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Conformation of Poly(1,3-dioxolane) in Dilute and Semidilute Aqueous Solutions

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ABSTRACT: The conformation of poly(1,3-dioxolane) (PDXL) in aqueous solution was studied by light and neutron scattering, by size-exclusion chromatography coupled with light scattering, and by viscosimetry. In the absence of salt, the solutions contain aggregates which cannot be eliminated either by centrifugation or by filtration. These aggregates result in an excess of scattered intensity, but in an intermediate range of q available in neutron scattering experiments, the behaviors in the dilute and in the semidilute regimes are those expected for a polymer in a rather good solvent. The scaling law for the concentration dependence of the screening length ξ was obtained: $\xi = 2.29c^{-0.73}$. In the presence of salt, (0.05 and 0.1 N NaCl), there are no more aggregates although the value of LCST is very close to that in pure water. The variation of the radius of gyration with molecular weight was determined as well as the temperature dependencies of the second virial coefficient and intrinsic viscosity for a given sample.

Introduction

The solubility of polyethers in water remains the object of numerous studies and theoretical approaches.[1,2] The poly(oxymethylene) is generally considered as insoluble while much attention has been devoted to the case of poly(ethylene oxide) (PEO) whose solubility diagram exhibits a "closed loop" form.[3] At room temperature, aqueous PEO solutions are transparent and phase separation occurs upon heating above 100 °C. This well-known phenomenon is generally attributed to the hydration of the monomer units via hydrogen bonding between water molecules and oxygen of the ether functions.[4,5] Heating induces a release of the hydration molecules and enhances the interactions between the hydrophobic parts of the polymer. Other explanations have been proposed, such as that of Saeki et al.[6] who applied the modified Flory-Huggins and Patterson theory[7,8] to the case of aqueous solutions. Moreover, the concept of solubility of PEO in water and in polar solvents even at room temperature is the object of some controversies. Indeed, while it is sometimes considered as molecularly dispersed,[9-12] light scattering or viscosity experiments often reveal the presence of large aggregates.[13-16] Polik and Burchard[15] have shown that the aggregation in aqueous solutions of a low molecular weight PEO sample (M_w = 20 000) increases markedly upon heating but decreases above 60 °C. In contrast, Devanand et al.[10-12] are able to prepare free aggregate solutions, and the molecular weight dependencies of the molecular dimensions reveal a behavior of a polymer in good solvent. In fact, the agreement between the different experimental studies is rather poor and the influence of the method of preparation and clarification of the solutions seems to be of paramount importance.[10,16]

However, de Gennes[17] has recently suggested that such association behavior presents a real physical significance and may correspond to particular phase separation between rich and poor polymer phases, in which the polymer chains remain expanded ($\chi < 0.5$). The rich polymer phase contains aggregates of expanded chains bound by a few hydrophobic segments. This theoretical approach is consistent with the findings of Polik and Burchard[15] which are interpreted in terms of the coexistence of high-density spherulites with low-density microgel aggregates. It assumes a demixing curve which is impossible to determine by the usual turbidimetric method but requires much more sophisticated techniques, since the solutions remain transparent.

In a recent work[18] we have compared the phase diagram of a water-PDXL system with that of aqueous PEO solutions. PDXL is a perfectly alternated copolymer made of units constitutive of POM and PEO.

$$\text{PDXL:}\ \ -[\mathrm{CH_2CH_2OCH_2O}-]_n$$

Differential scanning calorimetry, turbidimetry, and densimetry experiments have revealed that the solubility domain of PDXL is much more limited than that of PEO. The lower critical solubility temperature is 70 °C, while LCST is close to 100 °C for PEO. Moreover, the apparent solubility is limited to a polymer concentration range lower than 50% weight wise.

The purpose of the present paper is to determine the thermodynamic solution properties of PDXL in water at 25 °C and as a function of temperature in the dilute and the semidilute regimes. We have used viscosimetry, light scattering, and size exclusion chromatography coupled with multiangle light scattering and small angle neutron scattering. The lower "apparent" solubility of PDXL in water could suggest that a behavior of the type described by de Gennes[17] could be more likely than for PEO. Our results do not confirm such a behavior, and we will use another approach in an attempt at interpretation.

Experimental Section

Samples. The polydioxolane samples (PDXL) were prepared by cationic polymerization in methylene chloride at -25 °C using trifluoromethanesulfonic anhydride.[19] They were terminated with sodium methanolate, precipitated in methanol at -40 °C, and then washed with cold methanol and dried under vacuum at room temperature. The characteristics of these samples are reported in Table 1.

Two samples of PEO prepared using a Vandenberg-type catalyst ($M_w = 9 \times 10^5$ (sample 1) and 3.6×10^5 (sample 2) (with polydispersity index equal to 1.4 and 1.9, respectively) were kindly provided by Reibel. The end groups are not known with accuracy, but due to the high molecular weight of the samples used, this can be neglected.

Light Scattering (LS). Light scattering experiments were performed with two different experimental apparatuses operating

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Table 1. Characterization of the Polydioxolane Samples

sample	M_w	polydispersity
A	50 000[a]	
	20 000[b]	1.6
B	43 800[b]	1.7
	44 000[c]	
	42 000[d]	
C	160 000[b]	1.72

[a] From light scattering (LS) in water. [b] From SEC coupled with multiangle light scattering (SEC-MALS) in water–0.1 N NaCl. [c] From light scattering in water–0.05 N NaCl. [d] From light scattering (LS) in THF.

Table 2. Refractive Index Increment d*n*/d*c* of PDXL in Water Containing 0.05 N NaCl as a Function of Temperature

T (°C)	d*n*/d*c* (mL·g^{-1})
17	0.125
20	0.123
26	0.122
37	0.119
45	0.116
54	0.113

with a laser source of wavelength 6328 Å: (1) a home built apparatus working on the Wippler–Scheibling principle[20] and (2) an apparatus from Sematech (SEM-633) well adapted to measurements at high temperatures. They were calibrated as already described.[21]

In both cases, the scattered intensity was measured within a scattering angle θ ranging from 30 to 150° with increments of 5°. The cells were thermostated at ±0.1 °C. The solubilization of PDXL requires heating at 50 °C for 1 h. All stock solutions were prepared gravimetrically. Boiling water is the best way to remove bacteria; this is necessary for solutions in pure water and when the polymer is slow to dissolve. The water used in the preparation of our solutions was distilled three times in a quartz apparatus. Its conductivity is always less than 1 μS. When NaCl solutions were prepared, 200 ppm of sodium azide was added as bacteriostatic. Solutions were heated for 2 h at 45 °C and then gently stirred at room temperature for about 1 day. The optical clarification of the solutions was then obtained either by centrifugation at 20 °C at 20 000 rpm for 4 h or by filtration through hydrophilic 0.22-μm Millipore filters.

Refractometry. The refractive index increments d*n*/d*c* of PDXL in aqueous solutions were measured on a home-built apparatus, using the Brice–Phoenix principle.[22] This allows the measurements on solutions in the domain of low concentration used in light scattering experiments. The values found for 0.05 N NaCl are given in Table 2 as a function of temperature.

Due to the small difference between the refractive index of pure water or water–0.1 N NaCl or that of water–0.05 N NaCl used in these measurements, we can assume that the d*n*/d*c* values of the three solvents are similar.

Size Exclusion Chromatography Coupled with Multiangle Light Scattering (SEC/MALS). We used a SEC device working in aqueous medium and consisting of a Shimadzu pump, a degassing system, an automatic injector (Liquid Chromatograph LC-10AD), a precolumn, and three columns (TSK PW6, PW4 and PW2). Two detectors were used: a refractometer Waters 410 as concentration detector and a multiangle light scattering apparatus (MALS) (Wyatt)[23] allowing the determination of the molecular weight M_w and the radius of gyration R_g of the eluted macromolecules. The solvent was either water or water–0.1 N NaCl, and in both cases, 400 ppm of sodium azide as bacteriostatic was added. The solutions were always filtered on 0.22-μm Millipore filters before injection.

Fifteen detectors are available on the MALS instrument corresponding to a range of scattering angle θ between 3° and 151.8°. In most cases, only 12 detectors between 36° and 151.28° can be used. Figure 1 shows that, even with this configuration, a large scattering of the experimental points is observed at the smaller and higher angles of the Zimm-type plot ($Kc/\Delta I = f(\sin^2 \theta/2)$, where K is the optical constant of the system, c the polymer concentration expressed in g·mL^{-1}, and ΔI the difference of scattered intensity between the solution and the pure eluent) when the molecular weight and the radius of gyration are small. In addition, the program allows a treatment of the results according to a linear or second-degree regression whatever the range of qR_g (where q is the scattering vector: $q = (4\pi/\lambda)\sin(\theta/2)$). Some corrections must be made when $qR_g > 1$, i.e., outside the Guinier range.[24]

For each injection, it is possible to calculate the surface of the refractometric peak in order to check the absence of adsorption of the sample on the columns or its retention on the filters. This requires a good knowledge of the refractive index increment of the polymer in the eluent and of the volume and concentration of the injected solution.

