

Phase transition in swollen gels

29. Temperature dependences of swelling and mechanical behaviour of poly(*N*-vinylcaprolactam-*co*-1-vinyl-2-pyrrolidone) gels in water

M. Ilavský^{*1,2}, G. Mamytbekov^{2,a}, Z. Sedláková², L. Hanyková, K. Dušek²

¹ Faculty of Mathematics and Physics, Charles University, 180 00 Prague 8, Czech Republic

² Institute of Macromolecular Chemistry, Academy of Sciences of Czech Republic, 162 06 Prague 6, Czech Republic

^a Participant of the UNESCO-sponsored postgraduate course. On leave from the Academy of Sciences of the Kazakh Republic

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Summary

Ionized networks of statistical copolymers of *N*-vinylcaprolactam (VCL), 1-vinyl-2-pyrrolidone (VP) (mole ratios of VCL/VP = 1/0, 0.9/0.1, 0.8/0.2, 0.7/0.3 and 0.5/0.5), an ionic comonomer, *N,N*-diallyl-(*N,N*-dimethyl)ammonium chloride (mole fractions 0, 0.005, 0.01 and 0.02) and a crosslinker, 1,1'-divinyl-3,3'-(ethane-1,1-diyl)di(2-pyrrolidone) (mole fractions 0.016, 0.024, 0.032 and 0.048) were prepared by radiation polymerization in water/ethanol mixture (H₂O/EtOH = 0.5/0.5 by vol). Their swelling and mechanical behaviour was investigated in water at various temperatures. For all copolymers, a continuous transition was found from the expanded (at low temperatures) to collapsed (at high temperatures) state; the transition temperature T_r increases with increasing contents of VP and the ammonium salt in gels. The shift of T_r to higher temperatures is caused by hydrophilicity of network chains increasing with increasing VP contents. The decrease in swelling with increasing temperature is accompanied by an increase in equilibrium modulus, so that mechanical behaviour is predominantly determined by swelling.

Introduction

Polyelectrolyte hydrogels exhibit high swelling in water and a first-order phase transition (collapse) caused by a small change in external conditions such as temperature, electric field, solvent compositions, etc [1]. The presence of charges on the chain (1-10 mol %) seems to be an important condition for the occurrence of a jump change in gel volume [2,3]. Most results were obtained with charge-bearing networks of polyacrylamide (gels sensitive to solvent composition), poly(*N,N*-diethylacrylamide) (PDEAAm), and poly(*N*-isopropylacrylamide) (PNIPAAm) (temperature sensitive hydrogels). This transition, in particular temperature-induced collapse, can be widely used in practical applications [4].

Poly(*N*-vinylcaprolactam) (PVCL) exhibits unique physical properties including solubility in water and organic solvents, low toxicity, high complexing ability; it found application in many fields of technology, medicine and agriculture [5]. Crosslinked poly(*N*-vinylcaprolactam) (PVCL) hydrogel has shown under heating a sharp continuous shrinking region [6]. On the other hand, DSC experiments have revealed [7] that PVCL gel undergoes two transitions on heating (the low-temperature transition at 31.5 °C was associated with microsegregation due to the hydrophobic domain formation and the high-temperature transition at 37.5 °C was associated with the gel volume collapse. We have also shown that PVCL hydrogels with

* Corresponding author: Tel.: +420-2-21912363, Fax: +420-2-6885095, e-mail: ilavsky@kmf.troja.mff.cuni.cz

charges on the chain exhibited only one continuous shrinking region in dependence on temperature [8]; no jump in the volume was interpreted by the fact that for the uncharged PVCL network swollen in water, a high value of the Flory-Huggins interaction parameter $\chi = 0.522$ was found.

Also hydrogels based on poly(1-vinyl-2-pyrrolidone) (PVP) and its copolymers were extensively studied [5-9] and they found a variety of applications in biomedical devices, agriculture, and many others. In our previous papers [10] we reported on swelling and mechanical behavior of positively charged PVP networks in water/acetone mixtures and showed that ionized PVP hydrogels exhibit the first-order phase transition (collapse) at critical acetone concentrations $a_c \sim 75$ vol.%.

