Polymer Bulletin 43, 109–116 (1999)

Polymer Bulletin

Phase transition in swollen gels

27. Effect of negative charge concentration on swelling and mechanical behaviour of poly(*N*-vinylcaprolactam) gels

M. Ilavský[1,2,], G. Mamytbekov[2,*], K. Bouchal[2], L. Hanyková[1]**

[1] Faculty of Mathematics and Physics, Charles University, CZ-180 00 Prague 8,
Czech Republic
[2] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
CZ-162 06 Prague 6, Czech Republic

Received: 14 December 1998/Accepted: 16 June 1999

Summary

Ionized networks of copolymers of *N*-vinylcaprolactam with charged comonomer, sodium itaconate (mole fraction of ionic comonomer x_s = 0-0. 1) and of a crosslinker, 3,3'-(ethane-1,1-diyl)bis(1-vinyl-2-pyrrolidone) were prepared by radiation polymerization in water/ethanol mixture (H_2O/Et = 0.3/0.7 by vol.) and their swelling; mechanical behaviour in water was investigated as a function of temperature. On heating, a decrease in the swelling degree was observed. Increasing x_s shifts the volume transition temperature T_{tr} from the swollen to shrinked state to higher temperatures; in all cases, this transition is continuous. The observed decrease in swelling with temperature is accompanied by an increase in equilibrium modulus, so that mechanical behaviour is predominantly determined by swelling. The swelling of hydrogels can be in the first approximation described by the theory of polyelectrolyte networks in which repulsion of charges on the chain and finite chain extensibility were considered. In accord with this theory, as the Flory-Huggins interaction parameter χ = 0.522 for the uncharged network swollen in water, no jumpwise change in volume with increasing temperature was observed.

Introduction

One of the advantages of hydrogels consists in their capability of exhibiting a first-order phase transition (collapse) caused by a small change in external conditions such as temperature, electric field, solvent compositions (1). The presence of charges on the chain (~ 1-10 mole %) seems to be an important condition for the occurrence of a jumpwise change in gel volume (2-4). Most results were obtained with charged copolymers of acrylamide/ionic comonomers (solvent composition-sensitive gels), *N*,*N*-diethylacrylamide/ionic comonomers and *N*-isopropylacrylamide/ionic comonomesr (temperature-sensitive) hydrogels (1). This phenomenon, in particular temperature-induced collapse, can be used in practical applications (5).

Crosslinked poly(*N*-vinylcaprolactam) (PVCL) nonionic hydrogels have shown under heating one sharp continuous shrinking region (6), while DSC experiments have revealed (7) that this 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). It seems that ionic PVCL hydrogels have not been studied yet; one can expect that introduction of charges into the chain can lead to appearance of the 1st-order phase transition in these hydrogels depending on temperature.

In this work we investigate the effect of concentration of the negatively charged comonomer on the temperature dependence of swelling and mechanical behaviour of the poly [N-vinylcaprolactam-*co*-(sodium itaconate)] hydrogels in water.

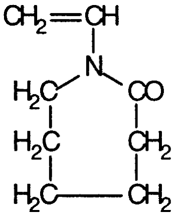
---

[*] Participant of the UNESCO-sponsored postgraduate course. On leave from Academy of Sciences of Kazakh Republic

[**] Corresponding author

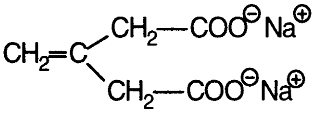
Experimental

Materials: *N*-vinylcaprolactam (Fluka)



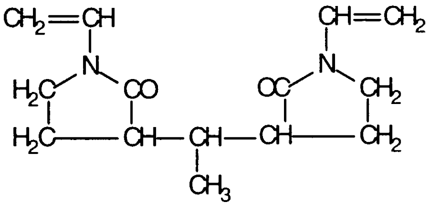
(VCL)

was distilled in vacuum at 76 °C/13 Pa. Itaconic acid (Fluka) was transformed to the sodium salt (S) by neutralization with aqueous NaOH solution



(S)

and was used as ionic comonomer. As a crosslinker (CR) was used 3,3'-(ethane-1,1-diyl)bis(1-vinyl-2-pyrrolidone)



(CR)

which was synthesised according to ref. (8).

