Contraction of a Polyelectrolyte upon Dilution. Light Scattering Studies on a Polycation in Basic and Acidic Water−Acetone Mixtures

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ABSTRACT: A polycation poly(methacryloylethyl trimethylammonium methylsulfate), PMETMMS, with molar mass $M_w = 26 \times 10^6$ has been studied by viscosity and light scattering in a mixture of water and acetone. Various amounts of a base (sodium hydroxide) or acids (hydrochloric, sulfuric, or phosphoric acid) have been added to the samples. PMETMMS shows typical polyelectrolyte behavior of the reduced viscosity in water−acetone mixtures with acetone mass fraction, γ, below 0.80. When $\gamma \geq 0.80$, PMETMMS undergoes a reversible coil-to-globule transition. The collapse can also be induced by dilution of the polymer solution, keeping the solvent composition constant, $\gamma = 0.70$. Correlation functions measured using dynamic light scattering show a decrease of the relaxation time as well as the narrowing of the size distribution of the polymer with dilution. It has been shown that a compact structure instead of an extended coil is formed in a very dilute solution. Base or acid added into the solvent increases the value of the critical polymer concentration at which the collapse occurs. In a medium with low dielectric constant, base or acid molecules strongly interact with the charged groups of the polycation. Addition of NaOH into the solvent (less than 6×10^{-4} mol/L) decreases the degree of ionization of the polycation. However, the addition of acid (0.3×10^{-4} mol/L) introduces counterions that not only screen the positive charges of the polymer chain but also form inter- and intramolecular links. The latter effect becomes more profound with increasing the counterion valency. Upon dilution of the polymer solution, the number of the contacts between the polymer and added base/acid increases, but the number of inter- and intramolecular ion pairs of the polycation decreases. The balance of inter- and intramolecular interactions changes, and at high dilution, the intramolecular interactions dominate, owing to the poor quality of the solvent.

Introduction

The conformation of charged macromolecules in solution is determined by a balance of Coulombic and van der Waals interactions. The molar mass of the polyelectrolyte and its concentration as well as the solvent quality and its ionic content and the valency of the counterions effect the balance and determine the macroscopic behavior of the polymer solution. In a medium with low dielectric constant polyelectrolytes form ion pairs that attract one another and may lead to a collapse of the polyions.[1,2] Ionomers either aggregate due to dipolar attractions in nonpolar solvents or show the polyelectrolyte behavior in polar solvents.[3,4] In solvents with low polarity intramolecular association dominates at low polymer concentration while at higher polymer concentrations, intermolecular interactions cause an increase of the solution viscosity and even the gelation of the solution.[1,5,6] It has been shown that it is difficult to avoid aggregation of ionomers dissolved in nonpolar solvent even at very low polymer concentration.[6] In some cases, however, it has been possible to observe isolated single coils, the size of which is smaller than that of the precursor noncharged macromolecules.[7,8]

Joanny has formulated a theory for random ionomers in a nonpolar solvent.[1] The theory predicts intramolecular collapse and demixing at low polymer concentration and temperature and gelation at higher concentration and temperature. It has been shown that the overall second virial coefficient, A_2, may be calculated taking into account the effect of dipolar interactions: $A_2 = A_2' + f^2 A_2''$. Here A_2' is the second virial coefficient due to the excluded volume of the nonionic part of the backbone chains[1] and also includes the interaction between the ionic groups and the solvent.[4] A_2'' owes to the attraction between dipoles and is always negative. f is the fraction of dipoles along the chain. In nonpolar solvents A_2' decreases with ion content while f^2 increases. Hence, A_2 is a decreasing function of ion content. This is not the case for polar solvents. Water is a poor solvent for nonpolar organic compounds, and A_2 increases with ion content. Therefore, highly charged polyelectrolytes dissolved in slightly polar solvents or in aqueous−organic mixtures can show effects similar to random ionomers dissolved in nonpolar solvents. Coils of highly charged polyelectrolytes dissolved in solvents with dielectric constant lower than that of water can be very dense.[9,10] Aqueous−organic mixtures are complicated owing to hydrophilic and hydrophobic interactions.

Properties of the water−acetone solutions of the high molar mass polycation poly(methacryloylethyl trimethylammonium methylsulfate), PMETMMS, have been recently discussed.[10−14] The polymer has the following

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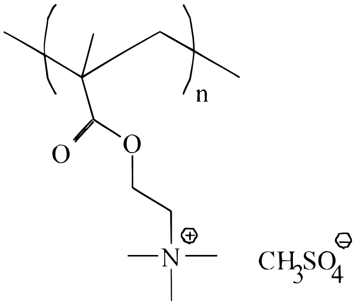
structure:



PMETMMS undergoes a reversible coil-to-globule transition in a mixture of water and acetone, in which acetone acts as a nonsolvent. If the mass fraction of acetone in the solvent, γ, is higher than 0.80, the polymer collapses, and single macromolecules adopt a globular state. This is observed as an increase of the intensity of scattered light and a decrease of the reduced viscosity, radius of gyration, R_g, and hydrodynamic radius, R_h. In the transition region $0.80 < \gamma < 0.82$ the second virial coefficient, A_2, equals zero and even less than zero. The decrease in A_2 owes to the poor solvent quality as well as the dipole–dipole interactions. The conductivity of the solution also decreases drastically in the transition region, but the macromolecules stay charged and soluble after the transition.

It has been shown that the collapse of PMETMMS dissolved in a water–acetone mixture may be induced by dilution of the polymer solutions, if γ is kept constant ($\gamma < 0.80$).[14] As ionomers dissolved in a polar solvent,[3,4] PMETMMS shows the polyelectrolyte effect, if γ is below 0.80. The effect is less pronounced in solutions with high acetone content. By light scattering measurements, it has been shown that, instead of expanding upon dilution, the polymer compresses. In a very dilute solution a compact structure with the radius of gyration $R_g \approx$ 50 nm, and the hydrodynamic radius $R_h \approx$ 30–40 nm is formed. These parameters are low for a polymer with molar mass $M_w = 26 \times 10^6$. The volume of the polymer in the collapsed state relative to the van der Waals volume was estimated as $V_w/V_h = 0.12$.[10]

This paper is a continuation of the study of the collapse of PMETMMS induced by the dilution of the solutions. It will be shown that when $\gamma = 0.70$, the addition of a base or an acid has an unexpectedly strong effect on the polymer conformation. The addition of a base or an acid into a PMETMMS solution increases the intensity of the scattered light, and thus, the accuracy of the analysis of the light scattering data increases. Also, the effect of the valency of the counterion has been studied.

