are the extrapolated linear regression lines which obtained using eq. (3) based on experimental data and 1–6 denote different mol % of AMPS: 1, 0 mol %; 2, 12.0 mol %; 3, 26.7 mol %; 4, 45.0 mol %; 5, 68.6 mol %; 6, 100 mol % AMPS. Angular frequency sweep from  $\omega = 0.63$  to  $10 \text{ s}^{-1}$  at strain 1% and  $20^\circ\text{C}$ . All data presented in Figure 2 are logarithm values.

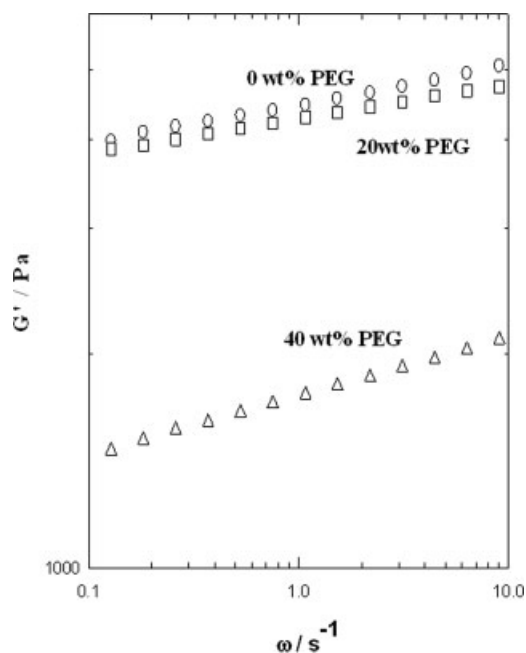
aggregates were closely interconnected by hydrophobic interactions. Because the gels were made at  $70^\circ\text{C}$  which was much higher than the normal LCSTs of NIPA-based polymers, the NIPA chain nanoparticles were believed smaller and denser packed during gel synthesis.<sup>12,35</sup> It was found, in general, that from 12 mol % of AMPS, the equilibrium storage moduli of both copolymer gels or SIPN gels increased with increasing AMPS to a maximum (26.7 mol % AMPS for NIPA-AMPS copolymer(a) and 45.0 mol % for PEG SIPN (b), respectively), then decreased with increasing AMPS mol %. This may be explained by hydrophobic NIPA units and existence of charges from AMPS unit. Zhang and Eastal<sup>36</sup> showed that average sequence length of NIPA units in NIPA-AMPS copolymers decreased with increasing AMPS concentration. The short chains of NIPA units will first formed smaller nanoparticles with elevated temperature but with time increasing eventually form larger but looser aggregates<sup>35</sup> which led to larger soft domains in gel structure that is lower in elasticity or strengthen under shear, on contrary, longer

chains of NIPA units formed eventually smaller but denser nanoaggregates in gels thus higher in elasticity. In another study,<sup>37</sup> the nanoparticle size of NIPA units decreased with increasing PEG in a PEG-NIPA grafted system. However, if AMPS concentration was near to a degree ( $\geq 68.6$  mol % AMPS in Table III) that NIPA aggregates are significantly decreased in size in AMPS-rich swollen structure, then gel strengthen was primarily contributed by more hydrated and ionic AMPS chains. It was reported elsewhere<sup>12</sup> that AMPS units was ionized in a PEG/AMPS-NIPA copolymer network. In a DMAA(electric neutral unit)-*co*-AMPS(ionic unit) hydrogel system, it was found that with an increase in AMPS mole fraction, the equilibrium storage moduli increased and then decreased, reaching its maximum at [AMPS] at 20 mol %<sup>38</sup> where in Table III(a) it was 26.7 mol %. The increase-then-decrease trend for equilibrium storage moduli was believed due mainly to the contribution of the electrostatic interaction of charged groups to the elastic energy of polyelectrolyte gels as well the pregel compositions.<sup>38</sup> In general if a macroscopic deformation acts on a polyelectrolyte gel, the spatial distribution of the distance between charges in the gel would be changed and that consequently the potential energy of the system would vary during the deformation.<sup>38</sup> On the other hand, one study<sup>12</sup> showed that PEG has strong interaction with AMPS-NIPA copolymer network. In PEG SIPN the PEG altered the hydration ability of the gels and changed the potential energy of the charged network responding to external shear deformation. The increase-then-decrease trend in equilibrium storage moduli in Table III(b), and the maximum value at 45.0 mol % AMPS now can be understood.

**TABLE III**  
 **$G'_e$  Data for (a) Copolymer Gels;**  
**(b) SIPN Gels with 50 wt % PEG**

AMPS (mol %)	$G'_e(\text{a})/\text{kPa}$	$G'_e(\text{b})/\text{kPa}$	$R^2(\text{a})$	$R^2(\text{b})$
0	0.97	15.1	0.98	1.00
12.0	0.12	2.30	0.99	1.00
26.7	1.51	3.93	0.99	1.00
45.0	1.35	5.36	0.99	1.00
68.6	0.70	3.18	1.00	1.00
100	0.10	0.73	1.00	1.00

$R^2$  denotes the coefficient of determination for each regression line in Figure 2 using eq. (3).



