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Notes

Small-Angle Neutron and X-ray Scattering Comparative Study of Polyacrylamide and Hydrophobically Modified Polyacrylamide in Aqueous Solution

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I. Introduction

Hydrophobically modified water-soluble polymers exhibit in aqueous solutions interesting thickening behavior due to the association of the hydrophobic parts into domains acting as temporary cross-links. Such polymers have a wide use for various applications in cosmetics, food processing, and paints industries. To optimize the rheological properties of these materials, a variety of different polymer architectures have been extensively studied in the literature[1,2] including end-modified polymers, grafted polymers, and block copolymers. The respective sizes of the parent polymer and of the hydrophobic modifiers as well as the hydrophobicity of the latter also have an influence on the rheological properties.

A large number of papers[1,2] have been devoted to the stress vs shear rate behavior of associating polymers. Fluorescence techniques have been used to show the existence of the hydrophobic domains. However, there have been relatively fewer attempts[3] to characterize the structure of the associating polymer solutions by scattering techniques although this information can help us to understand their flow behavior. One would like to get an idea about the structure of the transient associating network and how the fluctuations of polymer concentration are modified by the introduction of hydrophobic groups. Small-angle neutron scattering appears to be well suited to that purpose because of the possibility to label differently the hydrophilic and the hydrophobic parts of the chains. The contrast variation method would then allow one to distinguish the contributions of the hydrophilic backbone and of the hydrophobic domains to the total scattering intensity, possibly allowing one to determine the size and spatial distribution of the hydrophobic domains.[3]

This paper presents the first attempt to perform such experiments on acrylamide-based associating copolymers obtained by the micellar radical copolymerization of acrylamide and *N*-(4-ethylphenyl)acrylamide, resulting in long polyacrylamide chains containing random blocks of hydrophobic units. The steady state flow behavior of these polymers in aqueous semidilute solutions has been characterized for varying hydrophobe content and block length.[4] Also some attention has been paid to their transient rheological behavior in a shear flow.[5] Here we report on small-angle neutron and X-ray scattering results obtained with samples having a fixed molar fraction of hydrophobic units of about 0.01. The structure factor has been measured and compared to that of the corresponding homopolymer (pure polyacrylamide) solution with the same concentration.

Table 1. Characteristics of the Samples

Polymerization parameters			Polymer characterization		
sample	[SDS][a]	hydrophobe conc[b]	conversion[c]	hydrophobe content (mol %)	M_w (10^6 g/mol)
D	3	0	25	0	1.7
N	0	0	24.5	0	4.9
K	3	0.75	13	1.14	2.5
L	3	0.75	11	1.19	3.1

[a] SDS wt % in the feed, based on volume of water. [b] The mol % in the feed, based on monomer concentrations. [c] The wt %, based on initial monomer amount.

II. Experimental Section

The synthesis proceeds along the lines described in previous papers.[4,6] It is a micellar radical copolymerization where the sodium dodecyl sulfate surfactant (SDS) is used to solubilize the hydrophobic monomer, *N*-(4-ethylphenyl)acrylamide, in the aqueous solution of acrylamide monomers. The radical polymerization is initiated by potassium persulfate ($K_2S_2O_8$). A simple picture of the polymerization process is that, from time to time, growing acrylamide chains enter one micelle and the hydrophobic units polymerize until no free monomer is available in the micelle, the reaction then continuing again in the aqueous phase with the acrylamide monomers. The structure of the resulting copolymers should then consist of blocks of hydrophobic monomers randomly distributed along polyacrylamide chains, the average length of the blocks depending mainly on the hydrophobic monomer/surfactant ratio and their number on the initial composition of the feed comonomers. In practice, however, micelles can exchange hydrophobic monomers, and the average content of hydrophobic monomers in the micelles decreases during the reaction.[6] Moreover, it is known[7] that the reactivity of acrylamide and monosubstituted acrylamide monomers is larger when the local polarity of the medium decreases. Therefore the reactivity of the hydrophobic monomers located in the micelles is larger than the reactivity of acrylamide monomers that remain in the aqueous phase.[8] Both exchange and reactivity effects lead to an heterogeneity in composition for the copolymers, the chains formed at the beginning of the reaction being richer in hydrophobic units with larger blocks.[4,6,8] To reduce this heterogeneity, it is necessary to stop the reaction before completion. This is done by adding after a short reaction time a small amount of hydroquinone/methanol and cooling the reaction bath. The polymer is then precipitated and washed repeatedly in methanol, which is a solvent for the comonomers and the surfactant. After drying, the polymer is kept in airtight containers. The conversion of the reaction is obtained from the mass ratio of the polymer to initial mass of feed monomers and the average hydrophobe content is measured by routine UV spectroscopy. Pure polyacrylamide chains can be obtained under the same conditions in the absence of the hydrophobic monomer or by standard radical polymerization in the absence of surfactant. The weight average molecular weight of the samples is obtained in a standard way by static light scattering from dilute solutions of the polymers in formamide.[4] Table 1 summarizes the characteristics of the samples studied here.

