Macromol. Symp. **2004**, *210,* 393-401

Electrostimulated Shift of the Precipitation Temperature of Aqueous Polyzwitterionic Solutions

George Georgiev,[1] Anna Tzoneva,[1] Lyudmil Lyutov,[1] Stefko Iliev,[1] Irena Kamenova,[1] Ventseslava Georgieva,[1] Elena Kamenska,[1] Andreas Bund[2]*

[1]Faculty of Chemistry, University of Sofia, 1, J. Bourchier Avenue, 1164 Sofia, Bulgaria
[2]Institute of Physical Chemistry and Electrochemistry, Dresden University of Technology, D-01062 Dresden, Germany
E-mail: georgs@chem.uni-sofia.bg

Summary: The precipitation temperature (T_{pr}) value of aqueous poly(dimethylamino-ethoxyacryloyl-propylsulphonate) (PDMAPS) solutions decreases with the rise of electric field intensity both in the absence and in the presence of a low molecular salt. This electrostimulated T_{pr} shift is explained qualitatively by means of the model taking into account both the dominating intermacromolecular dipole-dipole interaction and the dipole cluster formation.

Keywords: phase separation; “sol-gel” transition; polyzwitterion

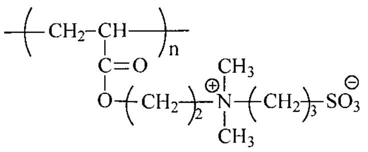
Introduction

The existence of both positive and negative electric charges in some or all the monomer units is a characteristic feature of polyzwitterions (PZ). The specific conformational transitions of PZ macromolecules and their aqueous solution properties (such as antipolyelectrolyte effect [1-3], electroviscosity [4, 5], phase separation [6-8]) are related to the strong dipole-dipole interactions [6-9]. The results obtained [4, 5] stimulated the investigation of the effect of the electric field on the reversible and thermally stimulated “sol-gel” transition in PZ aqueous solutions. The first results of this study are reported here. They are discussed in the light of the recently proposed qualitative model accounting the influence of the vector characteristic of the dipole moment on the dipole-dipole interaction, as a result of which the specific clusters from the antiparallel oriented dipoles (named “zip”-clusters) are formed.

Experimental

Poly(dimethylamino-ethoxyacryloyl-propylsulphonate) (PDMAPS, molecular weight $\overline{M_n} = 7.6 \times 10^4\ g/mol$, molecular weight distribution $\overline{M_w}/\overline{M_n} = 1.3$) was obtained according to a method reported in [2]. The optical transmittance (*Tr*) in electric field

DOI: 10.1002/masy.200450644



(PDMAPS)

of the aqueous PDMAPS solutions was determined by means of a Specol apparatus (Carl Zeiss-Jena) in a glass thermostatic cell with effective sample thickness of 0.5 *cm*. The optical path through the medium was 1.8 *cm*. Tantalum electrodes were placed on the two opposite walls of the cell, thus allowing the control of the changes in the electric field acting on the PZ solution. The distance between the electrodes was 1.1 *cm*. In order to provide a homogeneous electric field in the sample, the electrodes were longer than the cell by 0.3 *cm* at both sides. The electric field applied was perpendicular to the optical path. The precipitation temperature (T_{pr}) of the PDMAPS aqueous solutions used was determined from the maximum of the derivative $d(Tr)/dT = 0$, where T is the temperature.

The temperature dependence of the shear elasticity of the PDMAPS solutions was monitored with a piezoelectric thickness-shear mode (TSM) resonator. The corresponding measuring technique has been fully described earlier [10-12]. In short, the electrical admittance of a piezoelectric quartz crystal was monitored with a network analyzer (R3753BH, Advantest, Tokyo, Japan). Due to the piezoelectric effect the quartz transfers mechanical impedances into electrical ones.