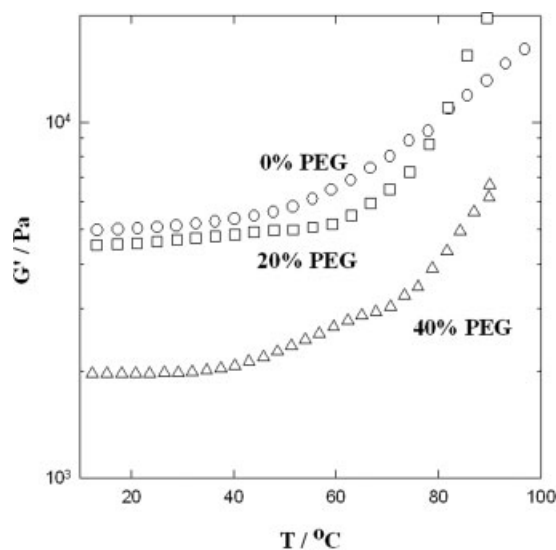
**Figure 3** Effect of PEG content on storage modulus as function of angular frequency for SIPN gels made with equimolar AMPS and NIPA and with  $0.016 \text{ mol L}^{-1}$  of MBAA. Angular frequency sweep from  $\omega = 0.63$  to  $10 \text{ s}^{-1}$  at strain 1% and at  $20^\circ\text{C}$ . All data presented in Figure 2 are logarithm values.

### Effects of PEG

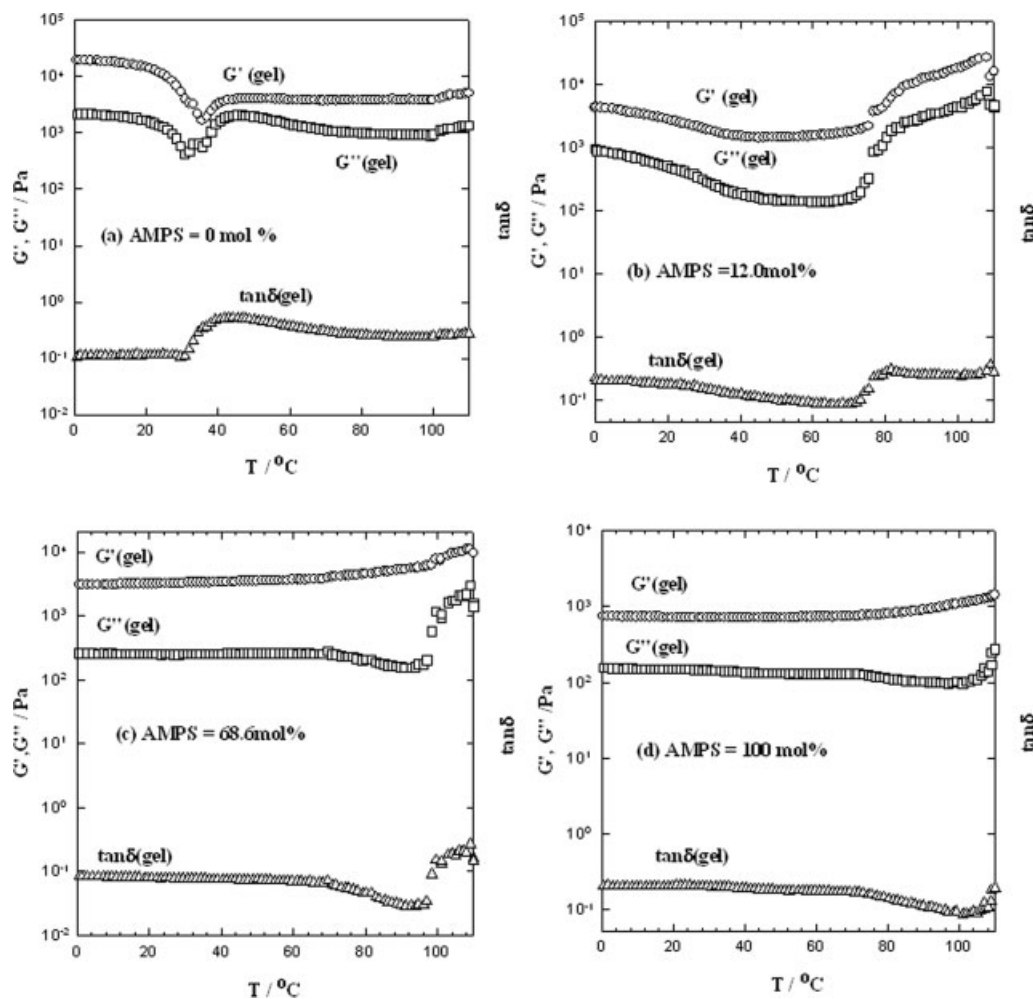
Because complete miscibility in a mixture (SIPN) of PEG6000 with AMPS-NIPA crosslinked network requires that the free energy of mixing is negative<sup>21,22</sup> and a negative heat of mixing is usually required. Therefore, strong interactions are expected and needed to produce a negative heat of mixing<sup>21</sup> while forming the gel in the presence of water. Because of the strong interactions between water, PEG and AMPS-NIPA copolymer network, PEG must play a role in the SIPNs in rheological properties.

Figure 3 shows that storage modulus of PEG SIPN gels is more frequency dependent (slope of  $G'$  to  $\omega$ ) than that from the highly crosslinked gels [Fig. 1(c,d)] and  $G'$  decreases significantly with increasing PEG content. The more frequency-dependent  $G'$  of the PEG SIPN gels indicates that the gels are incomplete crosslinked.<sup>32</sup> In general, addition of PEG6000 to AMPS-NIPA copolymer network modifies hydrogen bonding and hydrophobic interactions between PEG and the poly(AMPS-co-NIPA) network and more PEG molecules may generate less denser crosslink architecture of gels. The effects of PEG content and temperature on storage moduli  $G'$ s of the SIPN gels with 50 mol % AMPS were shown in Figure 4. A trend was that increasing PEG content reduces  $G'$