Small Angle Neutron Scattering (SANS). The SANS experiments were performed on the small angle neutron scattering instrument PACE of the L. Brillouin laboratory (LLB Saclay France). Two configurations were used where the wavelength was set at 9.98 Å or 5.74 Å. The total range of scattering vector q covered in these two configurations is (6×10^{-3})–0.3 Å^{-1}.

We investigated the dilute regime $c_w < 2.5\%$ w/w and the semidilute regime $2.5\% < c_w < 39\%$ w/w. The solutions were prepared in D_2O, homogenized by heating at 50 °C for 1 day, and kept at 25 °C for 2 days before any measurement.

The absolute values of the scattered intensity $I(q)$ were obtained from the following expression:

$$I(q) = \frac{\frac{1}{V}\left(\frac{I^{b}(q)}{T} - \frac{I^{b}_{cv}(q)}{T_{cv}}\right)}{\frac{1}{V_{water}}\left(\frac{I^{b}_{water}(q)}{T_{water}} - \frac{I^{b}_{cv}(q)}{T_{cv}}\right)}\left(\frac{d\Sigma}{d\Omega}\right)_{water} \qquad (1)$$

$I^{b}_{cv}(q)$, $I^{b}(q)$, and $I^{b}_{water}(q)$ are the measured values of the scattered intensities by the empty cell, the cell filled with the sample, and the cell filled with water used as a reference, respectively. T, T_{cv}, and T_{water} are the transmission values for the same cells. V and V_{water} are the scattering volumes of the sample and water. $(d\Sigma/d\Omega)_{water}$ is the effective section of water sample at the incident wavelength.

If ΔI is the excess of the coherent scattering intensity of the solution with respect to the solvent, ΔI is calculated by

$$\Delta I = I(q) - (1 - \Phi_p)I(q)_{D_2O} - \Phi_p I_p^{inc}(q) \qquad (2)$$

Φ_p is the volume fraction of the polymer and $I_p^{inc}(q)$ is the incoherent scattering intensity of the pure polymer. $I_p^{inc}(q)$ is measured from blanks (D_2O/H_2O = 21.39%) of increasing polymer concentration.

The classical Zimm expression can be used for the dilute solutions

$$K'c/\Delta I = 1/(M_w P(q)) + 2A_2 c \qquad (3)$$

where M_w is the weight average molecular weight and A_2 is the second virial coefficient. The contrast factor K' is determined by the scattering length density increment Δb of the solute:

$$K' = (\Delta b)^2/N_a \qquad (4)$$

N_a is Avogadro's number, and Δb is given by

$$\Delta b = b_2 - b_1 \rho_1^0 \upsilon_2^{\infty} \qquad (5)$$

ρ_1^0 and υ_2^{∞} are the mass density of the pure solvent and the partial specific volume of the polymer at infinite dilution, respectively. The specific scattering lengths of D_2O ($b_1 = 5.767 \times 10^{10}$ cm·g^{-1}) and of the monomer unit of PDXL ($CH_2CH_2OCH_2O$) ($b_2 = 0.746 \times 10^{10}$ cm·g^{-1}) are obtained from the tabulated atomic scattering lengths[25] and atomic numbers.[26] In the case of semidilute solutions, υ_2^{∞} is replaced in relation (5) by the value of the partial specific volume of PDXL at finite concentration, as previously measured by densimetry.[18]

Viscosimetry. The viscosity measurements were made with an automatic capillary viscosimeter of high accuracy.[27] The capillary diameter was 0.7 mm, and the water flow time was

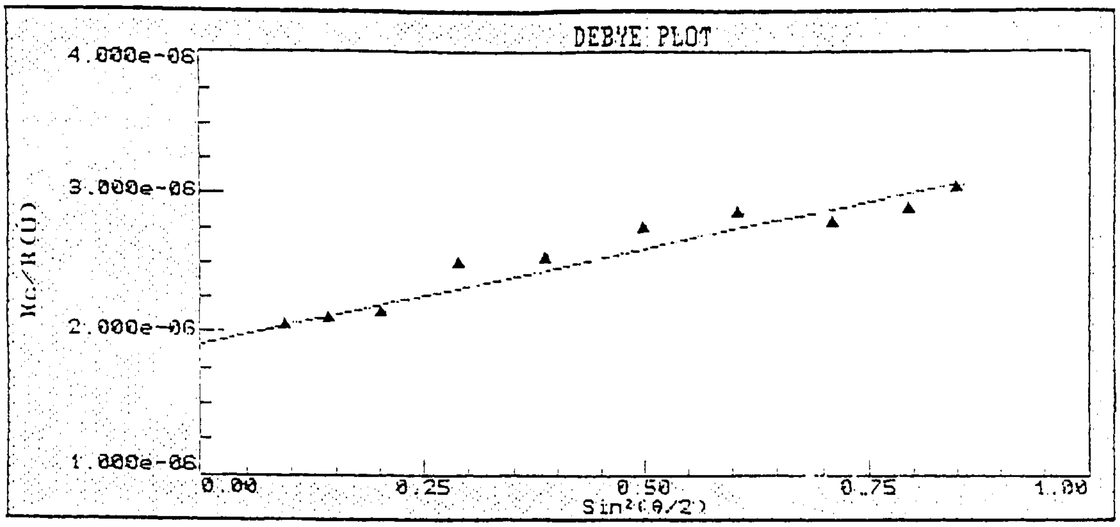

Figure 1. Example of variation of $Kc/\Delta I$ versus $\sin^2(\theta/2)$ obtained with MALS for a chromatographic fraction.

33.700 ± 0.001 s at 25 °C. The apparatus was thermostated at ±0.01 °C. The data treatment automatically includes the kinetics energy corrections.

Densimetry. The density of aqueous polymer solutions was obtained with a Kratky densimeter DMA02 equipped with a cell constructed in our laboratory.[28]

Results

(a) The Problem of Aggregation of PDXL in Aqueous Solutions. At this point, it is useful to recapitulate some results obtained in the same type of investigations performed on PEO solutions. Fortunately, the PEO sample studied in two different works by Strazielle[16] and Polik and Burchard[15] exhibit M_w values of the same order of magnitude (M_w = 20 000). Strazielle[16] showed that centrifugation can eliminate the aggregates from the aqueous solutions since no angular dependence was observed in the light scattering experiments and the expected value of M_w was obtained. For methanol solutions, which were not heated above the melting temperature of PEO ($T \approx 60$ °C), filtration on a 1-μm glass filter was able to provoke the formation of aggregates which could be removed by filtration on larger filters (4 μm). In all the cases, Strazielle has considered that heating the solutions is the better way to destroy the polymer aggregates, and this is confirmed by Layec and Layec-Raphaelen[14] who have obtained molecularly well-dispersed solutions of a PEO of higher molecular weight in methanol. These conclusions are completely different from those given in a more recent paper of Polik and Burchard.[15] These authors observed the presence of aggregates at 25 °C even in centrifuged solutions of PEO of the same M_w and an enhancement of this phenomenon upon heating up to 60 °C but a decrease of the apparent M_w above this temperature up to the phase separation. In addition to these two pieces of work, other contradictory results are reported in the literature. In solutions containing high molecular weight PEO (3 × 10^6), the presence of large aggregates made of about 50 molecules was shown by viscosimetric measurements.[13] In aqueous solutions obtained by dissolving a PEO sample (of intermediate molecular weight 2 × 10^5) in filtered water, Layec and Layec-Raphaelen[14] observed that the aggregates present at first disappear with time. A more recent work by Selser et al.[10-12] shows that aggregate free solutions can be obtained by simple filtration using carefully purified water.

On the other hand, it is well-known that the addition of most salts induces a decrease of the cloud point (or LCST, lower critical solution temperature) of the aqueous solutions of PEO.[6,29,30] Nevertheless, to the best of our knowledge, there is no available information on the influence of salts on the aggregation state of PEO.