Experimental Section

Materials and Methods. Poly(methacryloylethyl trimethylammonium methylsulfate) was prepared by free-radical polymerization. The monomer was prepared by quaternizing commercial (dimethylamino)ethyl methacrylate (Yarsintez, Yaroslavl, Russia), with dimethyl sulfate.[15]

The polymer has been characterized using static light scattering, in an aqueous 1 M sodium nitrate solution as well as in two saltless water–acetone mixtures with $\gamma = 0.82$ and 0.85.[10] The molar mass M_w is $(26 \pm 3) \times 10^6$ g/mol. The mean-square radius of gyration $\langle R_g^2 \rangle^{1/2}$ is 250 ± 10 nm in aqueous 1 M $NaNO_3$ and 53 ± 4 nm in solutions with $\gamma = 0.82$ and 0.85. The second virial coefficient A_2 is $(0.23 \pm 0.04) \times 10^{-4}$ cm^3 mol/g^2 in aqueous 1 M $NaNO_3$ but $(-0.33 \pm 0.05) \times 10^{-4}$ and $(-0.10 \pm 0.05) \times 10^{-4}$ cm^3 mol/g^2 in solutions with $\gamma = 0.82$ and 0.85, respectively.

The experiments described in this report were performed using solutions where the mass fraction of acetone in the solvent mixture was $\gamma = 0.70$. All the solutions were prepared using distilled deionized water and commercially available highly purified HPLC grade acetone (Labscan Ltd). PMETMMS was dissolved in deionized water for 4 days at +4 °C. Then the aqueous solution of PMETMMS was titrated with acetone for 10 h to get a solution with $\gamma = 0.70$. This solution was allowed to equilibrate at room temperature for 48 h.

Aqueous sodium hydroxide was titrated with acetone to get a solution with $\gamma = 0.70$ and the base concentration $c_b = 50 \times 10^{-4}$ mol/L. This stock solution was used for the preparation of base-containing solvents and polymer solutions. Four polymer solutions containing NaOH were studied, where the base concentrations, c_b, were 0.7×10^{-4}, 1.5×10^{-4}, 3.1×10^{-4}, and 6.3×10^{-4} mol/L. The viscosity of the solvent, i.e., the water–acetone–NaOH mixture, increases from 0.92 to 1.09 cP with sodium hydroxide concentration increasing from 0 to 10×10^{-4} mol/L. Solutions containing hydrochloric, sulfuric and *o*-phosphoric acids were prepared in a similar way. The concentration of acids was kept constant, $c_a = 0.3 \times 10^{-4}$ mol/L.

Solutions with varying polymer concentrations were prepared by consecutive dilution. The range of polymer concentrations, c_p, studied was 0.0002–0.037 mass %. After each dilution, the time dependence of the light scattering intensity was measured as a criterion of the stability of the solution. The solutions were purified of dust particles by centrifugation at 6000 rpm for 90 min. All measurements were done at 20° C.

Instrumentation. The viscosity measurements were performed using Ostwald's capillary viscometer.

Static light scattering (SLS) and dynamic light scattering (DLS) measurements were conducted with a Brookhaven Instruments BI-200SM goniometer and a BI-9000AT digital correlator. A helium/neon laser (Spectra Physics SP127-35, 35 mW) operating at 632.8 nm wavelength was used as a light source. The time autocorrelation function of the scattered light intensity $G_2(t) = \langle I(0)\, I(t) \rangle$ was measured in the self-beating mode[16] at the scattering angles 90°, 60°, 45°, and 30°. The shortest sample time varied from 1 to 10 μs, and the last delay was varied from 100 ms to 1 s. The number of correlator channels used was from 322 to 432. Brookhaven Instruments software was used (9KDLSW, Beta version 1.30). Time correlation functions were analyzed with a Laplace inversion program CONTIN (version 1.60). In the static measurements, the scattering angle was varied from 135° to 20°, in steps of 10°.

Results and Discussion

Solutions Containing Base. In general, the expansion of polyelectrolytes dissolved in a saltless aqueous solvent is observed upon dilution as an increase of the reduced viscosity. PMETMMS dissolved in a water–acetone mixture also shows the polyelectrolyte effect. One may expect that an increase of the pH of the medium decreases the degree of dissociation of the polycation and, hence, suppresses the polyelectrolyte effect. As can be seen in Figure 1, the polyelectrolyte effect becomes less pronounced with increasing the base concentration. The addition of NaOH decreases the value of the reduced viscosity of the solutions, and moreover, NaOH changes the shape of the $\eta_{sp}/c_p = f(c_p)$ dependence. For the solutions containing base, a considerable decrease of the reduced viscosity is observed upon dilution. A qualitatively similar dependence of the reduced viscosity on concentration has been observed earlier.[11,13] In the region of polymer concentrations studied, the value of the relative viscosity, η_r, changes upon dilution from 3.50 to 1.10. When $\eta_{sp}/c_p = f(c_p)$ passes the maximum, η_r = 1.30–1.40. The value of the

Table 1. Hydrodynamic Radius R_h of PMETMMS Dissolved in Aqueous 1 M $NaNO_3$ and in Water−Acetone Mixtures (γ = 0.70) with Various Concentrations of NaOH[a]

		water−acetone mixture				
solvent composition	aq 1 M $NaNO_3$	no base added	0.7×10^{-4} M	1.5×10^{-4} M	3.1×10^{-4} M	6.3×10^{-4} M
c_p at which $[c_m]/[c_b] = 1$, mass %			0.0021	0.0042	0.0089	0.0177
polymer concns studied, mass %	<0.015	<0.0004	<0.0015	<0.0036	<0.0059	<0.0163
R_h, nm	98 ± 10	30 ± 5	30 ± 4	32 ± 4	42 ± 3	59 ± 9

[a] c_p = polymer concentration in mass %, $[c_m]$ = the molar concentration of repeating units, $[c_b]$ = the molar concentration of NaOH.