Network preparation: Ionic networks, copolymers of *N*-vinylcaprolactam (VCL) with various amounts of sodium itaconate (ITNa, mole fraction, $x_s = 0 - 0.1$, Table 1) were prepared by γ-radiation copolymerization with various amounts of crosslinker (CR) (mole fraction $x_{CR} = 0.01 - 0.03$, Table 1) in water/ethanol mixture (0.3/0.7 by vol.). The volume fraction of mixed monomers was $v_m = 0.2$. Glass ampoules 10 mm in diameter were used as polymerization reactors and a required radiation dose γ-source Co^{60} with a dose rate of 0.8 kGy/h, Artim Prague) was used.

Table 1. Composition, swelling and mechanical parameters of ionic poly(*N*-vinylcaprolactam) hydrogels

Hydrogel	γ kGy	x_s	x_{CR}	G_l g cm^{-2}	$\nu_d\ 10^5$ mol cm^{-3}	T_{tr} °C	Q_{20}	ϕ
S1	2	0.000	0.01	66.8	1.65	32	13.4	–
S2	2	0.010	0.01	57.5	1.41	34	20.5	0.42
S3	2	0.030	0.02	42.9	1.06	36	27.2	0.27
S4	3	0.050	0.02	95.9	2.36	39	29.5	0.19
S5	4	0.070	0.03	100.2	2.46	50	32.1	0.13
S6	5	0.100	0.03	104.0	2.56	-	35.3	0.10

x_s is the mole fraction of ionic salt (ITNa); x_{CR} is the mole fraction of crosslinker (CR); γ is the radiation dose; G_l is the modulus after preparation; ν_d is the concentration of elastically active network chains relative to the dry state, T_{tr} is the transition temperature from the swollen to shrinked state, Q_{20} is the swelling degree at 20 °C and ϕ is the correction factor.

After crosslinking, the samples were removed from ampoules and cut to pieces of 10 mm in length and extracted with redistilled water. A sample ~ 1 cm^3 in volume was weighed and extracted in a large amount of water for evaluation of the sol fraction. After extraction, this sample was subsequently dried in vacuum at 90 °C to constant weight; from comparison of its dry weight with the dry weight theoretically expected it was found that in all samples, the sol fractions were less than 0.5 wt.%; this means that all three comonomers were completely bound in the structure.

Swelling and mechanical measurements: After extraction, the samples were kept at a chosen temperature (T) for about three days after which the inverse swelling ratio X, relative to the network formation state, was calculated from (4)

$$X = (D^*/D)^3 = V^*/V \tag{1}$$

where D^* and D, respectively, are sample diameters after preparation and swelling at temperature T, and V^* and V are the corresponding sample volumes. The diameters were measured with a travelling microscope (Abbe comparator). From X values, the volume fraction of dry polymer in the swollen state $v_2 = v^1 X$ (where $v^1 = v_m/\rho = 0.163$ is the volume fraction of dry polymer at network formation, $\rho = 1.23$ g/cm^3 is the dry density, $v_m = 0.2$) or the swelling degree relative to the dry state, $Q = 1/v_2$, were determined.

The mechanical experiments at given temperature were carried out in uniaxial compression. The specimen (10 mm high) was compressed to a ratio λ ($\lambda = l/l_o$ where l and l_o, respectively, are compressed and initial heights) and force f was measured after 30-s relaxation (time sufficiently long for attaining equilibrium). Usually ten values of λ and f were determined ($0.8 < \lambda < 1$); the shear modulus G was calculated from (4)

$$G = f/[S_o (\lambda^2 - \lambda^{-1}] \tag{2}$$

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

The mechanical experiments were done after preparation at room temperature (modulus G_1, Table 1) and with samples swollen to equilibrium in water at different temperatures (modulus G). From G_1, the concentration of elastically active network chains (EANCs) relative to the dry state ν_d was determined from

$$\nu_d = G_1/(Rv^1T^1) \tag{3}$$

where R is the gas constant and $T^1 = 298$ K is the network preparation (room) temperature (Table 1). From moduli G and G_1, the reduced modulus

$$G_r = G/G_1 \tag{4}$$

was also calculated.

