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Phase transition in swollen gels

30. Temperature-induced phase transition in positively charged poly(N-isopropylacrylamide) hydrogels in water and aqueous NaCl solutions

A. Fomenko[1], Z. Sedláková[2], M. Ilavský[1,2]

[1] Faculty of Mathematics and Physics, Charles University, 180 00 Prague 8, Czech Republic
[2] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
162 06 Prague 6, Czech Republic
e-mail: ilavsky@kmf.troja.mff.cuni.cz, Fax: +420-2-6885095

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Summary

The swelling and mechanical behaviour of ionized networks of *N*-isopropylacrylamide with an ionic comonomer, (2-acrylamidoethyl)trimethylammonium chloride (mole fractions x_S = 0-0.1), in the presence of a crosslinker, *N,N'*-methylenebisacrylamide, was investigated in water as a function of temperature and in aqueous NaCl solutions ($c_{NaCl} = 10^{-5} - 1$ M) at 23 °C. On heating, a continuous decrease in the swelling degree in water, Q_w, was observed; increasing x_S shifts the volume transition temperature, T_{tr}, (from the swollen to collapsed state) to higher temperatures. The expected decrease in the swelling degree, Q, with increasing NaCl concentration in aqueous NaCl solutions was observed and two shrinking regions in ionic gels were found. The decrease in Q_w with increasing temperature and the decrease in Q with increasing c_{NaCl} are accompanied by an increase in equilibrium shear modulus of gels, so that the mechanical behaviour of gels is predominantly determined by the swelling degree. The experimental swelling behaviour could 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.

Introduction

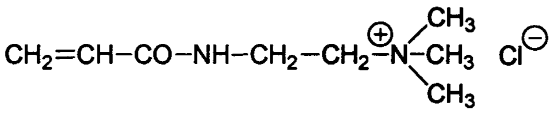
The first order phase transition (collapse) in polyelectrolyte hydrogels, caused by a small change of external condition such as temperature, electric field, pH and solvent composition, has received considerable attention in literature [1-3]. The presence of a low number of charges on the chain (~ 1−10 mol %) seems to be a necessary condition for the existence of a jumpwise change in the gel volume. SANS experiments showed that in the expanded state, the chains have a coil shape, while in the collapsed state they are in globular form [4]. It has been shown, both experimentally and theoretically, that the conditions of network formation (concentration of crosslinker and diluent) and of the charge concentration have a great influence on the appearance and extent of the collapse. The jump in volume is accompanied by a jump in other physical properties, such as shear modulus, refractive index, dielectric permittivity [1,2]. Most experimental results were obtained with charged poly(acrylamide)

(PAAm), poly(*N*-isopropylacrylamide) (PIPAAm), and poly(*N,N*-diethylacrylamide) (PDEAAm) hydrogels [1-3,5]. While in PAAm gels, the collapse can be brought about by the changes in the solvent composition, in PIPAAm and PDEAAm gels, the transition can be induced in water, by the temperature change.
Ionized PIPAAm gels with negative charges bound to the chains (as ionic comonomer, sodium acrylate was used, mole fractions $x_S = 0–0.1$) were already extensively investigated [2,6]; collapse was found in these networks in water dependent on temperature. Both, the extent of the collapse and transition temperature increased with increasing charge concentration. It was also shown [3] that the polarity and structure of the ionic comonomer plays a role in the collapse appearance and extent. In this contribution, we investigate swelling and mechanical behaviour of positively charged PIPAAm hydrogels in dependence on temperature in water and in aqueous NaCl solutions at room temperature. As an ammonium salt is used as ionic comonomer, we can consider full salt dissociation in water.

Experimental

Material

Commercial non-ionic monomer, *N*-isopropylacrylamide (IPAAm, Fluka) and a crosslinker, *N,N'*–methylenebisacrylamide (CR, Fluka) were used as received. As positively charged comonomer (S), (2-acrylamidoethyl)trimethylammonium chloride was used



$$CH_2{=}CH{-}CO{-}NH{-}CH_2{-}CH_2{-}\overset{\oplus}{N}(CH_3)_3 \quad Cl^{\ominus}$$

(S)

which was synthesized as shown previously [7].

