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TEMPERATURE - SENSITIVE POLYZWITTERIONIC GELS

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Summary: An abrupt change in the polyzwitterionic swelling ratio as a function of the temperature, sodium chloride concentration and chemical crosslinking density is established. These results are reasonably explained by the model presuming zwitterionic cluster formation in the segments between the chemical junction points. The zwitter-ionic clusters, produced at low chemical crosslinking density only, act as temperature- and salt concentration-dependent physical junction points. An irreversible temperature-stimulated swelling-shrinking behaviour of the polyzwitter-ionic hydrogels (swelling ratio-temperature hysteresis loop) at low chemical cross-linking density is also observed and analysed.

INTRODUCTION

Abrupt volume phase transitions in certain polymeric hydrogels caused by small changes in solvent composition [Refs. 1-6], temperature [Refs. 1, 6-9], pH [Ref. 10], ionic composition [Ref. 10], or by application of electric field across the gel [Ref. 11] have been extensively investigated in recent years. Each hydrogel system has its own unique chemistry, which determines to a great extent its swelling and deswelling characteristics. The specific properties of polyelectrolyte gels are related to the ionic nature of the chains and have been under intensive investigation during the last decade [Refs. 12-17]. Polyzwitterions (PZI) are polyampholytes (PA) in the isoelectric state, with two charges with opposite signs located on a separate monomer unit. They are now recognized as wellidentified classes of polymeric materials showing a broad spectrum of very specific and unique properties in solution and in the bulk, arising from the highly dipolar character of their functional unit (dipole moment values in the range 20-30 D) [Refs. 18-33]. They find application in water treatment, remediation, petroleum recovery, viscosification, formulation of coatings, cosmetics and pharmaceutics [Refs. 34-36], textile dyeing [Refs. 37, 38], emulsion properties improvement [Ref. 39], drug reduction [Ref. 40]. The antipolyelectrolyte behaviour, the absence of counterion condensation and the negligible Donnan effect in the PZI solutions and hydrogels

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characterize them as PA in the isoelectric state [Ref. 41]. However, their unique thermotropic phase behaviour seems to be the distinctive specific property of PZI which is not inherent to conventional PA [Refs. 41, 42]. An original model for a qualitative analysis of these properties has been developed [Refs. 41, 42], assuming a heterogeneous structure organization of PZI solutions and hydrogels as a result of the interaction between zwitterionic pendant groups. According to this model, the electroneutrality of these systems is due to the formation of the intragroup ionic pair (IG, Fig. 1a) and the zwitterionic clusters produced by the specific entropy-profitable "zip"-reaction between zwitterionic dipoles of different pendant groups (ZC, **Fig. 1b, c**). Depending on the temperature, PZI concentration and molecular weight, pH, and ionic strength, the dynamic equilibrium between IG, short (ZC_S) and long (ZC_L) ZC (1) is postulated:

$$ZG \rightleftharpoons ZC_S \rightleftharpoons ZC_L \qquad (1)$$

In the present report, the influence of this equilibrium on the PZI hydrogel properties is investigated. It is important to note that only ZC, produce the physical junction points in these hydrogels.

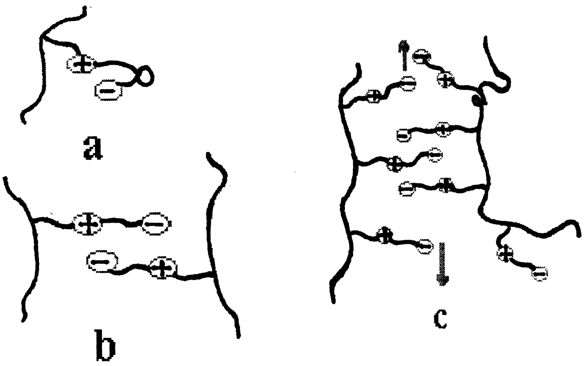
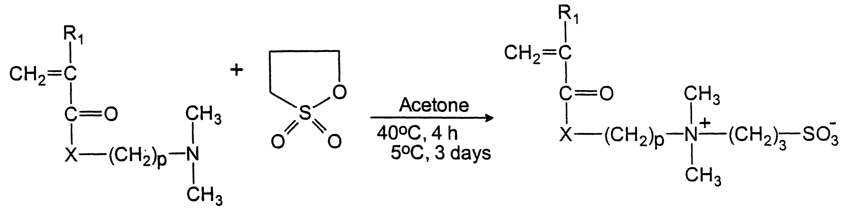


Figure 1. Scheme of the intragroup (**IG**) ionic pairs (**a**), inter/intra-macromolecular short zwitterionic clusters, (**ZC_S**) (**b**), and long inter/intramacromolecular zwitterionic cluster, (**ZC_L**), produced by the entropy-profitable zip-propagation mechanism (**c**). The arrows in Fig. **1c** show the zip-propagation directions.