Results and discussion

Effect of network formation conditions on their structure. The ionized network synthesis of the VCL had to be carried out in water/ethanol mixture as it was not possible to prepare homogeneous aqueous VCL solutions with low initial volume fractions of monomers, $v_m = 0.2$. As follows from Figure 1, the initial modulus after preparation G_1 increases with the radiation dose γ only in the range of the lowest γ. For $\gamma \geq 5$ kGy the G_1 values are virtually constant. From Figure 1 it can be also seen that G_1 decreases with increasing content of ionic comonomer x_s; for $x_s = 0.1$, the G1 value is almost independent of γ. Similar results were obtained (9,10) for poly(1-vinyl-2-pyrrolidone) crosslinked with the same CR by irradiation; in this case, the G_1 independence of γ (for $\gamma \geq 5$ kGy) and a decrease in G_1 with

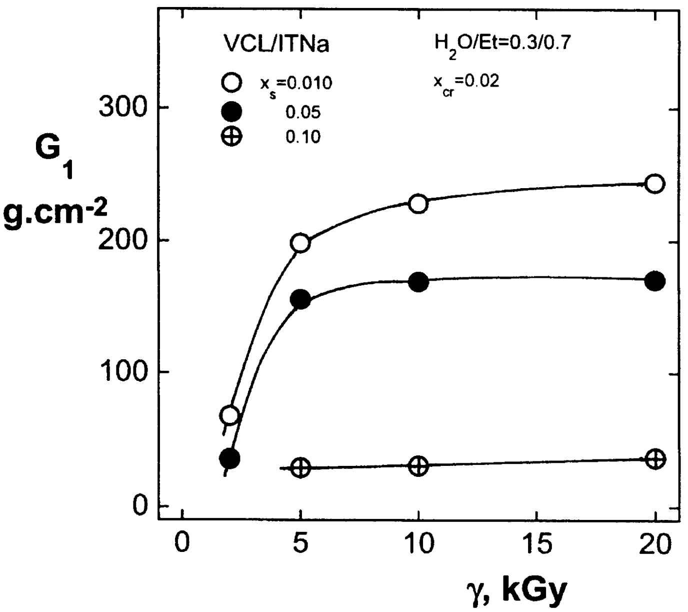


Figure 1. An example of measured dependence of modulus G_1 on radiation dose γ

increasing x_s at constant γ were also observed. We believe that the ethanol present in polymerization mixture causes a better solubility of growing polymermolecules in mixed diluent. The G_1 independence of γ suggests a negligible role of radiation crosslinking for $\gamma \geq 5$ kGy and the decrease in G_1 with increasing x_s means that the probability of chain transfer to the ionic comonomer increases with x_s. The results presented in Figure 1 allowed us to specify the network formation conditions used for preparation of samples S1-S6 shown in Table 1.

Swelling and mechanical behaviour. The dependence of the inverse swelling ratio X on temperature *T* is shown in Figure 2. On heating, only continuous transition from the expanded to shrinked gel state for all gels can be seen. One can see that increasing ionic comonomer concentration x_s shifts the transition temperature interval to higher temperatures. For the highest $x_s = 0.10$, there only a small increase in log X values appears up to 70 °C. As usually a jumpwise change in the volume of charged gels is observed (1), the continuous transition found for charged PVCL hydrogels is unexpected and will be discussed later.

From the dependences of log X on *T*, the transition temperatures T_{tr} were determined (Table 1) as temperatures corresponding to half increases in log X values going from the swollen to shrinked state. From Table 1, it can be seen that increasing charge concentration shifts the T_{tr} to higher temperatures quite efficiently (~ 20 °C for $x_s = 0.07$). The samples are transparent at the beginning of the transition, then become opalescent and finally turbid at highest temperatures. The turbidity indicates the coexistence of a stable two-phase structure with the dense and dilute phase. Such structure was observed earlier for PDEAAm (11) and PNIPAAm (12) hydrogels. While the transparent structure is homogeneous, the turbid one is due to microsegregates formed inside the gel. These microsegregate domains are due to a temperature change in inter- and intramolecular interactions (13) such as: (1) hydrophobic interactions associated with the change in water structure in the vicinity of chain; (2) non-polar interactions of hydrocarbon parts of side chains; (3) hydrogen bond interactions between carbonyl groups and water molecules.