of gels at a given temperature. A smaller proportion of free water (relatively higher proportion of bound water) in the SIPN gels and rotational C—C—O units of the PEG chains may also leads to a softer gel and smaller values of  $G'$  at given temperature. Storage moduli of the poly(AMPS-co-NIPA) copolymer gels increased with increasing temperature, at above  $60^\circ\text{C}$  a rapid increase of the  $G'$  was found, particularly, for 20 and 40 wt % of PEG in PEG/NIPA-co-AMPS SIPN gels. This phenomenon may be due to water vaporization where more bound water containing in higher PEG wt % SIPN networks became free water with higher dynamics and started outwards emigration from polymer network and lost to environment thus the water vaporization caused rapid gel dehydration and hardening ( $G'$  increasing). From another viewpoint, the variation of the PEG content changing the ratio of free to bound water in the gels and dynamics of water in gels is relevant to bound water.<sup>39</sup> The significant deflection points (shown in Fig. 4) for  $G'$  rapid increase at increment of temperature for equimolar AMPS and NIPA SIPN gels with 0, 20, and 40 wt % PEG were about:  $51$ ,  $63$ , and  $74^\circ\text{C}$ , respectively. Obviously, at a copolymer network with constant ratio of AMPS to NIPA, increasing PEG wt % increases phase transition temperature. It is known that PEG has a high capacity for water binding; a hydration number of 2.7 per polymer segment has been estimated for PEG and



**Figure 4** Dependence of storage modulus  $G'$  of SIPN gels at equimolar AMPS and NIPA on varying PEG6000 content (wt %) in association with temperature increasing. Crosslinker concentration as per Figure 3. Temperature sweep was performed at constant heating rate (mentioned previously in experimental section) at 2% strain and at 1 Hz. Data in  $y$ -axis presented in Figure 4 were logarithm values.



**Figure 5** Temperature dependence of rheological parameters for copolymer gels with varying AMPS content: (a) 0; (b) 12.0; (c) 68.6; (d) 100 mol %. [MBAA] = 0.016 mol L<sup>-1</sup>; rheological tests performed at strain 1% and frequency 1 Hz. Data in *y*-axis presented in Figure 5 were logarithm values, temperature sweeping from 0 to 110°C.

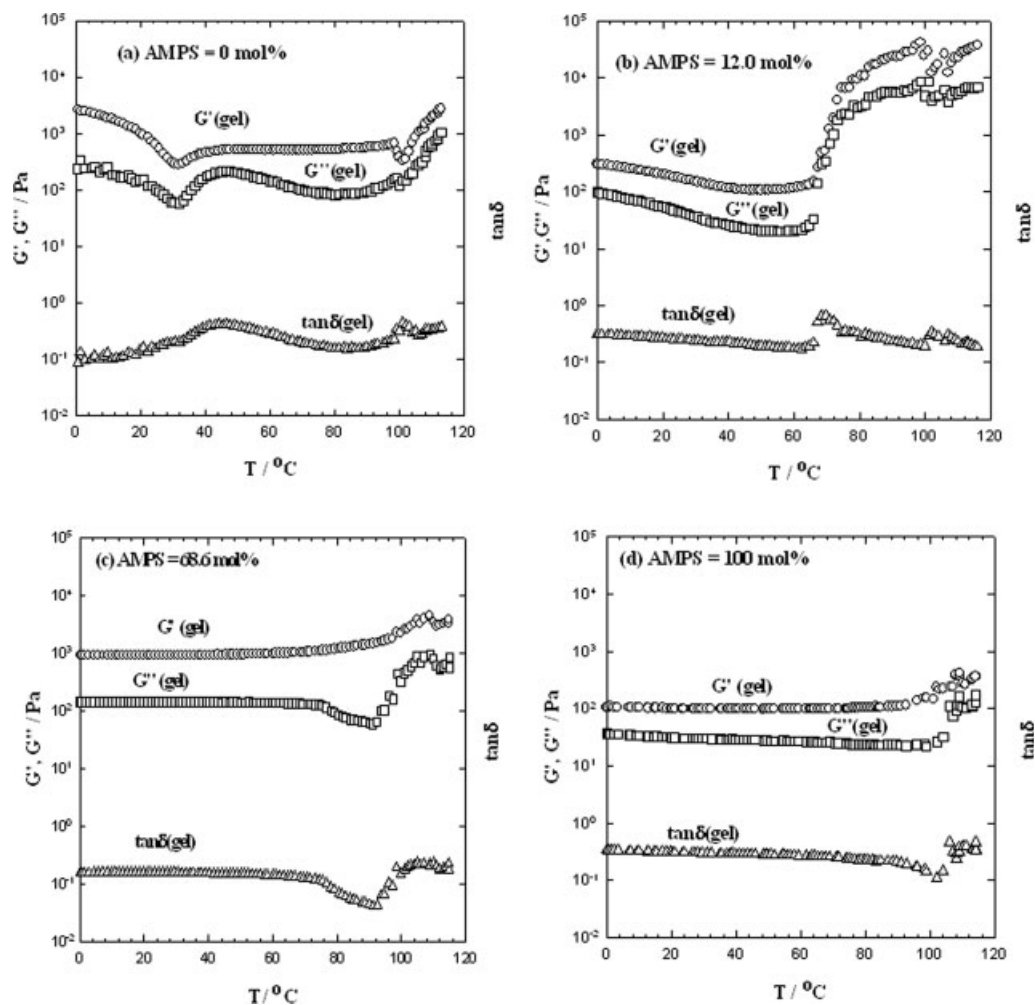
the free water melting temperature decreases with increasing PEG4000 concentration.<sup>14</sup>

