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# Swelling and elasticity of ionic poly(*N*-isopropylacrylamide) gels immersed in the melt of poly(ethylene glycol) chains

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## Abstract

The equilibrium network concentration  $\nu_2$  and the elastic modulus  $G$  of a series of poly(*N*-isopropylacrylamide) (PNIPA) gels immersed in the melt of poly(ethylene glycol) (PEG) chains were investigated. 2-Acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) was used as the ionic comonomer in the gel synthesis. The molecular weight of PEG was varied between 200 and 1000 g/mol. It was found that the decrease in  $\nu_2$  with increasing charge density of the gels is considerable weaker than expected with the assumption of Gaussian statistics. This deviation is interpreted as the ion pair and multiplet formation from the mobile counter ions of AMPS units of the gel in the presence of PEG chains. It was shown both theoretically and experimentally that the PNIPA gel undergoes a swelling–deswelling transition in PEG, if the chain length of PEG exceeds the critical value  $y_{cr} = N^{1/2}$ , where  $N$  is the network chain length calculated from the elastic moduli of gels immersed in PEG melt.

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## 1. Introduction

Polymer gels are important materials of both fundamental and technological interest. In recent years, considerable effort has been devoted to understanding of the swelling and collapse phenomena of polymer gels that are observed when a hydrogel network is brought into contact with a solvent [1]. The possibility of a first-order phase transition in polymer networks has been predicted theoretically and verified experimentally on ionic acrylamide-based hydrogels swollen in solvents [2–4]. It was shown that a small proportion of ionisable units on the polymer chains seem to be essential for a discontinuous shrinkage of the gel. More detailed calculations indicated that a strong concentration dependence of the polymer–solvent interaction parameter  $\chi$  may also induce a discontinuous shrinkage of the swollen gel, even in non-polar matrices [5–7]. However, experimental verification of this prediction is difficult to achieve due to the fact that the indicated requirement for the

polymer collapse is rare for real polymer–solvent systems [8].

Another possibility for the observation of phase transition in uncharged networks is to increase the number of lattice sites occupied by a solvent molecule, i.e. to bring the polymer network into contact with a polymer melt [9,10]. Calculations show that, even uncharged networks immersed in polymer melt may undergo a first order volume phase transition. The requirements for the critical state of a polymer network immersed in polymer melt are a high degree of dilution of the network at preparation and slightly incompatibility of the network chains with the linear polymer. Introduction of ionic units in the network facilitates attaining the critical state of the network immersed in polymer melt.

A first order volume phase transition of polymer network in the melt of linear polymer chains has not been observed experimentally as yet. In fact, the system consisting of a polymer network in equilibrium with polymer melt has not been studied before. Here, we report our results of the swelling and elasticity measurements carried out on poly(*N*-isopropylacrylamide) (PNIPA) networks of various charge densities immersed in the melt of poly(ethylene glycol) (PEG) chains. The molecular weight of PEG was varied

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between 200 and 1000 g/mol. The experimental results were explained within the framework of the Flory's theory of swelling equilibrium. As will be seen below, we observed a swelling–deswelling transition in PNIPA gels, if the chain length of PEG exceeds a critical value.

## 2. Theory of gel swelling immersed in polymer melt

The system under study is a two component system consisting of linear polymer chains (component 1) and a polymer network (component 2). The number of moles and the volume fractions of the components are represented by  $n_i$  and  $\nu_i$ , respectively ( $i = 1$  and  $2$  for linear polymer and polymer network, respectively and from the material balance  $\nu_1 = 1 - \nu_2$ ). This system is in thermodynamic equilibrium with a bulk linear polymer phase. We assume that the linear and the network chains consist of  $y$  and  $N$  segments, respectively. The energetic interaction between the linear polymer and the polymer network is represented by a single, concentration-independent  $\chi$  parameter. Qualitatively, if  $y \ll N$  and  $\chi = 0$ , the penetration of the linear chains into the network is both entropically and energetically favorable, so that the gel is swollen in the melt of polymer chains. If the chain length  $y$  of linear polymer is increased, the gel will deswell due to the reduction in the conformational entropy of linear chains entering the gel phase. In addition, a positive value of the  $\chi$  parameter, i.e. the incompatibility of the linear polymer with the polymer network will increase further the extent of deswelling of the gel in polymer melt.

