Macromolecules **1998,** *31,* 7717−7722

Contraction of a Polyelectrolyte upon Dilution. Light-Scattering Studies on a Polycation in Saltless Water−Acetone Mixtures

Vladimir O. Aseyev[†] **and Heikki Tenhu***

Laboratory of Polymer Chemistry, PB 55, FIN-00014 HY, University of Helsinki, Finland

Stanislav I. Klenin

Institute of Macromolecular Compounds, Russian Academy of Science, Bolshoi Prospect 31,
199004 St. Petersburg, Russia

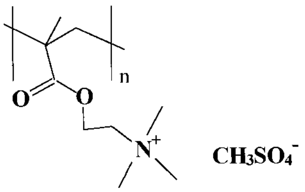
Received April 9, 1998; Revised Manuscript Received July 14, 1998

ABSTRACT: A superhigh-molar-mass polyelectrolyte, poly(methacryloylethyl trimethylammonium methyl sulfate) (PMETMMS), with molar mass 26×10^6 has been studied by viscosity and light scattering in saltless water−acetone mixtures of various compositions. PMETMMS is known to collapse on addition of acetone into an aqueous solution. It has been shown that the collapse of the polyelectrolyte chains may be induced also by dilution of the polymer solutions, leaving the solvent composition constant. The scattered light intensity measured as a function of polymer concentration shows a maximum at a certain concentration. The position of the maximum is dependent on the solvent composition. 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 in a very dilute solution where the value of the second virial coefficient A_2 is close to zero. The values of M_w measured by static light scattering in solutions with various solvent compositions were constant. Correlation functions measured using dynamic light scattering unambiguously show a decrease of the relaxation times as well as the narrowing of the size distribution of the polymer with dilution. This most probably is due to the change of the balance of inter- and intramolecular interactions upon dilution.

Introduction

A coil−globule transition of polymers occurs in dilute solutions when the solvent becomes poor. The solvent quality may be changed by changing the temperature as well as by changing the solvent composition. In both cases the decrease of the thermodynamic quality of the solvent tends to increase the polymer−polymer interactions at the expense of the polymer−solvent interactions. Aqueous polymer solutions are complicated due to the hydrophobic and hydrophilic interactions. The interactions in aqueous polyelectrolyte solutions are even more complex than those in solutions of neutral polymers. However, the existence of uncompensated charges of polyions prevents the aggregation and makes it possible to follow the coil-to-globule transition using various research methods.[1−6]

In this paper the concentration dependence of the conformation of the high-molar-mass polycation poly(methacryloylethyl trimethylammonium methyl sulfate) (PMETMMS) near the point of conformational transition will be discussed. The polymer has the following structure:



PMETMMS is known to undergo a reversible coil-to-globule transition in a water−acetone mixture, in which acetone acts as a nonsolvent.[1,3−5] If the mass fraction of acetone in the solvent γ is below 0.80, the viscosities of the solutions show the usual polyelectrolyte effect. When $\gamma > 0.80$, the polymer adopts a globular state. This is observed as a decrease of the reduced viscosity, the radius of gyration R_g, and the hydrodynamic radius R_h. In the transition region $0.80 < \gamma < 0.82$ the second virial coefficient A_2 becomes equal to zero and even less than zero, indicating that the transition occurs in a poor solvent. The correlation functions measured by dynamic light scattering change from bimodal to unimodal ones and indicate the formation of compact globular structures.[5] The conductivities of the solutions also decrease drastically in the transition region, but the macromolecules stay charged and soluble even after the transition.[4] In a medium of low dielectric constant, polyelectrolytes form ion pairs attracting one another which, in addition to other multiple interactions, result in the collapse of the polyion chains.[7]

In solutions with strong attraction between the polymer segments, the polymer concentration and the size of the polymer coils determine the macroscopic behavior of the system. Dilute aqueous solutions of polyelectrolytes are characterized by the expanded conformation of the polymers and strong intermolecular interactions. The existence of a specific concentration region in aqueous saltless solutions of high-molar-mass polyelectrolytes between concentrated and very dilute polymer solutions ("dilute lattice regime", "over-lap regime", or "crossover dilute regime") is widely discussed.[8] The possibilities to study experimentally a single polyelectrolyte chain in a dilute solution are often limited.