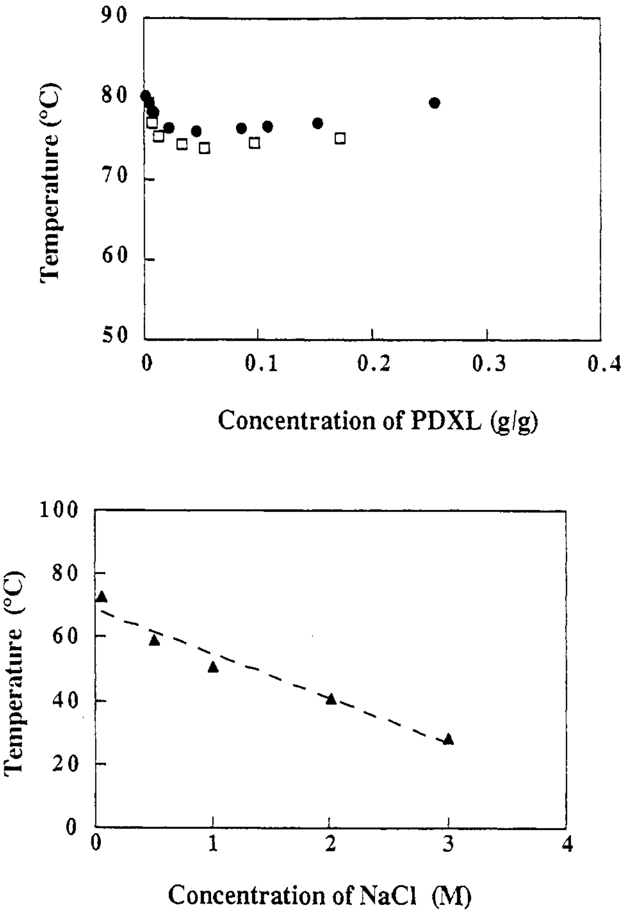

Figure 2. (Top) demixing curve of PDXL (sample B) in pure water (●) and in water–0.05 N NaCl (□). (Bottom) variation of the lower critical solution temperature as a function of the molar concentration of NaCl.

Our own investigations on the behavior of PDXL in aqueous solutions deal with the effects of the ways used to clarify and homogenize the solutions as well as with the influence of sodium chloride. Figure 2a shows the demixing curves of sample B in pure water and in water –0.05 N NaCl. The lower critical solution temperature is only slightly affected by the addition of this amount of salt, but the thermodynamic properties of PDXL in both solvents are expected to be similar at $T <$ LCST.

Light scattering measurements and SEC/MAL experiments were performed on dilute solutions of PDXL samples in THF, in pure water, and in salt-containing water.

Light Scattering. Although the molecular weight of sample A is relatively small, the scattering intensity was recorded in the whole scattering vector range available in order to study the aggregation. In this case, the solutions were simply centrifuged and the Zimm plot was already published and given in Figure 12 of ref 18. The angular dependence of $Kc/\Delta I$ was much larger than that expected for a sample of such a molecular weight, and the second virial coefficient A_2 was significantly negative. Besides, a downward curvature at lower angles suggests the presence of aggregates (whose radius of gyration ranges approximately from 300 to 500 Å), since the polydispersity of this sample (close to 2) is expected to yield a linear plot. The extrapolation to $c = 0$ and $\theta = 0$ leads to a value of $M_w = 50\,000$, which is much higher than that obtained in water 0.1 N NaCl ($M_w \approx 20\,000$). In a second experiment, sample C was dissolved in water and the solutions were filtered, with the same care as that described by Selser et al.[10-12] A molecular weight much too high (2.9×10^5 compared to 1.6×10^5 found by SEC in 0.1 N NaCl) was also obtained under these conditions. Moreover, the Zimm plots obtained with solutions of polymer B prepared in water 0.05 N NaCl (see Figure 3a, 20 °C) and filtered on 0.22-μm filters do not indicate the presence of aggregates.

Such systematic differences between the results obtained in the absence or in the presence of salt could be rationalized by invoking either a negative preferential adsorption of salt or a desaggregating effect of the salt present.

The first hypothesis may explain the lower molecular weight determined in the presence of salt only if the preferential adsorption is negative,[24] but several results run against this statement: (i) the dn/dc values either directly measured without previous dialysis procedure or by the integration of the refractometric peak in a SEC experiment do not differ by more than 0.0005 mL·g^{-1}, which clearly indicates that this possible effect is negligible, and (ii) the molecular weight of sample B determined by light scattering in THF is equal to that obtained in water, in the presence of salt (Table 1). Besides, in THF, the angular dependency of $Kc/\Delta I$ is linear and the slope leads to a lower value of R_g, as expected. It is to be noted that in any case the curvature of the Zimm plot could not have been explained by a preferential adsorption.

On the contrary, the assumption of a salt effect on the degree of association is supported by several self-consistent observations.

First, in order to obtain some information on the effect of filtration, we have checked the concentration of the solution by a densimetric method. A calibration curve of the variation of the density vs polymer concentration was established with nonfiltered solutions in pure water. This leads to the following relation:

$$d = 0.996\,19 + 0.184\,67c \ (\text{g}\cdot\text{mL}^{-1}) \qquad (6)$$

Table 3 shows that the polymer loss is about 10% after filtration in the case of solutions in pure water, while for c_{NaCl} equal to 0.05 and 0.1 N, the polymer concentration is not changed. We have assumed that the partial specific volume of the aggregates which may be kept by the filter is close to that of the dispersed macromolecules.

Secondly, polymer C was dissolved in pure water and a molecular weight value of 2.9×10^5 was determined by light scattering; upon addition of 0.04 N NaCl directly in the light scattering cells, the molecular weight value dropped to its normal value (1.6×10^5). Since the hypothesis of negative preferential adsorption could be discarded, this is direct evidence of the salt effect on the polymer association. Indeed, such an association phenomenon which occurs in pure water is sometimes interpreted by invoking the well-known difficulty to remove dust particles even from pure water itself and the possible role played by these particles as nuclei for associations. It is clear that the addition of salt cannot remove the dust particles.

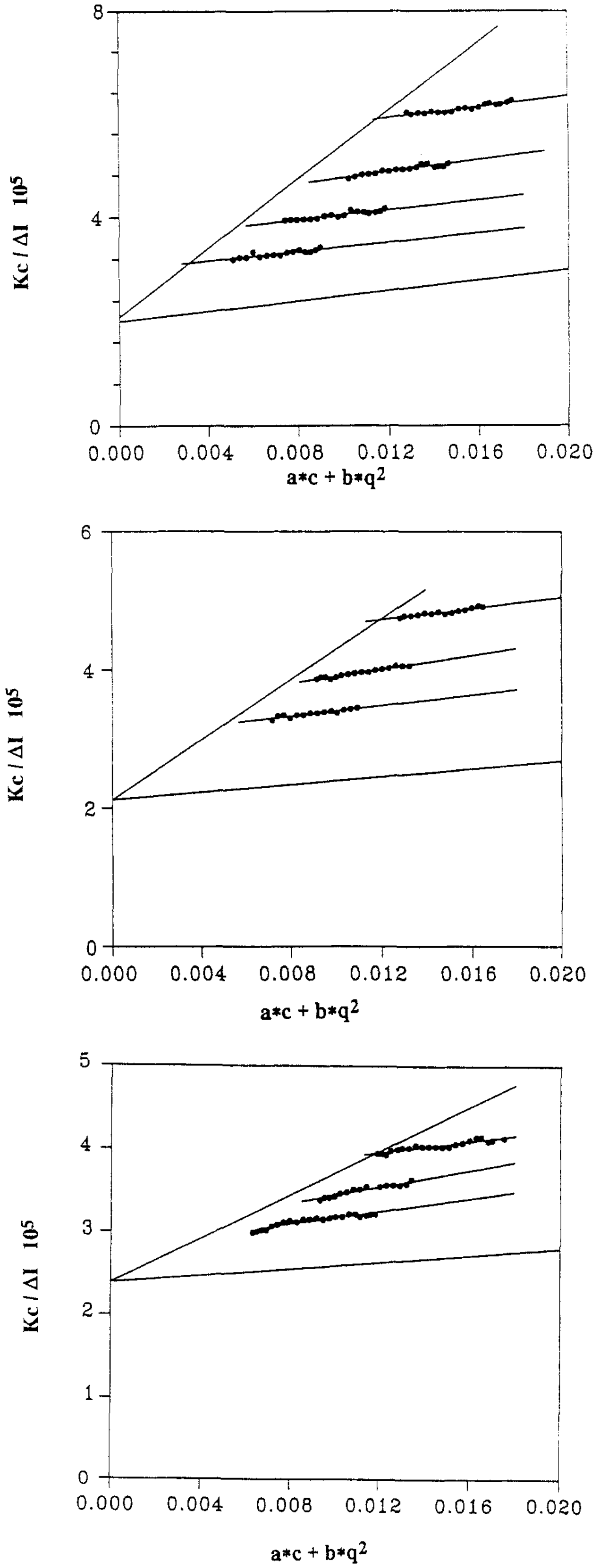

Figure 3. Zimm plots of PDXL (sample B) in water containing 0.05 N NaCl at (top) 20 °C; (middle) 30 °C; (bottom) 47 °C.