EXPERIMENTAL

N, N-Dimethyl(methacroylethyl)ammonium propanesulfonate (DMMAPS) and N, N-dimethyl(acrylamidopropyl)ammonium propanesulfonate (DMAAPS) are synthesized through the following scheme [Refs. 21, 43]:



$R_1 = CH_3$; X = O; p = 2 - DMMAPS; R_1 = H; X = NH; p = 3 - DMAAPS

Scheme 1. ***Synthetic route to the zwitterionic monomer production***

Aqueous solutions of the zwitterionic monomer (30, 40, 50 wt %), ethyleneglycol dimethacrylate (EGDM) as a crosslinking agent (0.2, 1.0, 2.0, 5.0 wt %), ammonium peroxodisulfate (0.1 wt %) and tetramethylethylenediamine (0.05 wt %) are prepared gravimetrically in siliconized glass cylindrical tubes (Φ = 8 mm). The polymerization is carried out at room temperature for 24 h, then the hydrogels are washed in a large amount of deionized water for 4 weeks (water is changed daily) to wash out low molecular weight compounds from the hydrogels. Dry hydrogel samples are prepared after water evaporation at 75°C and final drying in a vacuum oven at 40°C for 48 h.

The swelling ratio (SR) of the synthesized PZI hydrogels is determined gravimetrically as the ratio of the mass of gel swelling in water or in salt solution (m) and the mass of the dry gel (m_o). It was assumed that the studied systems attained equilibrium when the mass of the samples did not change for 4 days. Most experiments are performed over a period of 5 days.

RESULTS AND DISCUSSION

1. Temperature-stimulated swelling and contraction of PZI gels in deionized water

Temperature SR dependences of the PDMAPS hydrogels produced at different EGDM concentrations are presented in **Fig. 2**. Two peculiarities of these dependences are worth discussing. The first one is that the sharp SR increase (**Fig. 2**, curve 4) in the transition temperature region could be observed only at low EGDM concentration ($C_{EGDM} < 1.0$ wt %). The SR transition value decreases at higher cross-linking agent concentrations and even fades away at very high ones.The second one is that the temperature region of the SR transition is approximately that where the PZI hydrogels and concentrated PZI solutions become transparent. This coincidence shows that the abrupt change in SR could be related to the temperature-stimulated transformation of the PZI hydrogel physical (noncovalent) crosslinking.

At a dense chemical network (high EGDM concentration) such transformations are impossible because the segments between the covalent junctions are quite short.

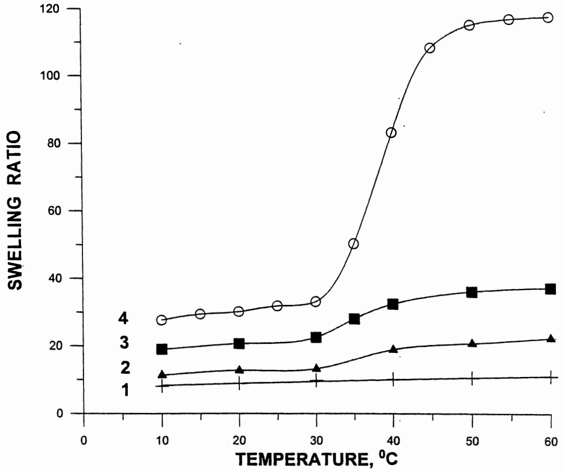


Figure 2. Swelling ratio as a function of the temperature of the PDMAAPS hydrogels, produced at the following monomer and cross-linking agent concentrations: **1**: $C_{DMAAPS} = 30.0$; 40.0 and 50.0 wt %, $C_{EGDM} = 5.0$ wt %; **2**: $C_{DMAAPS} = 40.0$ wt %, $C_{EGDM} = 2.0$ wt %; **3**: $C_{DMAAPS} = 40.0$ wt %, $C_{EGDM} = 1.0$ wt %; **4**: $C_{DMAAPS} = 40.0$ wt %, $C_{EGDM} = 0.2$ wt %;