During the investigations of PMETMMS in water−acetone mixtures, it has been observed that the reduced

---

* To whom correspondence should be addressed.

[†] Permanent address: Institute of Macromolecular Compounds, Russian Academy of Science, Bolshoi Prospect 31, 199004 St. Petersburg, Russia.

10.1021/ma980552q CCC: $15.00

viscosity η_{sp}/c has a maximum and decreases strongly at high dilution in solutions where $0.50 < \gamma < 0.80$ and $c < c^*$.[4] Even very low concentrations of base or acid added into the solutions ($(3-8) \times 10^{-5}$ mol/L) result in a shift of the critical polymer concentration where the η_{sp}/c curve inclines. At this concentration, an increase of the light-scattering intensity was detected. Preliminary investigations have shown that in a very dilute solution a compact structure with $R_g \approx 50$ nm is formed. This observation indicates that the intermolecular interactions of the polyelectrolytes influence also the intramolecular interactions.

Recently, a new theory of the collapse of linear, flexible, weakly charged polyelectrolytes in a dilute solution was presented by Kramarenko, Khokhlov, and Yoshikawa.[9] It was based on an assumption that a single polyelectrolyte chain is not electroneutral; some counterions may move to the outer solution. In good solvents not far from the Θ temperature the removal of the counterions was shown to lead to a significant decrease of the dimension of a single chain. In poor solvents the collapse of the polyelectrolyte is caused by non-Coulomb interactions and the swelling degree does not strongly depend on the fraction of counterions which are inside the coil. A Monte Carlo simulation[10] of strongly charged chains in solution far below the overlap concentration has also shown that at finite polymer concentration the single chains contract. The chains were concluded to begin to coil in order to stay as isolated objects rather than to maintain an elongated shape and overlap.

From an experimental and theoretical viewpoint, it is of interest to study dilute polyelectrolyte solutions to find out the factors that affect the polymer conformation. Light scattering is a method of choice to determine the size of a polymer in various solvents and concentrations. In this report, special attention is paid to the influence of the polymer concentration on the conformation of PMETMMS in water−acetone mixtures where the mass fraction of acetone is close to that where the conformational change is known to take place.

Experimental Section

Materials and Methods. The sample of poly(methacryloylethyl trimethylammonium methyl sulfate) was prepared by free-radical polymerization using a twice precipitated monomer.[11] The monomer was prepared by quaternizing a commercial monomer, dimethylaminoethyl methacrylate (purchased from Yarcintez, Yaroslavl, Russia), with dimethyl sulfate.

The polymer was examined using static light scattering in aqueous 1 M sodium nitrate solution as well as in saltless water−acetone mixtures with $\gamma \geq 0.82$. Static light-scattering data were treated using Zimm's double-extrapolation method. Specific refractive index increments, dn/dc, of the polymer dissolved in water−acetone mixtures and in aqueous 1 M $NaNO_3$ are equal within the experimental error. The value 0.166 mL/g was used. The experiments show that the values of M_w were not affected by selective sorption. Molar masses M_w measured for PMETMMS dissolved either in aqueous 1 M $NaNO_3$ or in a saltless water−acetone mixture with the mass fraction of acetone 0.82 are identical and equal to 26×10^6 g/mol. The mean-square radius of gyration $\langle R_g^2 \rangle^{1/2}$ is 250 nm in aqueous 1 M $NaNO_3$ and 53 nm in a solution with $\gamma = 0.82$. Detailed analysis of molar masses of PMETMMS samples has been presented in refs 4 and 5. The coincidence of the M_w values obtained by light scattering with that measured by sedimentation−diffusion indicates the narrow molar mass distribution of the sample studied. The polydispersity parameter of the sample was determined as $M_z/M_w = 1.15-1.20$ using the dispersion of the sedimentation constant distribution.[12] Assuming a Schulz distribution, M_w/M_n is equal to 1.6−1.8.