Table 3. Densimetric Titration of the PDXL Solutions in Pure Water after Filtration on 0.22-μm Filters

initial concn c_i (g/mL)	density after filtration	concn after filtration: c_f	$(c_i - c_f)/c_i$
0.004	0.99687	0.0037	0.098
0.0077	0.99755	0.00734	0.054
0.0175	0.99915	0.0160	0.078

Thus, from our results, we can conclude that neither centrifugation nor filtration is as efficient for the elimination of PDXL aggregates in pure water, as in the case of PEO. This behavior is consistent with our previous findings showing that the domain of solubility in the phase diagrams (temperature, polymer concentration) is much less extended for PDXL than for PEO.

SEC/MALS Experiments. The refractometric and light scattering chromatograms of sample C in pure water are given in Figure 4 as well as the plot of $M = f(V_e)$ (where V_e is the elution volume), obtained directly from the light scattering measurements. Two light scattering peaks are observed, both corresponding to high molecular weights ($\approx 10^7$), while the refractometric chromatogram exhibits one peak. Besides, integration of the refractometric peak reveals that 90% of the sample is lost. In fact, the poor results obtained with SEC in pure water are not only the consequence of some retention of the polymer on the filter (which has been already shown not to exceed 10%) but mostly due to adsorption on the columns.

The same experiments (SEC/MALS) performed with PEO in pure water led to satisfactory results. This shows that the tendency of PEO to adsorb on the support is lower.

As a general conclusion of our results obtained for PDXL in pure water, it turns out that it is impossible to obtain solutions where all the macromolecules are well dispersed. With respect to the case of PEO, the aggregation seems to be much more pronounced since we do not eliminate the low angle light scattering excess by simple centrifugation. This difference is consistent with our previous results[18] which show that the solubility of PDXL in water is lower than that of PEO; the LCST is lower and the concentration range of solubility is limited to $c < 40\%$.

(b) Conformation of PDXL in Dilute Aqueous Solutions. Neutron Scattering Experiments in Pure Water (25 °C). Since it was difficult to determine the dimensions of our low molecular weight PDXL samples by light scattering, whose measurements are moreover strongly perturbed by the presence of aggregates, we tried to use neutron scattering, using D_2O as solvent. The solutions were not filtered for these experiments because it is well-known that dust particles do not perturb the measurements. The Zimm plot obtained for the dilute solutions of sample A is given in Figure 5.

For the three higher concentrations, the curves of $K'c/\Delta I$ exhibit an excess of scattered intensity at the low values of q, and the second virial coefficient obtained from the extrapolations to $q = 0$ is negative. The plot obtained for the lower concentration is linear, and the value of $M_w = 20\,000$ deduced from the double extrapolation at $q = 0$ and $c = 0$ is in good agreement with that determined by SEC/MALS measurements in 0.1 N NaCl. This may be interpreted by considering that the influence of the aggregates becomes important only when $c > 9.2 \times 10^{-3}$ g·mL^{-1} in the range of q used in neutron scattering experiments. Indeed, for higher concentrations, the value of the radius of gyration of the aggregates (calculated from the slope of $Kc/\Delta I = f(q^2)$ at smaller values of q) is about 250 Å and it is easy to show that, if their concentration does not exceed 10%, their contribution to ΔI can be neglected for $q > 0.015$ Å^{-1}. Therefore, the curve of $K'c/\Delta I = f(q^2)$ at $c = 0$ can be analyzed in order to obtain the z average radius of gyration of the sample. A first approximate value of $R_g = 72$ Å is obtained from a simple linear fit of this curve. This shows that a large part of the q range investigated is outside the Guinier range. The adjustment of the results was made with the classical Debye function

$$P(q) = \left(\frac{2}{x^2}(\exp(-x) + x - 1)\right) \qquad (7)$$

or the modified function proposed by Oberthür[31]

$$P(q) = \left(\frac{2}{x^2}(\exp(-x) + x - 1)\right)\left(2 \operatorname{arctg}\left(\frac{25\pi}{x}\right)\right)^{-0.15} \qquad (8)$$

where $x = (qR_g)^2$. Figure 6 shows that a good agreement can be obtained between the experimental and calculated variations of $P(q) = f(qR_g)$ for $R_{gz} = 65$ Å. This value will be compared to the scaling law of $R_g = f(M)$ obtained below by SEC/MALS in the presence of salt.

SEC Coupled with MALS in 0.1 N NaCl (25 °C). Figure 7 gives the refractometric and light scattering (for scattering angle = 90°) chromatograms of sample B when water–0.1 N NaCl is used as eluent. They do not exhibit any apparent anomalies, and integration of the refractometric peak reveals that no polymer is lost either by filtration or by adsorption. The great advantage of this coupled technique is to allow the determination of the

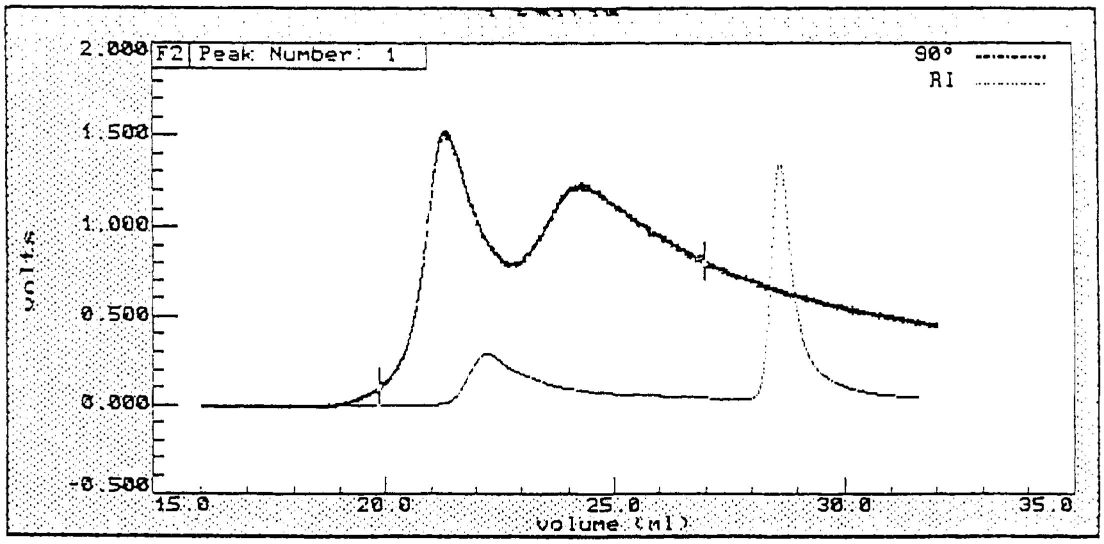

Figure 4. Refractometric and light scattering (90° angle) chromatograms of PDXL sample C in pure water.

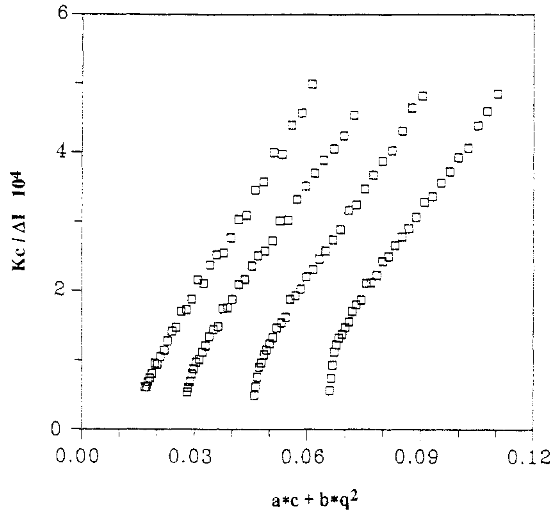

Figure 5. Zimm plot obtained by low angle neutron scattering, in the dilute regime for PDXL (sample A) in pure water (T = 25 °C).