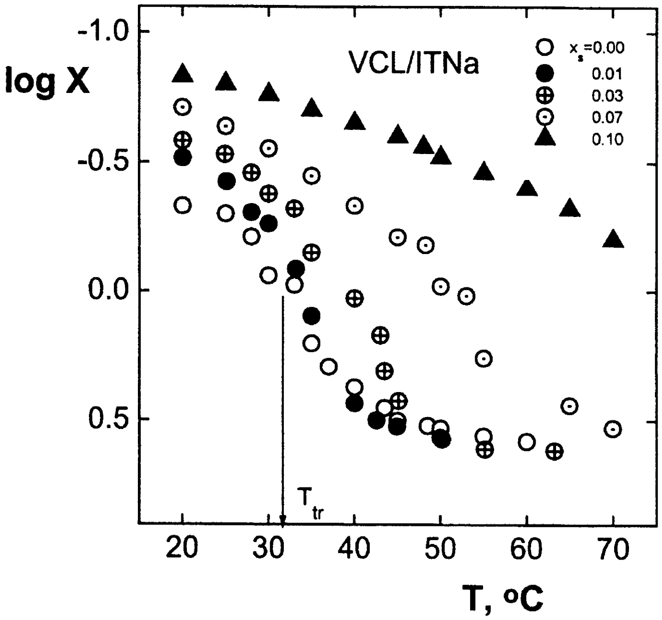


Figure 2. Dependence of the inverse swelling ratio X on temperature in water for gels with indicated ionic comonomer mole fractions x_s

The dependence of the reduced modulus, log G_r on log X measured at various temperatures is plotted in Figure 3. For comparison, the predicted rubber elasticity slope (s = 0.33) is also shown. It can be seen that they deviate from the theoretical slope s = 1/3 in the range of low (log X > 0.5) and high (log X < -0.5) swellings. We believe that departures at low swellings are due to vitrification (increase in G_1 due to the influence of the main transition) while those at high swellings are due to finite extensibility of the chain (4).

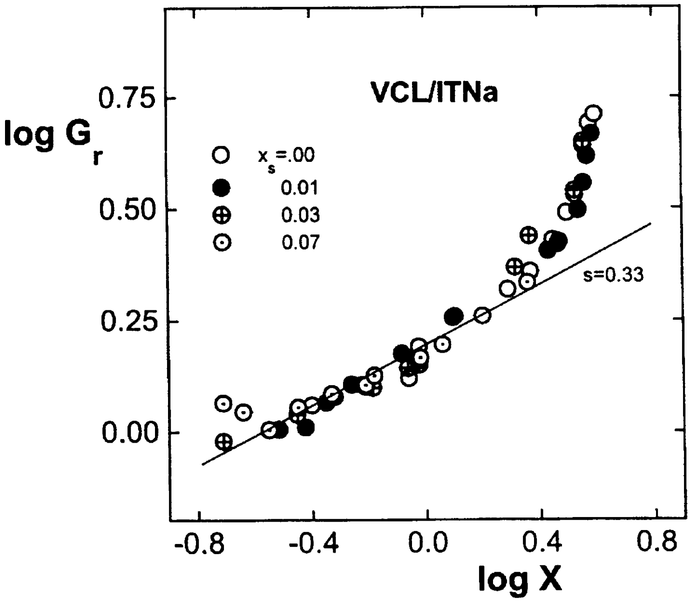


Figure 3. Dependence of the reduced modulus $G_r = G/G_l$ on the inverse swelling ratio X for variously ionized gels (the slope s = 0.33 is predicted by the rubber elasticity theory)

Comparison of swelling data with the theory of polyelectrolyte networks. Several models have been suggested for describing the swelling degree of charged gels (1,3,4). For comparison of our swelling results with theory, we will use the generalized model in which the effects of repulsion of charges on the chain and finite chain extensibility were included (3); 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 (4). The theory predicts the swelling pressure P as a sum of four terms (3)

$$P = \mu_1/V_1 = P_m + P_{el} + P_{os} + P_{els} \qquad (5)$$

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 the mixing of solvent molecules with chain segments (Flory-Huggins equation with interaction parameter χ), P_{el} is the elastic term 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 the interaction (repulsion) of bound charges on the chain. The individual terms P_i of eq.(5) were expressed in network molecular parameters (3): concentration of elastically active network chains ν_d (Table 1), density of polymer $\rho = 1.23$ g cm^{-3}, degree of ionization $\alpha = 2x_s$, average molecular weight of monomer unit M_0, molar volume of water $V_1 = 18.1$, dilution at network formation $v^1 = 0.163$ and the permittivity of water $\varepsilon = 80$. Using eq.(5), the dependence of the interaction parameter χ on the volume fraction of dry polymer in the swollen state, $v_2 = V^1X = 1/Q$, can be calculated from experimental equilibrium X (or Q) values measured in water (as the data were collected for free swelling, P = 0 in eq.(5)) by employing the same procedure described in detail earlier (3,4).