Preparation of networks

Ionic networks, copolymers of IPAAm with various amounts of ionic comonomer S (mole fraction of salt $x_S = 0–0.1$) and a constant mole fraction of crosslinker (x_{CR} = 0.003), were prepared by radiation polymerization. Glass ampoules, 10 mm in diameter (D^*), were used as polymerization reactors. After preliminary experiments, final network formation conditions (constant radiation dose of γ = 2 kGy and the volume fraction of all monomers in the system $v_m = 0.1$) were chosen for eight ionic networks. The basic requirements for network formation was to achieve a roughly constant modulus after network preparation G_1 (i.e., constant concentration of elastically active network chains at network formation, Table 1). After crosslinking copolymerization, the networks were removed from ampoules, cut into pieces ~ 10 mm in height and extracted with redistilled water.

Swelling and mechanical measurements

After extraction, the samples were immersed in 100 ml of water or in 100 ml of aqueous NaCl solutions ($c_{NaCl} = 10^{-5} – 1$ mol/l). Swelling proceeded at achosen temperature (T) for four days or in aqueous NaCl solutions for one month, after which the inverse swelling ratio X relative to the state of network formation was determined from [7,8]

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

where D^* and D, respectively, are the sample diameters after preparation and swelling at various temperatures or in aqueous solutions, respectively, and V^* and V are the corresponding swelling volumes. The diameters were measured with an Abbe comparator (accuracy ≈ 0.002 mm). From the X values, the volume fractions of dry polymer in the swollen state, $v_2 = v^0X$ (where $v^0 = v_m/\rho$ is the volume fraction of dry polymer at network formation, $\rho = 1.06$ g/cm^3 is the density of dry networks) and the swelling degrees relative to the dry state, $Q = 1/v_2$, were calculated (Q_w in water or Q in NaCl solutions).

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

x_S	G_1 g cm^{-2}	$\nu_d \cdot 10^3$ mol cm^{-3}	Q_w (23 °C)	T_{tr} °C	ϕ
0	43.3	1.776	27.63	30.7	-
0.01	43.2	1.771	69.07	40.9	0.671
0.02	46.4	1.908	126.56	47.8	0.495
0.03	46.7	1.920	156.06	51.7	0.371
0.04	47.2	1.938	206.21	55.0	0.345
0.05	43.3	1.775	221.98		0.303
0.07	46.9	1.927	258.41		0.238
0.10	45.3	1.861	333.66		0.196

x_S is mole fraction of ionic comonomer (S), G_1 is the modulus after preparation, $_d$ is the concentration of elastically active network chains (relative to the dry state), T_{tr} is the temperature of the transition from the expanded to the collapsed state, Q_w is the swelling degree in water at 23 °C and ϕ is correction factor for the degree of ionization of fixed charges.

Several copolymers after removing from ampoules and cutting into 10-mm pieces (~ 0.85 cm^3 in volume) were extracted with 10 cm^3 of redistilled water for the evaluation of sol fraction and ammonium salt determination. After extraction, samples were dried in vacuum at 90 °C to constant weight. By comparison of their dry weights with theoretical dry weights, it was found that in all samples, the sol fractions were less than 0.5 wt.%; this means that all the monomers were bound in the network structure. The same conclusions were obtained from the mercurimetric titration with 0.001 M $Hg(ClO_4)_2$. In this case, it was proved that virtually no ammonium salt was present in the extracted solutions.

Mechanical measurements were carried out in uniaxial compression in the earlier described apparatus [8]. The specimen, ~ 10 mm high, was compressed at the ratio λ ($\lambda = l/l_0$, where l and l_0 are the compressed and initial heights) and force f was measured after 15 s of relaxation. Usually 10 values of λ and f were determined. The shear modulus G was determined from the equation [7,8]

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

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

Swelling and mechanical experiments were carried out with samples immediately after preparation at room temperature (modulus G_1, Table 1) and with the samples swollen to equilibrium in water at various temperatures in the range 15–90 °C or in aqueous NaCl solutions (modulus G) at 23 °C. Using modulus G_1, the concentration of elastically active network chains relative to the dry state was calculated from (8)

$$\nu_d = G_1/(RT^0 v^0) \tag{3}$$

where R is the gas constant and T^0 = 296 K is the network preparation temperature (Table 1).