This picture of gel swelling in polymer melt can be quantified within the framework of the Flory–Huggins lattice theory. The change in the free energy due to the swelling of a polymer network in the melt of linear polymer chains can be given as [11]:

$$(RT)^{-1} \Delta G = n_1 \ln \nu_1 + n_2 \ln \nu_2 + y n_1 \nu_2 \chi + \frac{3}{2} \left( \frac{V}{N V_1} \right) \times \left[ \left( \frac{\nu_2^0}{\nu_2} \right)^{2/3} - 1 - \ln \left( \frac{\nu_2^0}{\nu_2} \right)^{1/3} \right] + \left( \frac{i}{N} \frac{\nu_2}{\nu_1} n_1 \right) \ln \left( \frac{i}{N} \nu_2 \right) \quad (1)$$

where  $V$  is the volume of crosslinked polymer,  $V_1$  is the molar volume of segment,  $\nu_2^0$  is the volume fraction of polymer network at the preparation conditions,  $i$  is the number of ionic segments in the network chain, and  $R$  and  $T$  are in their usual meanings.

Differentiation of Eq. (1) with respect to the number of moles of linear polymer  $n_1$  yields the following equation for the reduced chemical potential of linear polymer  $\Delta\mu_1$ :

$$\frac{\Delta\mu_1}{RT} = \ln(1 - \nu_2) + \nu_2 + y\chi\nu_2^2 + yN^{-1}[\nu_2^{1/3}(\nu_2^0)^{2/3} - 0.5\nu_2 - i\nu_2] \quad (2)$$

If the polymer network is in thermodynamic equilibrium with the linear polymer, the reduced chemical potential of linear polymer  $\Delta\mu_1$  will vanish. Thus, equating  $\Delta\mu_1$  to zero, Eq. (2) predicts the swelling ratio and the elastic modulus of polymer gels in equilibrium with polymer melt. Serial expansion of the logarithmic term of Eq. (2) and truncating at  $\nu_2^2$  yield the following equation for the equilibrium swollen gels in polymer melt:

$$\left( \chi - \frac{1}{2y} \right) \nu_2^2 + N^{-1} \nu_2^{1/3} (\nu_2^0)^{2/3} - 0.5N^{-1} \nu_2 - iN^{-1} \nu_2 = 0 \quad (3)$$

Three different regimes can be distinguished from Eq. (3), depending on the charge density  $i$  of the gel and, on the degree of polymerization of the linear polymer  $y$ :

1. For highly charged gels ( $i \gg 1$ ), the gels are highly swollen in the polymer melt. The swelling equilibrium is mainly determined by the mixing entropy of the counter ions (last term of Eq. (3)), which is balanced by the gel rubberlike elasticity (second term of Eq. (3)). Thus, for this regime, Eq. (3) leads to:

$$\nu_2 \sim i^{-3/2} \nu_2^0 \quad (4)$$

which indicates that the network concentration in the equilibrium swollen gel  $\nu_2$  decreases, i.e. the gel volume increases with increasing charge density. A scaling parameter of  $-1.5$  between  $\nu_2$  and  $i$  is expected for charged, swollen gels.

2. For non-ionic gels, if  $y < N^{1/2}$  and  $\chi \cong 0$ , the gels are swollen in polymer melt [9,12]. Eq. (3) for swollen, uncharged networks simplifies to:

$$\nu_2 \sim y^{3/5} (\nu_2^0)^{2/5} [N(1 - 2y\chi)]^{-3/5} \quad (5)$$

If one assumes that, similar to the single polymer coil, the initial polymer network concentration depends on the number of segments of the network chains by  $\nu_2^0 \sim N^{-1/2}$ , Eq. (5) becomes:

$$\nu_2 \sim y^{3/5} N^{-4/5} (1 - 2y\chi)^{-3/5} \quad (5a)$$

According to Eqs. (5) or (5a), the gel deswells ( $\nu_2$  increases) as the degree of polymerization of linear polymer  $y$  increases, or as the incompatibility of the linear polymer with the polymer network increases.

3. If  $y \geq N^{1/2}$ , the size of the linear polymer is too large to enter the mesh of the gel phase. In this case, the excluded volume interaction between the segments of the gel is completely screened by the linear polymer ( $\nu_2^2/y \cong 0$ ). In the athermal limit ( $\chi = 0$ ), the free energy is controlled only by the elastic terms [9,12]. Thus, Eq. (3) gives:

$$\nu_2 \sim \nu_2^0 \quad (6)$$

or, assuming that the network concentration scales with

$N$  as  $\nu_2^0 \sim N^{-1/2}$  :

$$\nu_2 \sim N^{-1/2} \quad (6a)$$

In this regime, the gel is unswollen in the polymer melt. In addition, a positive  $\chi$  parameter of the system results in a first order volume phase transition in the network from swollen to the collapsed state [9,10].

The theory thus predicts that the swelling to deswelling transition of polymer gels in polymer melt occurs if the degree of polymerization of linear polymer  $y$  exceeds the critical value  $y_{cr} = N^{1/2}$ .