Results and discussion

Electric and temperature effect on the "sol-gel" transition in PDMAPS aqueous solutions

The temperature dependencies of the optical transmittance of PDMAPS aqueous solutions at different PZ concentrations are shown in Figure 1. In the same temperature interval (24-45°C) the sharp transmittance increase is accompanied by a distinct increase of the storage shear modulus as indicated by the TSM resonator (Figure 2). Figure 2 shows only relative values in arbitrary units as no calibration of the TSM resonator was performed. The curves in Figure 1 are used as an origin to account the electric field effect on the "sol-gel" transition in the solutions. The obtained T_{pr} values are given in Table 1. As expected, they increase with the rise in PZ concentration. The shift to the right of the curves depicted in Figure 1 and the solution transmittance decrease with the rise in PDMAPS concentration are corollaries of the increased intermacromolecular interaction. According to the above mentioned model [6, 8, 9], the dipole-dipole interaction between monomer units is predominant, resulting in a dipole-dipole cluster formation according to the "zip"-mechanism ("zip"-clusters) [9].

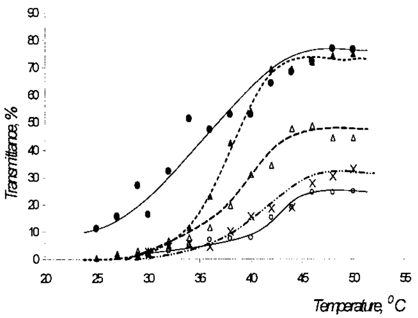


Figure 1. Temperature dependencies of the optical transmittance of PDMAPS aqueous solutions at different PZ concentrations: (●) 0.1, (▲) 0.2, (Δ) 0.3, (x) 0.4, and (○) 0.5 *wt. %*

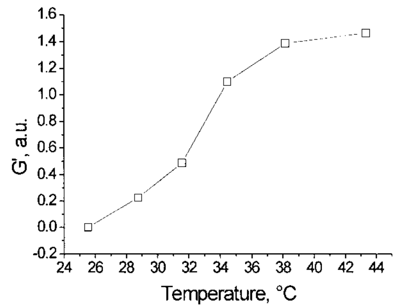


Figure 2. Temperature dependence of the storage shear modulus of 1.0 wt.% PDMAPS aqueous solution.

At higher temperatures, the number, length and structural perfection of these clusters decrease. The intermacromolecular "zip"-clusters form a PZ physical network and its destruction with the rise in temperature is the reason for the observed "sol-gel" transition, characterized by the T_{pr} value (Figure 1).

Table 1. Dependence of T_{pr} and transmittance reached at 50 °C of PDMAPS aqueous solutions on the PZ concentration.

PZ concentration (*wt. %*)	**T_{pr} (°C)**	**Transmittance at 50 °C (%)**
0.1	33.8	76.6
0.2	38.2	73.2
0.3	40.8	48.8
0.4	42.0	32.8
0.5	43.8	24.8

With the rise in PZ concentration, the number of junction points in the physical network also increases. This increase of the network density is a reason for both the T_{pr} increase and the decrease of the transmittance reached at 50 °C of PDMAPS aqueous solutions at higher PZ concentrations (Table 1).

In the presence of electric field, the above mentioned dependencies are shifted to the left (Figure 3 compared to Figure 1). This response to the electric field is in an opposite direction to the increasing PZ concentration effect (Figure 1). The curves depicted in Figure 3 suggest that the higher the E value, the more significant is the displacement against the references obtained at $E = 0$. This is a general trend, observed also with the other investigated PDMAPS concentrations (0.1, 0.2, 0.3, and 0.4 *wt. %*). In Table 2, the T_{pr} values determined from these dependencies are included. They are decreasing with the rise in E, suggesting that the applied electric field, similarly to the increasing temperature, destroys the junction points ("zip"-clusters) of the physical network formed at lower temperatures. This is a consequence of dipole orientation along the field, which is impossible if the "zip"-clusters with random orientation are not destroyed.

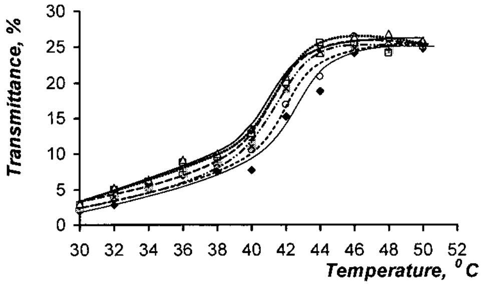


Figure 3. Temperature dependencies of the optical transmittance of 0.5 *wt. %* PDMAPS aqueous solutions at various intensities of the electric field: (♦) 0.0, (○) 1.0, (x) 2.0, (+) 2.4, (□) 3.0, and (Δ) 4.0 *kV/cm*.