The solutions were prepared using distilled deionized water and commercially available highly purified acetone of HPLC grade (Labscan Ltd). PMETMMS was dissolved in deionized water during 4 days at +4 °C. Then the aqueous stock solution of PMETMMS was titrated with acetone during 10 h to get a solution with a certain γ. This solution was allowed to equilibrate at room temperature for 48 h. Solutions with various polymer concentrations were prepared by consecutive dilutions. The range of polymer concentrations studied was 0.0002−0.037 mass %. After each dilution, the time dependence of the light-scattering intensity at a 90° angle was measured as a criterion of solution stability. The solutions were purified of dust particles by centrifugation at 6000 rpm for 90 min. All measurements were done at 20 °C. Molar mass measurements were repeated several times during the investigation to ensure the stability of the polymer.

Instrumentation. The viscosity measurements were performed using Ostwald's capillary viscometer, for which the shear rate is estimated as 700 s^{-1} for water.

Static light-scattering (SLS) and dynamic light-scattering (DLS) measurements were done 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 a 632.8 nm wavelength was used as a light source. The time autocorrelation function of the scattered intensity $G_2(t) = \langle I(0)I(t) \rangle$ was measured in the self-beating mode[13] at the scattering angles 90°, 60°, 45°, and 30°. All correlation functions were recorded in the real-time multi-τ mode (three multi-τ intervals). The shortest sample time was 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 the Laplace inversion program CONTIN (version 1.60). The value of dn/dc was measured using a WYATT/OPTILAB 903 interferometer operating at the wavelength 632.8 nm. In static measurements, the angle was varied from 135° to 20°, in steps of 10°.

Water was deionized with an ELGASTAT UHQ-PS device.

Results and Discussion

Viscosity. Polyelectrolytes dissolved in pure water expand upon dilution. The expansion is observed as an increase of the reduced viscosity with decreasing polymer concentration. PMETMMS dissolved in water−acetone mixtures with varying compositions also shows the polyelectrolyte effect. As can be seen in Figure 1, the polyelectrolyte effect becomes less pronounced with increasing acetone concentration. The addition of acetone decreases the thermodynamic quality of the solvent while the dielectric constant of the liquid decreases. When $\gamma = 0.82$, PMETMMS collapses and a considerable decrease of the solution viscosity is observed.

When $0.60 < \gamma < 0.82$, the reduced viscosity η_{sp}/c has a maximum at a certain polymer concentration. At very low polymer concentrations the reduced viscosity suddenly decreases. In this very dilute regime, the value of the relative viscosity $\eta_r = \eta_{solution}/\eta_{solvent}$ is in some cases less than 1.10. Correspondingly, the uncertainty in the exact value of the reduced viscosity increases. The regime where $\eta_r < 1.10$ is indicated with dotted lines in Figure 1. This range of polymer concentrations was studied using light scattering.

Static Light-Scattering Measurements. Figure 2 represents the concentration dependence of the intensity of light scattered at 90° from solutions with varying γ. The difference between the scattered light intensities

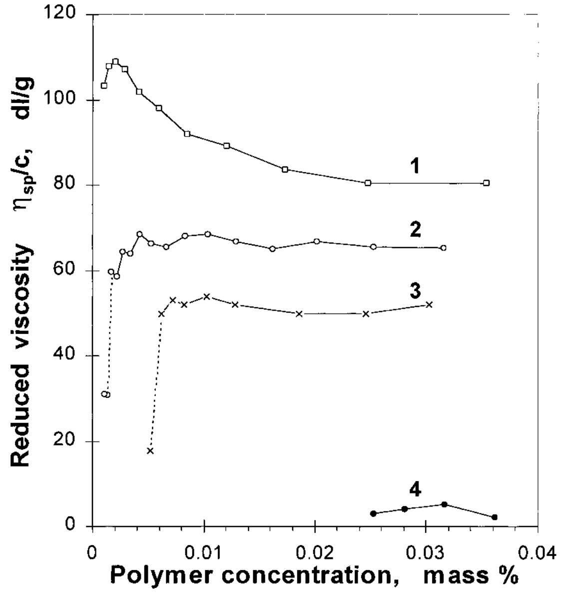


Figure 1. Concentration dependence of the reduced viscosity of PMETMMS dissolved in water−acetone mixtures with various compositions. Mass fraction of acetone: (1) 0.70; (2) 0.76; (3) 0.79; (4) 0.82.