### 3. Experimental

#### 3.1. Hydrogel preparation

PNIPA gels were synthesized by free-radical cross-linking copolymerization of the monomer *N*-isopropylacrylamide (NIPA) and the crosslinker *N,N'*-methylenebis(acrylamide) (BAAm) in aqueous solution at 5 °C. 2-Acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) was used as the ionic comonomer in the hydrogel synthesis. Ammonium persulfate (APS) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were used as the initiator system. In our experiments, the initial monomer and initiator (APS) concentrations were fixed at 0.71 M and 3.51 mM, respectively. The crosslinker ratio (mole ratio of the crosslinker BAAm to the monomers NIPA + AMPS) was also fixed at 1/85, while the concentration of the ionic comonomer AMPS was varied between 0 and 5 mol% (with respect to the monomers NIPA and AMPS). The hydrogels were prepared in glass tubes of about 5 mm internal diameter and about 100 mm long. The details for the preparation of the hydrogels were described previously [13].

#### 3.2. Swelling measurements in water

The cylindrical hydrogel samples of 4.5–5 mm in diameters and approximately 10 mm in length were placed in an excess of water at  $24 \pm 0.5$  °C. In order to reach the equilibrium degree of swelling, the gel samples were immersed in water for at least 2 weeks during which water was replaced every other day. The swelling equilibrium was tested by measuring the diameter of the gel samples. To achieve good precision, three measurements were carried out on samples of different length taken from the same gel. The interpretation of swelling measurements was made on the basis of volume fraction of crosslinked polymer at equilibrium swelling  $\nu_2$ .  $\nu_2$  was calculated as:

$$\nu_2 = \frac{\nu_2^0}{(D/D_0)^3} \quad (7)$$

where  $D$  and  $D_0$  are the diameter of hydrogels after equilibrium swelling in water and after synthesis, respectively. The volume fraction of crosslinked polymer after the gel preparation  $\nu_2^0$  was determined by extraction of the hydrogels with water followed by drying, as described previously [14].

#### 3.3. Swelling measurements in PEG melt

For the swelling measurements, reagent-grade PEGs (Fluka) of molecular weights 200, 300, 600, and 1000, designated by PEG-200, PEG-300, PEG-600, and PEG-1000, respectively, were used without further purifications.

Equilibrium swollen gel samples in water were first dried in vacuum at room temperature to constant weight, which took about 2 months. Thereafter, the dried network samples were immersed in PEG-200. To reach the equilibrium degree of swelling, the gels were immersed in a large excess of PEG-200 melt and, PEG-200 was replaced every other day over a period of at least one month until no volume change in the gel samples could be detected. The swelling ratio was then determined by measuring the diameter of the gel samples and by use of Eq. (7). Thereafter, the gel samples swollen in PEG-200 were successively immersed in PEG-300, PEG-600, and PEG-1000 and the swelling measurements were repeated as described above. All the swelling measurements, except those in PEG-1000, were conducted at  $24 \pm 0.5$  °C. Since PEG-1000 is a waxy liquid at this temperature, the swelling measurements in PEG-1000 were conducted at 37 °C. To investigate the temperature dependence of the swelling ratio of PNIPA gels in PEG melt, we also conducted the measurements at various temperatures between 15 and 60 °C. For example, Fig. 1 shows the temperature dependence of the  $\nu_2$  values of PNIPA gels swollen in PEG-200. It is seen that the swelling ratio in PEG-200 does not depend on the temperature in the range of 15 to 60 °C. Similar results were also obtained in PEG-300 and in PEG-600. Thus, we can conclude that the swelling data obtained in PEG-1000 at 37 °C can be compared with the data obtained in other PEG samples at 24 °C.

#### 3.4. Mechanical measurements

Uniaxial compression measurements were performed on gels after preparation as well as on gels in equilibrium with water or with PEGs of various molecular weights. All the mechanical measurements, except those in PEG-1000, were conducted at  $24 \pm 0.5$  °C. Gels in equilibrium with PEG-1000 were subjected to measurements at 37 °C. The stress–strain isotherms were measured by using an apparatus described before [15]. Briefly, cylindrical gel sample of about 5 mm in diameter and 7 mm in length, immersed in water or in PEG melt, was placed on a digital balance. A load was transmitted vertically to the gel through a rod fitted with a PTFE end-plate. The compressional force

