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Semidilute and Concentrated Solutions of a Solvophobic Polyelectrolyte in Nonaqueous Solvents

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ABSTRACT: We study the behavior of a solvophobic polyelectrolyte in a series of polar organic solvents of various quality and polarity. Small-angle X-ray scattering is used to measure the semidilute correlation length ξ as a function of polymer concentration. In polar solvents of good quality ξ varies as $c^{-1/2}$ in the whole concentration range, as expected. Contrastingly, in acetonitrile, a polar solvent of poor quality, the scaling exponent is found to change from $-^1/_2$ to $-^1/_7$, in qualitative agreement with the predictions of the pearl necklace model of Dobrynin and Rubinstein. This behavior is attributed to the crossover between “string” and “bead-colloid” controlled regimes of the isotropic transient network. At yet higher concentrations a gel-like phase is found attributed to bead interpenetration. It is thought to be driven by the small Debye−Huckel screening length at these concentrations, in agreement with recent molecular dynamics simulations of Micka et al. The crossover concentration for both string/bead-colloid and colloid/gel regimes can be adjusted by mixing solvents of varying dielectric constant and quality. The effect of added of salt and temperature is also studied.

1. Introduction

Flexible polyelectrolytes in good solvents have been well studied both experimentally and theoretically. Although a quantitative theory of their behavior in solution is still lacking, scaling approaches have been successful in providing a qualitative description of their solution-state features.[1−3] In these theories, a monomer−monomer correlation length ξ is introduced to describe the semidilute solution properties; it characterizes the average interchain mesh size of an assembly of overlapping chains above the overlap concentration c^*. ξ is easily measured in reciprocal space as the inverse of the position of a broad correlation peak in small-angle scattering techniques. ξ has been shown to depend on concentration as $c^{-1/2}$ by scaling theories,[1−3] experiments,[4−6] and molecular dynamics simulations.[7] Note that below c^* a peak is also observed by scattering techniques, when the range of the interchain repulsive electrostatic interaction is larger than the distance between them. In this case,[1,5] the 3-d order peak position scales as $c^{+1/3}$.

Flexible polyelectrolytes in poor solvents have experienced comparatively fewer experimental or theoretical studies. Theoretical progress has been made recently for the structure of single globular chains motivating further work.[8,9] Single chain globular structures are predicted to break up into a series of “beads” on “strings” as their charge increases, due to the Rayleigh charge instability, i.e., the increase in surface energy is balanced by a decrease in electrostatic energy, because of the mutual repulsion between charged segments, and the metastability is realized through capillary wave fluctuations on the surface of the globule. It is the pearl necklace model where highly stretched segments alternate with collapsed globules along the chain. This model, first proposed by Kantor and Kardar[8] for polyampholytes (chains containing both positively and negatively charged monomers), was introduced by Dobrynin, Rubinstein, and Obukhov[9] for polyelectrolytes. Extending their study into the semidilute regime, Dobrynin and Rubinstein[10] found two different regimes above c^*, labeled “bead controlled” and “string controlled”, depending on whether the concentration is sufficient for the interbead repulsion to become important or not. This theory has received partial corroboration with the experiments of Essafi et al.[11,12] and Spitteri et al.[13] on partially charged poly(styrenesulfonate) (PSS) in water. Essafi[11] found a ξ/c exponent which was a function of f; for instance, the exponent was −0.38 for 40% charged PSS ($f = 0.4$) in the whole semidilute regime while totally charged PSS displayed the typical −0.5 behavior. Similar findings were also reported by Heitz et al.[14] for poly(methacrylic acid) in water as a function of its neutralization (α): the ξ/c exponent was found to vary from −0.43 to −0.31 when α decreased from 0.95 to 0.09. Evidence for an intrachain bead correlation peak has also been seen in the single chain scattering function in semidilute solutions by small-angle neutron scattering.[13] A very recent investigation by Heinrich and Rawiso[15] of a more complex system of star PSS confirmed the general picture; the authors interpret the appearance of a peak whose position varies as $c^{+1/3}$ as being due to a correlation between hydrophobic aggregates, possibly the beads of the model, along the star arms. Moreover, the important question of counterion condensation[16,17] in these systems has also been studied experimentally and provides a further layer of rich phenomena; there is a strong reduction of the number of osmotically active counterions (or effective charge of the chains), compared to the prediction of Manning

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Table 1. Summary of the Solvent Properties

solvent	abbrev	dielectric constant, ϵ (25 °C)	Manning parameter ($f = b/l_b$)	solvent quality for methacrylate backbone	viscosity behavior[24 a]
acetonitrile	AC	35.9	0.164	poor	weak PE
dimethylformamide	DMF	36.7	0.167	good	PE
N-methylformamide	NMF	182	0.826	very poor	no PE
propylene carbonate	PC	64.9	0.298	good	strong PE
cyclohexanone	CH	15.6	0.071	good	very weak PE

[a] Polyelectrolyte effects.

condensation,[16] which depends on the bare charge fraction of PSS. Presumably, a proportion of the counterions are trapped into the hydrophobic globular structures.[12,18,19]

Micka et al.[20] have performed extensive molecular dynamics simulations of flexible polyelectrolytes in poor solvents which extend to higher charged fractions and higher polymer concentrations than the Dobrynin semidilute solution theory. Using discrete ions in their simulations, they show that pearl necklaces are not stable at high polymer concentrations, and they collapse into compact globular conformations which however do not phase separate. This is in contrast with the picture of Dobrynin et al., which has a stable bead necklace phase throughout the semidilute range. At yet higher polymer concentrations the globular colloids become unstable, and gelation occurs as the chains begin to interpenetrate. Further simulation results by Lyulin et al.[21] focus on the sharp first-order phase transitions displayed by dilute chains as the number of beads on a chain increases in discrete jumps as a function of increasing the charge, temperature, and solvent quality.