### Temperature responsiveness

It was anticipated that the copolymer and SIPN gels would be temperature responsive due to the NIPA component. NIPA chains are hydrophilic and soluble in water as individual random-coil chains when the temperature is lower than LCST. As the solution temperature increases, NIPA chains become hydrophobic and insoluble in water to form single chain globules or multichain aggregates (mesoglobules).<sup>40,41</sup> However, copolymerization of the highly hydrophilic, ionic monomer AMPS with comonomer NIPA may change the LCST of gels comparing to NIPA polymer gels. It was observed in our experiments that when the temperature approached the LCST of NIPA units, the copolymer and SIPN gels became opaque and some bulk water separated from

the gels. This leads to the volume reduction of the disc gel which collapses toward its center. This explains the decrease in  $G'$  and  $G''$  of the gels at the phase transition temperature. Above the LCST,  $G'$  and  $G''$  increase with increasing temperature due to expansion of the gel.<sup>42</sup> Figure 5(a) shows that NIPA homopolymer gel has LCST at 32°C. The copolymer gels with 12 and 68.6 mol % AMPS show [Fig. 5(b,c)] phase transitions at about 72 and 96°C, respectively, in accordance with the expected effect of incorporation of the hydrophilic AMPS units in the copolymer chains. It is interesting to note that the gel containing only AMPS units in the main chains appears to show [Fig. 5(d)] a similar phase transition at about 106°C, but there are obviously complications due to rapid vaporization of water from the gels at temperatures around 100°C.

The SIPN gel system shows very similar behavior, i.e., LCST increasing with increasing proportion of AMPS in the main chains (Fig. 6). The PEG compo-



**Figure 6** Temperature dependence of rheological parameters for SIPN gels with varying AMPS content: (a) 0; (b) 12.0; (c) 68.6; (d) 100 mol %, and all at 50 wt % PEG6000. [MBAA] = 0.016 mol L<sup>-1</sup>; rheological tests performed at strain 1% and frequency 1 Hz. Data in *y*-axis presented in Figure 6 are logarithm values, temperature sweeping from 0 to 110°C.

ment decreases the LCST slightly, but the LCST is determined primarily by the main chain composition.

Consequently from 0 to 110°C temperature sweep at constant PEG content, the phase transition temperatures of PEG SIPN gels were determined by copolymer main chain composition (Fig. 6) and at constant copolymer main chain composition (Fig. 4) the phase transition temperatures of PEG SIPN gels were modified by PEG content. The higher the phase transition temperature, the higher the thermal stability is for hydrogel against dehydration in association with temperature increasing.

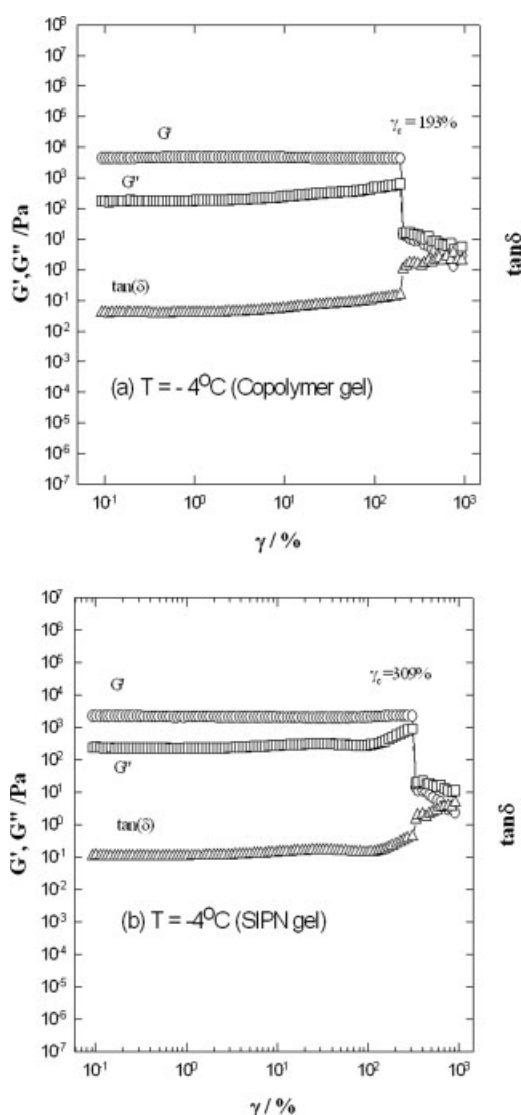
#### Gel behavior at low temperature

Amplitude sweeps for a copolymer gel and an SIPN with the same main chain composition are shown in Figure 7. In these gels, the water content is ~ 80 wt % and the contribution of water to the properties and structure of the gels at low temperature can be

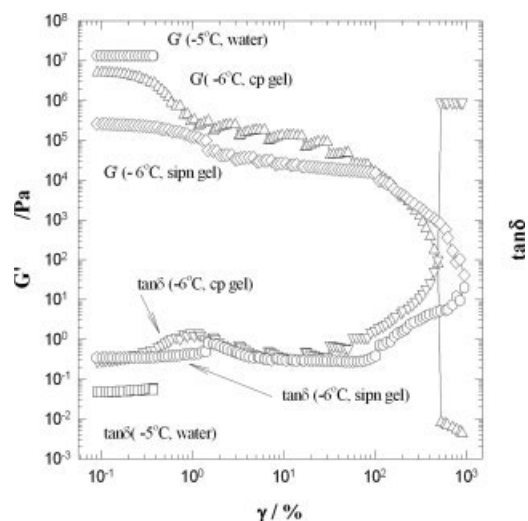
significant. It was occasionally that we found a narrow temperature region below 0°C where the hydrogels behave markedly different from soft gels. Albeit at -4°C and higher temperatures (up to temperatures below LCSTs), both copolymer and SIPN gels show the expected behavior as presented in the above sections as  $G' > G''$  and a plateau of  $G'$  within a temperature range. Figure 8 shows the rheological behavior of the hydrogels at -6°C although obvious slippage was found for gels at -6°C. At both low temperatures, the hydrogels were not observed phase separation as integrated gel discs. At strains less than 1%, the copolymer hydrogel shows similar behavior to ice at -5°C with very high  $G'$ . It was found that, at very low strain before the slippage occurred, the  $G'$  for water at -5°C is higher than for both copolymer and SIPN gels at -6°C. At small strains prior to slippage or plasticity the copolymer hydrogel shows similar behavior to ice with very high  $G'$ , very small extendable strain and small  $\tan \delta$