Table 2. T_{pr} values of PDMAPS aqueous solutions as dependent of the electric field intensity (E) at different PDMAPS concentrations.

PDMAPS (*wt. %*)	**T_{pr} (°C)**					
	0.0 (*kV/cm*)	**1.0 (*kV/cm*)**	**2.0 (*kV/cm*)**	**2.4 (*kV/cm*)**	**3.0 (*kV/cm*)**	**4.0 (*kV/cm*)**
0.1	33.8	32.4	31.8	30.4	30.2	29.5
0.2	38.2	37.6	37.2	36.6	36.3	35.8
0.3	40.8	38.9	38.6	38.4	38.3	38.0
0.4	42.0	40.0	39.8	39.6	39.2	38.9
0.5	43.8	42.8	42.1	41.8	41.6	41.4

Comparison of the dependencies depicted in Figures 1 and 3 suggests that the concentration effect on the "sol – gel" transition is stronger than that of E in the investigated PDMAPS concentration (0.1 – 0.5 *wt. %*) and E ranges (0 – 4 *kV/cm*). This is clearly seen from the data included in Table 2; the variation along the rows is smaller in absolute value than that in the columns.

It is seen that the curves in Figures 4 and 5 are shifted to the left at higher NaCl concentrations, *i.e.*, the "sol – gel" transition is realized at lower temperatures. Comparison of the dependencies in Figure 4 with those in Figure 1 suggests that the ionic strength influence is in a direction opposite to that of the PZ concentration, both effects being however similar in absolute value. The temperature dependencies registered in the presence of electric field (*E* = 1.0, 2.0, 2.4, 3.0, and 4.0 *kV/cm*) are similar to those of Figure 4. Figure 5 shows the temperature dependencies obtained at the highest value of *E* = 4 *kV/cm*. They all confirm the conclusions drawn from the comparison of Figures 1 and 4.

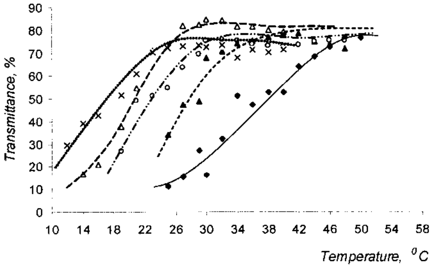


Figure 4. Temperature dependencies of optical transmittance of the 0.1 *wt. %* PDMAPS aqueous solution in the absence of electric field at different NaCl concentrations: (♦) 0.000, (▲) 0.010, (o) 0.050, (Δ) 0.075, and (x) 0.100 *wt %*

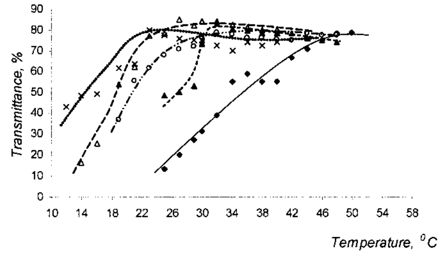


Figure 5. Temperature dependencies of the optical transmittance of the 0.1 *wt. %* PDMAPS aqueous solution in the presence of electric field (*E* = 4 *kV/cm*) at various NaCl concentrations: (♦) 0.000, (▲) 0.010, (o) 0.050, (Δ) 0.075, and (x) 0.100 *wt %*

Comparison of the results presented in Figures 4 and 5 with those of Figure 3 also leads to interesting conclusions. It is clear that the effect of ionic strength and *E* are unidirectional, but ionic strength plays a far more significant role, at least at the studied variation ranges. This conclusion is confirmed also by the observation that the change in *E* does not affect the maximal value of the PDMAPS aqueous solution transmittance (Figure 3) whereas changes in PDMAPS concentration influence considerably this transmittance (Figure 1).