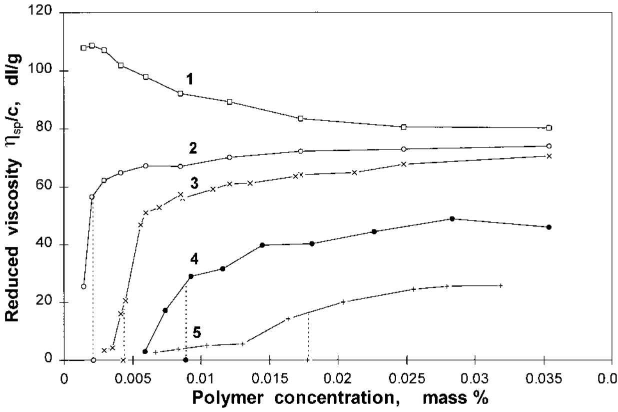


Figure 1. Concentration dependence of the reduced viscosity of PMETMMS dissolved in water−acetone mixture with the mass fraction of acetone γ = 0.70. The concentration of NaOH: (1) 0, (2) 0.7×10^{-4} mol/L, (3) 1.5×10^{-4} mol/L, (4) 3.1×10^{-4} mol/L, (5) 6.3×10^{-4} mol/L. The dotted lines show the values of the polymer concentration at which $[c_m]/[c_b] = 1$.

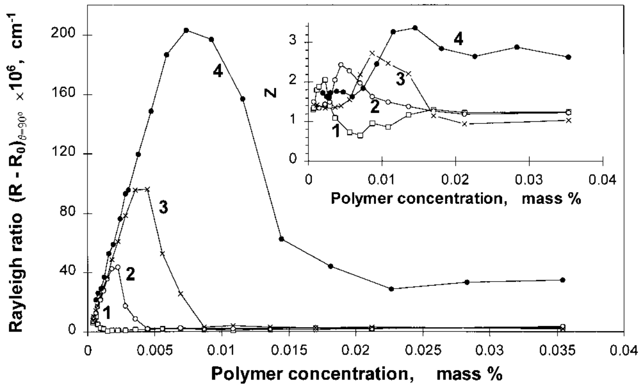


Figure 2. Concentration dependence of the scattering intensity (at 90° scattering angle), $R - R_0$, and the angular dissymmetry parameter, Z, of PMETMMS dissolved in the water−acetone mixture with γ = 0.70. The concentration of NaOH: (1) 0, (2) 0.7×10^{-4} mol/L, (3) 1.5×10^{-4} mol/L, (4) 3.1×10^{-4} mol/L. The intensity is given in absolute Reyleigh ratios.

critical polymer concentration where the reduced viscosity decreases is higher the higher is the base concentration. The viscosity decreases discontinuously upon dilution when the base concentration is low; with increasing amount of base, the change becomes more gradual.

For each series of polymer solutions with a certain base concentration, the equimolar concentrations where $[c_m]/[c_b] = 1$ ($[c_m]$ is the molar concentration of repeating units) were calculated. These values are tabulated in Table 1 and shown with vertical dotted lines in Figure 1. The observed decrease of the reduced viscosity occurs close to $[c_m]/[c_b] = 1$.

The range of polymer concentrations in which the considerable decrease of the reduced viscosity was observed was studied using light scattering. The intensity of light scattered at 90° from solutions with varying concentration of NaOH is represented in Figure 2 against the polymer concentration. The difference between the scattered light intensities from the solution and the solvent is given in absolute Rayleigh ratios. In the concentration region where the viscosity of the polymer solution decreases with decreasing polymer concentration, the scattered light intensity increases. The increase of the intensity of the scattered light upon dilution occurs even in solutions with no added base. This change, however, takes place in very dilute solutions that cannot be accurately enough studied by viscometry. The increase is more profound the higher is the base concentration. The intensity vs polymer concentration shows a maximum, the position of which depends on the base content of the solvent. The inset in Figure 2 shows the angular dissymmetry parameter $Z = I^{45}/I^{135}$ vs polymer concentration. The scattering intensity from solutions with high polymer concentration is low, and the value of Z is close to unity, which is typical for semidilute solutions. Increase of Z with decreasing polymer concentration may be understood as a transition from a semidilute to a dilute polymer solution. The overlap concentration, c^*, defined as the peak value of Z, increases with increasing base concentration. At concentrations $c < c^*$ the value of Z decreases due to a decrease of the size of the polyions. In very dilute polymer solutions Z is constant, indicating that the size of the macroions does not change. This conclusion is supported by the DLS studies discussed later in the text.

The static light scattering data were treated using the Zimm double extrapolation method, $Kc_p/\Delta R(\theta,c_p) = 1/M_wP(\theta) + 2A_2c_p$, where $\Delta R(\theta,c_p)$ is the excess reduced scattered intensity at angle θ from the solution with the polymer concentration c_p, K is an optical constant, $P(\theta)$ is the particle scattering factor, and A_2 is the second virial coefficient. Since M_w of the studied sample is known, the scattered light intensities were multiplied by a constant factor corresponding to $M_w = 26 \times 10^6$ g/mol to display relative differences in the measured molar masses. The logarithm of the normalized reduced scattered light intensity at zero angle, $\log(M_wKc_p/\Delta R_{\theta=0})$, is plotted against polymer concentration in Figure 3. For comparison, the data of PMETMMS dissolved in aqueous 1 M $NaNO_3$ and in a water−acetone mixture with γ = 0.85 are also shown. For all the solutions studied, except that with the highest NaOH concentration, the values of M_w were not affected by either selective sorption or aggregation.