though ice is more rigid than the gel. It appears that at small strains the rheological behavior of the copolymer gel is determined predominantly by the continuous free water phase, albeit an imperfect ice phase, in the gel structure. The imperfection of the ice structure is due to the copolymer network and its interactions with the water. The very high modulus of the copolymer gel at strains less than 1% is strongly attenuated by the 50 wt % PEG content in the corresponding SIPN gel to the extent that  $G'$  is reduced by more than one order of magnitude in the SIPN gel. The plasticity process (or slippage) that occurs in the copolymer gel at about 0.2% strain (corresponding to the maximum in  $\tan \delta$  at 0.6%



**Figure 7** Amplitude sweep for (a) copolymer gel, (b) SIPN gel at  $-4^{\circ}\text{C}$ . Main chains with equimolar proportions of AMPS and NIPA; 50 wt % PEG6000 in SIPN gel.  $[\text{MBAA}] = 0.016 \text{ mol L}^{-1}$ ; Amplitude performed at frequency 1 Hz.

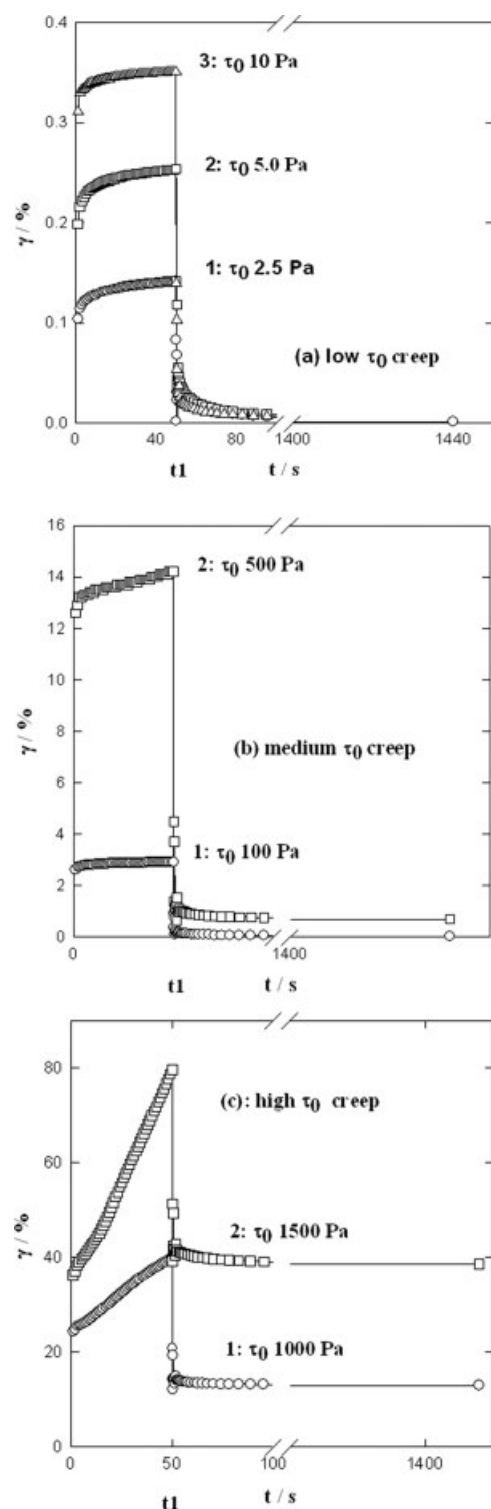


**Figure 8** Strain dependence of storage modulus for ice at  $-5^{\circ}\text{C}$ , and copolymer gel and SIPN gel at  $-6^{\circ}\text{C}$ . At strain higher than 1%, obvious slippage or plasticity was found for gels at  $-6^{\circ}\text{C}$ . Gel composition and experimental variables as per Figure 7.

strain) reduces  $G'$  by one order of magnitude: the SIPN gel undergoes a similar plasticity at about 0.8% strain (with a corresponding weak maximum in  $\tan \delta$  at about 1.3% strain) but the associated decrease in  $G'$  is much smaller than for the copolymer gel. The plasticity in the copolymer and SIPN gels may be associated with a strain-induced structure change in the ice component of the gels, analogous to the strain-induced phase changes that have been postulated to occur in glacier ice phase.<sup>43,44</sup> The onset of plastic flow is suggested by the marked decreases in slope of the  $G'$  versus  $\gamma$  curves (and increase in slope of  $\tan \delta$  curves) for the gels at about 100% strain. The bulk gel finally ruptures at a strain of nearly 500%, at which point there is a discontinuous increase in  $\tan \delta$  and decrease in  $G'$ .