Results and discussion

Swelling and mechanical behaviour in water

The dependences of the inverse swelling ratio in water, X, on the temperature, T, is shown in Figure 1. On heating, all gels show only continuous transition from the expanded to collapsed gel state that is reflected in increasing swelling ratio, X. In this respect, our positively charged hydrogels differ from those negatively charged PIPAAm gels prepared with sodium acrylate [6] where a jump change in volume was found. We believe that this difference is associated with the structure of the used ionic comonomers especially with the distance between the charge position and the main chain. It can be seen that increasing charge concentration x_S results in shifting of the transition temperature interval in which continuous collapse takes place, to higher temperatures (Table 1). For two highest concentrations of the charged groups ($x_S \geq 0.07$), there exists only a small increase in X at temperatures up to 90 °C.

From the dependences of log X on T, the transition temperatures T_{tr} were determined as temperatures where the slope d(log X)/dT has a maximum. In the inset of Figure 1 the dependence of T_{tr} on charge concentration is shown together with previously found results for negative charge [6]. In our case the shift of transition temperature is much higher than that for PIPAAm networks with negative charge. This result can be helpful in practical applications of the gels.

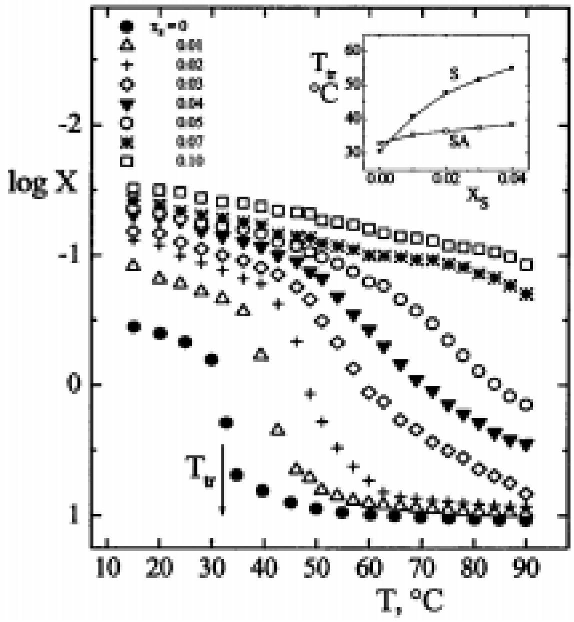


Figure 1. Dependence of inverse swelling ratio, X, on temperature in water for gels with indicated ionic comonomer mole fractions, x_S. In the inset, the dependence of transition temperature T_{tr} found for PIPAAm gels with negative charge [6] (curve SA) is also shown.

The dependence of the shear modulus log G on log Q_w measured in water at various temperatures is shown in Figure 2a. There can be seen some deviations from the predictions of the theory of rubber elasticity (the scaling exponent of G Q^s is expected to be $s = -1/3$), especially for low Q values (in the collapsed state). Katayama [9] has suggested that the deviations at low swelling may be due to complex gel structure in turbid (collapsed state) and transparent (expanded state) gels. While transparent structure is an ordinary homogeneous three-dimensional network, the turbid one is heterogeneous due to microsegregates formed inside the gel. Also vitrification, due to the effect of approaching the glass transition temperature at low swelling, can contribute to the increase in the modulus.