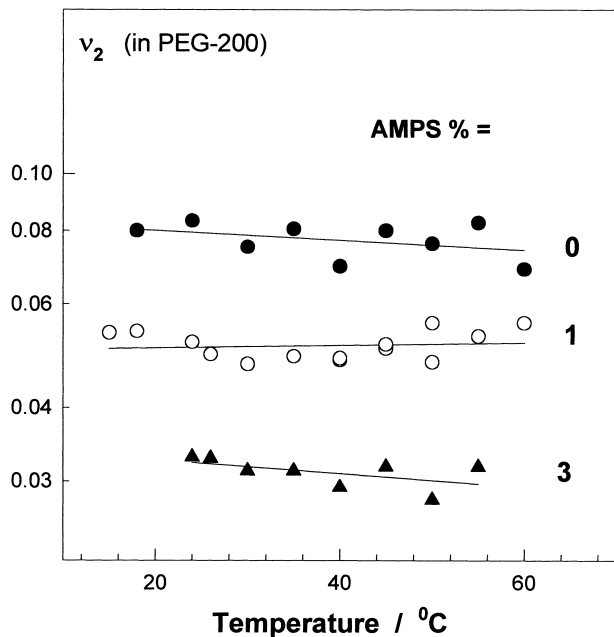


Fig. 1. Variation of the polymer network concentration  $\nu_2$  in PNIPA gels equilibrium swollen in PEG-200 with the temperature. The mole percent of AMPS in the gels is indicated in the Fig.

acting on the gel was calculated from the reading of the balance. The resulting deformation was measured after 20 s of relaxation by using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo Co.), which was sensitive to displacements of  $10^{-3}$  mm. The measurements were conducted up to about 15% compression. Reversibility of the isotherms was tested by recording the force and the resulting deformation during both force-increasing and force-decreasing processes. The two processes yielded almost identical stress–strain relations. From the repeated measurements, the standard deviations in the modulus value were less than 3%. The elastic modulus  $G$  was determined from the slope of linear dependence:

$$f = G(\lambda - \lambda^{-2}) \quad (8)$$

where  $f$  is the force acting per unit cross-sectional area of the undeformed gel specimen, and  $\lambda$  is the deformation ratio (deformed length/initial length). For a homogeneous affine network of Gaussian chains, elastic modulus of gels  $G$  relates to the average degree of polymerization of network chains  $N$  through the equation [11,16]:

$$G = (NV_1)^{-1} RT(\nu_2^0)^{2/3} (\nu_2)^{1/3} \quad (9)$$

The molar volume of a segment  $V_1$  is taken as the molar volume of water (18 ml/mol).

#### 4. Results and discussion

A series of PNIPA gels with charge densities ranging

from 0 to 5% AMPS were prepared at a fixed crosslinker ratio and monomer concentration. The characteristic data of the gels are compiled in Table 1. The polymer network concentrations after the gel preparation  $\nu_2^0$  are listed on column 2.  $\nu_2^0$  increases slightly with increasing charge density from 0.059 to 0.063. Elastic moduli of the gels after their preparation  $G_0$  are shown in column 3 of the Table. From the  $G_0$  values together with Eq. (9) for  $\nu_2 = \nu_2^0$ , we calculated the average number of segments of network chains  $N$ . The  $N$  values of the gels, listed on the last column of the Table, lie at 1200–1300. These gel samples were subjected to swelling and elasticity measurements in PEGs of various chain lengths. For comparison, measurements were also conducted in water.

##### 4.1. Charge density of the gels in polymer melt

Fig. 2 shows the network concentrations  $\nu_2$  in the equilibrium swollen gels plotted as a function of their AMPS contents. Measurements were carried out at 24 °C in water and in PEGs. The slopes of the double logarithmic  $\nu_2$  versus AMPS% dependencies are also shown in the Fig. A decrease in the network concentration  $\nu_2$  with increasing AMPS content of the gels is expected. This is a consequence of the osmotic pressure exerted by the counter ions ( $\text{Na}^+$ ) of AMPS units in the network chains. Furthermore, a scaling parameter of  $-1.5$  between  $\nu_2$  and the AMPS content is also expected (Eq. (4)). However, Fig. 1 shows that the slope of  $\nu_2$  versus AMPS% curve is equal to  $-0.71$  in water and, this value decreases further as the molecular weight of PEG increases and becomes zero in PEG-600.