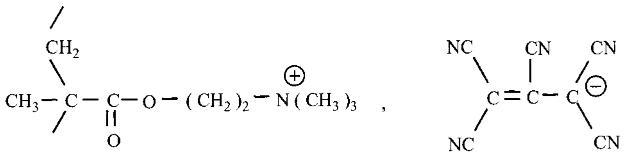
The motivation behind the current paper is toward a critical testing of the "necklace" model with respect to an ionic polymer, which exhibits variable polyelectrolyte behavior in nonaqueous solvents. The possibility to use a range of solvents allows one to test separately the influence of solvent quality and dielectric constant on the polyelectrolyte behavior. Varying the temperature also provides a way to control these two parameters. A further advantage is the possibility to circumvent the problems associated with the complex structure of water, its autodissociation, and difficulties in removing foreign particles.[22,23] The polymer is poly[2-(methacryloyloxy)ethyltrimethylammonium 1,1,2,3,3-pentacyanopropenide] (MPCP), which has been previously shown[24] to exhibit variable polyelectrolyte behavior in a series of nonaqueous solvents, as evidenced by the classic upturn in reduced viscosity at low polymer concentrations.

There have been a number of previous scattering experiments showing the polyelectrolyte behavior of ionomers (polymers containing less than 10−20% of ionizable monomers) in nonaqueous dissociating solvents,[22,25] but they were very weakly charged and their scaling behavior has not been studied. More relevant to the problem of solvophobic and hydrophobic interactions is the scaling study of Ermi and Amis,[26] who found that PMVP (poly(*N*-methyl-2-vinylpyridinium chloride) has the same peak position/concentration scaling exponent of $^1/_2$ whether the polyelectrolyte is in a good solvent (ethylene glycol) or a bad solvent (D_2O) for the backbone, in contradiction with the conclusion of the above-mentioned studies.

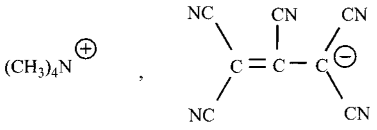
In this article we compare the structural characteristics of semidilute and concentrated solutions of MPCP. Five different nonaqueous solvents of varying quality and dielectric constant are studied for various salt contents and temperatures, by monitoring the position of the characteristic polyelectrolyte peak in SAXS.

2. Experimental Section

Materials. The polymer is an unfractionated sample of atactic poly[2-(methacryloyloxy)ethyltrimethylammonium 1,-1,2,3,3,-pentacyanopropenide] (MPCP) with a molecular weight M_w of 5.3×10^5 g/mol, corresponding to a degree of polymerization (DP) = 1600. Its polydispersity index is about 2 (free radical polymerization, low conversion rate). The reaction scheme for the synthesis is provided in detail in Jousset et al.[24] The monomer repeat distance b is 2.56 Å, and all the monomers are quaternary ammonium salts. MPCP is considered to be a flexible polyelectrolyte by comparison with the flexible character of the methacrylate backbone.[27] The added homoionic salt[28] is tetramethylammonium 1,1,2,3,3-pentacyanopropenide, $(CH_3)_4N^+PCP^-$. Polymer and salt have the following chemical structure:



Polyelectrolyte MPCP



Homoionic salt

The solvents—cyclohexanone (CH), acetonitrile (AC), *N*,*N*-dimethylformamide (DMF), *N*-methylformamide (NMF), and 1,2-propylene carbonate (PC)—of the best reagent grade available were used without further purification. The various solutions were prepared by weighing the polymer and the solvent, and their concentrations c in g/L were calculated assuming a simple volume additivity rule and a constant partial specific volume of MPCP, v, of 0.92 mL/g (pycnometric measurement in AC solution). The concentration range was extended from semidilute solutions up to the occurrence of a physical gel which could no longer flow; the fluidity limits were about 422 g/L in AC and 235 g/L in DMF and PC. Even for the highest concentrations no evidence for microphase demixing of the solvent (critical opalescence) was found. The dielectric constants of the various solvents and their variation with temperature were taken from literature compilation.[29] The solvent properties are summarized in Table 1. Salt concentrations were studied in the range 0−0.06 M.

SAXS Measurements. The X-ray experiments were performed on a laboratory-based Guinier camera with a rotating anode source at a wavelength λ of 1.54 Å (Cu Kα). The scattered X-ray photons were recorded on a linear gas detector with two sample-to-detector distances of 0.34 and 0.8 m, depending on the expected peak position. These configurations allow for q ranges $0.01 < q$ (Å^{-1}) < 0.4 and $0.009 < q$ (Å^{-1}) $<$

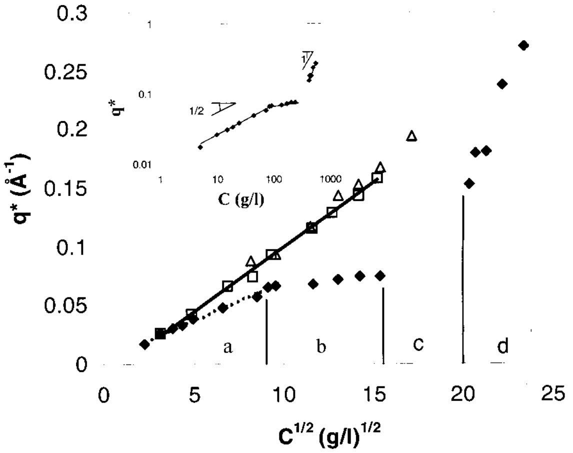


Figure 1. Scaling behavior of the peak position (q^*) as a function of concentration (c) with acetonitrile, AC (◆), dimethylformamide, DMF (□), and polycarbonate, PC (△), at 25 °C. The inset shows the data for AC plotted on a log/log scale. Note the change with AC at a concentration $c_b = 83$ g/L between $^1/_2$ and $^1/_7$ scaling exponents which is indicated by a dotted line. At yet higher concentrations of 260−547 g/L the structure factor peak is lost, only to return at 414 g/L (0.19 Å^{-1}).

0.17, respectively, where $q = (4\pi/\lambda) \sin (\theta/2)$ with θ the angle of the scattered radiation to the direct beam. The scattering profiles have been corrected for background scattering and are obtained as intensity (in relative units) vs q. Glass capillaries with a diameter of 1 mm were used as sample containers. The temperature was changed in situ using a Haake water bath attached to a brass sample holder with an accuracy of ±0.1 °C.

