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ON THE STATIC AND DYNAMIC SCATTERING FROM LINEAR AND BRANCHED POLYELECTROLYTES AT VARIOUS SCREENING LENGTHS

PROPRIETES DE DIFFUSION STATIQUE ET DYNAMIQUE DE POLYELECTROLYTES LINEAIRES ET RAMIFIES A DIVERSES LONGUEURS D'ECRAN

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ABSTRACT

During the two last decades, branched polyelectrolytes have been thoroughly studied from theoretical and experimental standpoints. In this report, we attempt to compare the behaviour of highly branched polyelectrolytes to that of their linear counterparts at low ionic strength. As expected, the expansion behaviour of the branched materials is considerably less than of that of the corresponding linear chains. Surprisingly, in the former case (sphere-like behavior), the ratio of the radius of gyration to the hydrodynamic radius $\rho=R_g/R_h$ shows an opposite behaviour as compared to the second one (rod-like behavior); indeed, contrary to the case of linear chains for which this ratio increases, that of branched homologous decreases as the ionic strength is lowered. Analyzis of the data, depicted in Kratky plots, reveals substantial discrepancies between the both polymeric structures. Moreover, at high ionic strength, one observes a rod-like structure that undergoes a transition to a disordered conformation which is not however that of a random coil, whereas, at low one, it appears that the two double- helix unfold and the loop strongly expands.

RESUME

Ces deux dernières décennies, les polyélectrolytes ramifiés ont été activement étudiés sur le double plan théorique et expérimental; le propos de cette étude est de tenter de comparer le comportement de polyélectrolytes fortement ramifiés à celui de leurs homologues linéaires pour des forces ioniques faibles. Comme attendu, l'expansion des matériaux ramifiés est considérablement moindre que celle des chaînes linéaires correspondantes. Cependant, il est surprenant que, dans le premier cas (comportement d'une sphère), le rapport du rayon de giration au rayon hydrodynamique $\rho=Rg/Rh$ montre un comportement opposé à celui correspondant au second cas (comportement de bâtonnet); en effet, contrairement au cas des chaînes linéaires pour lesquelles ce rapport croît, celui de leurs homologues ramifiés diminue à mesure que la concentration ionique est abaissée. L'analyse des données, mises en évidence dans la représentation de Kratky, indique des écarts substantiels entre les deux structures polymériques. Par ailleurs, pour une force ionique élevée, on observe une structure en forme de bâtonnet qui subit une transition vers une conformation désordonnée qui n'est cependant pas celle d'une pelote statistique, tandis que, pour des forces ioniques basses, il apparaît que les deux double-hélices ne se replient pas et la boucle s'étend fortement.

1. INTRODUCTION

The characterization of the nature of branchings in branched polymer molecules is an on- going effort. The pioneering work of Zimm and Stockmayer [1], followed by a wide variety of works reported in the literature [2,3] derived the mean-square radius of gyration of molecules with specific branching in the absence of any excluded-volume effects. In this limit $<S^2>_b$, is proportional to the mean-square radius of gyration $<S^2>$ of a linear molecule having the same number of segments than a branched molecule.

$$\left\langle S^2 \right\rangle_b = g \left\langle S^2 \right\rangle \tag{1}$$

For example, in the case of uniform stars, the proportionality constant g is given by

$$g = \frac{3f-2}{f^2} \tag{2}$$

where f is the number of branches in the star. Although branched polyelectrolytes have been extensively used in the colloid industry, they have recently attracted careful experimental investigation, particularly in the context of electrophoresis [4]. On this account, we present here the static and dynamic behavior at low ionic strength. Recently, some experimental measurements were performed by *Burchard et al.* [5] to collect reliable data on the expansion behavior and intermolecular interaction of these architectures in comparison to the corresponding linear chains. These data were thought to serve as a basis for suitable theories. For this purpose, static light scattering measurements were performed with a fully computerized instrument. Measurements were made in the angular range from 30° to 145° by steps of 5° and were represented as Zimm-plots and extrapolated to zero angle and zero concentration respectively. The evaluation of radius of gyration $R_g=[<S^2>_z]^{1/2}$ was made as usually. Because of the curvature of the angular dependence in Zimm-plots; the fitting of the curves were made by a 2nd order polynomial in which the linear term is $R_g^2/(6M_w)$. The dynamic light scattering measurements were carried out by the same instruments similar to those used in static LS in the angular range of 30°-150° but here by steps of 10°.