Small-angle neutron scattering experiments have been performed in Laboratoire Léon Brillouin, Laboratoire Commun CEA-CNRS, Saclay, France, on spectrometers PACE, PAXY,

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Table 2. Experimental Conditions Used in the SANS Experiments

series	spectrometer	λ (Å)	sample−detector distance (m)	q range (10^{-2} Å^{-1})	$d\Sigma/d\Omega$ (cm^{-1})
1	PAXY	6.0	3.26	1.3−11.5	0.856
2	PACE	10.0	3.00	0.63−6.7	0.972
3	PAXE	5.0	5.06	1.08−14.6	0.826
4	PAXY	8.0	5.015	0.63−5.6	0.916

and PAXE during separate experimental sessions. Table 2 lists the experimental conditions used and the corresponding range of scattering wavevectors q explored. Measurements were carried out in standard Hellma cells built from two quartz disks separated by an annular quartz spacer with a thickness of 1 or 5 mm. Standard data treatment was performed and involved correction for transmission and thickness, incoherent scattering subtraction, and normalization by the intensity scattered from 1 mm of H_2O. Incoherent scattering level for each sample was obtained from interpolation through a set of measurements performed on mixtures of D_2O/H_2O with different compositions. The interpolated value was calculated on the basis of the H content in the sample. The data were put on an absolute scale by using the values (see Table 2) for the incoherent scattering cross-section $d\Sigma/d\Omega$ of 1 mm of H_2O measured by Ragnetti et al.[9]

Small-angle X-ray scattering experiments have been performed on spectrometer D22 available at the LURE synchrotron facility. The wavelength of the incident photons and the distance between sample and detector were set to 1.38 Å and 1.620 m, respectively. Kapton was used for the cell windows, and data treatment involved correction for incident photon flux and for sample transmission and subtraction of the intensity scattered from pure water and kapton windows.

III. Results and Discussion

Our first goal was to answer the question whether we were able to distinguish the hydrophobic parts in the copolymer samples. Thus the first thing we tried was to find out what was the isotopic composition of the solvent that matches the contrast of the homopolymer. The contrast factor of the polymer with respect to the solvent is given by

$$K_{pp} = \left(b_p - \frac{V_p}{V_o} b_o\right)^2 \qquad (1)$$

$$b_o = x_D b_{D_2O} + (1 - x_D) b_{H_2O}$$

where b_p is the scattering length for the acrylamide monomer, V_p is the partial molar volume of acrylamide units in the polymer, and b_o, and V_o are the corresponding quantities for the solvent. In fact b_o is the effective scattering length of the H_2O/D_2O mixture with x_D being the molar fraction of deuterated water. The scattering length for each component is, within the small-angle scattering approximation, the sum of the scattering lengths of the constituting nuclei and does not depend on the scattering wavevector q. It can be calculated from tabulated values.[10] For a pseudo-two-component solution containing only the polymer and the effective solvent, the scattering intensity per unit volume $I(q)$ is simply

$$I(q) = K_{pp} S_{pp}(q) \qquad (2)$$

where $S_{pp}(q)$ is the structure factor of the polymer solution, i.e. the Fourier transform of its density−density correlation function.