Deviation of curves 1−3 in Figure 3 from linearity is typical for polyelectrolytes and has been observed also for ionomers dissolved in ionizing solvents.[3,4] The data in Figure 3 also show that the sudden decrease of the viscosity of the solutions with decreasing polymer concentration owes to a change of the polymer conformation. When $c_b = 3.1 \times 10^{-4}$ mol/L (curve 4), the dependence of $Kc_p/\Delta R_{\theta=0}$ on polymer concentration is

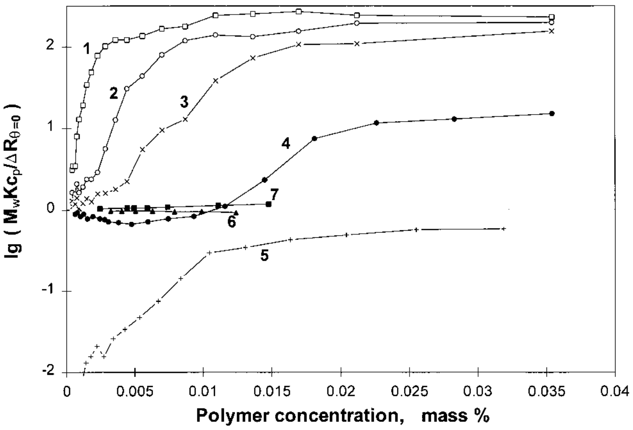


Figure 3. Inverse reduced scattering intensity at zero angle multiplied by molar mass 26 × 10^6 g/mol vs the concentration of PMETMMS. Concentration of NaOH: (1) 0, (2) 0.7 × 10^{-4} mol/L, (3) 1.5 × 10^{-4} mol/L, (4) 3.1 × 10^{-4} mol/L, (5) 6.3 × 10^{-4} mol/L. As references, (6) the polymer in $\gamma = 0.85$ with no base and (7) the polymer in aqueous 1 M $NaNO_3$.

linear and A_2 is negative, when $c_p < 0.0059$ mass %. In this range of polymer concentrations the angular dissymmetry parameter Z is concentration-independent (see curve 4 in Figure 2), and the parameters describing individual molecules can be obtained. The intensity of the scattered light from the solution with 6.3 × 10^{-4} mol/L NaOH is very high and could not be presented in the scale of Figure 2. Curve 5 in Figure 3 shows that the high intensity not only is due to the presence of the base but also owes to aggregates formed in solution.

The radius of gyration and the hydrodynamic radius were determined using solutions with the base concentration $c_b = 3.1 \times 10^{-4}$ mol/L and the polymer concentrations $c_p < 0.005$ mass %. It was found that $\langle R_g^2\rangle^{1/2} = 80 \pm 10$ nm. The size distribution obtained by dynamic light scattering shows a single peak, with a peak value of $R_h = 42 \pm 3$ nm. An approximate overlap concentration c_p* for such a solution, calculated as for noninteracting hard spheres using $c_p^* = M_w/[N_A\,(4\pi/3)R_g^3]$, is 1.81 mass %. However, the overlap concentration defined as a peak value of Z is 0.012–0.014 mass %. From the above reasoning it may be suggested that PMETMMS chains change their conformation in the concentration region where the reduced viscosity decreases dramatically and $Kc_p/\Delta R_{\theta=0}$ vs polymer concentration has the maximum. The difference between the c_p* values 1.81 and 0.012 mass % indicates that the polymers strongly interact with each other over $c_p = 0.012$ mass %.

Next, PMETMMS was studied by DLS in highly diluted solutions in which all the polyelectrolyte molecules are in a collapsed state (for the concentration range, see Table 1). For the solutions with $c_b \leq 3.1 \times 10^{-4}$ mol/L, no concentration and angle dependence of R_h was found. An example of the size distribution obtained at five scattering angles is shown in Figure 4. A CONTIN fit of the correlation functions was performed within an error less than 1%. The R_h value of the collapsed PMETMMS given in Table 1 was calculated as an average of the peak values of the size distributions obtained for 4–8 polymer concentrations at 4–7 scattering angles. The hydrodynamic size of PMETMMS in the collapsed state slightly increases with increasing c_b in the solvent.

The DLS measurements were performed in a region of polymer concentrations where the decrease of the reduced viscosity takes place. Correlation functions obtained for the solution with $c_b = 6.27 \times 10^{-4}$ mol/L at the scattering angle 90° are shown in Figure 5a,b. The measured correlation functions $G_2(t)$ were normalized as follows:

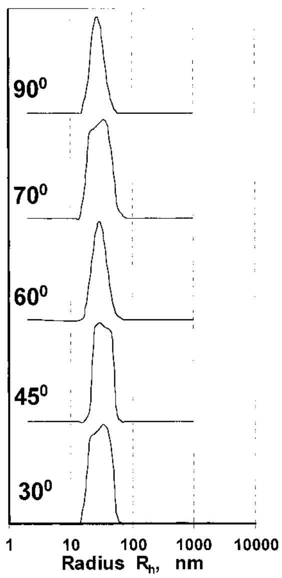


Figure 4. Angle dependence of the size distribution of PMETMMS dissolved in a water–acetone mixture with $\gamma = 0.70$. Sodium hydroxide concentration is 1.5 × 10^{-4} mol/L, and the polymer concentration is 0.0036 mass %.

$$|G_2(t)| = \frac{G_2(t) - G_2(\infty)}{G_2(0) - G_2(\infty)}$$

It is clearly seen that the relaxation time decreases with a decrease of the polymer concentration; see Figure 5a. The inset shows that the logarithmic correlation function of the most concentrated solution deviates strongly from a straight line representing a single-exponential decay. Further dilution, however, makes the relaxation time to increase again; see Figure 5b. With high dilution, the polymers aggregate and the amount of the aggregates increases upon dilution. The inset in Figure 5b shows only one relaxation process that is due to aggregates in the solution with $c_p = 0.0022$ mass %. It should be noted that the shape of curve 1 in Figure 5a is due to a broad distribution of the particle size, but not to a broad molar mass distribution.[10] It is evident that the most concentrated samples shown in Figure 5b are semidilute. More concentrated samples, with $c_p = 0.3$ mass %, were also measured. In this region of polymer concentrations, two relaxation processes are distinguished. The investigation of this concentration regime, however, was not the purpose of the present study.