3. Results

Effect of Solvent Quality. In AC, DMF, and PC the scattering profiles show a single broad maximum characteristic of polyelectrolytes. These solutions also exhibited polyelectrolyte behavior in viscometry experiments.[24] No peak was observed in CH or NMF. Since there is no obvious reason for the X-ray contrast to be insufficient in either case (the electron density of NMF is very close to that of DMF), we thus attribute to these solutions weak or nonexistent polyelectrolyte behavior, also in agreement with the previous viscosity measurements.[24]

The concentration dependence of the peak position q^* is markedly different for the three solvents where it is visible. With DMF and PC the behavior is similar, and there is a $\sim c^{+1/2}$ behavior throughout the data set ($9.9 < c < 292$ g/L) as seen in Figure 1 as a straight line in a q^* vs $c^{1/2}$ representation. More precisely for a c^{α} fit we have $\alpha = 0.57$ and $\alpha = 0.56$ for DMF and PC, respectively. This is the expected scaling for a semidilute polyelectrolyte solution in a good solvent within experimental error since q^* is proportional to ξ^{-1}.[1−3] In contrast to this behavior, in AC one observes four different regimes in the same concentration range (noted a, b, c, and d in Figure 1). In the low concentration *regime a* (5−83 g/L) the exponent α is 0.45 over a decade of concentrations. (A linear dependence with a different slope is seen in Figure 1.) There is then a strong saturation as concentration increases: this is *regime b,* which extends up to 235 g/L. Fitting to a scaling law gives an exponent of 0.134, close to $^1/_7$. Note that this value is imprecise as it is determined over half a decade of concentrations only (83−235 g/L). The critical concentration at which there is a change of regime is 83 g/L (c_b in Figure 1), and the corresponding value of the correlation length $\xi = 2\pi/q^*$ is 97 Å. A monotonic increase of the total scattered intensity with concentration is seen in regimes a and b up to 235 g/L (Figure 2a). *Regime c* corresponds to a featureless region (235−404 g/L) where there is no polyelectrolyte peak in the accessible q range and where the intensity decreases as concentration increases until 422 g/L (Figure 2b). In *regime d,* above 422 g/L a peak returns at still higher q values; it corresponds to spacings of 30−22 Å at 422−547 g/L, respectively, when the solutions are gel-like. Note that regimes c and d appear at much higher concentrations than normally studied in semidilute solutions.

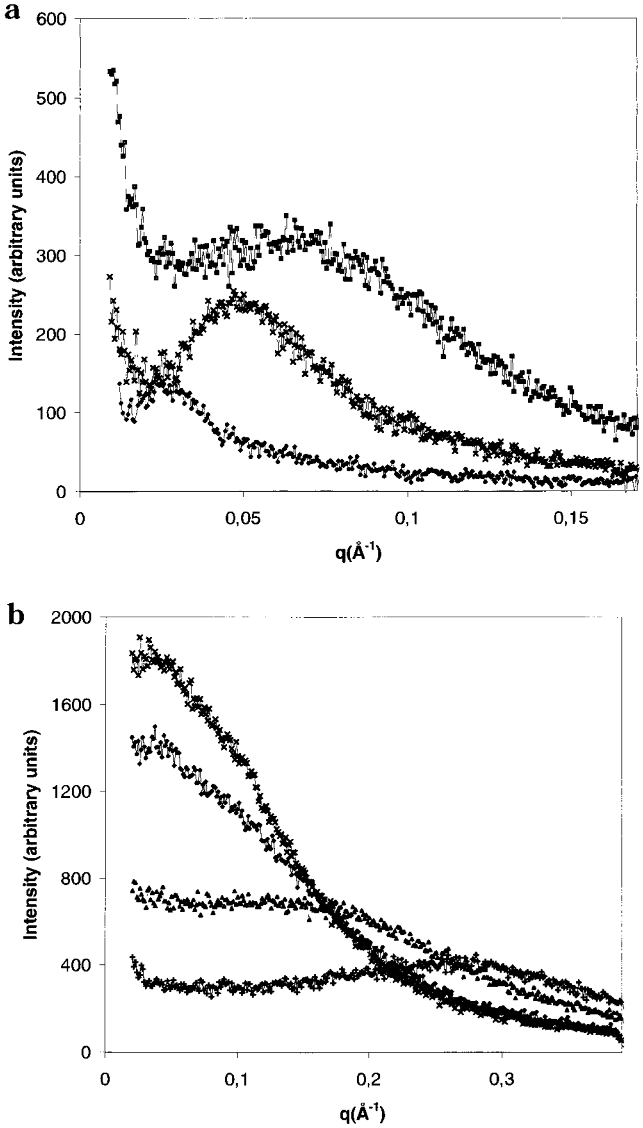


Figure 2. Small-angle X-ray scattering curves from MPCP in AC at a series of different concentrations (9.9−169 g/L). The scattered intensity in relative units is shown as a function of the momentum transfer (q). (a) Lower concentrations: ●, 9.6 g/L; ×, 43.5 g/L; □, 169 g/L. (b) Higher concentrations: ×, 260 g/L; ●, 340 g/L; ▲, 414 g/L; +, 546.7 g/L. Note the sharp decrease in intensity between 404 and 422 g/L followed by the reappearance of a peak.