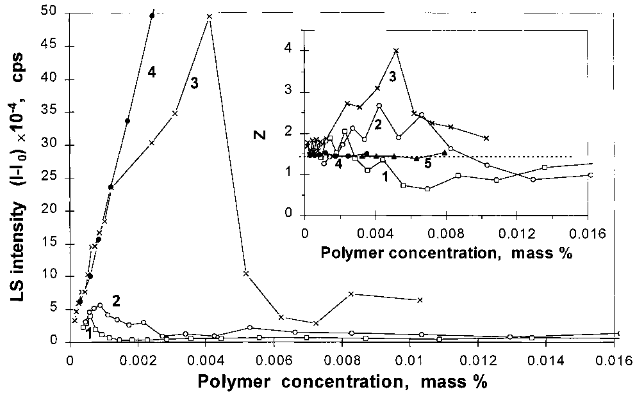


Figure 2. Concentration dependencies of the scattering intensity and the angular dissymmetry parameter *Z* of PMETMMS dissolved in water−acetone mixtures with varying composition. Mass fraction of acetone: (1) 0.70; (2) 0.76; (3) 0.79; (4) 0.82; (5) 0.85. The intensity is given in counts of photons per second (cps).

from the solutions and the solvents, $I - I_0$, is given in counts of photons per second. In the low-concentration region, where the viscosity of the solution decreases (and/or the possibilities to accurately measure the viscosity are restricted), the scattered light intensity increases. The increase is more profound the higher γ is. It may be seen that the solutions with high γ scatter strongly. The increase of the intensity with increasing γ is due to the change in the solvent quality followed by the compactization of the polymers. The intensity versus concentration shows a maximum, the position of which depends on the solvent composition.

The inset in Figure 2 shows the angular dissymmetry parameter $Z = I^{45}/I^{135}$ versus polymer concentration. For the solutions with $\gamma \leq 0.79$ and high polymer concentration, the scattering intensity is low and the value of *Z* is close to unity, which is typical for semidilute solutions. The increase of *Z* with decreasing polymer concentration may be understood as a transition from a semidilute to a dilute polymer solution. Polyelectrolyte coils are more expanded in solutions with low γ,

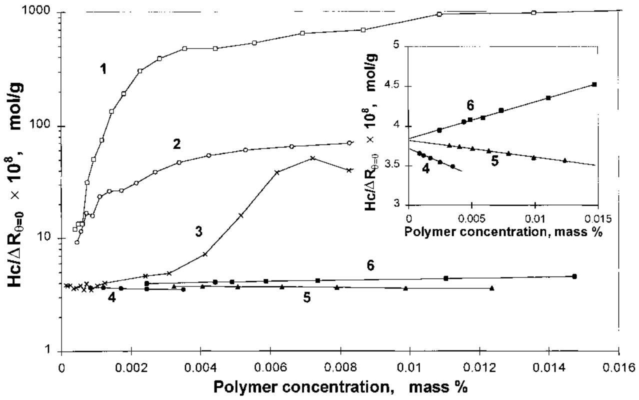


Figure 3. Concentration dependence of the inverse reduced scattering intensity of PMETMMS in water−acetone mixtures with various compositions: (1) 0.70; (2) 0.76; (3) 0.79; (4) 0.82; (5) 0.85. (6) Polymer in aqueous 1 M $NaNO_3$.

and thus, the overlap concentration *c**, defined as a peak value of *Z*, increases with increasing acetone content of the solvent. The decrease of *Z* at concentrations $c < c^*$ could only be due to a decrease of the size of the polyions. As will be shown later, this hypothesis is supported by DLS results. The scattered light intensity from concentrated solutions (concentration ≤ 0.037 mass %) with $Z \approx 1$ is insufficient for DLS studies. In addition, strong intensity fluctuations make a quantitative analysis difficult.