The driving force for both IG and ZC is the coulombic interaction. IG are formed between the two opposite electrical charges of the particular zwitterionic pendant group, while ZC are produced from two and more dipoles of two or more pendant zwitterionic groups (**Fig. 1**) [Ref. 41, 42]. This structural difference between IG and ZG results in a distinct influence of these two types of associates on the conformation state of the PZI macromolecules or the PZI segments between any two arbitrary chosen covalent junction points of the PZI hydrogel. IG do not affect this conformation state while the ZC formation is virtually the physical node formation (**Fig. 3**), having a considerable influence on the conformation state of the two PZI macromolecules as a whole, and on the aforementioned segments between the junction points, too. For the discussed PZI hydrogels with short segments between the covalent nodes (PZI

Figure 3. Scheme of the PZI hydrogel with chemical (○ , EGDM bridges) and physical (■▬, ZC) junction points.

○ - chemical, ■▬ - physical (ZC_S and ZC_L) junction points.

gels produced at high EGDM concentration), the gel electroneutrality could be due to the IG formation only. The impossibility for the conformational variation of these short segments, in this case, practically excludes the ZC formation, i. e., an additional temperature dependent physical cross-linking could not be realized. For this reason, the SR temperature-dependent variations in PZI hydrogels, produced at high EGDM concentration is not observed.

The probability of formation of ZC with different length and density, and of temperature-stimulated conformation transformations of the internode segments increases with the growth of the length of these segments (EGDM concentration diminution). In practice, this means a shift of equilibrium (1) to the right. The temperature is the determining external factor for the realization of this possibility. Equilibrium (1) is shifted to the left with the temperature increase, to the dominant IG formation, providing the gel electroneutrality. In doing so, the additional physical cross-linking decreases and the SR value tends to its maximum, determined by the degree of chemical cross-linking. In an opposite case, with the temperature decrease, equilibrium (1) shiftes more and more to the right. ZC, produced at these temperatures, causes an additional physical cross-linking of the PZI gel, and as a result, the abrupt SR decrease is observed. Naturally enough, this effect should appear in both PZI solutions and PZI hydrogels: in the former, it is manifested by the clear temperature-stimulated sol-gel transition [Ref. 41] and in the latter - by the sharp SR variation of the PZI gels with low degree of chemical cross-linking (**Fig. 2**) discussed here.

The quantitative analysis of the suggested explanation of the abrupt PZI hydrogel swelling in a specific temperature region could be performed by the modified *T. Tanaka* et al. [Ref. 44] dependence for the equilibrium swelling of the polyampholite gels. Despite the advantages of this relationship, over other simulations of the polyampholite gels [Refs. 12, 45-51] to account for the contributions of the mixing, elasticity, ion transport and coulombic interaction to the total free energy of swelling, its modification is imposed because it does not account for the nonhomogeneous charge distribution in the PZI solutions and hydrogels [Refs. 41, 42]. These peculiarities and, in particular, that the difference between the two electrical charges of these solutions and hydrogels $N_{f+} - N_{f-} = 0$, and the Donnan potential $\Phi_D = 0$ are partiallty taken into account in the following equation for the equilibrium swelling of the PZI gels:

$$-\frac{1}{v_{site}}\left[\ln(1-\phi)+\phi+\chi\phi^{2}\right]+\frac{\phi_o}{N_x v_{site}}\left[\frac{1}{2}\left(\frac{\phi}{\phi_o}\right)^{1/3}\right]$$

$$-\frac{A}{24}\frac{N_{fe}}{N_A V}\frac{e^2}{\pi\varepsilon k_B T}\left(\frac{1+kr}{r}\right)\exp(-kr)=0 \qquad (2)$$

where v_{site} is a lattice site volume, Φ and Φ_0 are the PZI volume fraction after and before the swelling, χ is the PZI solvent interaction parameter, N_x is the average number of monomers between crosslinks, $N_{fe} = N_{f+} + N_{f-}$, V is the hydrogel volume, A is the Madelung constant order than unity, *e* is the electron charge, N_A is Avogadro's number, k_B is the Boltzmann constant, *r* is the nearest neighbor distance between charges, such that

$$r \approx 2\left(\frac{3V}{4\pi N f_e}\right)^{1/3}, \qquad (3)$$

and *k* is the reciprocal Debye length in the hydrogel

$$k = \left(\frac{e^2 N_A C_o 10^3}{\varepsilon k_B T}\right)^{1/2}, \qquad (4)$$