#### Creep and recovery of strains and stress relaxation behaviors

Creep and strain recovery<sup>31,45–48</sup> experiments were carried out to investigate the observed extraordinary elasticity of the SIPN gels. For the creep experiments, carried out at  $20^{\circ}\text{C}$ , the change in strain of a gel disc was measured continuously at constant applied stress for a time, and immediately at the time following removal of the stress. For a viscoelastic material, the deformation produced by the application of stress is partially reversed over a period of time on removal of the stress, i.e., strain recovery occurs. Figure 9 shows the creep behavior of an SIPN gel with AMPS:NIPA mol ratio 1 : 1 and 50 wt % PEG, with low, medium and high applied



**Figure 9** Creep and strain recovery at 20°C as a function of applied stress. (a) low between 2.5 and 10 Pa; (b) medium 100 and 200 Pa; (c) high stress 1000 and 1500 Pa. Gel composition: AMPS:NIPA = 1 : 1 (mol/mol), 50 wt % PEG. [MBAA] in 0.016 mol L<sup>-1</sup>; Plate gap 2.25 mm.  $t_1$  is the time length of constant stress applied to gels. The lines are guides for the eye.

**TABLE IV**  
Creep and Strain Recovery for SIPN Gel

$\tau_0$ /Pa	$\gamma_i$ (%)	$\gamma_f$ (%)	$(\gamma_i - \gamma_f)/\gamma_i$ (%)
2.5	0.142	0.0001	99.9
5.0	0.254	0.0002	99.9
10	0.351	0.0014	99.6
100	2.91	0.026	99.1
500	14	0.69	95.1
1000	40	12.9	67.7
1500	80	38.5	51.6

$\tau_0$  = applied stress;  $\gamma_i$  = strain at  $t_1 = 50$  s;  $\gamma_f$  = strain at 1440 s after release of stress;  $(\gamma_i - \gamma_f)/\gamma_i$  = strain recovery ratio.

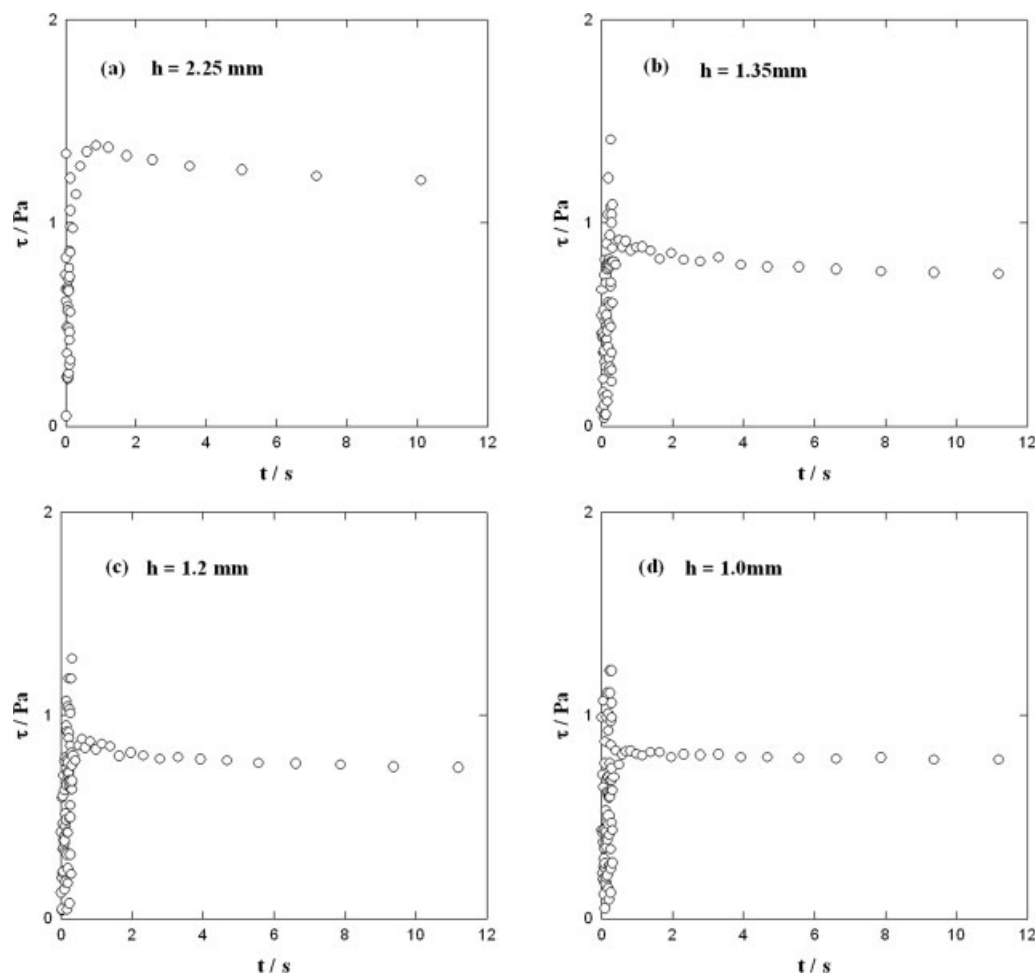
Gel composition: AMPS:NIPA = 1 : 1 (mol/mol); [MBAA] in 0.016 mol L<sup>-1</sup>; 50 wt % PEG.

stress ( $\tau_0$ ). In all cases the shear strain increased very rapidly initially, via the elastic response of the gel, and the strain continued to increase with time to  $t_1$ , at a reduced rate of increase. For applied stress < 500 Pa the strain approached a limiting value in the period ( $t_1 = 50$  s) for which the stress was applied and the gel behaved as an almost ideal elastic solid,<sup>49</sup> with almost total strain recovery within 1440 s. For applied stress  $\geq 500$  Pa, the very rapid initial increase in strain was followed by approximately linear increase with time, and the gels showed a permanent set (strain recovery < 100%). The experimental data are summarized in Table IV.