The reduced scattered light intensity at zero angle $Hc/\Delta R_{\theta=0}$ is plotted against polymer concentration in Figure 3 for all the studied solutions. For comparison, the data for aqueous 1 M $NaNO_3$ are also shown. It is worth noting that the molar mass of the polymer, measured by the Zimm method in water−acetone mixtures and in the aqueous−salt solution, is constant (see Table 1). The change of the polymer conformation induced by dilution occurs in a thermodynamically good solvent, where $\gamma \leq 0.79$; A_2 is positive. When $\gamma = 0.82$, A_2 is negative, but it increases again with a further increase of γ due to the increasing solubility of the hydrophobic parts of the polymer.

Ionomer solutions have been studied by light scattering, for example, by MacKnight[14] and Hara.[15] Although some similarities between the present case and the quoted systems exist, the present system has a profound difference: the polymer is dispersed in a mixture of a good solvent (water) and a nonsolvent (acetone). Intermolecular ion pairs keep the polymers in solution when $\gamma < 0.80$ and polymer concentration is sufficiently high.

The molecular parameters can be reliably determined only for solutions with $\gamma \geq 0.82$. The approximate overlap concentration for such solutions may be calculated as for non-interacting hard spheres using $c^* = M_w/[N_A(4\pi/3) R_g^3]$. For PMETMMS the value of *c** is 7.7 mass % in a water−acetone mixture with $\gamma = 0.82$ in comparison to 0.066 mass % in an aqueous saline solution. This shows that all the measurements have been conducted with dilute solutions. Without any detailed knowledge of the structure of the macromolecule in the solution, this conclusion is, however, somewhat uncertain.

Dynamic Light-Scattering Measurements. For the systems with $\gamma = 0.70$, 0.76, and 0.79, the DLS measurements were performed in the concentration region where the scattering intensity has the maximum, that is, at very low polymer concentrations, where the

Table 1. Molecular Characteristics Obtained for PMETMMS Dissolved in Mixed Solvents with Varying Water−Acetone Ratio γ

solvent	1MNaNO$_3$	γ=0.70	γ=0.76	γ=0.79	γ=0.82	γ=0.85	γ=0.90
range of polymer conc, mass %	<0.015	<0.0004	<0.0013	<0.0022	<0.0036	<0.0193	<0.01
M_w, $\times 10^{-6}$ g/mol	26				27	26	
A_2, $\times 10^{-4}$ cm^{3}mol/g^2	0.23				−0.33	−0.09	
$\langle R_g{}^2\rangle^{1/2}$, nm	250				53	54	
R_h,[a] nm	98 ± 10	30 ± 5	31 ± 4	32 ± 5	35 ± 2	35 ± 2	43 ± 2

[a] The given error is the experimental error from several measurements.