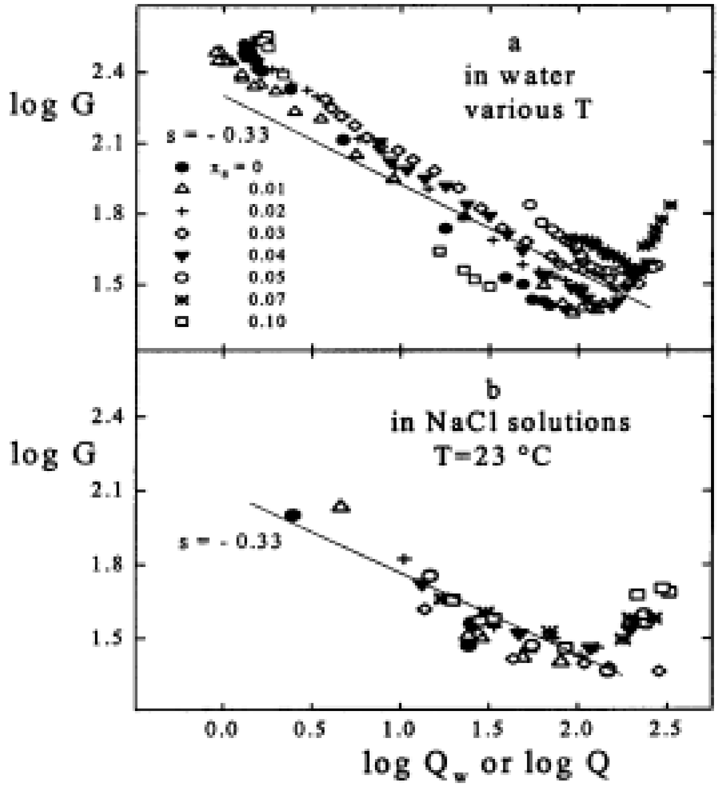


Figure 2. Dependence of shear modulus, G, on swelling degree: (a) Q_w (in water) or (b) Q (in aqueous NaCl solutions) for variously ionized gels

Swelling and mechanical behaviour in aqueous NaCl solutions

The dependences of the swelling ratio in aqueous NaCl solutions, Q, on NaCl concentration, c_{NaCl}, measured at T = 23 °C are given in Figure 3. While for uncharged network, only one transition at the highest NaCl concentrations ($c_{NaCl} \geq 10^{-1}$ M) is observed, for charged networks, two transition regions are clearly detected. The decrease in Q found with charged networks in the expanded state at low c_{NaCl} values ($c_{NaCl} < 0.1$ M) can be associated with increasing concentration of counter-ions (Na^+) in the gel volume with increasing external c_{NaCl} concentrations (Donnan equilibrium). As expected, the transition regions shift to higher NaCl concentrations with increasing x_S (polyelectrolyte effect). In the transitions, external aqueous NaCl concentrations

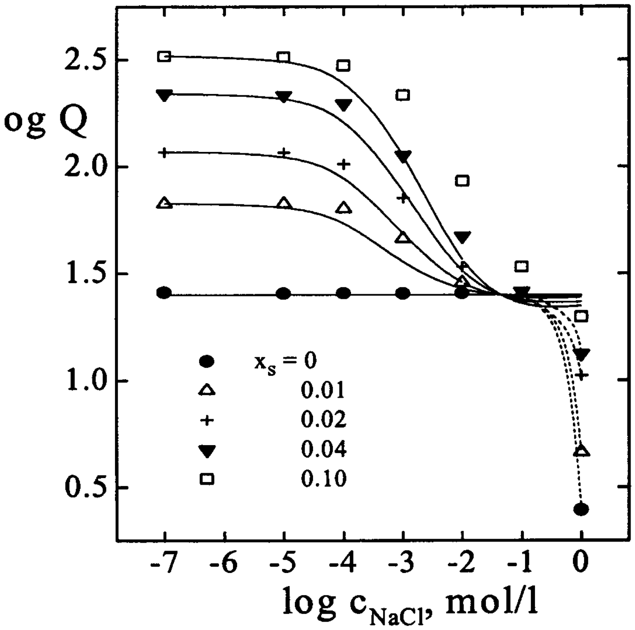


Figure 3. Dependence of swelling degree, Q, on aqueous NaCl concentrations, c_{NaCl}. Lines are theoretical dependences from Eq. (4).

exceed the molar ratios, x_S and screen the charges bound to the chain. The second transition observed at highest NaCl concentrations, $c_{NaCl} \geq 0.1$ M for all networks are due to suppression of phase transition temperature of PIPAAm by NaCl. A similar effect was observed earlier for charged poly(*N*-vinylcaprolactam) hydrogels [10].