Figure 6 shows an example of the size distributions measured at 45° scattering angle for the same polymer solutions that were used to produce Figure 5. The decrease of the size of the molecules as well as the narrowing of the size distribution upon dilution is evident. The size distributions measured at five scattering angles are shown in Figure 7. The solution with the polymer concentration 0.0280 mass % (Figure 7a) shows a strong angle dependence of the apparent size distribution, this indicating that the actual particle size distribution is very broad. At low scattering angles the bimodality of the size distribution, obtained using the

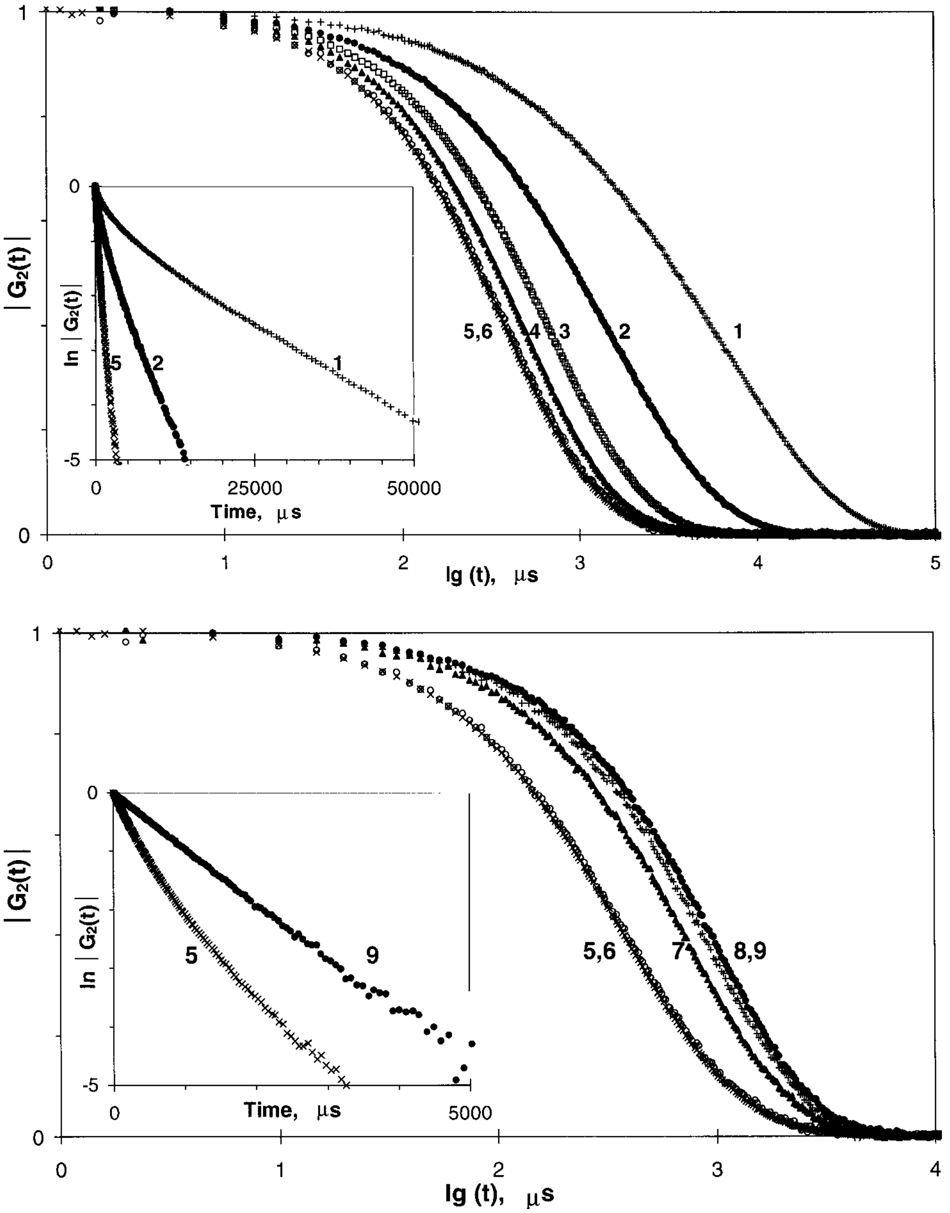


Figure 5. (a) Correlation functions (at 90° scattering angle) of PMETMMS dissolved in a water–acetone mixture with $\gamma = 0.70$ and sodium hydroxide concentration of 6.3×10^{-4} mol/L. The polymer concentration: (1) 0.0319 mass %, (2) 0.0280 mass %, (3) 0.0255 mass %, (4) 0.0204 mass %, (5) 0.0163 mass %, (6) 0.0131 mass %. (b) Continuation of (a). Polymer concentration: (5) 0.0163 mass %, (6) 0.0131 mass %, (7) 0.0054 mass %, (8) 0.0034 mass %, (9) 0.0022 mass %.

polymer concentration 0.0131 mass %, is clearly seen; see Figure 7b. The peak corresponding to small R_h is due to the collapsed molecules, and its value is in accordance with the size of collapsed molecules existing in other solvents; see Table 1. At high dilution (Figure 7c) only aggregates exist in the solution. Practically no angle dependence of the apparent particle size can be seen because of the narrow size distribution of the aggregates and their high density. The hydrodynamic radius of the aggregates is about 200 nm for all the solutions with $c_p \leq 0.0163$ mass %. This probably is the maximum size of soluble PMETMMS aggregates.

Investigation on the PMETMMS solutions with lower base concentrations, $c_b \leq 3.1 \times 10^{-4}$ mol/L, has also shown a decrease of the relaxation time and the narrowing of the size distribution in the transition region upon dilution. In highly diluted solutions, no aggregates were found, and the correlation functions approach single exponential.

Figure 8 is a summary of the conformational changes occurring upon dilution of the PMETMMS solutions. The upper part of the scheme represents how the size distribution changes with concentration. In addition to the observed maximum and minimum values of the R_h distribution, also the peak value is shown. The concentration dependencies of the reduced viscosity, curve 1, light scattering intensity, curve 2, and the angular dissymmetry parameter, curve 3, are represented in the bottom part of the figure. Narrowing of the size distribution and the decrease in the coil dimension upon dilution starts at the polymer concentration at which the reduced viscosity of the solution decreases. At this polymer concentration the scattered light intensity shows a maximum. In a very dilute solution, $c_p < 0.005$ mass %, the intensity of the scattered light decreases linearly with decreasing polymer concentration, and the size of the molecules is constant.