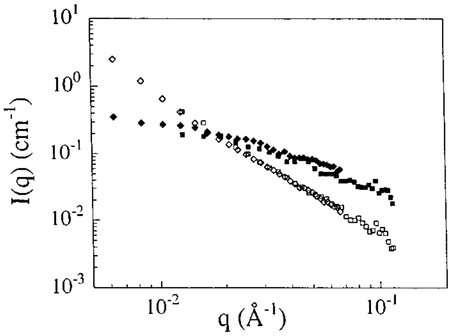

Figure 1. SANS intensities scattered from polyacrylamide solutions ($C = 0.03$ g/cm^3) in H_2O (closed symbols) and in D_2O (opened symbols). Squares and diamonds correspond to data obtained in two different series of experiments (series 1 and 2, respectively; see Table 2 for experimental conditions).

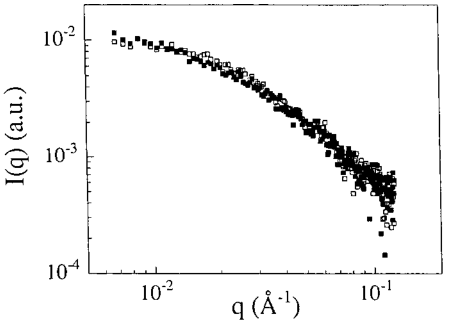

Figure 2. SAXS intensities scattered from the same samples as in Figure 1. Opened and closed symbols have the same meaning as in Figure 1.

Experiments performed with varying D_2O content should thus yield intensity curves with same shapes but different amplitudes, based on the assumption that the isotopic composition affects only the contrast factor of the polymer with respect to the solvent. Clearly this expected behavior is not seen in Figure 1 where we have plotted the intensities scattered from a polyacrylamide solution (sample D) with concentration $C = 3 \times 10^{-2}$ g/cm^3 in pure H_2O ($x_D = 0$) and in pure D_2O ($x_D = 1$) solvent: the two curves have obviously different shapes. In fact isotopic substitution is known to also affect the polymer solvent interactions, and this effect can be best seen for systems close to their compensation temperature (e.g. polystyrene−cyclohexane[11] or poly(acrylic acid)−water[12] solutions). Such an effect could be invoked here, and the change in the shape of the scattering curves would be consistent with a quality of the solvent getting poorer as x_D is increased from 0 to 1. However the estimation of contrast factors in the two experiments were inconsistent with the results, and we felt uncomfortable in drawing a conclusion from this single result. Therefore we turned to SAXS, where the contrast between polymer and solvent is not affected by the isotopic substitution and only possible thermodynamic effects would remain. The results displayed in Figure 2 allow one to definitely rule out any isotopic effect on the quality of the solvent since the scattering curves obtained with the two solvents $x_D = 0$ and $x_D = 1$ superpose perfectly within the experimental noise. At that point only contrast effects can explain the results in Figure 1.

A first possibility would be the presence of another component in the polymer solution. Remaining surfactant from the polymerization step might well be incriminated. Therefore, we synthesized a new homopolymer sample without the use of surfactant (sample N) and compared the scattering intensities from the two samples. Figure 3 shows the combination of all SANS and SAXS intensities scattered from samples D and N

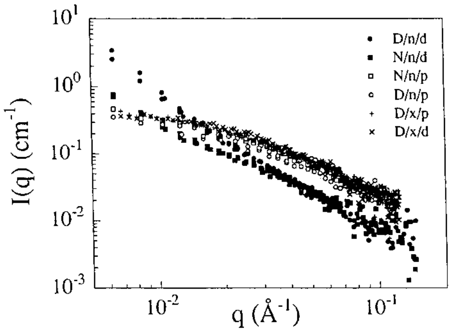

Figure 3. Comparison of all SANS and SAXS intensities scattered from two polyacrylamide samples ($C = 0.03$ g/cm^3) synthesized in the presence (sample D) or in the absence (sample N) of surfactant. In the legend are indicated the nature of the incident particles (n or x, for neutrons and X-rays, respectively) and the labeling of the solvent (p or d, for H_2O or D_2O, respectively). Note that D/n/d, N/n/d and D/n/p data points combine the results obtained from respectively four, three, and three different experiments performed with varying spectrometers or experimental setups (See Table 2).