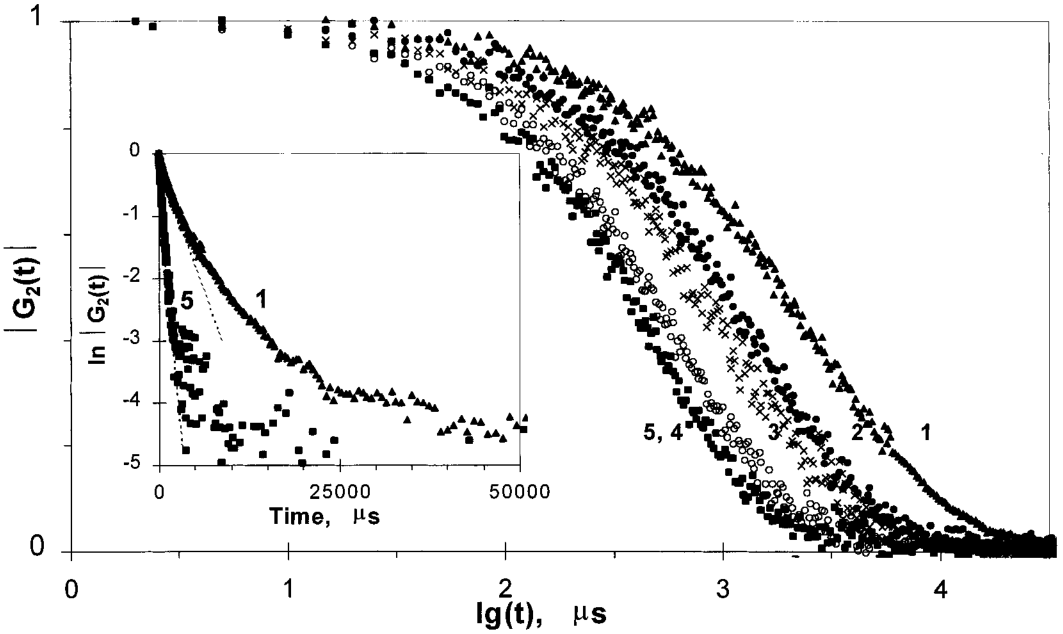


Figure 4. Correlation functions (at 45° scattering angle) of PMETMMS dissolved in a water−acetone mixture with γ = 0.76. Influence of the polymer concentration: (1) 0.0053 mass %; (2) 0.0034 mass %; (3) 0.0022 mass %; (4) 0.0014 mass %; (5) 0.0005 mass %.

correlation functions were close to monomodal ones. Typical correlation functions obtained for the solution with γ = 0.76 at the scattering angle 45° are shown in Figure 4. The measured correlation functions $G_2(t)$ were normalized as follows

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

It is clearly seen that the relaxation time decreases with a decrease of the polymer concentration. Another representation of the same relaxation processes is seen in the inset in Figure 4, and it shows that the logarithmic correlation function of the most concentrated solution deviates strongly from a straight line representing a single-exponential decay. The distributions of the hydrodynamic radii obtained with CONTIN are shown in Figure 5. The decrease of the hydrodynamic radius upon dilution is evident. The size distribution is broad at higher concentrations but becomes narrow with a decrease of the polymer concentration. The narrowing of the size distribution upon dilution is due to the changing balance between the inter- and intramolecular interactions. During the dilution of the solution, the polymer adopts gradually a globular conformation. As was shown in Figure 4, the correlation function approaches a single-exponential one upon dilution. This points to the probable coexistence of polymers in a coil and a globular conformation at the upper concentration limit shown in Figures 4 and 5. At the lower limit, most of the polymers have already adopted a globular conformation; a further dilution does not decrease the relaxation time. A similar behavior was observed also for the other solutions studied, with varying ratio of acetone and water. Yoshikawa et al. have also reported the coexistence of polymers in two different conformations during the coil-to-globule transition.[6]

PMETMMS in the collapsed state was studied more closely, using highly diluted solutions (for concentrations, see Table 1) with varying γ. No concentration and angle dependence of R_h was found up to γ = 0.90. Water−acetone mixtures with $\gamma \geq 0.82$ are poor solvents for PMETMMS, and the scattering intensity from such solutions is high. Therefore, the correlation functions can be obtained and analyzed with good accuracy. A CONTIN fit of the correlation function obtained at a scattering angle of 30° for the PMETMMS solution with γ = 0.85 and the concentration 0.0193 mass % is presented in Figure 6. The residuals shown in the inset in Figure 6 show that the fit was done within an error less than 1%. Distributions of R_h calculated by CONTIN, using the correlation functions like the one in Figure 6, are shown in Figure 7. Practically no angle dependence may be detected. A peak corresponding to an R_h of about 200 nm may be due to a small amount of aggregates in the solution. However, no aggregates were found in solutions with polymer concentration less than 0.013 mass %, and $0.82 < \gamma < 0.90$.