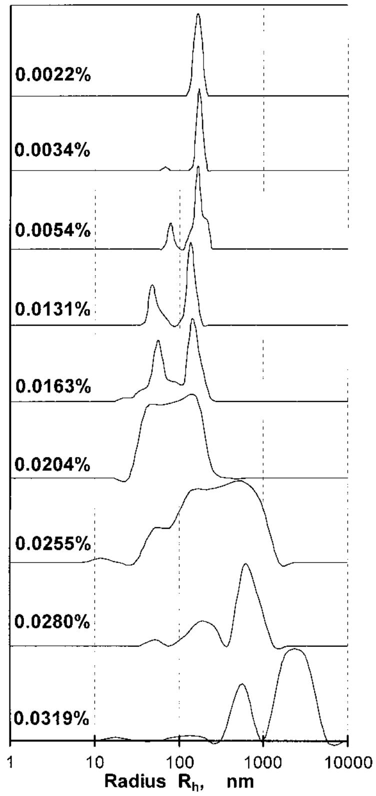


Figure 6. Dependence of the apparent R_h on the polymer concentration. Results are obtained for PMETMMS solution with $\gamma = 0.70$ and NaOH concentration of 6.3×10^{-4} mol/L at 45° scattering angle.

At the upper limit of the studied region of polymer concentrations, the macromolecules strongly interact with each other via ion pairs as well as due to the attraction of the repeating units in a thermodynamically poor solvent. A transient network is formed. This conclusion is supported by the very low scattering intensity and by the decrease of the dissymmetry parameter with increasing concentration. Dilution breaks down the network.

Two processes can be distinguished upon dilution. The role of the intramolecular interactions increases at the expense of the intermolecular contacts. In addition, because the base concentration of the solvent is kept constant, the number of base molecules per one repeating unit of the polymer increases upon dilution. The latter is especially important in a media with low dielectric constant. Base strongly interacts with the charged groups of the polycation, and the polymer–polymer contacts are replaced by the polymer–base contacts. The increase of the amount of sodium hydroxide per repeating unit of the polymer decreases the degree of dissociation and changes the mechanism of the mutual interaction of the chains. Intramolecular attraction makes the PMETMMS molecules collapse while uncompensated charges, together with hydrophobic groups, keep the polymer soluble.

It should be noted that the value of A_2 obtained for PMETMMS dissolved in water–acetone mixture is apparent and reflects the balance of multiple interactions. From comparison of A_2 of curves 4 and 6 in Figure 3 it may be concluded that the solvent with $\gamma = 0.70$ and $c_b = 3.1 \times 10^{-4}$ mol/L is poorer than the solvent with $\gamma = 0.82$ and no base added. Because PMETMMS dissolves in water due to the basic ammonium groups, screening of these charges makes the solvent poorer. Addition of acetone not only decreases the dielectric constant of the solvent and thus the degree of dissociation of the basic groups of PMETMMS. Increase in γ also increases solubility of hydrophobic parts of PMETMMS. Total screening of charges of PMETMMS in solvent with $\gamma = 0.70$ causes aggregation. This is the case in the solution with $\gamma = 0.70$ and $c_b = 6.3 \times 10^{-4}$ mol/L. Introduction of NaOH may also change the structure of the water–acetone mixture. This effect, however, is supposed to be of minor importance in comparison to ion pair formation.

The broad size distribution shown in Figure 8 is probably due to the coexistence of the transient network (a), single coils (b), and partially (c) or fully (d) globulized molecules. PMETMMS adopts the globular conformation gradually. This suggestion is in accordance with the observed coexistence of two different conformations of DNA during a coil-to-globule transition.[17] The structure of the PMETMMS globules differs from the structure of the globules of uncharged polymers.[10,14] A toroidal donutlike structure of PMETMMS, similar to DNA,[17] as well as a spherical flow-through grapelike

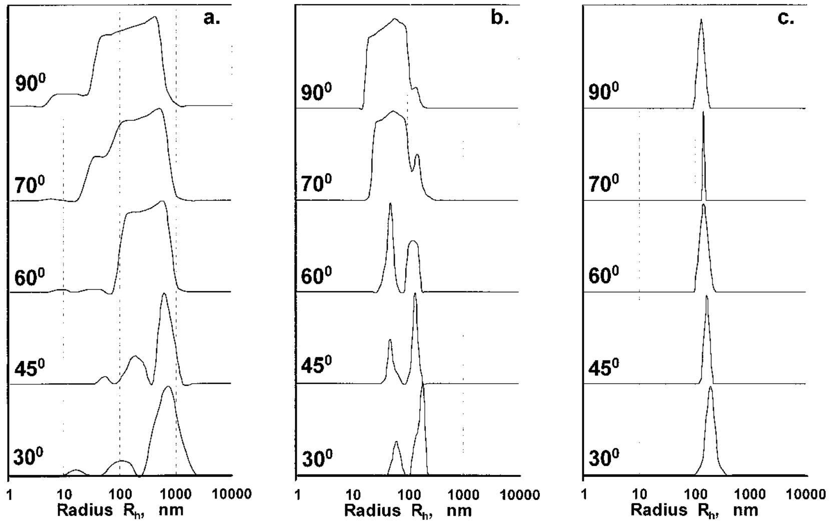


Figure 7. Angle dependence of the size distribution of PMETMMS dissolved in a water–acetone mixture with $\gamma = 0.70$ and sodium hydroxide concentration of 6.3×10^{-4} mol/L. The polymer concentration is (a) 0.0280 mass %, (b) 0.0131 mass %, and (c) 0.0022 mass %.