Mixtures of Solvents. The qualitative behavior of MPCP in binary solvent mixtures of AC was studied, since it allowed the dielectric constant and quality of the solvent to be tuned (Figure 3). There was no optical evidence of demixing at any concentration, which could

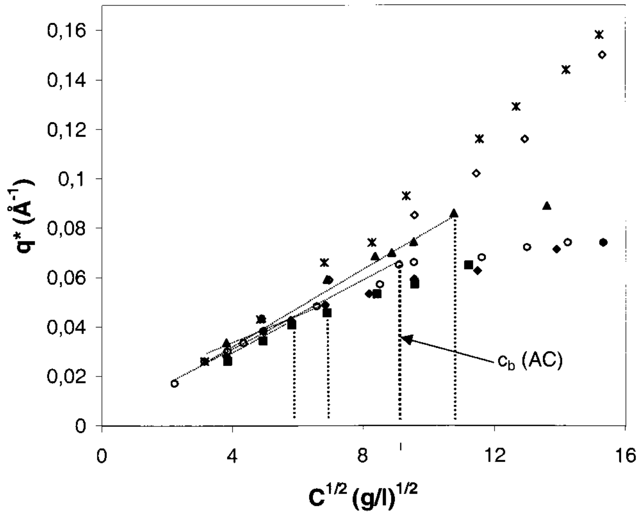


Figure 3. Scaling of the peak position (q^*) of MPCP in a mixture of solvents: CH, AC, and DMF. The behavior of the polymer in 100% DMF and in AC is shown for guidance. Vertical lines on the figure indicate the crossover concentration (c_b) between the $^1/_2$ and $^1/_7$ exponents at low regimes, identified as the "string controlled" and "bead controlled" regimes (see text). Symbols: ◆, 75:25 AC:CH; ■, 50:50 AC:CH; ▲, 75:25 AC:DMF; ◇, 50:50 AC:DMF; *, 100 DMF; ○, 100 AC. Note that the regime where the intensity decreases occurs at 126 g/L for 50:50 AC:CH (■).

be due to a reduced solubility in mixed solvents. However, note that a quantitative analysis in binary solvents is difficult because of the possibility of preferential solvation of parts of the chain by one of the two solvents. Addition to the MPCP in AC solution of DMF, a solvent of same dielectric constant but of better quality causes the crossover concentration (c_b) to move to higher values (116 g/L, $\xi = 73$ Å for 75/25 AC/DMF); the concentration domain of regime a is thus increased as expected for a better solvent. Conversely, addition of CH, a solvent of lower dielectric constant but better quality, to MPCP in AC causes c_b to move to smaller values (47 g/L, $\xi = 130$ Å for 75/25 AC/CH; 33.9 g/L, $\xi = 153$ Å for 50/50 AC/CH). Here the effect of the dielectric constant is seen to be more important than the quality of the solvent. Furthermore, the concentration at which the structure factor peak is lost follows a similar trend, e.g., 126 g/L, $\xi = 97$ Å for 50/50 AC/CH, compared to 235 g/L, $\xi = 85$ Å for pure AC.

Effect of Temperature. The effect of temperature is expected to be slight on the correlation length with hydrophobic polyelectrolytes.[12] To improve the experimental sensitivity, we considered a whole series of concentration measurements and used the scaling behavior of the multiplicative constant (k) in the $q^* = kc^{1/2}$ plots to magnify these small changes. This is helpful, since the temperature is decoupled from the polymer concentration dependence in the scaling theories and still allows easy comparison with experiment. With DMF and PC there is a gradual reduction in the scaling constant (k) as a function of temperature (Figure 4); the variations are almost identical for both solvents, at least for $T > 20$ °C. For AC in contrast k is barely sensitive to temperature and is consistently much lower than with PC or DMF.

Effect of Added Salt. The novel behavior of MPCP in AC solutions was investigated in the presence of the homoionic salt $(CH_3)_4N^+PCP^-$, in the "a" and "b" regimes noted in Figure 1. The salt concentrations c_s were kept lower than 0.06 M,[30] a concentration range where the SAXS peak was still clearly visible. In both regimes, acceptable linear correlations were found (Figure 5):

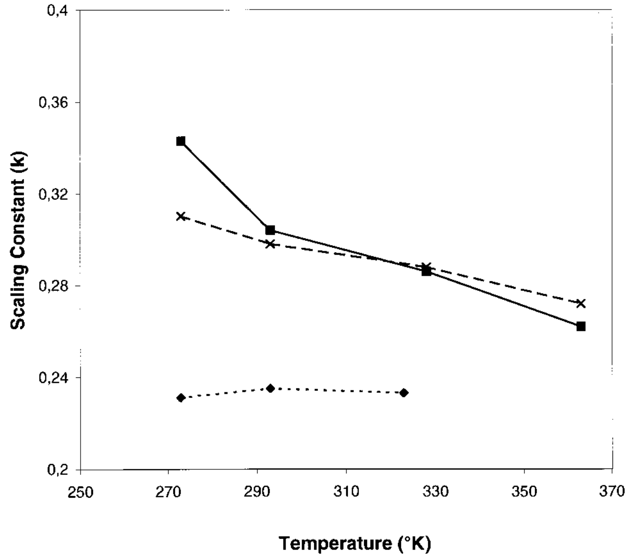


Figure 4. Dependence of the scaling constant (k) as a function of temperature ($q^* = k(T)c^{1/2}$) with AC (◆), PC (■), and DMF (×).

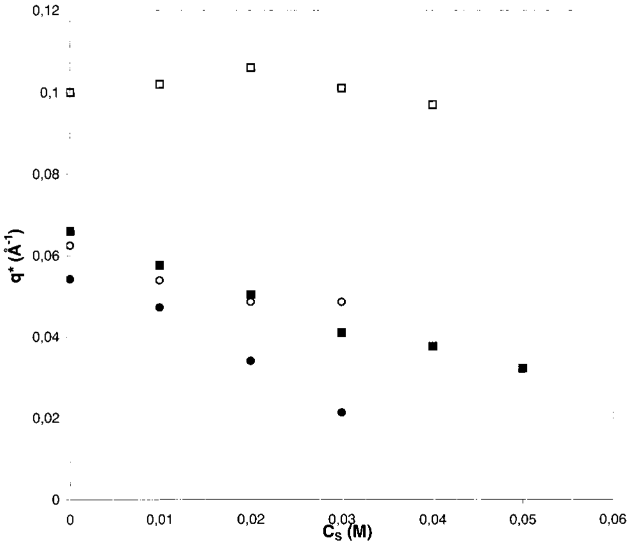


Figure 5. Scaling of the peak position (q^*) as a function of salt concentration (c_s in M) with AC for bead and string controlled regimes. The corresponding behavior in DMF is shown for comparison. ○, 45 g/L DMF; ●, 43.5 g/L AC; □, 117 g/L DMF; ■, 135 g/L AC.