Combined effect of temperature, electric field, and low molecular salt on the "sol – gel" transition in PDMAPS aqueous solutions

The characteristic antipolyelectrolyte effect [1-3] of PZ aqueous solutions is related to the influence of low molecular salts on the dipole-dipole interactions between the monomer units in the PZ macromolecule. For this reason, the analysis of the influence of ionic strength on the electric and thermal effect discussed in the previous section is important.

Figure 6 shows the curves for 0.1 *wt.%* NaCl and 0.1 *wt. %* PDMAPS at different E values. It is clearly seen, that with the rise in *E* values, the temperature dependencies are shifted to the left, *i.e.,* the "sol-gel" transition takes place at a lower temperature. A similar weak displacement of the curves is established also at the other NaCl concentrations. Table 3 includes T_{pr} values determined from the curves of Figures 4 – 6 for the 0.1 *wt. %* PDMAPS aqueous solution. The changes in these numerical characteristics of the investigated "sol – gel" transition are in full agreement with the conclusions drawn from the graphical dependencies: unidirectional effects of ionic strength and *E* on the transitions, that of ionic strength being more significant.

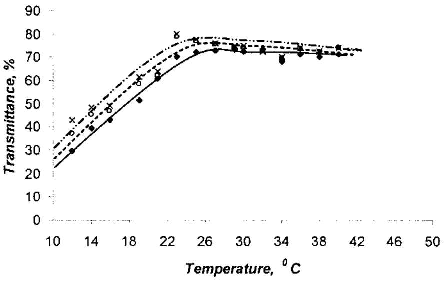


Figure 6. Temperature dependencies of the optical transmittance of the 0.1 *wt. %* PDMAPS aqueous solution in the presence of 0.10 *wt. %* NaCl and electric field with intensity: (♦) 0.0, (○) 2.4, and (x) 4.0 *kV/cm*

The observed salt effect on the "sol-gel" transition should be considered as a new demonstration of the antipolyelectrolyte effect. Actually, the shielding action of the low molecular ions on the dipole-dipole interaction results in the destruction of intermacromolecular "zip"-clusters to a different extent and the transition is realized at lower temperatures; the curves in Figures 4 and 5 are shifted to the left, and the T_{pr} values in all columns of Table 3 decrease.

Table 3. T_{pr} values of the 0.1 *wt. %* PDMAPS aqueous solution as dependent on E and NaCl concentration.

NaCl concentration, (*wt. %*)	**T_{pr} *(°C)***					
	0.0 (*kV/cm*)	**1.0 (*kV/cm*)**	**2.0 (*kV/cm*)**	**2.4 (*kV/cm*)**	**3.0 (*kV/cm*)**	**4.0 (*kV/cm*)**
0.000	33.8	32.4	31.8	30.4	30.2	29.5
0.010	29.5	29.7	29.8	29.6	29.5	29.5
0.050	27.5	25.2	24.8	23.8	24.6	24.4
0.075	20.8	20.4	19.8	19.1	18.8	18.6
0.100	19.8	20.2	19.4	18.9	18.0	16.4

The application of an external electric field in the presence of a low molecular salt has a bilateral effect on the "sol-gel" transition in PDMAPS aqueous solutions. On the one hand, the above mentioned orientational effect of the field should cause additional destruction of intermacromolecular "zip"-clusters and displacement of the temperature dependencies to the left (decrease in T_{pr}), as shown in Figure 6 and Table 3. On the other hand, the higher mobility of low molecular ions compared to that of PZ monomer units results in a decrease of their concentration in the PZ globules, their shielding effect decreases; hence the curve displacement is to the right. The influence of this mobility difference on the electroviscous properties of PZ aqueous solutions has been discussed in more details in previous our works [4, 5]. The observed opposition of the consequences of dipole orientation and different mobilities of low molecular ions and macromolecular zwitterions, hence their compensation, is one of the likely explanations of the weak influence of E on the "sol-gel" transition. However, the fact that in the presence of NaCl (when there are no reasons for curve displacement to the right) the influence of E is again quite weak (first row in Table 3) shows that this explanation is at least fragmentary. One should assume that the effect of the dipole-dipole orientation on the dipole-dipole "zip"-cluster destruction is weak, at least within the limits of the E variations studied.