Copolymerization of two monomers is one of the effective methods of modification of physical properties of gels. Several authors [11,12] who have studied temperature collapse in poly(*N*-isopropylacrylamide) hydrogels reported that while incorporation of a hydrophilic comonomer leads to a higher transition temperature (LCST), incorporation of a hydrophobic comonomer lowers the transition temperature. In this work, we investigate the effect of composition of ionized networks of statistical copolymers of *N*-vinylcaprolactam and 1-vinyl-2-pyrrolidone prepared by radiation polymerization in water/ethanol mixtures on their swelling and mechanical behaviour in water at various temperatures.

Experimental

Materials: Purification of *N*-vinylcaprolactam (VCL, Fluka) and 1-vinyl-2-pyrrolidone (VP, Fluka) was described previously [8,10]. *N,N*-diallyl-*N,N*-dimethylammonium chloride (Fluka, 65 vol.% aqueous solution of monomer/water), was used as ionic comonomer (S). As the crosslinker was used 1,1'-divinyl-3,3'-(ethane-1,1-diyl)di(2-pyrrolidone) (CR), which was synthesized as shown previously [10].

Network Preparation: A series of networks, statistical copolymers of *N*-vinylcaprolactam and 1-vinyl-2-pyrrolidone (mole ratios of VCL/VP = 1/0, 0.9/0.1, 0.8/0.2, 0.7/0.3 and 0.5/0.5) with various amounts of the ammonium salt (mole fractions, $x_s = 0, 0.005, 0.01$ and 0.02) and various amounts of the crosslinker (mole fractions, $x_{CR} = 0.016, 0.024, 0.032$ and 0.048), were prepared by γ -radiation copolymerization in a water/ethanol mixture (0.5/0.5 by volume) in glass ampoules 10 mm in diameter (Table 1). The volume fraction of the mixture of monomers was $v_m = 0.2$. A constant radiation dose, $\gamma = 2$ kGy, was used for polymerization (γ -source ^{60}Co with a dose rate of 0.8 kGy/h, Artim Prague) at room temperature. After crosslinking, the copolymers were removed from ampoules, cut into 10 mm pieces and extracted with redistilled water. A sample (≈ 1 cm³) was weighed and extracted with a large amount of water for evaluation of the sol fraction. After extraction, this sample was dried under reduced pressure at 90 °C to constant weight. By comparison of its dry weight with the theoretical value, it was found that in all samples, the sol fractions were less than 0.5 wt.%; this means that all the monomers were virtually bound in the network structure.

Swelling and Mechanical Measurements: After extraction, the samples were immersed in water; swelling proceeded at a chosen temperature for a week. Then the swelling degree relative to the dry state, Q , was calculated from

$$Q = 1/v_2 = (\rho/v_m)(D/D^*)^3 = V/V_d \quad (1)$$

Table 1. Composition, swelling and mechanical parameters of poly(*N*-vinylcaprolactam-*co*-1-vinyl-2-pyrrolidone) (VCL/VP) hydrogels

VCL/VP	x_{CR}	x_S	G_1 g cm ⁻²	$v_d \cdot 10^6$ mol cm ⁻³	T_{tr} °C	Q_w	Φ	χ
1.0/0.0	.016	0	34.6	8.53	31	13.6	-	0.520
0.9/0.1	0.016	0	29.8	7.20	33	16.1	-	0.516
0.8/0.2	0.016	0	29.1	7.02	40	17.6	-	0.512
0.7/0.3	0.016	0	30.4	7.28	43	18.5	-	0.509
0.5/0.5	0.016	0	28.6	6.91	53	22.6	-	0.503
1.0/0.0	0.024	0.005	29.8	7.20	45	47.5	0.90	-
0.9/0.1	0.024	0.005	31.9	7.75	51	35.5	0.86	-
0.8/0.2	0.024	0.005	32.7	7.89	53	33.9	0.78	-
0.7/0.3	0.024	0.005	35.7	8.55	65	37.1	0.62	-
0.5/0.5	0.024	0.005	32.2	7.68	70	38.9	0.61	-
1.0/0.0	0.032	0.010	32.0	7.77	51	52.5	0.53	-
0.9/0.1	0.032	0.010	39.8	9.65	62	48.7	0.52	-
0.8/0.2	0.032	0.010	33.3	7.97	68	45.7	0.47	-
0.7/0.3	0.032	0.010	30.2	7.23	70	52.4	0.42	-
0.5/0.5	0.032	0.010	37.2	8.85	-	52.4	0.39	-
1.0/0.0	0.048	0.020	41.3	10.02	63	45.5	0.12	-
0.9/0.1	0.048	0.020	45.2	10.96	67	40.6	0.11	-
0.8/0.2	0.048	0.020	43.9	10.57	81	48.4	0.09	-
0.7/0.3	0.048	0.020	44.8	10.75	83	50.1	0.12	-
0.5/0.5	0.048	0.020	41.5	9.90	-	50.2	0.14	-