2. RESULTS

2.1 SWELLING BEHAVIOUR

In order to illustrate the dependence of the radius of gyration with the inverse of Debye-Hückel screening length in the case of linear and crosslinked chains, we have depicted in figure 1, the variation of Rg as a function κ.

Figure 1 shows the variation of the radius of gyration as a function of the ionic screen length for the linear chains (filled circles) and intermolecular crosslinked chains (open circles). In the light of this figure, one observes that the radius of gyration strongly increases in the case of linear chains but a slight swelling for the branched ones. This difference in behavior could be expected, since the cross-linked structure is characterized only by a restricted swelling where-as the linear one can stretch out freely.

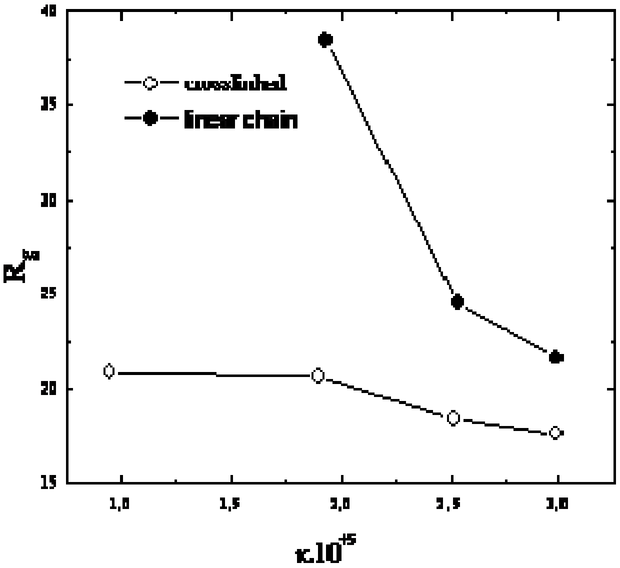

Figure 1: dependence of the radius of gyration R_g with the inverse Debye-Hückel screening length for the linear (filled circles) and crosslinked (open circles) polymer.

The fact that, the hydrodynamic radii are not much changed in both cases is not surprising. Thus, the pronounced opposite behavior, through the $\rho=R_g/Rh$ parameter, is shown in figure 2. For linear chains, an increase of ρ is found as the ionic strength is lowered, and this is in agreement with a chain expansion to a rather stiff conformation. For the branched material, a decrease of ρ to the value of homogeneous spheres is obtained. At first, due to the expanding force of the charges, the bell-shaped high segment density distribution around the center of mass is smoothed out to a homogeneous segment density.

2.2 ANGULAR DEPENDENCE

However, striking effects became apparent when the angular dependence of the scattered light was studied. Figure 3 shows a kratky plot of the particle scattering factor as a function of q for the branched polyelectrolyte. For comparison, the corresponding theoretical curves for monodisperse and polydisperse coils, are shown as solid lines. The experimental curves look similar to that for monodisperse linear chains in a θ-solvent.