The discrepancy between the theory and experiment observed in water may be related to the non-Gaussian behavior of fully swollen PNIPA gels in water. The theory (Eq. (1)) assumes that the polymer network is a collection of Gaussian chains, which can be extended to infinity. For the highly swollen hydrogels in water, deviation from the Gaussian statistics may appear due to the finite extensibility of the network chains. For Gaussian chains, elastic free energy increases with the square of the linear swelling ratio  $\alpha = (\nu_2^0/\nu_2)^{1/3}$  (fourth term of Eq. (1)). As the network

Table 1

Characteristic data of the hydrogels.  $\nu_2^0$  = Volume fraction of crosslinked polymer after gel preparation,  $G_0$  = elastic modulus of gels after their preparation,  $N$  = average number of segments between two successive crosslinks calculated from the  $G_0$  values and using Eq. (9) for  $\nu_2 = \nu_2^0$ . The numbers in parenthesis are the standard deviations of at least three separate measurements

AMPS %	$\nu_2^0$	$G_0$ (kPa)	$N$
0	0.059	6.12 (0.65)	1322 (127)
1	0.060	6.48 (0.08)	1271 (14)
2	0.061	6.94 (0.46)	1205 (74)
3	0.061	7.14 (0.05)	1180 (7)
4	0.062	7.33 (0.04)	1165 (5)
5	0.063	6.48 (0.26)	1340 (53)

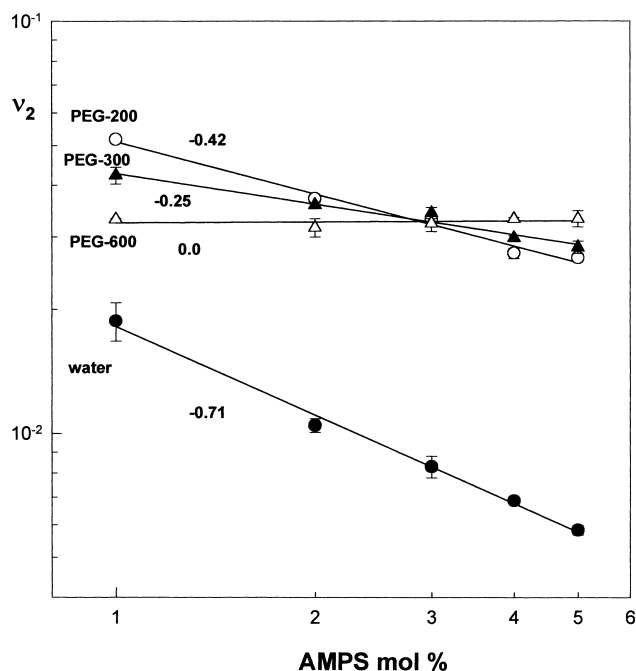


Fig. 2. The network concentrations  $\nu_2$  in the equilibrium swollen gels shown as a function of the AMPS content. Measurements were carried out at 24 °C in water, PEG-200, PEG-300, and PEG-600. The solid curves are the best fitting curves to the experimental data. The slopes of the curves are also shown in the Fig.

chains deviate from the Gaussian statistics, the elastic free energy will increase with a higher power of the linear swelling ratio. For example, assuming that the elastic free energy increases with fourth power of  $\alpha$ , a scaling parameter of 0.75 can be obtained from Eq. (1), which is close to the observed behavior of the hydrogels in water. Further evidence for the non-Gaussian behavior of the network chains swollen in water comes from their elastic moduli data, as will be seen later.

However, due to the relatively low degree of swelling of the gels in PEG melt, the discrepancy between theory and experiment cannot be explained with the non-Gaussian behavior. Instead, formation of ion pairs and their aggregates (multiplets) from the mobile counter ions ( $\text{Na}^+$ ) of AMPS units may explain this discrepancy. The formation of ion pairs is known to be more pronounced for solutions with a lower dielectric constant [17–19]. Moreover, the probability of the formation of multiplets increases with increasing charge density, as was shown both theoretically and experimentally for the gels in media of rather low polarity [20,21]. Although the counter ions are mobile in water due to the high dielectric constant of water (80), they become increasingly immobile as the dielectric constant of the medium decreases. Since the dielectric constant of PEGs decreases with increasing molecular weight and approaches to unity at high molecular weights [22], experimental results can be explained by the formation of an increasing number of ion pairs and multiplets, as the molecular weight of PEG increases. As seen in Fig. 2, the

network concentration  $\nu_2$  is independent on the AMPS content in the melt of PEG-600, indicating that the ionic gels immersed in PEG-600 behave like an uncharged gel. These results show that the use of ionic gels to facilitate a first order volume phase transition in polymer melt, as predicted theoretically [9,10], is experimentally not achievable.