$$\text{a regime at } c_p = 43.5 \text{ g/L}, \quad q^* \propto -64c_s + 0.060$$

$$\text{b regime at } c_p = 135 \text{ g/L}, \quad q^* \propto -34c_s + 0.0645$$

For comparison in the good solvent DMF at similar polymer concentrations, linear correlations were also observed (Figure 5):

$$c_p = 45 \text{ g/L}, \quad q^* \propto -32c_s + 0.0615$$

$$c_p = 117 \text{ g/L}, \quad q^* \propto -3.5c_s + 0.103$$

4. Discussion

Solvent Quality and Dielectric Properties. For a comparison with the theory and simulations let us

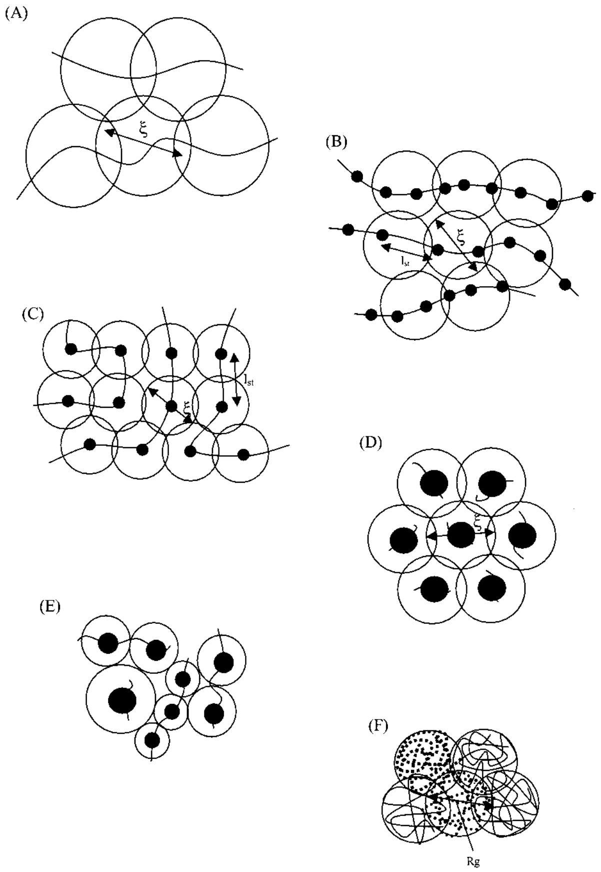


Figure 6. Possible schematic diagram for the concentration dependence of the correlation length ξ of a polyelectrolyte in (A) good solvent (MPCP in DMF or PC); (B) poor solvent "string" regime (MPCP in AC, zone a in Figure 1); (C) poor solvent "bead" regime (zone b); (D) poor solvent "colloidal" regime (zone b); (E) poor solvent "polydisperse colloidal" regime (zone c); (F) interpenetrating "gel" regime. Black circles indicate globular aggregates. l_{str} is the average distance between "beads". Counterions and electrostatic blobs are not shown. (C) and (D) correspond to the pearl necklace model of Dobrynin et al.[10] (D), (E), and (F) are inspired by the simulations of Micka et al.[20]

first define some relevant variables. Consider chains with a degree of polymerization N, monomer size b, and fraction of charged monomers f; the dimensionless interaction parameter describes the strength of the electrostatic interaction as

$$u = l_b/b \tag{1}$$

where $l_b = e^2/(4\pi\epsilon k_B T)$ is the Bjerrum length, b is the monomer repeat distance (equal to 2.56 Å for a polymethacrylic backbone), e is the electron charge, k_B is the Boltzmann constant, T is the temperature, and ϵ is the solvent dielectric constant. For polymer solutions, the reduced temperature, $\tau = (\theta - T)/\theta$, gives a measure of the quality of the solvent as the relative variation from the θ temperature; $\tau = 0$ in a θ solvent where the behavior is quasi-ideal and is negative in a good solvent and positive in a poor solvent.

For a flexible polyelectrolyte *in a good solvent*[1,2] such as DMF and PC, the semidilute correlation length (Figure 6A) is found to be

$$\xi \approx \left(\frac{B}{cb}\right)^{1/2} \propto c^{-1/2} \tag{2}$$

Here B defines the expansion of the chain and is the ratio of the contour length (Nb) to actual extended size L; in good solvent conditions ($T \gg \theta$),

$$B \approx \left(\frac{1}{uf^2}\right)^{2/7} \qquad T \gg \theta \tag{3}$$

In varying the dielectric constant of the solvent, one has to consider the effect of counterion condensation on highly charged polyelectrolyte chains.[26] Assuming complete dissociation of each salt group, the fraction of free counterions (or the effective charge fraction f_{eff} on the polymer) has an upper limit determined by the condition that $u = 1$ (or $f_{\mathrm{eff}} = b/l_b$). All counterions in excess of this condition stay in the close vicinity of the chain in order to reduce its charge. This effect is known as the Manning−Oosawa condensation and is rather well supported by experiments, at least qualitatively. The values of u^{-1}, known as the Manning parameter, in the different solvents are listed in Table 1.