The R_h value of collapsed PMETMMS shown in Table 1 was calculated as an average of R_h peak values of the size distributions obtained for three to six polymer concentrations at four scattering angles. Below a

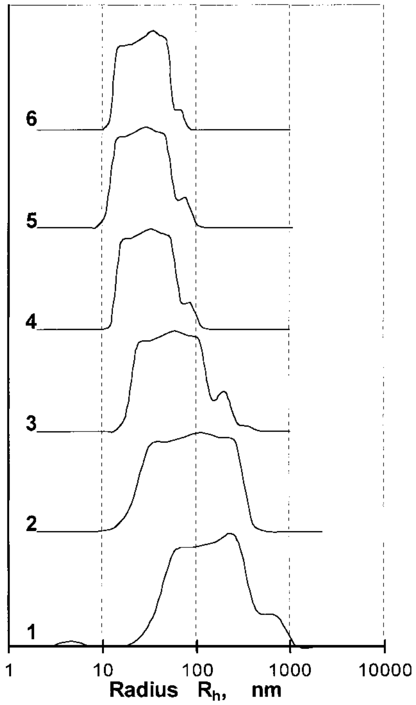


Figure 5. Dependence of the apparent R_h on the polymer concentration calculated with CONTIN from the correlation functions in Figure 4: (1) 0.0053 mass %, (2) 0.0034 mass %; (3) 0.0022 mass %; (4) 0.0014 mass %; (5) 0.0007 mass %; (6) 0.0005 mass %.

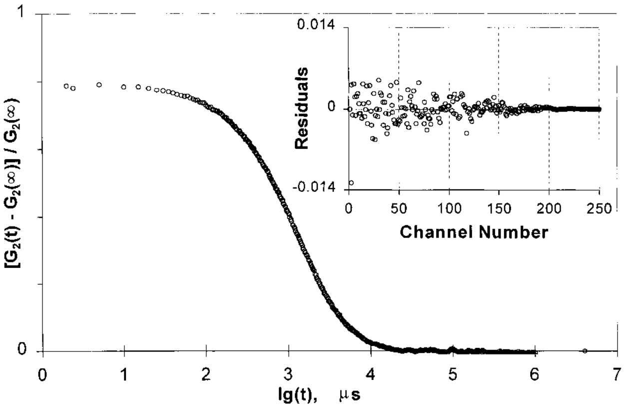


Figure 6. Correlation function of a PMETMMS solution with $\gamma = 0.85$ and the polymer concentration 0.0193 mass %.

certain polymer concentration, the size distribution is no longer concentration dependent. Thus, R_h in Table 1 is the peak maximum, for example, like that in curve 6 in Figure 5. The hydrodynamic size of PMETMMS in the collapsed state slightly increases with increasing γ. This is in accordance with the observed increase of A_2 and is most probably due to the increasing solubility of the hydrophobic parts of the polymer with increasing acetone concentration.

As can be seen in Table 1, for PMETMMS in an aqueous saline solution the ratio R_g/R_h is 2.5, a value typical for a charged polyelectrolyte coil. For the uncharged polymers in the globe state the ratio R_g/R_h is close to 0.77, which corresponds to a solid isotropic sphere.[16] Flow birefringence measurements have shown that during the transition induced by the addition of acetone the conformation of PMETMMS changes from a Gaussian coil into a symmetrical particle without the macroform effect.[1] For collapsed PMETMMS the ratio R_g/R_h is about 1.50. The average density of PMETMMS in its collapsed state for a solution with $\gamma = 0.82$ equals 0.24 g/cm^3, calculated using a simple approximation $\rho \approx M_w[N_A(^4/_3\pi R^3)]^{-1}$. The van der Waals volume of PMETMMS V_W was also calculated and compared with the volume occupied by the molecule in the collapsed state $V_W/V_h \times 100\% = 12\%$. Thus, the results show that the structure of the PMETMMS globules differs from the structure of the globules of uncharged polymers.

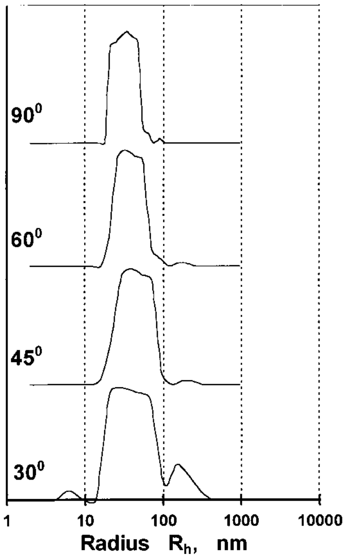


Figure 7. Angle dependence of the size distribution of PMETMMS dissolved in a water–acetone mixture with $\gamma = 0.85$ and the polymer concentration 0.0193 mass %.