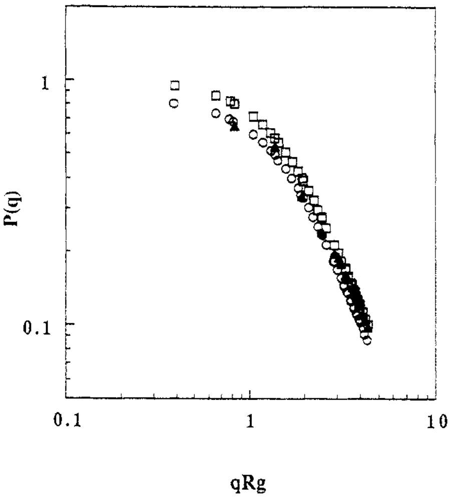

Figure 6. Variation of $P(q)$ at $c = 0$ versus qR_g from the neutron scattering experiments of Figure 5 (R_g = 65 Å): values calculated from eqs 7 (□) and 8 (○) and experimental values (▲).

scaling law of the molecular weight dependence of R_g, even for low molecular weight samples, provided that the distribution is large enough. In the case of this sample M_w/M_n is equal to 1.72.

The $R_g = f(M)$ variations as directly deduced from SEC/MALS measurements without changing the treatment of the data are reported in Figure 8 for PDXL and for PEO (two PEO samples were used in these experiments). The following scaling laws are obtained by the least-squares analysis:

$$R_g = (0.222 \pm 0.03)M^{0.57\pm0.02}\ (\text{Å})\ \text{for PDXL} \qquad (9)$$

$$R_g = (0.082 \pm 0.03)M^{0.64\pm0.02}\ (\text{Å})\ \text{for PEO} \qquad (10)$$

For the fractions of higher molecular weight, when $qR_g >$ 1, we have corrected the R_g values by treating the data through a fit by the complete Debye expression. This does not change the PDXL law but improves that of PEO:

$$R_g = (0.106 \pm 0.03)M^{0.62\pm0.02}\ (\text{Å}) \qquad (11)$$

This last result is well consistent with the results of Strazielle, reported in ref 32

$$R_g = 0.135M^{0.62}\ (\text{Å}) \qquad (12)$$

and is also rather close to that obtained by Selser et al.:[10]

$$R_g = 0.215M^{0.583\pm0.03}\ (\text{Å}) \qquad (13)$$

Relation (9) yields a value of R_g of about 63 Å for M = 20 000, which is in good agreement with the value obtained in pure water by neutron scattering for sample A. On the other hand, the exponent is close to the value expected for a good solvent, and this explains that the behavior observed for the semidilute regime is rather well described by the theoretical predictions for such conditions.

Light Scattering and Viscosity as a Function of Temperature. Some solutions of polymer B were prepared in water in the presence of 0.05 N NaCl, filtered on 0.22-μm filters and characterized by light scattering at different temperatures, T. The results are given in Figure 3. Whatever the temperature, the angular dependence is very low and leads to values of $R_g \leq 100$ Å. The variations of A_2 versus T are plotted in Figure 9 for PDXL in water–0.05 N NaCl. A_2 is close to zero for T = 73 °C, the temperature close to the LCST value obtained by turbidimetry and significantly lower than that of a PEO sample of similar M previously studied by Strazielle.[16]

The intrinsic viscosity of PDXL sample B was measured as a function of temperature. It strongly decreases upon heating and at T = LCST = 74 °C reaches an estimated value of 35 mL·g^{-1}, as obtained by extrapolation of the

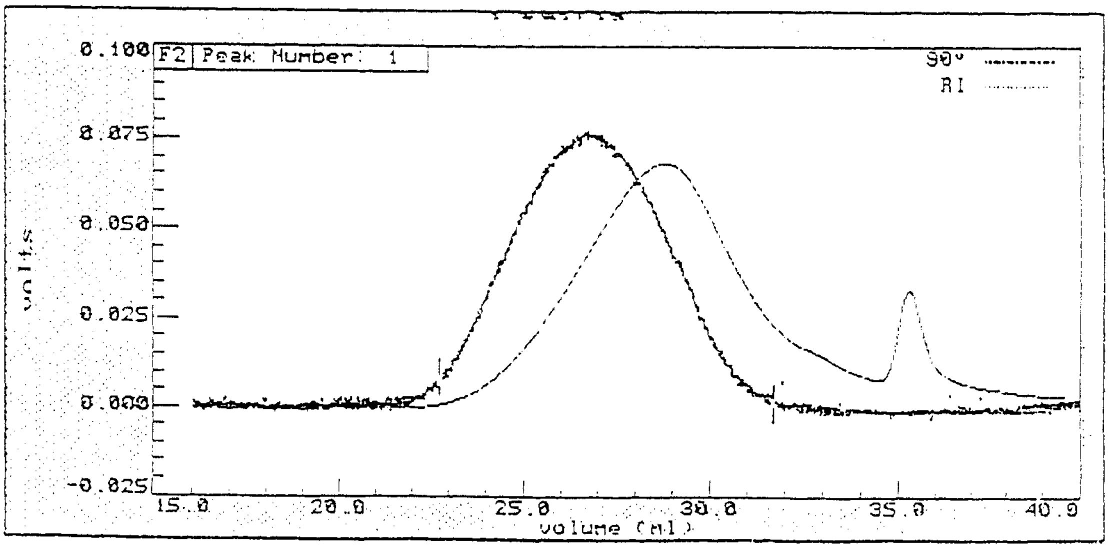

Figure 7. Refractometric and light scattering (90° angle) chromatograms of PDXL (sample B) in water–0.1 N NaCl.

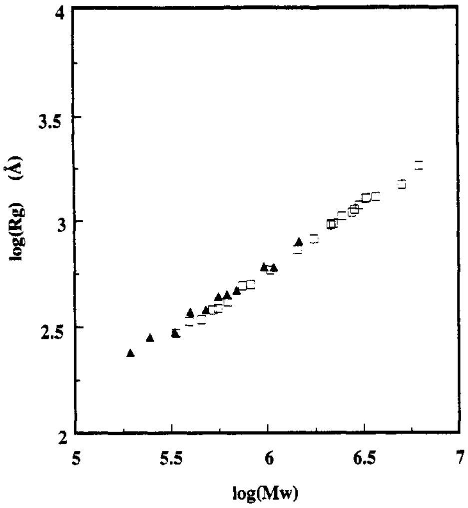

Figure 8. Logarithmic plot of R_g versus M as deduced from SEC/MALS experiments for PDXL (sample B) (▲) and PEO (samples 1 and 2) (box).

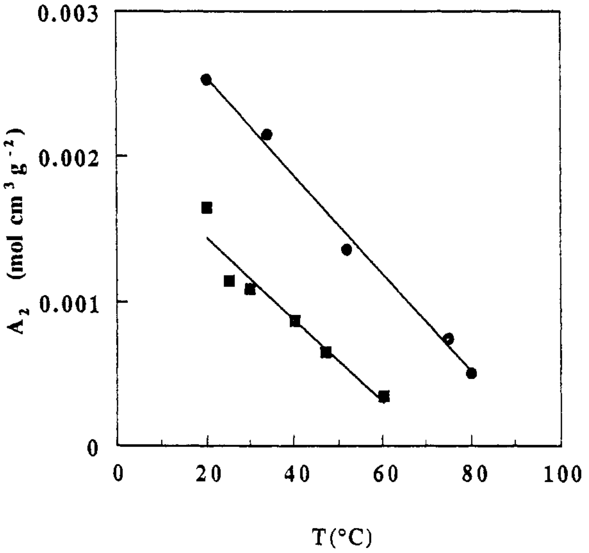

Figure 9. Variation of the second virial coefficient A_2 versus temperature for PDXL (sample B) in water containing 0.05 N NaCl (■) and for PEO in water–0.1 N NaCl from ref 16 (●).