Comparison of the theory of swelling equilibria for polyelectrolyte networks and experiment

Several models for interpretation of thermodynamic properties of charged gels have been suggested [2,11,12] in which also the effect of repulsion of charges on the chain and finite chain extensibility were included. For comparison of experimental swelling data with theoretical prediction, we use the theory discussed in Refs [8,11]. This theory predicts the swelling pressure P as a sum of four terms

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

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 of solvent 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 the finite chain extensibility was included, P_{os} is the osmotic term given by mixing of network ions with the solvent, P_{els} is the electrostatic term determined by the interactions (repulsion) of charges on the chain. For the uncharged case, only two first terms in Eq. (4) remain as the degree of ionization $\alpha = 0 = x_S$, i.e., $P_{os} = P_{els} = 0$. From the knowledge of network parameters (v_d, ρ, v^0, determined independently), and using reduced Eq. (4), the dependence of the interaction parameter χ on the volume fraction of dry polymer in the swollen state, v_2, could be calculated from experimental v_2 (or Q_w) values of the uncharged network measured in water at various temperatures (Figure 4). As swelling

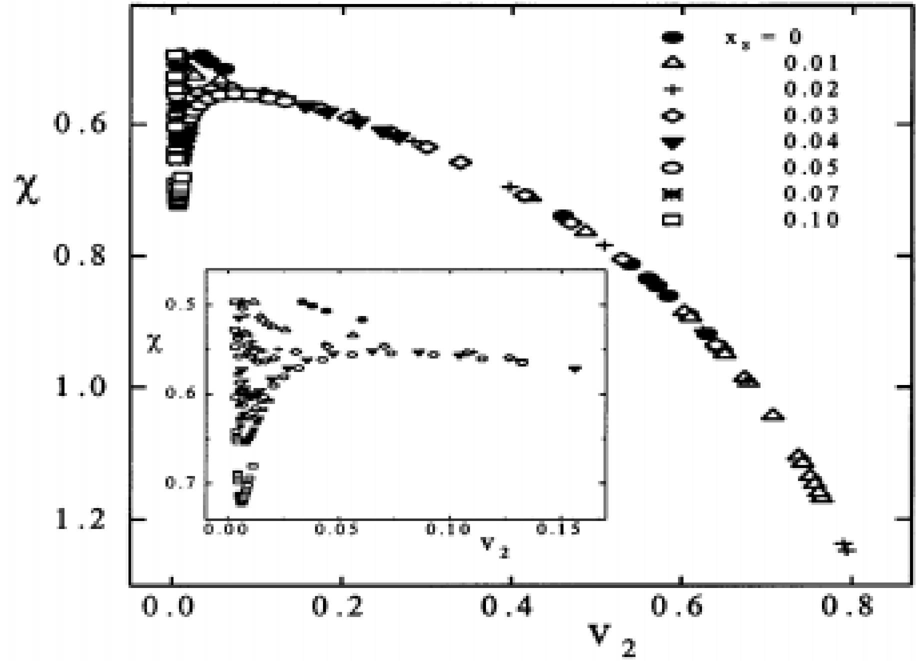


Figure 4. Dependence of interaction parameter, χ, on volume fraction of dry network in the swollen state, v_2, measured in water at various temperatures for gels with indicated ionic comonomer mole fractions, x_S.

data were collected for free swelling, $P = 0$ in Eq. (4). In such way, the value of $\chi = 0.496$ was found at 23 °C. As expected, with increasing v_2 (increasing temperature), χ values of uncharged network increase as the overall hydration of the PIPAAm chains decreases. This is due to increasing extent of the hydrophobic interactions between side groups of IPAAm, which makes water a poorer solvent with increasing temperature.