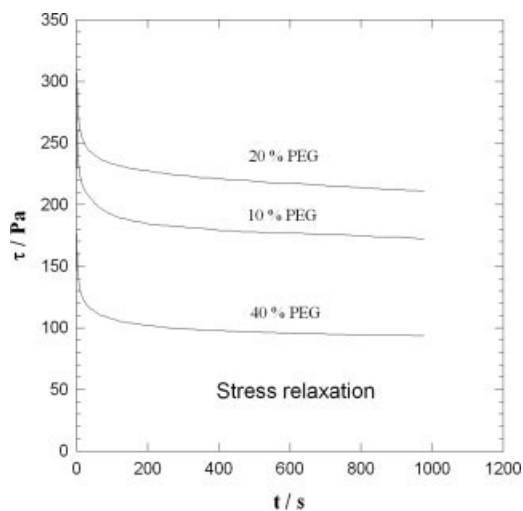
Stress relaxation experimental data for one of the SIPN gels are presented in Figure 10. These experiments were carried out by applying a constant shear strain to the gel under different gap widths, and determining the variation with time of the stress required to maintain the strain. In contrast to plastic materials, the gels exhibit a smaller stress relaxation, and the stress rapidly attains its equilibrium value. This behavior is typical of a highly elastic body. The relaxation behavior for SIPN gels, with the same main chain composition and different PEG contents, is strongly dependent on the PEG content (Fig. 11), due to the strong interactions between copolymer network and PEG.<sup>12,26</sup>

## CONCLUSIONS

The viscoelastic properties of the copolymer and SIPN gels are determined primarily by crosslinker concentration, copolymer main chain composition, proportion of PEG6000 and water content. The larger equilibrium storage moduli of SIPN gels compared with the copolymer gels with the same main chain composition are attributable to strong interactions between PEG and copolymer main chains and rheological properties of AMPS-NIPA copolymer net-



**Figure 10** Stress relaxation after instantaneous 0.05% strain, with varying plate-plate gap width ( $h$ ). (a) 2.25 mm; (b) 1.35 mm; (c) 1.2 mm; (d) 1.0 mm. Gel composition: AMPS:NIPA = 1 : 1 (mol/mol), [MBAA] in  $0.016 \text{ mol L}^{-1}$ ; 50 wt % PEG (For clarification, stress relaxation versus gap width were presented in separate charts due to the overlapping points so close).



**Figure 11** Effect of PEG6000 content on stress relaxation of SIPN gels with equimolar proportions of AMPS and NIPA. Relaxation tests at 10% strain. PEG6000 proportion: 10, 20, and 40 wt % PEG, respectively; [MBAA] in  $0.016 \text{ mol L}^{-1}$ ; Gels formed at  $70^\circ\text{C}$ , 2 h. Gap width ( $h$ ):1.35 mm.

work were modified by the presence of PEG. The rheological data indicate that the copolymer and SIPN gels are thermosensitive due to the NIPA units in the main chains, and the LCST depends predominantly on main chain composition. The low temperature behaviors of copolymer and SIPN gels are similar to that of ice at small low strain. At larger strain, gel slippage or plasticity was found in the amplitude sweep.

**TABLE V**  
Regression Equations for Densities of Dried Gels

Polymer system	Regression equation	$R^2$
poly(AMPS-co-NIPA)	$\rho = 3.2 \times 10^{-3} M_a + 1.09$	0.96
PEG/poly(AMPS-co-NIPA)		
SIPN	$\rho = 2.1 \times 10^{-3} M_a + 1.12$	0.95

Note:  $M_a$  is mol% of AMPS.  $R^2$  denotes the coefficient of determination.

The authors are grateful to Paar Physica, Germany for providing training on the operation of Paar Physica UDS200 rheometer.

## APPENDIX

The densities at room temperature for NIPA monomer, amorphous NIPA homopolymer, completely crystalline NIPA homopolymer and monomer AMPS were reported<sup>50,51</sup> as 0.970, 1.070, 1.118, and 1.45 g cm<sup>-3</sup>, respectively. The density of PEG6000 was measured as 1.226 g cm<sup>-3</sup>. The densities of dried copolymer gels (in a range of 1.09–1.41 g cm<sup>-3</sup>), and SIPN gels containing 50 wt % PEG6000 are given in Table V in the form of linear functions of main chain composition.