x_{CR} and x_S are molar fractions of the crosslinker and ionic salt, respectively; G_1 is the modulus after preparation, v_d is the concentration of elastically active network chains (relative to the dry state), T_{tr} is the transition temperature determined from Fig. 1 as temperature corresponding to a half decrease in log Q values from the expanded to the collapsed state, Q_w is the swelling degree in water 22 °C, χ is the Flory-Huggins interaction parameter and Φ is correction factor for the degree of ionization of fixed charges.

where D^* and D , respectively, are sample diameters after preparation and swelling in water at various temperatures, V and V_d are the swollen and dry sample volumes, v_2 is the volume fraction of the dry polymer in the swollen sample and ρ is the dry density ($\rho = 1.23, 1.22, 1.21$ and 1.20 g cm⁻³ for molar ratios of VCL/VP = 1/0, 0.8/0.2, 0.6/0.4 and 0.5/0.5, respectively). From v_m also the volume fraction of dry copolymer network at network formation, $v_1 = v_m/\rho$, can be determined. The diameters were measured with a travelling microscope (Abbe comparator).

Mechanical experiments, at given temperatures, were carried out in a uniaxial compression apparatus [3]. A specimen (10 mm high) was compressed to a ratio λ ($\lambda = l/l_0$ where l and l_0 , respectively, are compressed and initial heights) and force f was measured after 30 s relaxation (sufficient time for attaining equilibrium). Usually ten values of λ and f were determined ($0.8 < \lambda < 1$); the shear modulus G was calculated from Eq. (2) (see Ref. [3])

$$G = f/[S_0(\lambda^2 - \lambda^{-1})] \quad (2)$$

where S_0 is the initial cross-section of the specimen.

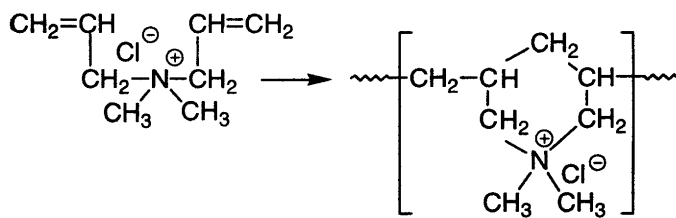
The mechanical experiments were made just after network preparation at room temperature $T_1 = 298$ K (modulus G_1 , Table 1). From G_1 , the concentration of elastically active network chains (EANCs) relative to the dry state v_d was determined from Eq. (3)

$$v_d = G_1 / (R v_1 T_1) \quad (3)$$

where R is the gas constant (Table 1). As T_1 is the same as temperature of network preparation the memory term $\langle \alpha_0^2 \rangle = v_1^{2/3}$ so that the total correction for the dry state is $\langle \alpha_0^2 \rangle = v_1^{1/3} = v_1$ [3]. From moduli G and G_1 , the reduced modulus $G_r = G/G_1$ was calculated.

Results and discussion

Effect of Network Formation Conditions on Network Structure: The synthesis of neat ionized PVCL networks [8] as well as the copolymerization of P(VCL/VP) networks had to be carried out in water/ethanol mixtures as it was not possible to prepare homogeneous aqueous solutions at low initial volume fraction of monomers ($v_m = 0.2$). We believe that the presence of ethanol in the polymerization mixture improves the solubility of growing polymer molecules in the mixed diluent and homogeneous networks can be formed. As follows from Table 1, the moduli G_1 after preparation at constant radiation dose $\gamma = 2$ kGy are virtually constant for individual series with constant amounts of crosslinker, x_{CR} . Hence, the efficiency of radiation crosslinking is not much affected by VP content. From Table 1, it can also be seen that the G_1 values for all series prepared with various contents of the ammonium salts, x_s , are virtually constant (a small exception can be seen for series with the highest x_s) even though the amount of crosslinker increased with increasing salt content. This fact suggests that ionic comonomer (S), though having two double bonds, does not act as a crosslinker. Actually, it was found by Butler et al. [13] that polymerization of diallylammonium salts of the S type in water leads to the formation of linear cyclic structures [10,12] which are incorporated into the chain and thus the positively charged copolymer chains are formed. Similar results were obtained [8,10] for ionized PVCL and PVP hydrogels crosslinked with the same crosslinker in the presence of the same ammonium salt by irradiation; in both cases, a decrease in G_1 with increasing x_s was observed at constant γ . The decrease in G_1 with increasing x_s was interpreted by a transfer reaction followed by isomerization and ring closure of the radicals [10].