#### 4.2. Swelling and elasticity of PNIPA gels in PEG melt

In Fig. 3, the network concentration in PNIPA gels equilibrium swollen in PEG,  $\nu_2$ , is plotted as a function of the molecular weight of PEG. The AMPS contents of the gels are indicated in the Fig. In the  $x$ -axes, the number of segments per linear chain  $y$  is also given, which was calculated from the molecular weight  $M$  of PEG as:

$$y = \frac{M}{dV_1} \quad (10)$$

where  $d$  is the density of PEG (1.12 g/cm<sup>3</sup>). For PNIPA gels with less than 3% AMPS, increasing molecular weight of PEG from 200 to 600 g/mol results in a decrease in the  $\nu_2$  value, i.e. in an increase in the PEG concentration in the gel. This reveals that the attractive interactions between the isopropyl groups of PNIPA network and the ethylene units of PEG become stronger as the molecular weight of PEG increases. Thus, as the molecular weight of PEG increases from 200 to 600 g/mol, although the conformational entropy of PEG chains penetrating into the gel decreases due to the

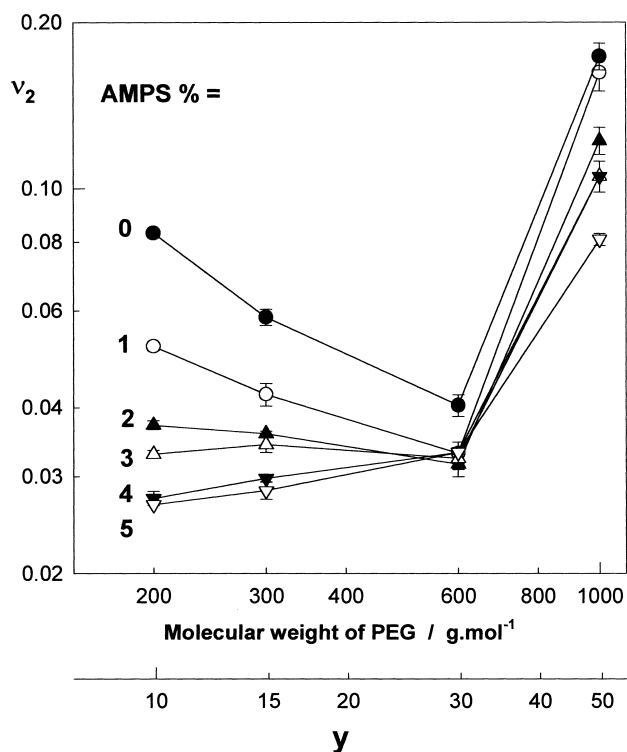


Fig. 3. The network concentration  $\nu_2$  in the gels, equilibrium swollen in PEG, shown as functions of the molecular weight and the number of segments  $y$  of PEG. The mole percent of AMPS in the gels is indicated in the Fig. The curves only show the trend of data.

reduction in the number of their arrangements, the energy gain due to the contact between PEG and PNIPA segments exceeds the decrease in the conformational entropy, so that the chains easily penetrate into the gel. In order to quantify these results, we calculated the interaction parameter  $\chi$  between PNIPA and PEG chains. Since both the crosslink densities  $N$  and the swelling ratios of the gels are known, Eq. (2) for free swelling ( $\Delta\mu_1 = 0$ ) can be used to calculate the interaction parameter  $\chi$  between the non-ionic PNIPA network and PEG. The results of calculations are shown in Fig. 4 plotted as a function of  $y$ .  $\chi$  decreases as the chain length of PEG increases and becomes close to zero at  $y = 20$ –30. This trend of  $\chi$  is similar to that of the second virial coefficient  $A_2$  in a binary solution, which also decreases with increasing molecular weight [23]. The molecular weight dependence of  $\chi$  was also observed previously in several systems [23–25].

Fig. 3 also shows that, at AMPS contents higher than 3%, the gels slightly deswell with rising PEG molecular weight from 200 to 600 g/mol. For these highly charged gels, one has to consider two opposite effects of the molecular weight of linear polymer on the gel swelling. The first effect is the increasing extent of attractive PEG–PNIPA interactions with increasing PEG molecular weight, which leads to gel swelling, as was observed in the slightly charged gels. Opposing this, increasing extent of ion pair formation with increasing PEG molecular weight reduces the gel swelling in PEG melt (Fig. 2). This second effect seems to dominate the swelling process of highly charged gels in PEG melt. Another interesting point shown in Fig. 3 is that all the gels undergo a swelling to deswelling transition between PEG molecular weights 600 and 1000 g/mol, which corresponds