and $C_o = C_{H+}$. The first term of equation (2) accounts for the mixing contribution, the second one - for the elasticity contribution, and the third - for the contribution of the electrostatic interaction to the total swelling free energy. From this equation it becomes clear that its third negative term should decrease with the temperature rise. One possibility for the compensation of this term reduction is the diminution of the second (elasticity) term because of both the Φ value reduction, and the growth in N_x. However, with the V increase, the reduction of the third term becomes more considerable due to both the presence of V in third term denominator and the increase in *r*. From this discussion, one gets the impression that the ratio between these two terms reflects the temperature-stimulated transformation of the electrostatic interaction between electrical charges and dipoles of the PZI hydrogels (causing the gel shrinking) and the entropy- determined gel stretching of the bent segments between junction points as well as their approximation, in this way, to the limited Gaussian conformation state. However, this equation does not allow the rigorous quantitative analysis of this transformation. Its solution, aiming at the determination of the critical values of the parameters controlling the observed SR variation (**Fig. 2**), confirms this statement. This inadequate description of the experimental results by equation (2) could be related just to the aforementioned nonhomogeneity of the charge distribution which should be reflected in all three terms of this equation. This requires another approach to the development of the relationship of the PZI hydrogel equilibrium swelling, which will be the subject of the next theoretical analysis.

The inability of equation (2) to provide a more rigorous quantitative analysis of the SR temperature dependence (**Fig. 2**), could be also regarded as an indirect proof of the model of the dipole-dipole ZC formation proposed in our previous works [Ref. 41, 42]. More direct evidences of this dipole-dipole association in the PZI hydrogels with a low degree of the chemical cross-linking are the T-SR hysteresis loops, shown in **Fig. 4** (curves 1 - 4) for the reversible gel swelling-shrinking in deionized water and in 0.12 wt % sodium chloride aqueous solution, respectively. These hysteresis dependences are a convincing proof of the metastable structure of the segments between the chemical junctions of the PZI hydrogels. This structure formation testifies to the specific dipole-dipole interactions in these PZI gels, approximates these hydrogels to some biopolymers, where hydrogels show a similar hysteresis dependences [Ref. 52], allows the model investigation of the protein "folding-unfolding" problem, and is of the undisputable applied interest.

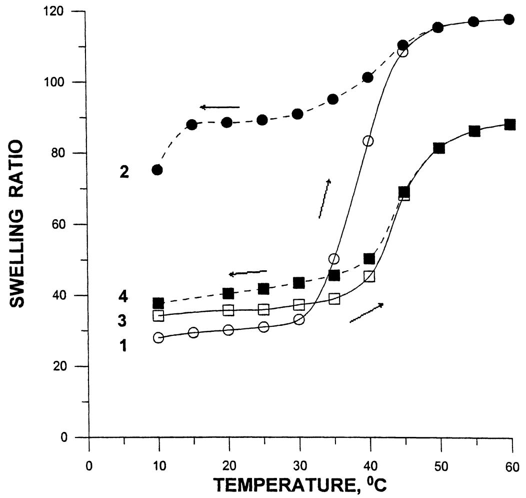


Figure 4. Temperature-stimulated swelling-shrinking hysteresis of the PDMAAPS hydrogels, produced at C_{DMAAPS} = 40.0 wt % and C_{EGDM} = 0.2 wt %. Curves 1 and 2 - deionized water, Curves 3 and 4 - C_{NaCl} = 0.12 wt %; — heating; ---- cooling

2. Temperature-stimulated PZI hydrogel swelling and shrinking in salt aqueous solutions

The temperature dependences of SR of the PDMAAPS hydrogels with a fixed degree of cross-linking (C_{EGDM} = 0.2 wt %), low enough for a considerable conformational variation of the interjunction segments in aqueous solutions with different sodium chloride concentrations, are shown in **Fig. 5.** It is clear that SR increases with the rise of C_{NaCl}. However, it appears that the abrupt change in the SR value decreases with the rise in salt concentration. The first dependence could be explained again by the heterogeneous structure of the PZI solutions and hydrogels composed of IG and ZC [Refs. 41, 42]. The salt addition leads to the destruction of ZC - the physical junction points of the PZI hydrogel. The reduction of the total (chemical and physical) degree of crosslinking (with the sodium chloride increase) results in SR growth. Together with this, the temperature influence on SR decreases as the temperature-sensitive physical junction concentration also decreases with the rise in salt concentration actually, the salt addition effect is a ZC "chemical melting". The process competing the temperature provoked ZC destruction. As is to be expected at temperatures, high enough for a complete ZC destruction, the salt influence is negligible.