Next we consider a flexible polyelectrolyte in a *poor solvent*. In the limit of very weak charge, the chain is collapsed into a globule. According to the pearl necklace model of Dobrynin, Rubinstein, and Obukhov,[9] there exists a phenomenon akin to the Rayleigh charge instability when the charge on a isolated chain is increased in a poor solvent. The necklace chain consists of a series of beads separated by thin strings. More specifically, the number of monomers in each bead created by this instability is found to be $m_b \approx \tau/(uf^2)$. The semidilute regime is still described by a single correlation length ξ.[10] In the "string controlled regime" (SCR), ξ is larger than the average distance between beads (Figure 6B) and is given by

$$\xi \approx b m_b^{1/4} (cb^3)^{-1/2} \tag{4}$$

which has the same $c^{-1/2}$ concentration dependence as in (2) with a good solvent. The sole difference is that the correlation length increases for a poorer solvent due to the decrease in excluded volume and thus effective chain concentration. This would be expected to cause a loss in the gradient (k) of a $q^*/c^{1/2}$ plot. Upon increasing the pearl necklace concentration, the correlation length becomes of the same order as the distance between pearls, and we find the "bead controlled regime" (BCR) with a correlation length (Figure 6C) given by

$$\xi \approx \left(\frac{m_b}{c}\right)^{1/3} \tag{5}$$

The $c^{-1/3}$ dependence is unusual in polyelectrolyte semidilute solutions; in this regime the chain could be viewed as a dilute solution of beads where the electrostatic interactions are screened, and there is one bead per correlation volume. The crossover concentration c_b between SCR and BCR is predicted to be when the string and bead controlled correlation lengths given in (4) and (5) become of similar magnitude, i.e.

$$c_b \approx b^{-3}\left(\frac{\tau}{uf^2}\right)^{-1/2} \tag{6}$$

In the poor solvent case, counterion condensation is more complex since it can take place on strings, with the usual Manning condition, on beads controlled by their size and charge and on the whole necklace controlled by its total charge. In what follows, short of more quantitative information, we will consider that the usual Manning condition gives an upper limit for f in all cases.

Comparing this theory with our experiments, we confirm that DMF and PC are good solvents for MPCP with eq 2 applicable for the correlation length, since there is a $c^{1/2}$ behavior of q^* throughout the data set (Figure 1). For AC the reduction in gradient (k, Figure 5) and change in scaling at 83 g/L ($\xi = 96.7$ Å) leads us to assume that we are studying a poor solvent behavior, and eqs 4 and 5 are relevant. Comparing the dielectric constants for DMF ($\epsilon = 36.7$) and AC ($\epsilon = 35.9$), we observe that there is only a small difference in their values and thus conclude the electrostatics of the monomer/monomer interactions are similar in the two solvents. We deduce that it is the second virial coefficient for the backbone (or quality of solvent) which is driving the change in phase behavior. Further evidence for the poor solvent polyelectrolyte behavior in AC was previously found[24,31] in viscosimetry measurements, and a rough estimate of the number of effective charges per chain showed that it is about twice lower in AC than in DMF. The contrasted behaviors of MPCP in DMF and AC thus directly reflect the solvation power of these solvents for the chain backbone. This may be modeled by poly(methyl methacrylate) (PMMA) which has the same chemical structure as MPCP, but without the ionic groups. It is found that DMF is actually a fairly good solvent of PMMA,[32] while AC is a Θ solvent at 28 °C, with an even more collapsed chain conformation than in other Θ solvents.[33]

A definite phase transition is seen with AC in the semidilute regime as concentration increases with q^*/c exponents of 0.45 and 0.134. We tentatively identify these two regimes as the string and bead controlled regimes, keeping in mind that the apparent exponent in the BC regime is much smaller than the predicted value, and thus the structural description of the phase may be different. Although a quantitative comparison of c_b with the theory is not possible, the relative variations of c_b in binary solvents of AC mixed with CH or DMF is rather revealing. According to the model and assuming homogeneous solvent mixtures, addition to AC ($\epsilon = 35.9$) of DMF (good solvent, similar $\epsilon = 36.7$) causes the size of the beads to reduce and the chains to extend as the solvent quality improves. Similarly, with a 50:50 AC/DMF mixture a loss in slope (k) of the q^*/c is seen compared to 100% DMF, as the solvent gets poorer and the chains form more compact conformations; but the pearl controlled regime is not experimentally realizable with this mixture since it occurs at too high concentrations to allow solubility. On the other hand, addition to AC of the low dielectric constant ($\epsilon = 15.6$), good solvent CH decreases the electrostatic interactions due to counterion condensation and causes the bead size to increase, the correlation length increases, and the crossover between bead-colloid and string regimes should occur at longer length scales, and thus at lower concentrations as observed, ($c_b \sim \epsilon^{+1/2}$, assuming $f = b/l_B$) (Figure 3).

The pearl necklace model seems adequate to describe the moderate concentration regimes in poor solvent. However, in its present state it breaks down at very high polymer concentrations (>235 g/L in AC) since it does not predict the existence of the two regimes "c" and "d". In this region it is useful to examine the Monte Carlo simulations of Micka et al.[20] of highly charged chains with discrete counterions in poor solvent, where the charges, including counterions, all interact via the full Coulomb potential. The results show a variety of conformations as concentration increases which includes the stretched pearl necklace chain at lower concentration but also shows very collapsed isolated chains at higher concentrations which eventually at still higher concentrations will open up. We do have to remember that the simulated chains are much shorter than ours, which is a possible reason for disagreement, especially concerning the fact that the simulated chains do not overlap until very high concentrations. Still it can be interesting to compare these simulations with our scattering results and note some similar trends. However, one should also keep in mind that the X-ray scattering experiments provide the total scattering functions which include all the partial scattering functions whereas the simulation results are limited to the relevant partial structure functions. At high concentrations there is a monotonic decrease in the scattered intensity, as we observe; we find that there is no longer a correlation peak in the scattering profile for 235−404 g/L (Figure 2b). However, at yet higher polymer concentrations the experiments show a high q peak in the scattered intensity at a q value corresponding to the order of magnitude of the radius of gyration (R_G) of a single chain (Figure 6F). This has as yet not been seen in the simulations, and the predictions of this reentrant appearance of the small-angle peak would be a good test for them. An order of magnitude estimate for a single compact MPCP globule gives $R_G \approx bN^{1/3} \sim 30$ Å, which is similar to the value of the peak position 30.2 Å (ξ_g). Thus, it is likely that the chains are interpenetrated since the volume available to a single chain at 422 g/L is only (108 Å)^3, three gel correlation lengths. Furthermore, we note that the loss in low-q intensity in the polydisperse colloid regime (Figure 1c, Figure 6E) could be explained by the globules opening out and releasing their counterions, thereby screening the long wavelength fluctuations. Indeed, the zero q limit of the structure factor is related to the number of free counterions f through osmotic compressibility[2] $\partial c/\partial \Pi$ by

$$S(0) \approx kT \frac{\partial c}{\partial \Pi} \approx \frac{1}{f} \qquad (7)$$

Thus, a loss of low q scattering could be related to either an increase in the effective value of f or equally the loss of large globular structures in the solution. To a first approximation the final gel-like regime (Figure 1d, Figure 6F) could be expected when the Debye−Huckel screening length in this semidilute gel solution

$$r_D = \left(\frac{B}{bc}\right)^{1/2} \qquad (8)$$

a decreasing function of the polymer concentration,[34] becomes equal to the length scale of the solvophobic interaction. These interactions lead to cross-links at high polymer concentrations and the formation of a percolating gel structure.