at $C = 0.03$ g/cm^3. SAXS intensities have been arbitrarily shifted on the vertical scale to match the SANS data. From these data it is clear that, in H_2O solvent, all data for D and N samples superimpose on a single curve within experimental errors. The SAXS data for sample D in D_2O follow the same trend as well (see also Figure 2). On the other hand, the SANS curves measured in D_2O solvent exhibit markedly different shapes, with the ones corresponding to sample N synthesized in the absence of surfactant being closer to the curves measured in H_2O. Thus the presence of surfactant during the synthesis seems to play a role.

The presence of remaining surfactant is rather surprising at first sight. The repeated washing of the samples in methanol is expected to remove the surfactant since it is soluble in this solvent, and moreover SDS and polyacrylamide are known not to associate.[13] A better possible explanation would consist in a transfer reaction during the polymerization of some radicals to 1-dodecanol, which is likely to be present in the micellar solution, due to remaining impurities in the SDS or even to hydrolysis of the sulfate group in water. Thus a few growing chains would start up with a C_{12} alkyl chain. In fact, the average molecular weight of polyacrylamide synthesized in the presence of SDS is generally smaller (see Table 1) than when synthesized without micelles, and this effect shows that some transfer reactions do occur. From the comparison of typical molecular weights values obtained with and without the presence of SDS, we can estimate that roughly 10% of the chains would start with an alkyl chain if this transfer reaction were the single reason for the decrease in molecular weight.[14] This would correspond to a molar ratio of about 10^{-5} for chains with an average degree of polymerization around 2×10^4.

Hill[15] has searched by elemental analysis for remaining traces of sulfur in the samples. His conclusion is that the weight fraction of sulfur is less than 0.3%, which is the limit of sensitivity for the method. This seems to exclude the presence of surfactant but gives no indication about the alkyl chains that would no longer contain the sulfate group if 1-dodecanol is the transfer agent. The sensitivity of the SANS curves to the presence of SDS during the synthesis is less surprising if we take a look at the contrast factors listed in Table 3. The large number of H atoms in the alkyl chain give it a very large contrast in D_2O solvent, larger than the contrast of monomer units by a factor about 200. Similarly the cross-correlation term between the alkyl chain ends, and the polymer is also weighted by a rather large contrast value. These effects are much less important in H_2O (see Table 3). We can mention here that, to calculate these contrast values, the scattering length of the acrylamide units is estimated by taking into account the isotopic exchange on the NH_2 group,[16,17] assuming that its equilibrium value corresponds to the isotopic composition of the solvent. For the partial molar volumes, we use the values $V_p = 50.9$ cm^3/mol and $V_a = 215$ cm^3/mol.[18]

Table 3. Contrast Factors K_{ij} of Polyacrylamide and C_{12} Alkyl Chains with Respect to H_2O and D_2O[a]

Solvent	K_{pp} (b)	K_{pa} (b)	K_{aa} (b)
D_2O	2.86	81.5	582
H_2O	4.49	14.7	12.0

[a] Subscripts p and a refer to polyacrylamide and alkyl chains, respectively.