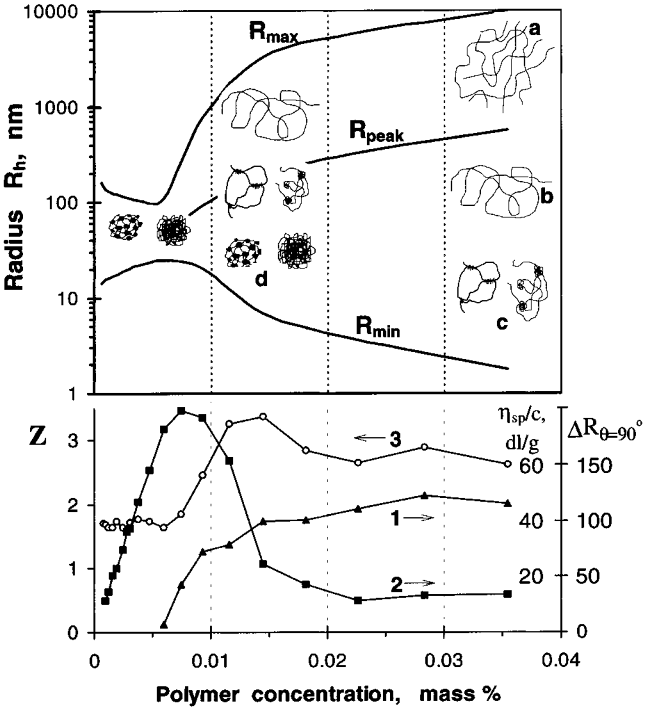


Figure 8. Scheme of the conformational change of PMETMMS in a water–acetone mixture with $\gamma = 0.70$, having the sodium hydroxide concentration of 3.1×10^{-4} mol/L. The upper part of the scheme represents the change of the size distribution with the polymer concentration. Probable structures existing in the solution: a transient network (a), single coils (b), partially (c) or fully (d) globulized molecules. Data obtained at 90° scattering angle represent average maximum and minimum values of R_h in size distribution and the distribution highest peak value. The lower part of the scheme shows the concentration dependence of the reduced viscosity (1), light scattering intensity (2), and the angular dissymmetry parameter, Z (3). The viscosity data are given in dL/g, while the intensity is given in Rayleigh ratios, $\text{cm}^{-1} \times 10^6$.

structure with a heterogeneous density distribution[18] may describe the compact conformation. We suppose that the structure of PMETMMS globule is a dense but flow-through structure. Preferable sorption of water to polymer is expected to take place.

Solutions Containing Acid. As has been recently observed, acid and base have a similar effect on the viscosity of a PMETMMS solution with $\gamma = 0.70$.[13] Therefore, the effect of acids on the PMETMMS conformation as well as the influence of the counterion valency has been studied using light scattering.

The effect of various acids on the viscosity of the PMETMMS solutions is shown in Figure 9. A very small amount ($c_a = 0.3 \times 10^{-4}$ mol/L) of HCl acts like salt ($NaNO_3$ in ref 13) screening the charges and suppressing the polyelectrolyte effect, curve 2. When the concentration of HCl is increased 10-fold, $c_a = 3.3 \times 10^{-4}$ mol/L, the concentration dependence of the reduced viscosity changes considerably, curve 3. Below the equimolar polymer concentration, $c_p = 0.009$ mass %, the reduced viscosity decreases in a way similar to that observed for the basic solutions.

Curves 2, 4, and 5 in Figure 9 show the concentration dependence of the reduced viscosity of the solutions containing 0.3×10^{-4} mol/L hydrochloric, sulfuric, and phosphoric acid, respectively. The polyprotic acids induce a sharp decrease of the viscosity upon dilution. Concentration dependencies of LS intensity and the angular dissymmetry parameter of the solutions containing polyprotic acids are similar to those obtained for PMETMMS solutions containing base; see Figure 10.

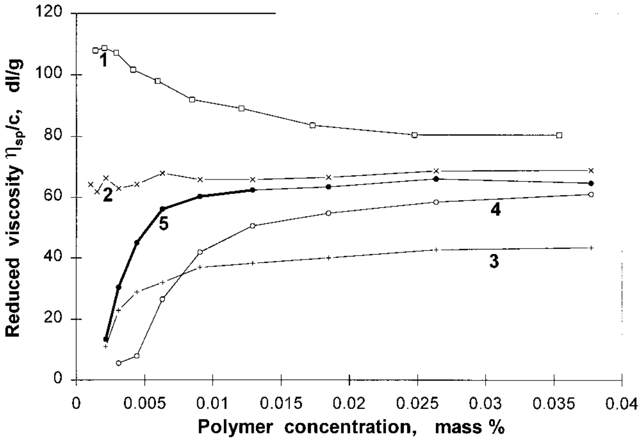


Figure 9. Concentration dependence of the reduced viscosity of PMETMMS dissolved in a water–acetone mixture with $\gamma = 0.70$ containing various acids: (1) no acid added, (2) 0.3×10^{-4} mol/L of HCl, (3) 3.3×10^{-4} mol/L of HCl, (4) 0.3×10^{-4} mol/L of H_2SO_4, (5) 0.3×10^{-4} mol/L of H_3PO_4. The bold line marks the polymer concentration range at which the DLS measurements have been performed.

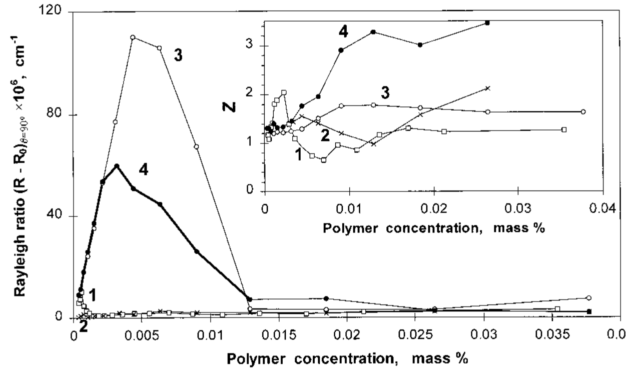


Figure 10. Concentration dependencies of the scattering intensity (at 90° scattering angle), $R - R_0$, and the angular dissymmetry parameter, Z, of PMETMMS dissolved in water–acetone mixed solvents with mass fraction of acetone $\gamma = 0.70$ and various acids of the same concentration 0.3×10^{-4} mol/L: (1) no acid added, (2) HCl, (3) H_2SO_4, (4) H_3PO_4. The intensity is given in Rayleigh ratios. The bold line marks the polymer concentration range at which DLS measurements were performed.