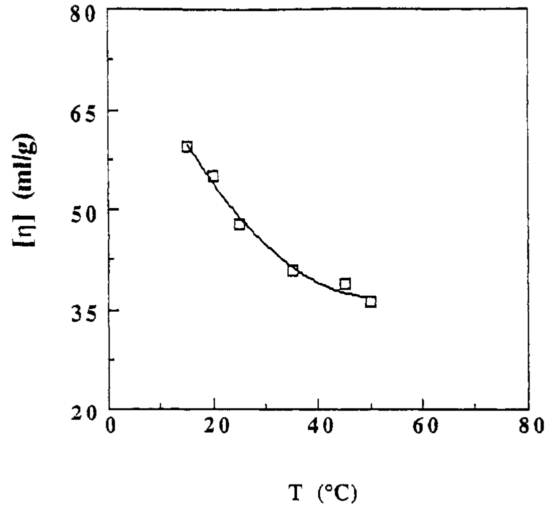

Figure 10. Temperature dependence of the intrinsic viscosity of PDXL sample B.

values given in Figure 10. Due to experimental problems, no measurements were performed at temperatures very close to the LCST value, but Figure 10 shows that the value of 35 mL·g^{-1} is probably overestimated. This value corresponds to unperturbed dimensions, which are interesting to compare with those obtained through a procedure of the Stockmayer–Fixman[33] type at 25 °C. Indeed, by extrapolation of $(6R_g^2/M)^{3/2} = f(M^{1/2})$ at $M = 0$, one can obtain the term $(6R_g\theta^2/M)^{3/2} = A^3$, where $R_g\theta$ is the unperturbed radius of gyration. From the values of Figure 8, we find $A^3 = 1.29 \times 10^{-24}$ cm^3·g$^{-3/2}$·mol$^{3/2}$ at 25 °C. For sample B of $M_w = 44\,000$, $R_g\theta = 93$ Å while from the value $[\eta] = 35$ cm^3·g^{-1} at 74 °C and through the Fox–Flory relation[34] one finds $R_g\theta = 72$ Å. If credence can be given to these results, the chain rigidity decreases when the temperature increases. Since the unperturbed dimensions of polymers in solutions are believed to depend only slightly upon temperature, such a variation could then be attributed to the change of hydration of the PDXL chain between the two temperatures considered. The length of the statistical segment b should be of about 10 Å at 25 °C.

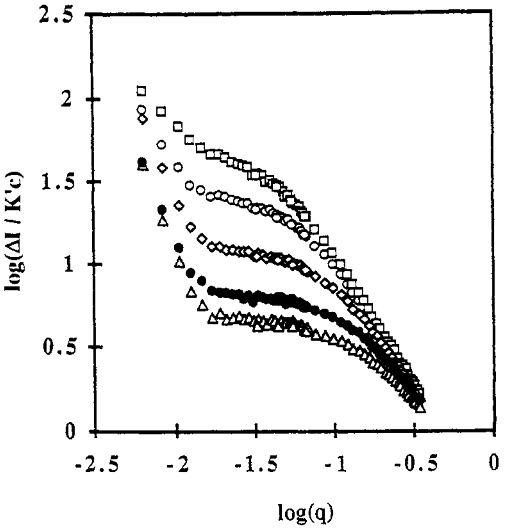

Figure 11. Neutron scattering experiments in the semidilute regime for PDXL (sample A) at 25 °C: variation of log $\Delta I/K'c$ versus log q for c = 0.0524 (□), 0.098 (○), 0.18 (◇), 0.296 (●), and 0.398 (△) g·mL^{-1}.

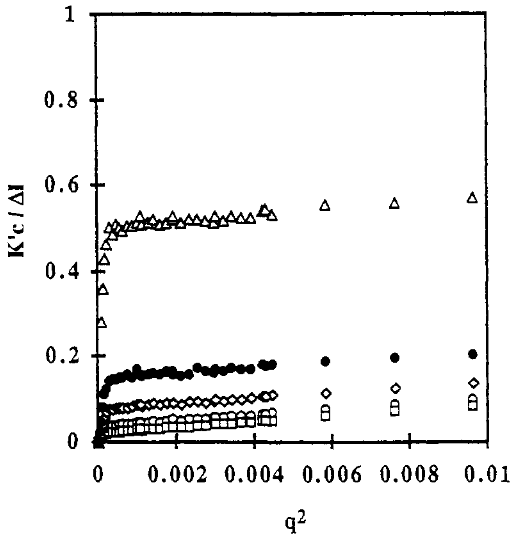

Figure 12. Neutron scattering experiments in the semidilute regime: variation of $K'c/\Delta I$ versus q^2 for c = 0.0524 (□), 0.098 (○), 0.18 (◇), 0.296 (●), and 0.398 (△) g·mL^{-1}.

(c) Structure of Semidilute PDXL Solutions. Neutron scattering experiments were performed for different concentrations of polymer A in pure water in the semidilute regime.

Figures 11 and 12 show the variations of $\Delta I/c$ versus q in logarithmic scales and $c/\Delta I$ versus q^2. Generally, for moderately concentrated solutions of flexible chains, the scattering law is of a Lortentzian type,[35] leading to

$$\frac{\Delta I}{c} \propto \frac{1}{q^2 + \xi^{-2}} \qquad (14)$$

where ξ is the screening length defined by Edwards.[35] This relation only applies for $q < \xi^{-1}$. Scaling laws predict a variation of ξ as a function of polymer concentration[36]

$$\xi \propto c^{\nu/(1-3\nu)} \qquad (15)$$

where ν is the excluded volume exponent and if $c > c^*$, c^* being the overlap threshold. By assuming that the value of $R_g = 65$ Å is correct, we obtain $c^* = 0.029$ g·mL^{-1} from the usual expression:[36]

$$c^* = \frac{M}{{}^4/_3 \pi N_a R_g^{\,3}} \qquad (16)$$

In the appropriate range of q, $c/\Delta I$ vs q^2 is expected to be linear and ξ can be deduced from relation 14 by equating $c/\Delta I = 0$. For $q > 1/b$, ΔI varies as q^{-1}, if b is the statistical length and in an intermediate range $1/\xi < q < 1/b$ ΔI is expected to decrease as $q^{-1/\nu}$.

The results obtained with our sample are qualitatively in agreement with such a description, if one excepts the low q behavior. One indeed observes a large range of q where $c/\Delta I$ versus q^2 is linear with a slope which is a decreasing function of c (Figure 12). Besides, the $c/\Delta I$ values for a particular q within this q range increase with increasing c, as predicted by the Benoit and Benmouna theory.[37] In the higher q range, a significant divergence from the q^2 behavior is observed and ΔI tends to vary as q^{-a}, with $a < 2$.

In the range of small values of q, an excess of intensity indicates the presence of heterogeneities. Such a behavior has already been observed for many different systems in nonpolar[38-43] or polar systems[44-47] and was the object of controversies. This phenomenon is generally considered to be specific of the semidilute regime and is generally attributed to an attractive potential between polymer chains.[47] The same type of behavior can be observed with PDXL in water, but in this case, an excess of scattered intensity is also observed in the dilute regime.

Figure 12 shows that the low q anomalies do not interfere with the linear section of the curves ($c/\Delta I$ versus q^2) and that therefore it is possible to deduce a scaling law for the variation of ξ versus c:

$$\xi = 2.29 c^{-0.73} \text{ (Å)} \qquad (17)$$

This relation was deduced by a least-squares analysis on all the experimental points, as shown in Figure 13. In the so-called universal law, one generally expresses ξ/R_g as a function of c/c^*. The predictions of Muthukumar and Edwards[48] are

$$\frac{\xi}{R_g} = 0.26\left(\frac{c}{c^*}\right)^{-0.75} \qquad (18)$$

while the experimental law obtained by Lapp et al.[49] with various systems of polymer in good solvents is

$$\frac{\xi}{R_g} = 0.43\left(\frac{c}{c^*}\right)^{-0.74} \qquad (19)$$

By taking $R_g = 65$ Å, we obtain for PDXL

$$\frac{\xi}{R_g} = 0.26\left(\frac{c}{c^*}\right)^{-0.75} \qquad (20)$$

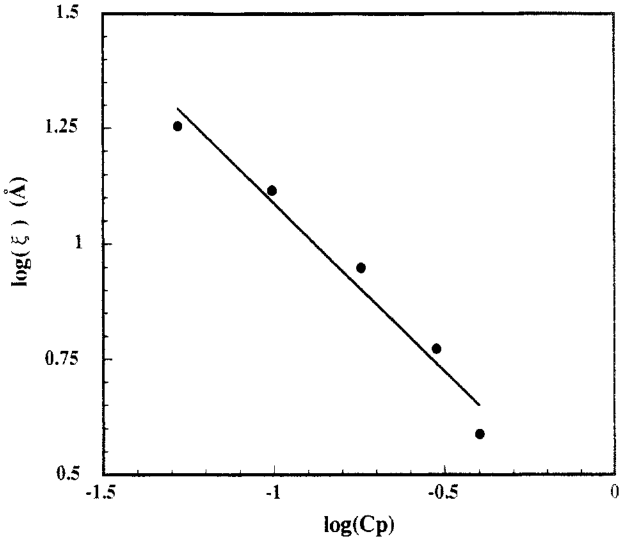

Figure 13. Variation of the screening length ξ versus PDXL concentration (sample A, 25 °C) from neutron scattering experiments.

which differs very slightly from the previous one. This seems to indicate that the semidilute solutions of PDXL exhibit a classical behavior of polymers in good solvents. The heterogeneities which affect the low angle scattering do not perturb the scattering in the intermediate q range which corresponds to the structure of the whole semidilute network. The same conclusions were obtained by Medjahdi et al.[46,47] and Gan et al. for polyacrylamide–water or polystyrene in carbon disulfide.[42]

One can, however, observe that the slope of the logarithmic plot of Figure 13 tends to increase with increasing concentration. This is expected if one considers that the excluded volume effect tends to decrease with increasing concentration, the limit of the exponent in relation 15 being −1, under θ conditions. A continuous increase of the absolute slope has already been observed for other systems.[50] Such an effect must be more pronounced for PDXL–water which exhibits a solubility limit around 50%.