Swelling and Mechanical Behaviour. A continuous change in the swelling degree Q in water with increasing temperature can be seen in Figure 1. Incorporation of VP, the more hydrophilic component, results in a pronounced shift of the transition region from the expanded (at low temperatures) to collapsed (at high temperatures) state to higher temperatures in all the four series; at the same time, the steepness of the transition region decreases. From $\log Q$ vs. T dependences, the transition temperatures T_{tr} were determined as temperatures corresponding to a half decrease in $\log Q$ values from the expanded to the collapsed state (Table 1). From Table 1 it can be seen that both the increasing VP and S contents shift the transition to higher temperatures very efficiently (by more than 20 °C). This indicates that with increasing VP and with increasing salt content, the extent of

hydrogen bonding increases and water becomes a better solvent for gels. Accordingly, no temperature transition was observed earlier [10] for uncharged PVP gels in water. These results can be helpful in practical application of hydrogels. They show the possibility of adjusting T_{tr} by changing the composition of the copolymer. Generally, the samples were transparent at the beginning of the transition and became opalescent and finally turbid at the highest temperatures. The turbidity indicates the existence of a two-phase structure in gels with concentrated and dilute phases. Such structures were observed earlier for PDEAAm and PNIPAAm [9] hydrogels. The dependences of the reduced shear modulus, $G_r = G/G_1$ on temperature are also shown in Figure 1. As expected, a decrease in the volume of the gel is reflected in an increase in the reduced shear modulus. For all copolymers, continuous dependences of G_r on T are observed.

The dependences of the reduced modulus, $\log G_r$ on $\log Q$ for four series of copolymers with constant x_s are plotted in Figure 2. For comparison, the predicted rubber elasticity slope, s , for the dependence of $\log G_r$ vs $\log Q$, $s = -0.33$, is also shown [3]. For uncharged hydrogels, departures from a straight line in the region of low swelling degrees ($\log Q < 0.5$) can be seen; the larger increase in G_r is probably due to the influence of the main transition region (vitrification) at high temperatures due to low swelling.

The value of $s = -0.33$, independent of charge concentration, was also found [8] for charged poly(1-vinyl-2-pyrrolidone) networks. On the other hand, the value of $s = -0.7$, independent of charge concentration, was found [3] for charged polyacrylamide (PAAm) networks in water/acetone mixtures. A swelling dependence of the modulus with the slope $s = -5/6$ was recently suggested by the theory of Rubinstein et al. [14] based on the scaling concept of the polyelectrolyte chain. As a good correlation exists between the change in volume and the modulus, we can conclude