To summarize, we tentatively propose that the four separate regimes that we have observed as a function of polymer concentration in the semidilute region (Figure 1) correspond to the following regimes. At low concentration where the chains begin to overlap we have the "string" controlled regime (Figure 6B), next the "bead-colloid" controlled regime (Figure 6C,D), then the polydisperse colloid (Figure 6E), and finally the interpenetrating "gel" regime (Figure 6F), according to the nomenclature of Micka et al.[20] No evidence was found for microphase separation in line with the simulation results, which indicate homogeneous distributions of chains in concentrated regimes. More experiments are clearly needed to validate this picture which can only be considered so far as a possible scenario.

Effect of Temperature. A previous SANS study of Boué et al.[35] of 100% charged PSS showed no effect of temperature on both inter- and intrachain interactions. However, Essafi et al.[12,13] observed that decreasing the charge fraction of PSS below 100%, thus increasing the hydrophobicity, causes the peak height to become more and more temperature sensitive. A similar temperature dependence of the peak height was found in the present study for MPCP in AC, indicating again that it is also in the poor solvent regime. For a more accurate understanding of the temperature-dependent behavior, we need to take into account the temperature dependence of the dielectric constant.[29]

Considering Figure 4, we see that the correlation length decreases with temperature as predicted by the theory for the good solvents PC and DMF (eqs 2 and 3), i.e., $k \propto (T\epsilon)^{1/7}$. Comparison with experiment however shows that the temperature dependence is largely underestimated by the theory for both solvents. The temperature dependence in the bad solvent string regime is predicted to be $k \propto (T\epsilon\tau)^{1/4}$, in qualitative agreement with experiment for the relative magnitudes of the temperature sensitivity.

Effect of Salt. For a semidilute polyelectrolyte in high salt concentration (c_s) and good solvent conditions, Dobrynin et al.[9] predict that the correlation length (ξ) is given by

$$\xi \approx b(cb^3)^{-1/2}B^{1/2}\left(1 + \frac{2c_s}{fc}\right)^{1/4} \qquad (9)$$

and is in qualitative agreement with our experimental results when linearized for small c_s.

In a poor solvent two predictions by the same authors of the semidilute scaling behavior for polyelectrolytes are

string controlled regime (SCR):

$$\xi \approx b{m_b}^{1/4}(cb^3)^{-1/2}\left(1 + \frac{2c_s}{fc}\right)^{1/4} \qquad (10)$$

bead controlled regime (BCR):

$$\xi \approx {m_b}^{1/3}c^{-1/3}\left(1 + \frac{2c_s}{fc}\right)^{5/12} \qquad (11)$$

Qualitatively, the effect of salt in BCR is less strong than SCR. This agrees with experiment, and in Figure 5 it is seen that the effect of salt concentration follows the series (in increasing order of effect) DMF (high c (9)), DMF (low c (9)), AC (high c (10)), and AC (low c (11)).

General Remarks. The phase behavior of MPCP in the present SAXS experiments is strikingly reminiscent of that of poly(styrenesulfonate) (PSS) in the intermediate concentration range. In principle, MPCP provides a more ideal system for molecular modeling than typical aqueous polyelectrolytes. Only weak hydrogen bonding is involved in AC solutions and is actually lacking for the other organic solvents. Thus, the second virial coefficient could, in principle, be calculated, because more tractable interchain potentials exist for the other interactions.

With such complex systems as polyelectrolytes the theory of Dobrynin et al. offer a number of useful predictions. However, we must note certain practical reservations as to its applicability with MPCP in the low-concentration semidilute regime. First of all, it is not evident whether the globular structures are above or below their glass transition temperature with MPCP as well as with PSS, as already noted.[12] There could be a glassy ionomer-like[36] behavior in the globular regions due to dipole/dipole interactions and low plasticization in the poor solvent AC. Another problem is that our polyelectrolytes are highly charged, and blob theory is strictly accurate for $fu^2 \ll 1$, which is clearly not obeyed in the current study. Finally, the pentacyanopropenide counterions are large, planar, and highly polarizable species, and their possible role as a point of departure from the theories cannot be definitely ruled out. Previously, studies with PSS[37] have however shown a negligible effect of ion size.

It is interesting to question why the succession of different regimes has not been seen before for polyelectrolytes in poor solvents. For example, referring to the work of Ermi and Amis,[26] we see that their analyses have been conducted in the low-concentration semidilute regime (2−25 g/L), and thus we propose that much higher concentrations would need to be studied to find the novel phase behaviors seen in the present study.

5. Conclusion

We have studied with small-angle X-ray scattering the correlation length of semidilute and concentrated solutions of a model flexible polyelectrolyte, MPCP, in a range of nonaqueous solvents of variable quality and dielectric properties. Classic polyelectrolyte behavior is found in dissociating good solvents, such as dimethylformamide and propylene carbonate, confirming earlier viscometric experiments.[24] Solvophobic polyelectrolyte effects are observed in semidilute solutions with dissociating poor solvents, similar to those observed with the hydrophobic partially charged poly(styrenesulfonate).[11−13,15] The crossover behavior from $-1/2$ to $-1/7$ of the scaling exponent of the semidilute correlation length in acetonitrile is in qualitative agreement with the theory of Dobrynin and Rubinstein[9] for a new mesophase and provides further experimental evidence for the existence of the pearl necklace structure. The transition between the "string controlled regime" and the "bead controlled regime" is found to be fairly sharp and is reminiscent of a first-order phase transition. Temperature and salt dependence of the correlation length are in qualitative agreement with theory. At very high polymer concentrations (concentrated regime) two new regimes are observed, corresponding to a loss of the correlation peak followed by a reappearance at higher q values. A possible scenario is provided by the Monte Carlo simulations of Micka, Holm, and Kremer[20] as a "bead necklace/colloid" to gel phase transition driven by the extremely small Debye screening lengths in these systems. Clearly more extensive X-ray, neutron, and light scattering as well as NMR experiments are needed to understand these new effects and to rigorously classify the mesophases a, b, c, and d in Figure 1. It is hoped that these data will stimulate more focused simulations and further theoretical developments.