It was also shown that in semidilute solution ΔI at $q = 0$ varies with c as[36]

$$\Delta I \propto c^{3\nu-2/3\nu-1} \qquad (21)$$

Variations in $c^{-1/4}$ and c^{-1} are expected for conditions of good and θ solvent, respectively. By taking into account the four lower concentrations of Figure 12, an exponent of about −0.22 is obtained, which corresponds rather well to a good solvent while a calculation on the five investigated concentrations leads to −0.4. This confirms the decrease of the excluded volume effect when concentration increases.

In the intermediate range, and for the two lower concentrations, ΔI decreases as $q^{-1.6}$, which is also consistent with good solvent conditions. From such a value of $b = 10$ Å, the q^{-1} dependence of the scattered intensity is expected for $q > 0.5$ Å^{-1}. The higher slope in Figure 11 (at higher q) may be due to a slight overestimation of the incoherent scattering, particularly at the lower concentrations. This error does not affect the range of lower q.

Discussion

(a) Aggregation in Pure Water. Solutions of PDXL in pure water contain aggregates in the dilute and in the semidilute regimes. Many polymer–solvent systems are characterized by an excess of scattered intensity at small angle but this is generally limited to the semidilute solutions. Polyacrylamide is an example of water-soluble polymer which can be well dispersed in dilute solution[46] without taking much care in the preparation of the solutions. The polymer–polymer interactions seem to be more important with PDXL and also with PEO since the perfect dissolution of this last polymer requires special conditions when the solutions are prepared.

One of the questions which has to be resolved deals with the swelling degree of the aggregates. The theory of de Gennes[17] assumes that aggregates are constituted of expanded macromolecules. In the dilute regime, and in a first approximation, the scattered intensity can be supposed to be the sum of two contributions, that of aggregates (M_2, R_{g2}) and that of the dispersed molecules (M_1, R_{g1})

$$\Delta I = (1 - x)cM_1P_1(q) + xcM_2P_2(q) \qquad (22)$$

where x is the weight fraction of the aggregates. The Zimm plot of Figure 12 of ref 12 shows an extrapolation at $q = 0$ which leads to an average molecular weight $M = 50\,000$. From such a value, we cannot derive both the molecular and the fraction of the aggregates. We can only conclude that if this fraction is $x = 0.1$, $M_2 = 3.2 \times 10^5$, if $x = 0.01$, $M_2 = 3 \times 10^6$, and if $x = 0.001$, $M_2 = 4.9 \times 10^7$. It is easy to show that the slope of $Kc/\Delta I$ versus q^2 in the light scattering range is very close to that which corresponds to the radius of gyration of the aggregates (it was found to be of about 400 Å) since the radius of gyration of the dispersed molecules is small (65 Å). If the aggregates are constituted of pure polymer, the radius of such particles should be 45, 96, and 208 Å for $M_2 = 3.2 \times 10^5$, 3×10^6, and 4.9×10^7, respectively. These values are lower in all cases than the measured value of R_g, and this comparison could indicate that the aggregates remain expanded and can be considered as interpenetrated coils. Moreover, one can calculate that whatever the couple of values x, M_2 considered, the dimensions of the aggregates must be large enough to perturb only slightly the neutron scattering. Let us recall that even in pure water the Zimm plot leads to a good value of M_1 and R_{g1}.

If one extrapolates this description to the case of the semidilute solutions, one could use a model of the type proposed by Medjahdi et al.[47] who considered a distribution of screening lengths ξ. In some regions of the solution, ξ is lower than in the whole solution due to an attractive potential between chain segments, and this can explain the excess of intensity at low angle. Such a picture may be a better approach than the model of Koberstein et al.[43] who assume the presence of particles of pure polymer in semidilute solutions and calculate the resulting scattering functions through the Debye–Bueche theory.[51]

In our previous work,[18] we have described a phase diagram of PDXL in water completely different from that obtained with PEO. At room temperature, the solubility is limited to 50% of polymer. We could expect in the semidilute regime a behavior different from that generally observed for polymers in good solvents. A way to consider this system is to divide the phase diagram into two different regions: (1) $c < 50\%$, where, in fact, the polymer in solution is not PDXL but the hydrated complex (PDXL + three water molecules per monomer unit); this complex, whose concentration is 1 at 50% of dry PDXL, may be considered as in rather good solvent at 25 °C and (2) $c > 50\%$, where the complex is no more compatible with the pure PDXL.

In the solubility region, the behavior in pure water is qualitatively consistent with the de Gennes theory which assumes that even for polymers in good solvent ($A_2 > 0$) polymer–polymer interactions can lead to associations and to the formation of swollen aggregates. Nevertheless, the problem is to determine the origin of this attractive potential. The densimetric measurements performed on PEO or PDXL aqueous solutions reveal a decrease of the absolute value of the excess mixing volume (generally negative for water-soluble polymers) upon heating. Then the stoichiometry of the complex polymer–water is expected to change when the temperature increases and the hydration number must be close to 0 at T = LCST. At a given temperature $T_m < T <$ LCST (where T_m is the melting temperature of the complex: 15 °C for PDXL) the polymer may be considered as a kind of "copolymer" constituted by hydrated monomer units and nonhydrated monomer units. The segment–segment interactions invoked by de Gennes may correspond to these later species, while the hydrated segments have a positive contribution to the second virial coefficient. In fact, the change of hydration is considered in many theoretical approaches as the main origin of the demixing by heating of the nonionic polymer–water systems. Tanaka,[52] for example, introduces in the Flory–Huggins theory the solvent–polymer interactions through an equilibrium law and modifies the entropic term of the free energy, without changing the temperature dependence of the χ parameter. This approach explains well why strongly hydrated PEO is soluble in a range of temperature where the simple solubility parameter would predict it to be insoluble. It may be proposed to take into account of both approaches of de Gennes and Tanaka in order to get a good description of the behaviors of such systems, in an extended range of temperature.

On the other hand, the solubility of a polymer, whatever the solvent, depends on its crystallinity. This property is, for example, invoked to explain the insolubility in water of poly(oxymethylene) (POM) which is highly crystalline with a melting point of 180 °C. PDXL was found to be 50% crystalline, and its melting point is 55 °C. Then this difference in crystalline properties may simply explain the different solubility behaviors. However, Stockmayer et al.[53] have shown that POM can be solubilized in a mixture of water and hexafluoroacetone through a very strong hydrogen bonding provided by the hexafluoroacetone monohydrate. It appears, therefore, that the solubility and the good dispersion of a polymer are related to both its crystallinity and the solvation effects.

(b) Effect of Salt on the PDXL Aggregation. One of the most striking and well-established results of our study is the dispersive power of sodium chloride on PDXL in water when added in small quantity. An improvement of the solvent quality when the NaCl concentration increases leading to a better solubilization may be considered as incompatible with the lowering of the LCST value shown in Figure 2b. Such an effect is classically called "salting out effect" and is observed for many nonionic polymers in aqueous solutions.[6,29,30] The aggregation of PDXL in pure water and the salting out effect are probably thermodynamic phenomena of quite different origins. As proposed by de Gennes,[17] in the first case, the polymer chains within the aggregates may remain expanded while in the second case, the phase separation corresponds to a collapse of the chains. This assumption is consistent with a positive value of A_2 and an excluded volume exponent >0.5 at 25 °C in the presence of small amounts of salt as well as in pure water when aggregates are not considered.

The question which remains is the exact role played by the salt. We can imagine that the sodium ions occupy selectively the binding sites causing the polymer aggregation. Therefore, a polyelectrolyte-like behavior should be observed with the occurrence of intermolecular electrostatic repulsions provoking chain disentanglement.

Such a hypothesis is supported by several works which claim the formation of a "pseudo-polyelectrolyte" (in the case of PEO) in aqueous salt solutions through the interaction of the oxide group with various hydrated cations.[54] Further investigation on the PEO and PDXL interactions with cations are now in progress in our laboratory in order to clarify this point.