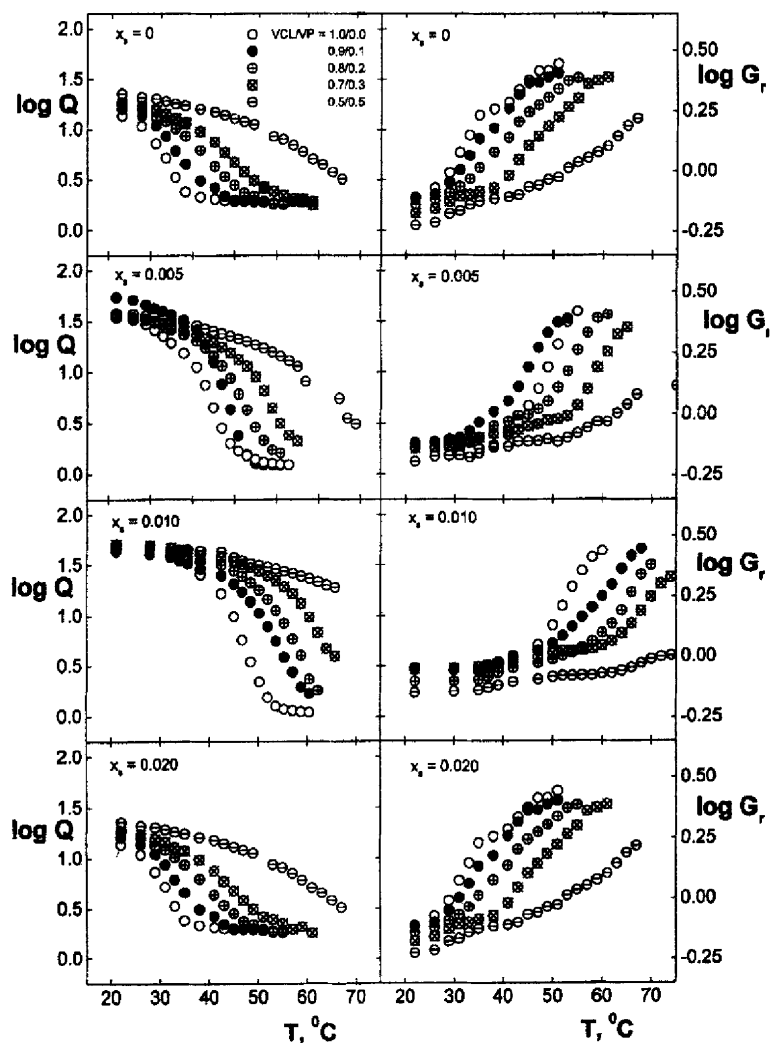


Figure 1. Dependence of swelling degree in water Q and the reduced modulus $G_r = G/G_1$ on temperature for indicated VCL/VP compositions and x_s values

that mechanical behaviour of all the hydrogels is predominantly determined by the swelling degree. As can be seen from Table 1, the swelling degree Q_w in water at 22 °C slightly increases with increasing content of VP comonomer in the series of uncharged networks, in accord with a more hydrophilic character of the VP comonomer in comparison with VCL. As expected, an increase in Q_w values with increasing content of the ammonium salt was found; on the other hand, no systematic changes in Q_w were found while increasing VP contents in individual series at constant x_s .

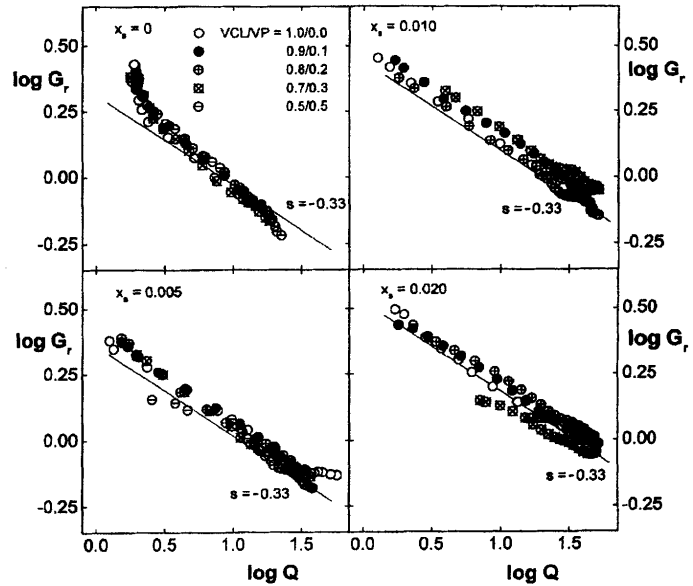


Figure 2. Dependence of the reduced modulus $G_r = G/G_1$ on the swelling degree Q for indicated VCL/VP compositions and x_s values