To understand the mechanism of the transition, it would be important to check its reversibility in solutions with $\gamma < 0.82$. To accomplish this, however, no experimental possibilities have been found yet.

Conclusions

A collapse of PMETMMS with the molar mass 26×10^6 occurs on addition of acetone into an aqueous solution. The collapse of polyelectrolytes is gradual, so that coils and globules probably coexist during the process. The polyelectrolyte concentration significantly affects the transition. It has been shown that PMETMMS molecules adopt a compact structure also upon diluting the polymer solutions. The conformational change induced by the decreasing polymer concentration takes place in solvent mixtures which may be regarded as good solvents despite their high acetone content. The change in conformation is gradual. Because of the coexistence of polymers with different shapes, the size distributions are somewhat broad at higher concentrations but become narrower upon dilution. The results obtained are in agreement with the recent theory by Kramarenko et al.[9]

The structure of the PMETMMS globules differs from the structure of the globules of uncharged polymers. A toroidal structure of PMETMMS, similar to that of DNA,[6] as well as a spherical flow-through grapelike structure with a heterogeneous density distribution[17] may be suggested as hypothetical models describing the compact conformation.

Acknowledgment. V.A. acknowledges the Laboratory of Polymer Chemistry of the University of Helsinki for a study grant.

References and Notes

(1) Klenin, S. I.; Baranovskaya, I. A.; Valueva, S. V. *Polym. Sci. USSR* **1993**, *35*, 934.
(2) Kipper, A. I.; Valueva, S. V.; Bykova, E. N.; Samarova, O. E.; Rumyantceva, H. B.; Klenin, S. I. *Vysokomol. Soedin., Ser. A* **1994**, *36*, 976.
(3) Klenin, S. I.; Baranovskaya, I. A.; Aseyev, V. O. *Macromol. Symp.* **1996**, *106*, 205.
(4) Aseyev, V. O.; Klenin, S. I.; Tenhu, H. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1107.
(5) Aseyev, V. O.; Klenin, S. I.; Tenhu, H. *Polymer*, in press.
(6) Yoshikawa, K.; Takahashi, M.; Vasilevskaya, V. V.; Khokhlov, A. R. *Phys. Rev. Lett.* **1996**, *76*, 3029.
(7) Morawetz, H.; Wang, Y. *Macromolecules* **1987**, *20*, 194.
(8) Förster, S.; Schmidt, M. *Adv. Polym. Sci.* **1995**, *120*, 51.
(9) Kramarenko, E. Yu.; Khokhlov A. R.; Yoshikawa, K. *Macromolecules* **1997**, *30*, 3383.
(10) Schäfer, H.; Seidel, C. *Macromolecules* **1997**, *30*, 6658.
(11) Kurljankina, V. I.; Molotkov, V. A.; Dobrodumov, A. V.; Eizner, Y. E.; Denisov, V. M.; Panarin, E. F. *Dokl. Akad. Nauk* **1995**, *341*, 358.
(12) Tsvetkov, V. N. *Rigid-Chain Polymers. Hydrodynamic and Optical Properties in Solution*; Consultants Bureau: New York and London, 1989; p 120.
(13) Chu, B. *Laser Light Scattering: Basic Principles and Practice*, 2nd ed.; Academic Press: San Diego, 1991; p 74.
(14) Lantman, C. W.; MacKnight, W. J.; Peiffer, D. G.; Sinha, S. K.; Lundberg, R. D. *Macromolecules* **1987**, *20*, 1096.
(15) Hara, M.; Wu, J.-L. *Macromolecules* **1988**, *21*, 402.
(16) Sun, S.-T.; Nishio, I.; Swislow, G.; Tanaka, T. *J. Chem. Phys.* **1980**, *73*, 5971.
(17) Dobrynin, A. V.; Rubinstein, M.; Obukhov, S. P. *Macromolecules* **1996**, *29*, 2974.

MA980552Q