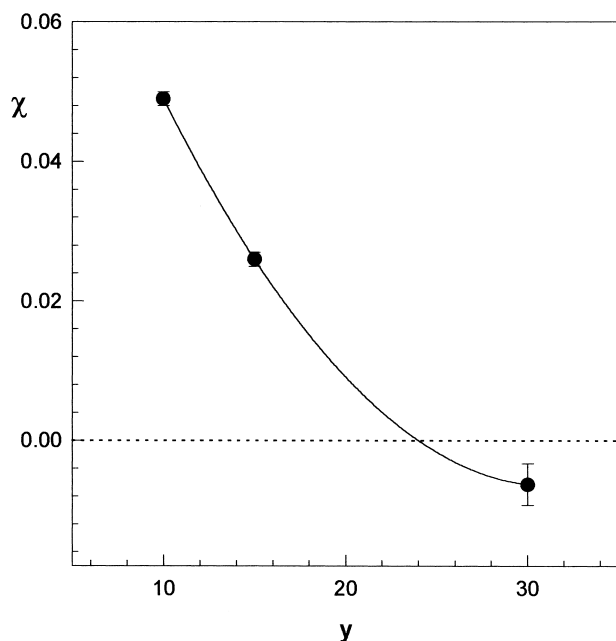


Fig. 4.  $\chi$  parameter for PNIPA–PEG system calculated from the swelling degree and the elasticity of PNIPA gels immersed in PEG plotted as a function of the number of segments of PEG  $y$ .

to  $y = 30$ –50. As a result of this transition  $\nu_2$  value rapidly increases from 0.04 to 0.1–0.2.

In Fig. 5, the elastic moduli  $G$  of PNIPA gels are plotted as a function of the network concentration  $\nu_2$ . Data were obtained from gel samples equilibrium swollen in water and in PEGs. The dotted line illustrates the theoretical slope of 1/3 (Eq. (9)), assuming that the network crosslink density  $N$  remains constant. Three different regimes can be observed from the Fig.

1. For  $\nu_2 < 0.01$ , i.e. for ionic gels swollen in water (filed circles in Fig. 5),  $G$  slightly decreases with increasing  $\nu_2$  value. This type of dependence is an indication of the limited extensibility of the network chains swollen in water, which is in accord with the results of the previous section.
2. For the gels swollen in PEG,  $G$  increases with increasing  $\nu_2$ . The slope of  $G$  versus  $\nu_2$  dependence is close to the theoretical value of 1/3. Thus, PNIPA gels in this regime behave Gaussian. Furthermore, at a given value of  $\nu_2$ , the higher the molecular weights of PEG are, the larger  $G$  is.
3. For the gels with 0 and 1% AMPS immersed in PEG-1000 (two data points at the upper right corner of Fig. 5), the elastic moduli were found to be in the range of  $10^6$  Pa. These samples are expected to be in the glassy state during the measurements.

From the elastic moduli of gels together with Eq. (9), we calculated the network crosslink densities in terms of  $N$ . The results are collected in Fig. 6. For comparison, the initial values of  $N$ , calculated from the moduli of gels after their

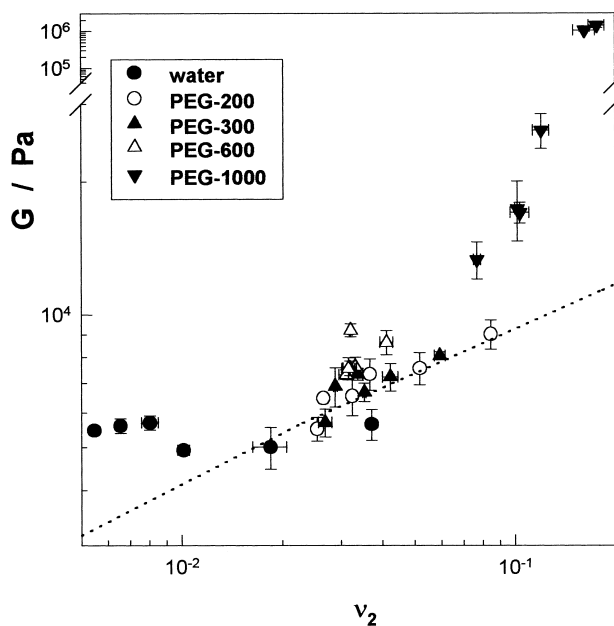


Fig. 5. The elastic modulus  $G$  shown as a function of the equilibrium network concentration  $\nu_2$ . The data were obtained from gel samples equilibrium swollen in water and in PEGs. The dotted line illustrates the theoretical slope of 1/3 (Eq. (9)), assuming that the network crosslink density  $N$  remains constant.