(c) Conformation of PDXL in Aqueous Solution. In pure water, as long as the aggregates do not perturb the measurements (large enough values of the scattering vector) or in the presence of 0.05 N and 0.1 N NaCl, PDXL does exhibit the behavior of a polymer in rather good solvent with an excluded volume exponent close to 0.6. However, the second virial coefficient is lower than that of PEO, under comparable conditions of temperature and molecular weight. This is consistent with the lower LCST value as compared to that of PEO. The variation of the expansion coefficient $\alpha = R_g/R_g\theta$ versus the reduced temperature $[(T - \mathrm{LCST})/\mathrm{LCST}]$ is close to those obtained for PEO[55] and copolymers of ethylene oxide and propylene oxide.[56] It was demonstrated that these later polymers behave in good agreement with the theory of Flory[7] or the predictions of the blob model,[36] generally applied for $T >$ UCST (if UCST is the upper critical solution temperature). Nevertheless, a comprehensive study of the PDXL conformation should include an inelastic light scattering investigation coupled to viscosity measurements in a wider range of molecular weight.

Conclusion

In this work, we have investigated the behavior of PDXL in aqueous solutions by viscosimetry, elastic light, and neutron scattering and coupled size exclusion chromatography–multiangle light scattering. We can conclude that, at room temperature and in pure water, aggregates are present which seem to be thermodynamically stable and that could be taken into account by a recent de Gennes theory. These aggregates may be considered as formed from expanded macromolecules. This is consistent with the behavior of a polymer in a good solvent found for salt-containing solutions or in pure water when aggregates can be neglected. This is the first investigation of conformational properties of PDXL in water, and its results are consistent with the previously published phase diagrams. Presently, further investigation is in progress in two main directions: to determine the influence of salts upon the aggregation state and to establish the hydrodynamic behavior on a wider range of molecular weights.

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References and Notes

(1) Bailey, F. E.; Koleske, J. V. *Alkylene Oxides and their Polymers*; Marcel Dekker, Inc.: New York and Basel, 1991.
(2) Bakanova, Z. Kh.; Bekturov, E. A. *Izv. Akad. Nauk. Kaz. SSR. Ser. Khim.* **1977**, *3*, 63.
(3) Saeki, S.; Kuwahara, N.; Nakata, M.; Kaneko, M. *Polymer* **1976**, *17*, 685.
(4) Kjellander, R.; Florin, E. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2053.
(5) Matsuyama, A.; Tanaka, F. *Phys. Rev. Lett.* **1990**, *65*(3), 341.
(6) Saeki, S.; Kuwahara, N.; Nakata, M.; Kaneko, M. *Polymer* **1977**, *18*, 1027.
(7) Flory, J. P. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1978.
(8) Patterson, D.; Delmas, G. *Trans. Faraday Soc.* **1969**, *65*, 708.
(9) Carpentier, D. K.; Santiago, G.; Hunt, A. H. *J. Polym. Sci., Polym. Symp.* **1974**, *44*, 75.
(10) Devanand, K.; Selser, J. C. *Macromolecules* **1991**, *24*, 5943.
(11) Woodley, D. M.; Dam, G.; Lam, H.; LeCave, M.; Devanand, K.; Selser, J. C. *Macromolecules* **1992**, *25*, 5283.
(12) Devanand, K.; Selser, J. C. *Nature, London* **1990**, *343*, 739.
(13) Wolf, C. *Can. J. Chem. Eng.* **1980**, *58*, 634.
(14) Layec, Y.; Layec-Raphalen, M.-N. *J. Phys. Lett.* **1985**, *44*, L120.
(15) Polik, W.; Burchard, W. *Macromolecules* **1983**, *16*, 978.
(16) Strazielle, C. *Makromol. Chem.* **1968**, *119*, 50.
(17) de Gennes, P. G. *C. R. Acad. Sci. Paris* **1991**, t. 313, Serie II, 1117.
(18) Benkhira, A.; Franta, E.; François, J. *Macromolecules* **1992**, *25*, 5697.
(19) Chwialkowska, W.; Kubisa, P.; Penczek, S. *Makromol. Chem.* **1982**, *183*, 753.
(20) Libeyre, R.; Sarazin, D.; François, J. *Polym. Bull. (Berlin)* **1981**, *4*, 53.
(21) Schwartz, T.; Sabbadin, J.; François, J. *Polymer* **1981**, *22*, 609.
(22) Sarazin, D.; François, J. Licence ANVAR no. 85. 5888. 00 D. 53043, Automatisation d'un réfractomètre differentiel, 1988.
(23) Wyatt, P. J. In *Differential Light Scattering Techniques to Microbiology*; Norris, P. J., Ribbons, D. W., Eds.; Academic Press: London, 1973.
(24) Huglin, M. B. *Light Scattering from Polymer Solutions*; Huglin, M. B., Eds.; Academic Press: London, New York, 1972.
(25) Koester, L.; Steyerl, A. In *Neutron Physics*; Springer: Berlin, 1977.
(26) *Handbook of Chemistry and Physics*, 54th ed.; CRC Press: Cleveland, OH, 1973.
(27) Gramain, P.; Libeyre, R. *J. Appl. Polm. Sci.* **1970**, *14*, 383.
(28) Sarazin, D.; LeMoigne, J.; François, J. *J. Appl. Polym. Sci.* **1978**, *22*, 1377.
(29) Bailey, F. F.; Callard, R. W. *J. Appl. Polym. Sci.* **1959**, *1*, 56.
(30) Boucher, E. A.; Hines, P. M. *J. Polym. Sci.* **1976**, *14*, 234.
(31) Vennemann, N.; Lechner, M. D.; Oberthür, R. C. *Polymer* **1987**, *28*, 1738.
(32) Cabane, B. *J. Phys.* **1982**, *43*, 1529.
(33) Stockmayer, W. H.; Fixman, M. *J. Polym. Sci. Part C: Polym. Lett.* **1963**, 137.
(34) Flory, P. J.; Fox, T. G. *J. Am. Chem. Soc.* **1951**, *73*, 1904.
(35) Edwards, S. F. *Proc. Phys. Soc. London* **1966**, *88*, 265.
(36) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, and London, 1979.
(37) Benoit, H.; Benmouna, M. *Polymer* **1984**, *25*, 1059.
(38) Benoit, H.; Picot, C. *Pure Appl. Chem.* **1966**, *12*, 545.
(39) Dautzenberg, H. *J. Polym. Sci., Part C: Polym. Lett.* **1972**, *39*, 123.
(40) Dautzenberg, H. *J. Polym. Sci., Symp.* **1977**, *51*, 83.
(41) Guenet, J. M.; Wilmott, N. F. F.; Ellsmore, P. A. *Polymer Commun.* **1983**, *24*, 230.
(42) Gan, J. Y. S.; François, J.; Guenet, J. M. *Macromolecules* **1986**, *19*, 173.
(43) Koberstein, J. T.; Picot, C.; Benoit, H. *Polymer* **1985**, *26*, 641.
(44) Hara, M.; Nakajima, A. *Polym. J.* **1980**, *12*, 701.
(45) Hara, M.; Nakajima, A. *Polym. J.* **1980**, *12*, 711.
(46) Medjahdi, G.; Sarazin, D.; François, J. *Eur. Polym. J.* **1990**, *26*, 823.
(47) Medjahdi, G.; Sarazin, D.; François, J. *Macromolecules* **1991**, *24*, 4138.
(48) Muthukumar, M.; Edwards, S. F. *J. Chem. Phys.* **1982**, *76*, 2720.
(49) Lapp, A.; Picot, C.; Strazielle, C. *J. Phys. Lett.* **1985**, *46*, 1031.
(50) Pouyet, G.; François, J.; Dayantis, J.; Weill, G. *Macromolecules* **1980**, *13*, 176.
(51) Debye, P.; Buech, A. M. *J. Appl. Phys.* **1949**, *20*, 518.
(52) Mattsuyama, A.; Tanaka, F. *Phys. Rev. Lett.* **1990**, *65*(3), 341.
(53) Stockmayer, W. H.; Chan, L. L. *J. Polym. Sci. A2* **1966**, *4*, 437.
(54) Erlander, S. R. *J. Colloid. Interface Sci.* **1970**, *34*, 53.
(55) Bakanova, Z. Kh.; Bekturov, E. A. *Izv. Akad. Nauk. Kaz. SSR. Ser. Khin.* **1977**, *3*, 63.
(56) Louai, A.; Sarazin, D.; Pollet, G.; François, J.; Moreaux, F. *Polymer* **1991**, *32*, 703.