Back to Figures 2 and 3, it is clear that the replacement of H_2O by D_2O does not change the quality of the solvent and that the presence of surfactant during the synthesis is not able to explain all of the observed effects. Thus the most realistic explanation for the remaining part of the difference appears to be linked to contrast effects that are likely to originate from an incomplete or nonrandom isotopic substitution on the NH_2 groups. Specific labeling of styrene monomers has been found to modify the asymptotic large *q* behavior of the form factor of the chains while the small *q* behavior remained unaffected except for an obvious numerical contrast factor.[19] In the present case, however, the larger effects are observed at small *q* values and can be compared to previous results obtained by Balsara et al.[20] These authors reported the measurement of a *q*-dependent coherent intensity scattered from a melt of a pure D-saturated polybutadiene. They showed that this effect arises from a partial H−D exchange on the monomers that reveals the form factor of the individual chains in the melt. In the case of a melt, this effect could be analyzed quantitatively by performing the full random phase calculation for the structure factor and by obtaining the average number of deuterium atoms per monomeric unit from density measurements.[20] Interestingly, the contribution of the form factor of the individual chains was found to be weighted by the variance of the labeling distribution and to be still significant in more usual situations, like in mixtures of deuterated and protonated identical chains with equal volume fractions. This contribution had to be taken into account to get meaningful values of the interaction parameter.[20] In the present case, such a quantitative analysis would be more delicate owing to the questionable validity of the random phase approximation to describe the structure of the semidilute solutions. However, it seems very likely that a similar effect of the form factor of the large individual chains arises from an uneven isotopic substitution and explains the large difference in the intensities measured for the homopolymer N in H_2O and D_2O at small *q* values.

Such effects can be expected similarly in the SANS curves measured on copolymer solutions, which contain in addition hydrophobic units. Under these conditions it seems hopeless trying to extract the intensity arising from these hydrophobic units and to get information on their organization. It is nevertheless possible to get some qualitative ideas about the effect of hydrophobic

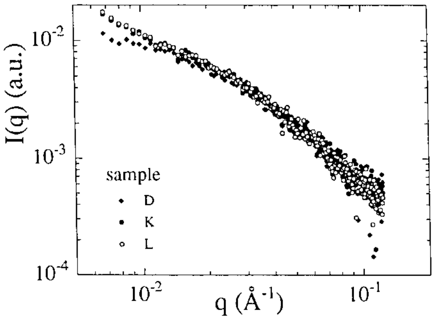

Figure 4. SAXS intensities from homopolymer D and copolymers K and L in H_2O (C = 0.03 g/cm^3).

units on the structure of the samples. In fact SAXS experiments or SANS experiments performed in pure H_2O should be rather insensitive to the multicomponent nature of these systems and can be expected to probe overall fluctuations of polymer concentration. Indeed, for a given sample, the SAXS curves can be superposed by using an arbitrary normalization factor onto the SANS curves measured in pure H_2O.

As an example, Figure 4 shows the comparison of SAXS intensities scattered from homopolymer and copolymer solutions in H_2O. The intensity curves for copolymers K and L are the same within experimental errors. They are essentially the same as in the homopolymer solution on length scales smaller than about 100 Å (when $C = 0.03$ g/cm^3), which is the same order of magnitude as the correlation length[21] $\xi \sim 50$ Å obtained when plotting $I^{-1}(q)$ vs q^2 for the data corresponding to the homopolymer semidilute solution, However for larger length scales (i.e. $q < 10^{-2}$ Å^{-1}), copolymer solutions show enhanced fluctuations of polymer concentration due to the presence of hydrophobic units.

IV. Conclusion

We have compared the small-angle neutron and X-ray scattering intensities measured from aqueous solutions of polyacrylamide and of hydrophobically modified random block copolymers based on acrylamide.

Experiments performed under varying contrast conditions show that these systems are multicomponent solutions. In the case of the homopolymer, there is evidence for some alkyl groups bound to the extremities of the chains due to transfer reactions during the radical copolymerization in micellar solution. However this not sufficient to explain all of the observed effects, and isotopic substitution on the NH_2 groups might play also a role. The same phenomena are likely to occur in copolymer samples, which prevents the separation of the contributions arising from the different components by contrast variation methods.

We have found that the fluctuations of overall polymer concentration are the same for the two systems for small length scales while they are enhanced in the copolymer solutions at larger distances. The limit between these two regimes corresponds approximately to the correlation length of the semidilute solution of the homopolymer. These results suggest that it would be interesting to probe the fluctuations of polymer concentration on larger length scales by light-scattering techniques. A forthcoming paper[22] will show that this is indeed the case.

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