PMETMMS solutions containing polyprotic acids (0.3×10^{-4} mol/L) and HCl (3.3×10^{-4} mol/L) were studied using dynamic light scattering in the transition region. Correlation functions and the size distributions obtained for the solution containing H_3PO_4 are presented in Figure 11. For this solution, the region of polymer concentrations studied by light scattering is indicated on Figures 9 and 10 with thick lines.

In a medium with low dielectric constant acid molecules screen the charges of the polycation and/or form ion pairs of the polymer with the acid. Multivalent counterions $SO_4{}^{2-}$ and $PO_4{}^{3-}$ form intra- and intermolecular links. A similar effect has been observed for a DMF solution of sulfonated polystyrene with zinc as a counterion.[3] The effect of the counterion valency has been observed even in aqueous solutions. It has been shown that the higher the valency of a precipitant added in aqueous DNA solution, the smaller is the amount of the precipitant needed for the collapse of the DNA molecules.[19] It has also been shown that the addition of Al^{3+} causes the gelation of a solution of sulfonated

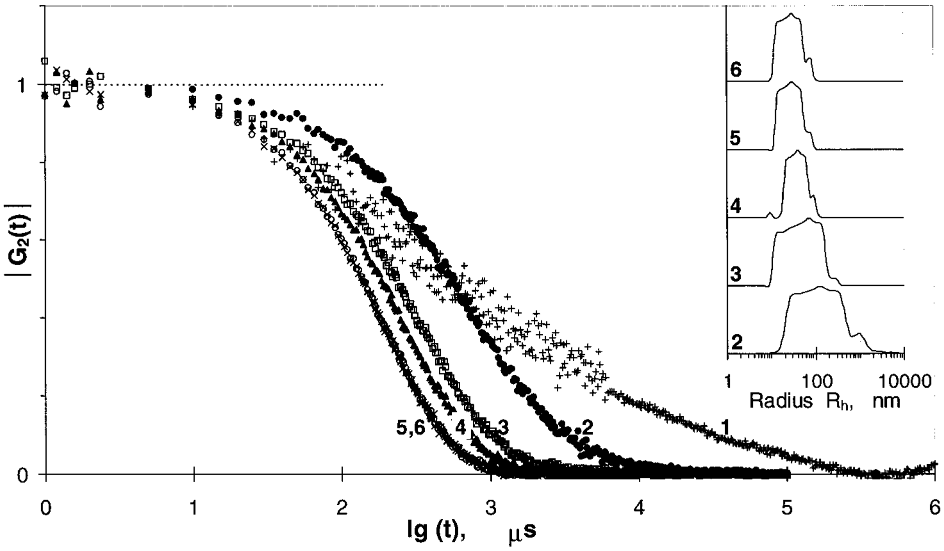


Figure 11. Correlation functions and corresponding hydrodynamic size distributions (at 90° scattering angle) of PMETMMS dissolved in water−acetone mixture with $\gamma = 0.70$ containing *o*-phosphoric acid of concentration 0.3×10^{-4} mol/L. The polymer concentration: (1) 0.0129 mass %, (2) 0.0091 mass %, (3) 0.0063 mass %, (4) 0.0044 mass %, (5) 0.0022 mass %, (6) 0.0015 mass %.

polystyrene at high polymer concentration.[20] The transient physical network formed in concentrated PMETMMS solutions containing trivalent counterions is stronger than that in the case of bivalent counterions. Reduced viscosity of phosphate-containing solutions is higher than that of the sulfate-containing solution; see Figure 9. The number of contacts between polymer and acid increases upon decreasing the polymer concentration, and at a high dilution the PMETMMS molecules collapse. Decrease in the dimension of PMETMMS occurs in solutions containing polyprotic acids when c_a is 10 times smaller than c_b in the basic solutions studied. A further increase of concentration of the polyprotic acids in the solvent mixture causes strong aggregation of PMETMMS molecules and precipitation.

Conclusions

PMETMMS with a molar mass 26×10^6 collapses on addition of acetone into an aqueous solution. Collapse of PMETMMS can be induced by the dilution of the polymer solution, having the solvent composition constant.

Solution properties of PMETMMS were studied with $\gamma = 0.70$. PMETMMS−water−acetone solutions show the polyelectrolyte effect similar to that observed for ionomers dissolved in polar organic solvents. A drastic decrease of the polymer dimension is observed upon dilution. Addition of base or acid in a water−acetone mixture screens Coulombic interactions, suppresses the polyelectrolyte effect, and increases the value of the polymer concentration at which the polymer collapses. Two polymer concentration regions are observed: the higher concentration regime, where the coils interpenetrate, and the lower concentration regime, where all the PMETMMS molecules are collapsed. In the intermediate region, the collapse of PMETMMS is gradual, and coils and globules probably coexist during the process. The transition from a transient network to single coils differs in this case from that taking place in an aqueous solution of a polyelectrolyte. The so-called “ordinary−extraordinary” transition occurs in aqueous polyelectrolytes in which $A_2 > 0$ and ion pairs do not form.[21] PMETMMS molecules collapse upon dilution and adopt a globular structure instead of an extended coil.

The conformational change upon dilution owes to a change in the balance of inter- and intramolecular interactions. The number of contacts between the polymer and the added base or acid increases, while the number of polymer−polymer ion pairs decreases. Base or acid added in PMETMMS dissolved in a solvent mixture with low dielectric constant strongly interacts with the charged groups of the polycation and introduces additional counterions in the system. The base causes a decrease in the degree of dissociation. The base also lowers the solvent quality and thus increases the polymer concentration where PMETMMS shrinks. Multivalent counterions create additional intermolecular and intramolecular links. When the amount of the base or the acid is small enough, the charges of the polycation as well as the hydrophobic parts of the polymer soluble in the solvent mixture prevent the aggregation of PMETMMS globules.

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