Comparison of Swelling Data with a Theory of Polyelectrolyte Networks. Several models have been suggested for describing the swelling of gels on the degree of ionisation [1]. For comparison of swelling results with theory, we will use our generalized model in which the effects of repulsion of charges fixed on the chain and finite chain extensibility are included [2]. In this model, all molecular parameters are independently accessible. This theory semiquantitatively described the collapse phenomenon in water/acetone mixtures and in aqueous NaCl solutions of various charged gels [3,8,10]. The theory predicts the swelling pressure P as a sum of four terms [2,3]

$$P = \mu_1/V_1 = P_m + P_{el} + P_{os} + P_{els} \quad (4)$$

where μ_1 is the chemical potential of the solvent, V_1 is the molar volume of the solvent; P_m is the mixing term given by mixing solvent molecules with chain segments (Flory-Huggins equation with interaction parameter χ); P_{el} is the elastic term (based on the affine deformation model) given by the change in elastic energy with swelling, in which finite chain extensibility was included; P_{os} is the osmotic term given by mixing network ions with the solvent and P_{els} is the electrostatic term determined by interaction (repulsion) of charges on the chain. The individual terms P_i of Eq. (4) were expressed in network molecular parameters [3]: concentration of elastically active network chains v_d (Table 1), density of polymer ρ , degree of ionization $\alpha = x_s$, average molecular weight of monomer units, molar volume of water V_1 , volume fraction of dry polymer at network formation v_1 and the relative permittivity of water, $\epsilon = 80$. Using Eq. (4), the dependence of the interaction parameter χ on the volume fraction of dry polymer in the swollen state, $v_2 = 1/Q$, can be calculated from experimental equilibrium Q values measured at various temperatures (as the data were collected for free swelling, $P = 0$ in Eq. (4)) by employing the same procedure described in detail earlier [3].

The application of Eq. (4) to the uncharged series (for $\alpha = x_s = 0$, $P_{os} = P_{els} = 0$, classic Flory-Huggins equation is obtained) and using the Q_w values measured at 22 °C (expanded state of gels, Table 1), leads to the values of interaction parameters χ shown in Table 1. As expected, χ slightly decreases with increasing VP content due to an increase in Q_w values (for the uncharged PVCL network swollen in water, the value of $\chi = 0.522$ was found earlier at 20 °C [8]); for all copolymers these values are higher than 0.5. The decrease in χ indicates that increasing content of hydrophilic VP in copolymers slightly increases the overall hydration of P(VCL/VP) chains in pure water. Finally, from Q data of uncharged networks measured at various temperatures (Figure 1), a universal increase in χ with increasing v_2 was obtained (Figure 3a), independent of the VP content in hydrogels. Such universal dependences were observed earlier [8].

As expected, the swelling degree in water Q_w , measured at 22 °C increases with increasing content of charged groups x_s in the chain (Table 1). Similarly to previous case [3,8,10], the use of Eq. (4) for ionic networks with the degree of ionization $\alpha = x_s$ gives unrealistically high χ values as calculated from Q_w (for networks of various compositions with $x_s = 0.005$, 0.01 and 0.02, the χ values in the region 0.55-0.60, 0.58-0.70 and 0.82-0.85 were calculated). Since, as mentioned in the used theory, χ is a measure of polymer-water interactions when all charges are screened (the effect of charges is included in P_{os} and P_{els} terms), χ values shown in Table 1 for uncharged networks may be, in the first approximation, required also for corresponding ionic hydrogels swollen in water at 22 °C. With this requirement, the Q_w data shown in Table 1 can be described by Eq. (4) assuming that the effective degree of ionization α^* is lower than the salt concentration, i.e., $\alpha^* = \alpha\Phi = \Phi x_s$, where Φ is the correction factor. This factor is related to the activity coefficient of counter-ions, and to clustering of counter-ions due to possible heterogeneity of highly dilute networks. The Φ values thus calculated lie in the range 0.11-0.90 (Table 1) and are strongly dependent on the content of the ammonium salt in hydrogels (with increasing x_s , the Φ values decrease). While for the ionized series with $x_s = 0.005$ and 0.01 a decrease in Φ is observed with increasing VP content, for the series with the highest $x_s = 0.02$, Φ was found virtually independent of composition.

Finally, using known molecular parameters and the effective degree of ionisation, $\alpha^* = \Phi x_s$, the dependence of χ on v_2 was calculated from Q values measured at various temperatures (Figure 1) for all ionized samples. A continuous universal dependence of χ on v_2 for all samples, regardless of their composition and ionic salt concentration, was found (two