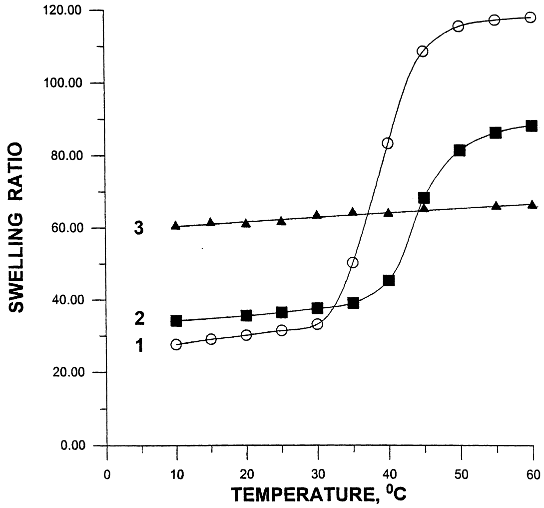


Figure 5.
Swelling ratio as a function of the temperature of the PDMAPS hydrogels, produced at C_{DMAAPS} = 40.0 wt % and C_{EGDM} = 0.2 wt %. 1. swelling in deionized water 2. swelling in aqueous NaCl solution. C_{NaCl} = 0.12 wt % 3. swelling in aqueous NaCl solution. C_{NaCl} = 1.0 wt %

The results obtained prove that at T = const a chemomechanical transformation is possible and it is expressed as SR variation with the salt concentration alteration. According to A. Katchalsky et al. [Ref. 53], the total differential of the thermodynamic potential of the hydrogel discussed is

$$d\Psi = fdl - \varepsilon d\mu_s \qquad (5)$$

where $\varepsilon = (n_s - n^o_s)/ n^o_w$ is the solute enrichment of the gel, n_s, μ_s and n_w , μ_w are the salt and water mole numbers and chemical potentials, respectively.

The last equation could be used to show that ε decreases with the gel shrinking. As dΨ is a total differential, from Cauchy's condition it follows that

$$-\left(\frac{d\varepsilon}{dl}\right)_{\mu_s} = \left(\frac{df}{d\mu_s}\right)_l \qquad (6)$$

Then

$$\left(\frac{df}{d\mu_s}\right)_l = -\left(\frac{dl}{d\mu_s}\right)_f \left(\frac{df}{dl}\right)_{\mu_s}, \tag{7}$$

and because of the salt screening effect, the gel length (l) increases with the salt concentration

$$-\left(\frac{dl}{d\mu_s}\right)_f \prec 0 \tag{8}$$

On the other hand, the multiplier $(df/dl)\mu_s$ is a positive one, as the more gel stretching, the larger force is necessary to overcome the electrostatic interaction between PZI dipoles. From these two inequalities, it follows that

$$\left(\frac{df}{d\mu_s}\right)_s = -\left(\frac{d\varepsilon}{dl}\right)_{\mu_s} \prec 0 \tag{9}$$

The last inequality shows that when the gel is expanded ($- dl < 0$) at a constant salt concentration, the solute ε also increases. This is a phenomenological expression of the consequence of the antipolyelectrolyte PZI properties. Certainly, this phenomenological discussion does not allow to express the detailed structured inhomogeneity of the PZI solutions and gels, and hence, the essential difference between the conventional PA and PZI gels also. To this aim, more vigorous statistical simulations [Ref. 54] are of great importance.

CONCLUSION

It is shown that the model for the PZI solution and hydrogel heterogeneous structure, proposed in our previous works [Ref. 41, 42], allows the temperature-stimulated abrupt changes in SR of PZI hydrogels in deionized water and in salt aqueous solutions to be explained reasonably. To this end the influence of temperature and salt concentration on the PZI gel physical cross-linking expressed by the equilibrium (1) shift is of a crucial significance. The results obtained, and the model used for their explanation, open new possibilities for an amphyphilic copolymer diversification by ZC addition to the classical amphyfile blocks (hydrophilic and hydrophobic, elastomeric and plastomeric, CO_2-phobic and CO_2-philic, etc.).

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