## References

- Umezawa, K.; Osada, Y. *Chem Lett* 1987, 9, 1795.
- Sato, T.; Takei, S.; Sunamoto, J. *Kenkyu Hokoku—Nagasaki Daigaku Kogakubu* 1986, 16, 183.
- Bilia, A.; Carelli, V.; Colo, G. D.; Nannipieri, E. *Int J Pharm* 1996, 130, 83.
- Ono, T.; Sugimoto, T.; Shinkai, S.; Sada, K. *Nature Mater* 2007, 6, 429.
- Bronstein, L. M.; Platonova, O. A.; Yakunin, A. N.; Yanovskaya, I. M.; Valetsky, P. M.; Dembo, A. T.; Makhaeva, E. E.; Mironov, A. V.; Khokhlov, A. R. *Langmuir* 1998, 14, 252.
- Jabbari, E.; Tavakoli, J.; Sarvestani, A. S. *Smart Mater Struct* 2007, 16, 1614.
- Richter, A.; Bund, A.; Keller, M.; Arndt, K.-F. *Sens Actuat B: Chem* 2004, B99, 579.
- Ladet, S.; David, L.; Domard, A. *Nature* 2008, 452, 76.
- Wang, C.; Stewart, R. J.; Kopecek, J. *Nature (London)* 1999, 397, 417.
- Meewes, M.; Ricka, J.; De Silva, M.; Nyffenegger, R.; Binkert, T. *Macromolecules* 1991, 24, 5811.
- Chen, G.; Hoffman, A. S. *Macromol Chem Phys* 1995, 196, 1251.
- Zhang, C.; Easteal, A. J. *J Appl Polym Sci* 2007, 104, 1723.
- Hardy, L. C.; Shriver, D. F. *J Am Chem Soc* 1985, 107, 3823.
- Hager, S. L.; Macrury, T. B. *J Appl Polym Sci* 1980, 25, 1559.
- Shojaei, A. H.; Li, X. *J Control Release* 1997, 47, 151.
- Francis, G. E.; Fisher, D.; Delgado, C.; Malik, F.; Gardiner, A.; Neale, D. *Int J Hematol* 1998, 68, 1.
- Chen, G.; Hoffman, A. S. *Nature* 1995, 373, 49.
- Shibayama, M.; Fujikawa, Y.; Nomura, S. *Macromolecules* 1996, 29, 6535.
- Jung, J.-H.; Sung, Y.-K.; Cho, C.-S.; Lee, Y.-M. *Adv Sci Technol* 1995, 12, 205.
- Cho, H.-K.; Kim, B.-S.; Noh, S.-T. *Polymer (Korea)* 2001, 25, 186.
- Hale, A.; Bair, H. E. In *Thermal Characterization of Polymeric Materials*; Turi, A., Ed.; Academic Press: San Diego, 1997; Vol. 1, p 745.
- Eisele, U. *Introduction to Polymer Physics*. Springer-Verlag: New York, 1990.
- Zhang, C.; Easteal, A. J. *J Appl Polym Sci* 2004, 94, 2083.
- Zhang, C.; Easteal, A. J. *J Appl Polym Sci* 2004, 91, 3635.
- Schroder, U. P.; Oppermann, W. In *Physical Properties of Polymeric Gels*; Addad, J. P. C., Ed.; Wiley: Chichester, 1996; p 19.
- Melekaslan, D.; Okay, O. *Macromol Chem Phys* 2001, 202, 304.
- Clark, A. H.; Ross-Murphy, S. B. *Adv Polym Sci* 1987, 83, 57.
- Michailova, V.; Titeva, S.; Kotsilkova, R.; Krusteva, E.; Minkov, E. *Colloids Surf A: Physicochem Eng Aspects* 1999, 149, 515.
- Kantaria, S.; Rees, G. D.; Lawrence, M. J. *J Control Release* 1999, 60, 355.
- Stepto, R. F. T. Appendix: International Union of Pure and Applied Chemistry Macromolecular Division-Commission on Macromolecular Nomenclature. Blackie Academic & Professional: London, 1998; p 316.
- Ferry, J. D. *Viscoelastic Properties of Polymers*, 2nd ed.; Wiley: New York, 1970.
- Miquelard-Garnier, G.; Demoures, S.; Creton, C.; Hourdet, D. *Macromolecules* 2006, 39, 8128.
- Saunders, D. W. In *The Rheology of Elastomers: Proceedings of a Conference Organized by the Br Society of Rheology and held at the Br Rubber Producers' Research Association, Welwyn City, in May 1957*; Mason, P.; Wookey, N., Eds.; Pergamon Press: London, 1958; p 30.
- Zhang, C.; Easteal, A. J. *J Appl Polym Sci* 2003, 89, 1322.
- Qiu, X.; Kwan, C. M. S.; Wu, C. *Macromolecules* 1997, 30, 6090.
- Zhang, C.; Easteal, A. J. *J Appl Polym Sci* 2003, 88, 2563.
- Qiu, X.; Wu, C.; *Macromolecules* 1997, 30, 7921.
- Tong, Z.; Liu, X. *Macromolecules* 1993, 26, 4964.
- Netz, P. A.; Dorfmueller, T. *J Phys Chem B* 1998, 102, 4875.
- Siu, M.; Zhang, G.; Wu, C. *Macromolecules* 2002, 35, 2723.
- Wu, C.; Zhou, S. *Phys Rev Lett* 1996, 77, 3053.
- Akiyoshi, K.; Kang, E.-C.; Kurumada, S.; Sunamoto, J.; Principi, T.; Winnik, F. M. *Macromolecules* 2000, 33, 3244.
- Russell-Head, D. S.; Budd, W. F. *J Glaciol* 1979, 24, 117.
- Gow, A. J. *Deep Core Studies of the Crystal Structure and Fabrics of Antarctic Glacier Ice*; Cold Reg. Res. and Eng. Lab.: Hanover, NH, 1970; p 25.
- Tanner, R. I.; Walters, K. *Rheology: An Historical Perspective*; Elsevier Science: New York, 1998; Vol. 7.
- Mackley, M. R. In *Rheological Measurement*; Collyer, A. A.; Clegg, D. W., Eds; Elsevier: London, 1988.
- Ferry, J. D.; Ninomiya, K. In *Viscoelasticity Viscoelasticity; Phenomenological Aspects*; Bergen, J. T., Ed.; Academic Press: New York, 1960; p 150.
- Mezger, T. *Paar Physica's Little course in rheology*, Parts 1, 2, and 3. In Paar Physica, Germany.
- Tanner, R. I. *Engineering Rheology*; Oxford University Press: New York, 1985; p 451.
- Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; Wiley: New York, 1999.
- AcrosOrganics, 98/99 Catalogue of fine chemicals. A Fisher Scientific Worldwide company: Geel, Belgium, 1999.