As expected, the swelling degree in water Q at 20 °C increases with increasing content of charged groups in the chain x_s (Table 1, Fig. 4). The use of eq.(5) for the uncharged case ($\alpha = 2x_s = 0$, P_{os}, $= P_{els} = 0$) gives the value of interaction parameter $\chi = 0.522$; from X data for the uncharged network measured at various temperatures (Fig. 2),

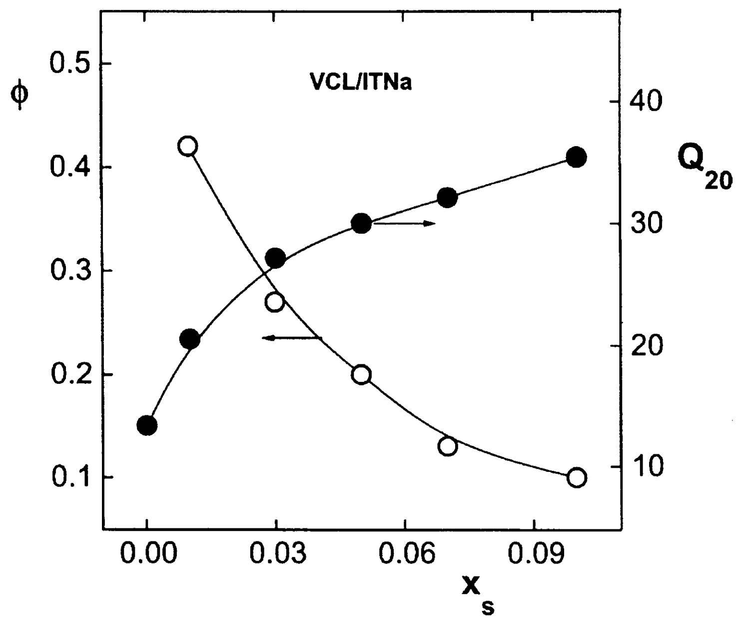


Figure 4. Dependence of swelling degree Q measured in water at 20 °C and of correction factor ϕ on the mole fraction of ionic comonomer x_S

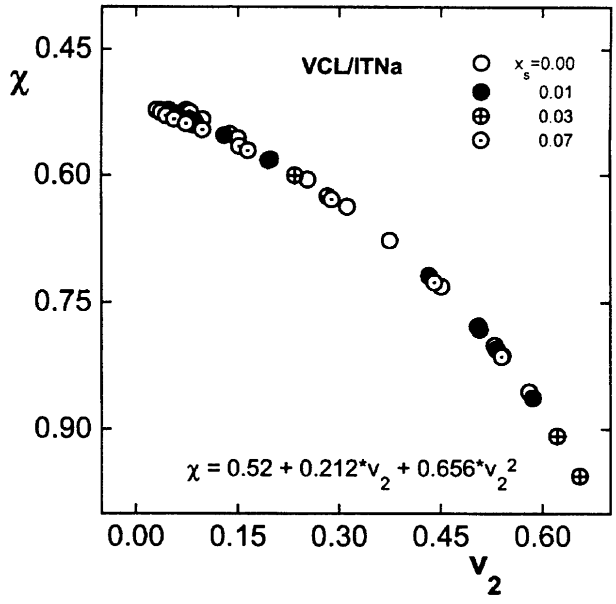


Figure 5. Dependence of interaction parameter χ on the volume fraction of the dry network in the swollen state v_2 measured in water at various temperatures for gels with indicated ionic comonomer mole fractions x_s