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References and Notes

(1) de Gennes, P. G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys.* (*Paris*) **1976**, *37*, 1461.
(2) Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. *Macromolecules* **1995**, *28*, 1859.
(3) Barrat, J. L.; Joanny, J. F. In *Advances in Chemical Physics;* Prigogine, I., Rice, S. A., Eds.; Wiley: New York, 1996; Vol. XCIV, and references therein.
(4) Nierlich, M.; Williams, C. E.; Boué, F.; Cotton, J. P.; Daoud, M.; Farnoux, B.; Jannink, G.; Picot, C.; Moan, M.; Wolf, C.; Rinaudo, M.; de Gennes, P. G. *J. Phys. (Paris)* **1979**, *40*, 701.
(5) Kaji, K.; Urakawa, H.; Kanaya, T.; Kitamaru, R. *J. Phys. (Paris)* **1988**, *49*, 993.
(6) Förster, S.; Schmidt, M. *Adv. Polym. Sci.* **1995**, *120*, 51 and references therein.
(7) Stevens, M. J.; Kremer, K. *J. Chem. Phys.* **1995**, *103*, 1669.
(8) Kantor, Y.; Kardar, M. *Europhys. Lett.* **1994**, *27*, 643.
(9) Dobrynin, A. V.; Rubinstein, M.; Obukhov, S. P. *Macromolecules* **1996**, *29*, 2974.
(10) Dobrynin, A. V.; Rubinstein, M. *Macromolecules* **1999**, *32*, 915.
(11) Essafi, W.; Lafuma, F.; Williams, C. E. *J. Phys. II* **1995**, 1269.
(12) Essafi, W. PhD Thesis, Paris VI, 1996.
(13) Spitteri, M. N. PhD Thesis, Paris XI, 1997.
(14) Heitz, C.; Rawiso, M.; Francois, J. *Polymer* **1999**, *40*, 1637.
(15) Heinrich, M.; Rawiso, M., preprint.
(16) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(17) Oosawa, F. *Polyelectrolytes*; Marcel Dekker: New York, 1971.
(18) Essafi, W.; Lafuma, F.; Williams, C. E. *Eur. Phys. J. B* **1999**, *9*, 261.
(19) Essafi, W.; Lafuma, F.; Williams, C. E. Manuscript in preparation.
(20) Micka, U.; Holm, C.; Kremer, K. *Langmuir* **1999**, *15*, 4033.
(21) Lyulin, A. V.; Dumweg, B.; Borisov, O. V.; Darinskil, A. A. *Macromolecules* **1999**, *32*, 3264.
(22) Hara, M. In *Polymeric Materials Encylopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 5, p 3473.
(23) Schmitz, K. S. *Macroions in Solutions and Colloidal Suspensions*; VCH Publishers: New York, 1993.
(24) Jousset, S.; Bellissent, H.; Galin, J. C. *Macromolecules* **1998**, *31*, 4520.
(25) Lantman, C. W.; MacKnight, W. J.; Sinha, S. K.; Peiffer, D. G.; Lundberg, R. D.; Wignall, G. D. *Macromolecules* **1988**, *21*, 1344.
(26) Ermi, B. D.; Amis, E. J. *Macromolecules* **1997**, *30*, 6937.
(27) Analysis of the viscosity/molecular weight data for the homologous poly[(2-methacryloyloxy)ethyltrimethylammonium benzenesulfonate] in aqueous KCl 0.5 M solution lead to a steric factor of 3.1 corresponding to a persistence length p of about 15 Å. Ignoring as a first approximation the potential influence of the counterions, fairly close σ and p values may be reasonably anticipated for MPCP (identical polycationic chain) which should be thus considered as an intrinsically flexible polyelectrolyte. Stejskal, J.; Benes, M. J.; Kratochvil, P.; Peska, J. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1941.
(28) Middleton, W. J.; Little, E. L.; Coffmon, D. D.; Engelhardt, D. T. *J. Am. Chem. Soc.* **1958**, *80*, 2795.
(29) Variation in $\epsilon = f(T)$. Wohlfarth, C. In *Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1996.
(30) Quantitative dissociation of $(CH_3)_4N^+PCP^-$ in AC and DMF according to the literature; see: Boyd, R. H. *J. Chem. Phys.* **1963**, *67*, 737.
(31) Fits of viscosimetric data with the Fuoss law in its simplified form, $\eta_{red} = A/(1 + Bc^{1/2})$; i.e., reduced viscosity as a function of concentration where A and B are constants; the A/B ratio reflects the number of effective charges per chain.
(32) Spychaj, Y.; Bohdanecky, M.; Berek, D. *Acta Polym.* **1986**, *37*, 93.
(33) Quadrat, O.; Bohdanecky, M.; Mrkvickova, M. *Makromol. Chem.* **1981**, *182*, 445.
(34) Rubinstein, M.; Colby, R. H.; Dobrynin, A. V.; Joanny, J. F. *Macromolecules* **1996**, *29*, 398−406.
(35) Boué, F.; Cotton, J. P.; Lapp, A.; Jannink, G. *J. Chem. Phys.* **1993**, *101*, 2562.
(36) Kim, J. S.; Eisenberg, A. *Ionomers*; Wiley: New York, 1998.
(37) Nallet, F.; Jannink, G.; Hayter, J. B.; Oberthur, R.; Picot, C. *J. Phys. (Paris)* **1983**, *44*, 87.

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