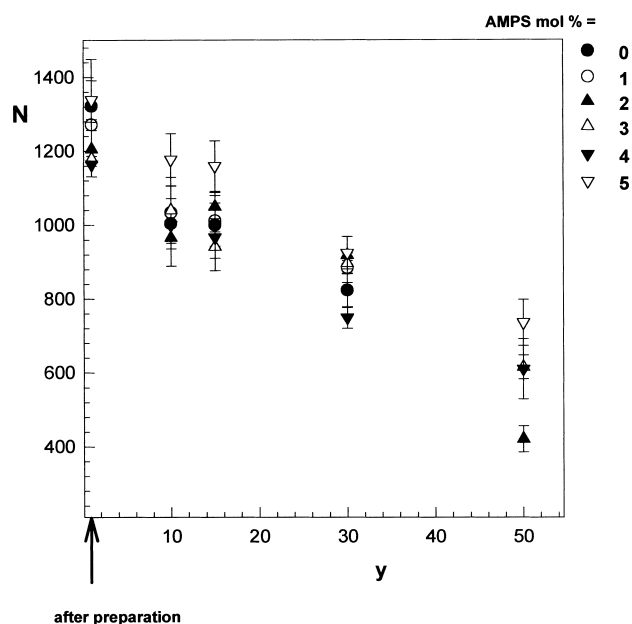


Fig. 6. The number of segments of network chains  $N$  shown as a function of the number of segments in PEG  $y$ . The mole percent of AMPS in the gels is indicated in the Fig.

preparation are also included in the Fig. It is seen that the number of segments of elastically effective network chains  $N$  decreases as the molecular weight of PEG increases. This shows that the PEG chains penetrating into the gel entangle with the PNIPA network and thus, decrease the elastically effective chain length by creating physical crosslinks. According to Fig. 5, the number of these additional crosslinks increases with increasing molecular weight of PEG.

As mentioned in Section 2, the theory predicts a swelling to deswelling transition in polymer gels if the chain length of linear polymer exceeds the critical value  $y_{cr} = N^{1/2}$ . If  $y < y_{cr}$ , we expect that the gel is swollen while for  $y \geq y_{cr}$ , the gel is collapsed. In Fig. 7,  $\nu_2$  values of the gels are plotted as a function of  $y/y_{cr}$ , where  $y_{cr}$  was calculated from the crosslink densities  $N$  of the gels in respective PEGs. It is seen that the shape of the curves below and above  $y/y_{cr} = 1$  are completely different. The gel rapidly deswells if  $y/y_{cr}$  exceeds unity, i.e. if the molecular weight of PEG is higher than 600 g/mol. The experimental findings are in fully accord with the prediction of the Flory's lattice theory applied to polymer network-linear polymer systems.

## 5. Conclusions

The equilibrium network concentration  $\nu_2$  and the elastic modulus  $G$  of a series of PNIPA gels immersed in the melt of PEG chains were investigated. It was shown that the decrease in  $\nu_2$  with increasing charge density of the gels is considerable weaker than expected with the assumption of Gaussian statistics. This deviation is interpreted as the ion

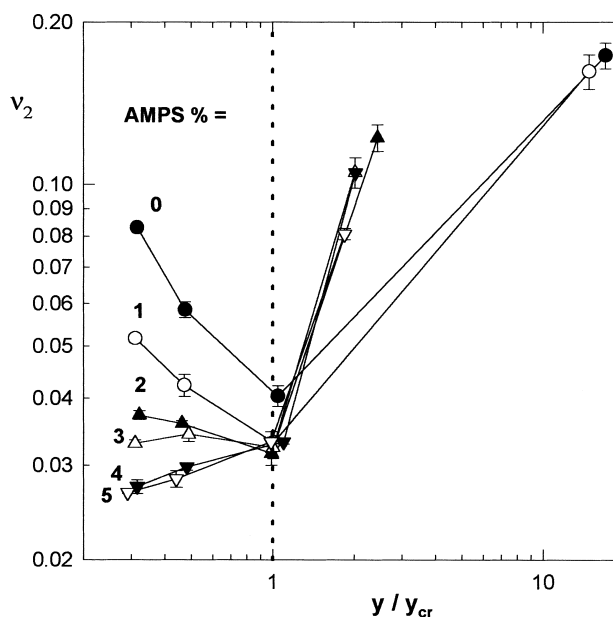


Fig. 7. The equilibrium network concentration of gels  $\nu_2$  plotted as a function of  $y/y_{cr}$  where  $y_{cr} = N^{1/2}$ .

pair and multiplet formation from the mobile counter ions of AMPS units of the gel in the presence of PEG chains. The swelling and elasticity data of the gels immersed in PEG melt indicate increasing extent of attractive interactions between PNIPA and PEG segments with increasing molecular weight of PEG from 200 to 600 g/mol. A further increase in the PEG molecular weight resulted in an abrupt increase in the network concentration  $\nu_2$  of the gels. It was shown both theoretically and experimentally that the gel undergoes a swelling–deswelling transition if the chain length  $y$  of PEG exceeds the critical value  $y_{cr} = N^{1/2}$  where  $N$  is the network chain length calculated from the elastic moduli data of the gels immersed in PEG melt.

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