Unlike the dependencies shown in Figure 1, those in Figures 4 – 6 do not reveal substantial changes in the reached value of the optical transmittance. This means that neither the ionic strength (Figures 4 and 5) nor *E* (Figure 6) affect this value as the PZ concentration does. The observed weak (by no more than 10 %) decrease in optical transmittance at higher temperatures, ionic strengths (Figures 4 and 5), and *E* values (Figures 6), *i.e.*, when the dipole–dipole clusters (including the intermacromolecular ones) should be destroyed to a great extent, deserves attention. The explanation of this interesting result resides in the transformation of intramacromolecular dipole-dipole contacts into intermacromolecular ones under the conditions indicated. During the process of destruction of dipole–dipole "zip"-clusters, the size and shape of the PZ macromolecules change; the size increases because some intramacromolecular clusters are also destroyed. This means that the probability of intermacromolecular dipole-dipole contacts (not necessarily clusters) is increased. This is actually an increase in junction points and network density under these extremely conditions for "zip"-cluster formation.

Conclusions

It is established that the electric field intensity is a factor influencing the "sol-gel" transition of aqueous PDMAPS solutions in the absence (Figure 3) and in the presence (Figure 6) of low molecular salt. The electric field effect is lower than those of ionic strength (Figures 4 and 5) and PZ concentration (Figure 1), at least within the limits of variation ranges of these quantities used in the present study. It is essential that the effects of *E* and ionic strength are in the same direction and are opposite to that of PZ concentration. The proposed explanation of this observation is based on the recently developed qualitative model of the structural organization and transformations of PZ macromolecules [6, 8, 9]. According to this model, the higher the PZ concentration, the higher the intermacromolecular "zip"-cluster concentration and the T_{pr} value. The clusters act as junction points in the physical network formed [9]. With the ionic strength increase, the shielding effect of low molecular ions facilitates the destruction of these intermacromolecular dipole-dipole clusters. The density of the physical network decreases leading to a decrease in the T_{pr} value of the PDMAPS aqueous solution.. Nevertheless, the results of the present work add a new, easily realized and controlled factor to the classical approaches of affecting the "sol-gel" transition of PZ aqueous solutions (*e.g.*, ionic strength, PZ concentration), namely the electric field intensity.

Acknowledgement

The financial support of this work was provided by a grant from the Bulgarian National Scientific Foundation (Grant № X-1307). The authors would like to thank of Dr. Velin Spassov for his helpful discussions.

[1] J. C. Galin, in: "*Polyzwitterions, the Polymeric Materials Encyclopedia*", J. C. Salomone, Ed., CRS Press, Boca Raton, **1996**, *9*, 7189.

[2] V. M. Monroy Soto, J. C. Galin, *Polymer* **1984**, *25*, 254.

[3] T. A. Wielema, J. B. F. N. Engberts, *Eur. Polym. J.* **1990**, *26 (6)*, 639.

[4] G. S. Georgiev, A. A. Tzoneva, V. A. Spassov, *e-Polymers* **2002**, 037 (http://www.e-polymers.org).

[5] G. S. Georgiev, A. A. Tzoneva, V. A. Spassov, *J. Univ. Chem. Technology and Metallurgy* **2002**, *XXXVII (1)*, 109.

[6] J. L. Bredas, R. R. Chance, R. Siley, *Macromolecules* **1988**, *21*, 1633.

[7] D. N.Schulz, D. G. Peiffer, P. K. Agarwal, J. Larabee, J. J. Kaladas, L. Soni, B. Handwerker, R. T. Garner, *Polymer* **1986**, *27*, 1734.

[8] G. S. Georgiev 1st Int. Symp. Reactive Polymers, Dresden, Abstracts, 2000, P7.

[9] G. S. Georgiev, Z. P. Mincheva, V. T. Georgieva, *Macromol. Symp.* **2001**, *164*, 301.

[10] G. Schwitzgebel, Ber. Bunsenges, *Phys. Chem.* **1997**, *101*, 1960.

[11] A. Bund, G. Schwitzgebel, *Anal. Chem.* **1998**, *70*, 2584.

[12] A. Bund, H. Hmiel, G. Schwitzgebel, *Phys. Chem. Chem. Phys.* **1999**, *1*, 3938.