the dependence of χ on v_2 was obtained (Fig. 5). Similarly to the previous case (9,10), for water swollen ionic networks with the degree of ionization $\alpha = 2x_s > 0$, eq.(5) gives unrealistic high χ values calculated from X measured at 20 °C (for $x_s = 0.01$, 0.03, 0.05, 0.07 and 0.10, the values $\chi = 0.560$, 0.650, 0.820, 1.150, and 2.850 were found). Since, as it was introduced 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), $\chi = 0.522$ may be, in the first approximation, required also for all ionic hydrogels swollen in water at 20 °C. With this requirement, the Q data shown in Fig. 4 can be described by eq.(5) assuming that the effective degree of ionization α^* is lower than the salt concentration, i.e. $\alpha^* = \alpha\phi = 2\phi x_s$, where ϕ is the correction factor. This factor is related to the activity coefficient of counter-ions, especially for the highest x_s values, or to clustering of counter-ions due to possible heterogeneity of highly diluted networks. The ϕ values thus calculated lie in the range ~ 0.1-0.45 (Fig. 4).

Using known molecular parameters and the degree of ionization $\alpha^* = 2\phi x_s$, the dependence of χ on v_2 was calculated from swelling in water, X, at various temperatures (Fig. 5) for all the ionized samples. As follows from Fig. 5, a continuous universal dependence χ on v_2 was found. As was discussed previously (1,3), the van der Waals loop in the dependence of χ on v_2 is a necessary condition for the appearance of a jumpwise change in the gel volume (1st-order phase transition). Such dependences were found for many ionized network systems swollen in mixed solvents or in water at various temperatures (1,3,4,9). Detailed examination of eq.(5) has revealed (3) that the necessary condition for the van der Waals loop appearance is that water is a good solvent for uncharged polymer ($\chi < 0.5$). As $\chi = 0.522$ was found for uncharged network at 20 °C, no 1st-order transition was found for ionized PVCL gels

The phase state of PVCL gel in water is determined by interactions of polar and nonpolar groups in the chain and water molecules. As for a poly(1-vinyl-2-pyrrolidone) network in water, $\chi = 0.495$ was found (9), increasing length of the side group of

N-vinylcaprolactam has decreased the overall hydration of PVCL chain as number of hydrophobic groups in side chain of monomer increased. In aqueous solutions of linear PVCL, macromolecules adopt more or less dense conformation with hydrophobic micelles-like structure near LCST (13,14). Such structure can be promoted by chemical junctions in network. High-sensitive DSC measurements of uncharged PVCL gel revealed two cooperative transitions in water (7). Only one continuous transition at ~ 32 °C can be seen in Figure 2, which was found in the previously published (6) swelling curve of uncharged PVCL gel.

Acknowledgement

The financial support of Ministry of Education of the Czech Republic (Project No VS 97115) and of the Grant Agency of the Charles University (Grants Nos 46/1998/B and 72/1998/B) is gratefully acknowledged. For irradiation of samples, we thank Dr M. Řeřichová from Artim Co., Prague, Czech Republic

References

1. Dušek K (ed), Responsive Gels: Volume Transitions I and II, Adv Polym Sci 109 and 110(1993).
2. Tanaka T, Fillmore DJ, Sun ST, Nishio L, Swislow G, Shak S (1980) Phys Rev Lett 45:1636.
3. Ilavský M (1981) Polymer 22:1687.
4. Ilavský M (1993) Adv Polym Sci 109:173.
5. De Rossi D, Kajiwara K, Osada Y, Yamauchi A (eds). Polymer Gels. Fundamentals and Biomedical Applications. Plenum Press, New York 1991.
6. Makhaeva EE, Thanh LTM, Starodubtsev SG, Khokhlov AR (1996) Macromol Chem Phys 197:1973.
7. Mikheeva LM, Grinberg NV, Mashkevich AYa, Grinberg VI, Thanh LTM, Makhaeva EE, Khokhlov AR (1997) Macromolecules 30:2693.
8. Haaf F, Sanner A, Straub F (1985) Polym J 17:143.
9. Mamytbekov GK, Bouchal K, Ilavský M, Bekturov EA (1998) Polym. J. 30:713.
10. Mamytbekov GK, Bouchal K, Ilavský M, Eur Polym J, submitted.
11. Ilavský M, Hrouz J, Havliček I (1985) Polymer 26:1514.
12. Zhang X, Hu Z, Li Y (1997) J Appl Polym Sci 63:1851.
13. Kirsh YuE (1993) Prog Polym Sci 18:519.
14. Kirsh YuE, Sus TA, Karaputadze TM, Kobyakov VV, Sinitsina LA, Ostrovskii SA (1979) Vysokomol Soedin 21A:2734.