As can be seen from Table 1, the swelling degree in water at 23 °C, Q_w strongly increases with ammonium salt concentrations. As we know all network parameters (v_d, ρ, v^0), and if we further assume that the degree of ionization $\alpha = x_S$, we can use Eq. (4) for the description of dependence of Q_w on x_S. We obtain unrealistic high χ values (ranging from 0.6 to 10). As it was introduced in the used theory [8,11], χ is a measure of polymer–water interactions when all charges are screened. It is therefore reasonable to require the same value of $\chi = 0.496$ for all charged networks at 23 °C. This requirement is possible to fulfil by the assumption that the effective degree of ionization α^* is lower than the ammonium salt concentration x_S, i.e., $\alpha^* = \phi\alpha = \phi x_S$, where ϕ is the correction factor; the values ϕ in the range ~ 0.67–0.20 were found (Table 1). This factor is related to the osmotic coefficient of counter-ions and to the clustering of counter-ions due to possible heterogeneity of highly dilute networks and accounts for the effects which were not considered in the above discussed theory. Similar ϕ values were found earlier [8] for charged poly(*N*,*N*-diethylacrylamide) hydrogels with sodium methacrylate (MNa) ($\phi = 0.56$–0.38 for $x_{MNa} = 0.005$–0.07).

Using known molecular parameters and the effective degree of ionization $\alpha^* = \phi x_S$, the dependences of χ on v_2 were calculated from X values measured at various temperatures (Figure 1) for all ionized networks (Figure 4). An increase in χ on v_2

regardless of ionic comonomer concentrations was found; the increase in χ with v_2 was commonly observed earlier [8,10,12] being related to the decreasing solvent quality with increasing temperature (as in uncharged network). As was discussed previously [8,11], a van der Waals loop in the dependence of χ on v_2 is a necessary condition for the appearance of a jump change in the gel volume (1st-order phase transition). As follows from the inset in Figure 4, networks with $x_S \geq 0.04$ show the tendency to exhibit such van der Waals dependences. Figure 1 shows that in these networks, a proper collapse state was not achieved at the highest temperatures. We believe that this can be one of the reasons why a jump change in volume was not found in these networks. Another possibility is that Eq. (4) overestimates the effect of charges on swelling equilibria and van der Waals loops in the inset are artificial (e.g., correction factor ϕ should be temperature-dependent).

Equation (4) can be used also for description of swelling degree Q measured in various aqueous NaCl solutions at constant $T = 23$ °C. In this case, as factor ϕ was determined at the same temperature, the use of theory is more grounded. The knowledge of the concentration of mobile co-ions c_{Na^+} inside the gel phase for various external NaCl concentrations, c_{NaCl}, is required together with previously used network parameters. Due to the presence of positive charges on the chain, the c_{Na^+} concentrations inside the gel are lower than that of external c_{NaCl} values. For calculations of c_{Na^+} , we used Eq. (6) from Ref. [13], which was based on Donnan equilibrium analysis. The values c_{Na^+} , together with other network parameters (v_d, ρ, v^0), $\chi = 0.496$ and $\alpha^* = \phi\alpha = \phi x_S$, were used in Eq. (4) for description of the data shown in Figure 3. As can be seen, the calculated Q vs. c_{NaCl} dependences agree reasonably well with experimental ones. For gels with highest ionizations, the theoretically predicted abrupt decrease in swelling is shifted by 0.5 logarithmic decades to lower c_{NaCl} concentrations than experimentally observed ones.

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References

1. De Rossi D, Kajiwara K, Osada Y, Yamauchi A, Eds (1991) Polymer Gels. Fundamentals and biomedical applications. Plenum Press, New York
2. Dušek K, Ed (1993) Responsive Gels, Volume Transition I and II, Adv Polym Sci, vol 109 and 110
3. Ilavský M, Bouchal K (1988) In Biological and Synthetic Polymer Networks, Elsevier, London
4. Pleštil J, Ostanevich Yu, Borbely S, Stejskal J, Ilavský M (1987) Polym Bull 17:465
5. Saito S, Kanno M, Inomata H (1993) Adv Polym Sci 109:207
6. Hirotsu S (1993) Adv Polym Sci 110: 1
7. Ilavský M, Sedláková Z, Bouchal K, Pleštil J (1995) Macromolecules 28:6835
8. Ilavský M, Adv Polym Sci (1993) 109:173
9. Katayama S (1967) J Phys Chem B 101:10607
10. Mamytbekov G, Bouchal K, Ilavský M (1999) Eur Polym J 35:1925
11. Ilavský M (1981) Polymer 22:1687
12. Onuki A (1993) Adv Polym Sci 109:63
13. Mamytbekov G, Bouchal K, Ilavský M, Bekturov EA (1998) Polym J 30:713