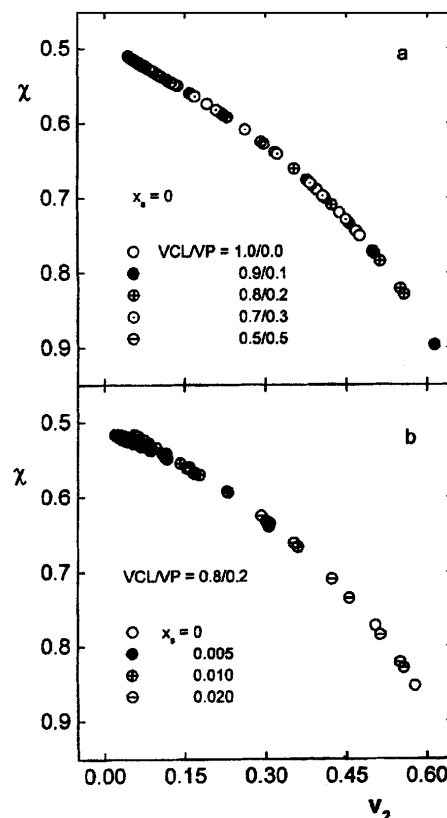


Figure 3. An example of dependence of the interaction parameter χ on the volume fraction of the dry network in swollen gel $v_2 = 1/Q$ for indicated VCL/VP compositions and x_s values

examples of such dependences for networks, with constant $x_s = 0$ in Fig. 3a and constant ratio VCL/VP = 0.8/0.2 in Fig. 3b are shown). As was discussed previously [2,3], the van der Waals loop in the dependence of χ on v_2 is a necessary condition for the appearance of a jump in the gel volume (collapse). Such dependences were found earlier for many ionized network systems swollen in mixed solvents or in water at various temperatures [1,3,9,10]. Detailed examination of Eq. (4) has revealed [3] that the necessary condition for the van der Waals loop appearance is water being a good solvent for uncharged polymer ($\chi < 0.5$). As $\chi > 0.5$ was found for all uncharged copolymer networks at 22 °C, no jump in volume was found for ionized P(VCL/VP) gels.

The phase state of our P(VCL/VP) gels in water is determined by interactions of polar and non-polar groups on the chain and their interaction with water molecules. As $\chi = 0.495$ and $\chi = 0.520$ were found for PVP [8] and PVCL [10] uncharged networks in water, the decreasing bulkiness of the side group of VP has increased the overall hydration of the P(VCL/VP) chains as the number of hydrophobic groups in the side chain of the VP monomer decreased. In aqueous solutions of linear PVCL, it was found [15] that macromolecules adopt more or less dense conformations with hydrophobic micelle-like structure near LCST. Such structure can be promoted by chemical junctions in network; due to this structure only one continuous transition can be seen in Figure 1 for all gels.

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References

1. Dušek K (ed) (1993) Responsive Gels: Volume transition I and II, Adv Polym Sci 109 and 110
2. Ilavský M (1981) Polymer 22:1687
3. Ilavský M (1993) Adv Polym Sci 109:173
4. De Rossi D, Kajiwara K, Osada Y, Yamauchi A (eds) (1991) Polymer Gels Fundamentals and Biomedical Applications, Plenum Press, New York
5. Bekturov EA, Bakauova ZKh (1986) Synthetic Water Soluble Polymers in Solution, Huethig-Wepf Verlag, Basel, p. 242
6. Mikhaeva EE, Thanh LTM, Starodubtsev SG, Khokhlov AR (1996) Macromol Chem Phys 197:1973
7. Mikheeva LM., Gringerg NV, Mashkeevich AZa, Grinberg VK, Thanh LTM, Makhaeva EE, Khokhov AR (1997) Macromolecules 30:2693
8. Mamytbekov G, Bouchal K., Ilavský M (1997) Eur Polym J 35:1925
9. Blanco MD, Trigo RM Garcia O, Teijon JM (1997) J Biomater Sci, Polym Ed 8:709
10. Mamytbekov G, Bouchal K, Ilavský M, Bekturov EA (1998) Polym J 30:713
11. Yoshida R, Uchida K, Kaneko Y, Sakai K, Kikuchi A, Sakurai Y, Okano T, Nature (1995) 374:240
12. Shin BC, Jhon MS, Lee HB, Yuk SH (1998) Eur Polym J 34:171
13. Butler GB, Crawshaw A, Miller WL (1958) J Am Chem Soc 80:3615
14. Rubinstein M, Colby HR, Dobrynin VA, Joanny J-F (1996) Macromolecules 29:398
15. Kirsh Yu E (1993) Prog Polym Sci 18:519