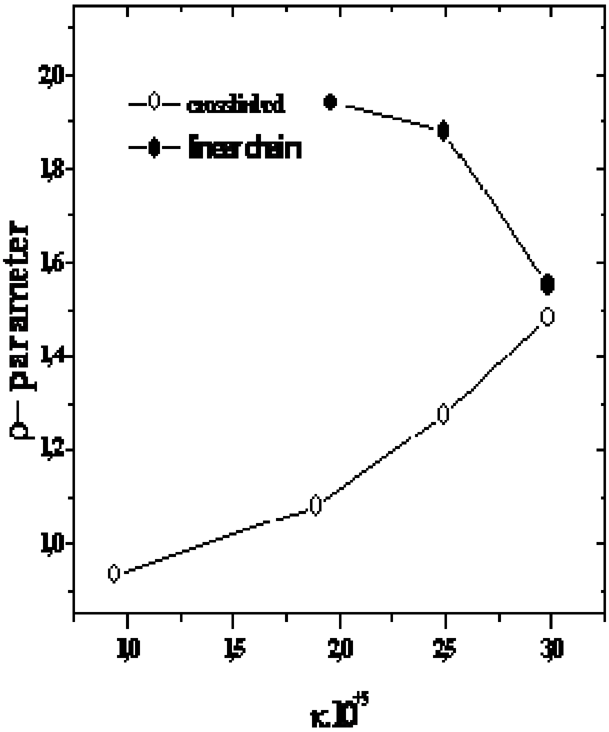

Figure 2: Variation of the structure parameter ρ =Rg/Rh as a function of the inverse of screening length for the linear and cross-linked polymer. The meaning of the both symbols is identical to that indicated in figure 1.

However, the salt solutions are typical good solvents. Interestingly, the shape of the curve does not change significantly with the expansion. Obviously, the expansion does not affect the type of the segment density distribution.

Figure 4 shows the results for the charged linear polyelectrolyte at various ionic strengths. In contrast to our expectation, a rod like structure was obtained at high ionic strength. This was the first surprise but can be explained by the tendency of linear polyelectrolyte to form double helices [6, 7].

This helix conformation is not broken up at the high ionic strength in spite of the charges along the chain because of the strong electrostatic shielding. However, the helix became destructured when the ionic strength was lowered, and several intermediate states of an order-disorder transition could be observed. Surprisingly this transition to disorder does not approach the conformation of a random coil as may be seen by comparison with the random coil curve. The final particle scattering factor resembles more a star-branched macromolecule with about 20 polydisperse arms [8].

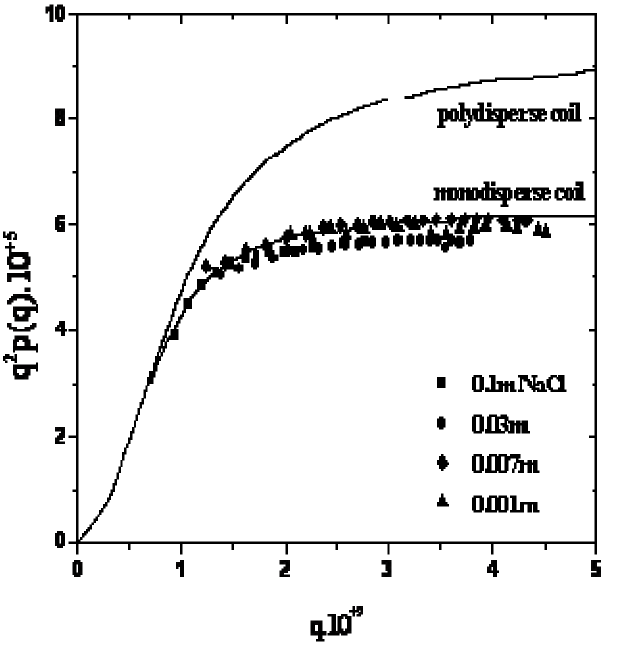

Figure 3 :Kratky plot q2p(q) versus q for branched polyelectrolyte derivative at 4 different ionic strengths. The solid curves represent the behavior of monodisperse and polydisperse random coils of linear chains at θ-conditions.

DISCUSSION

The angular dependence, observed for the linear polyelctrolyte allows us to think of a model which is able to explain the behavior of this polyelectrolyte. Before showing the suggested model, two further observations have to be mentioned. The first point is that already the non-substituted linear polyelectrolyte showed an increase of the molar mass in sodium hydroxide and this factor remained the same of derivatized samples. Hence, a double helix structure existed already before the derivatization was made. The second point is that the linear mass density of the rodlike chains could be determined from the asymptotic plateau of the scattering curves in a Casassa-Holtzer representation. The linear mass density of the linear polyelectrolyte double helix can be calculated from the well documented crystalline structure [9].

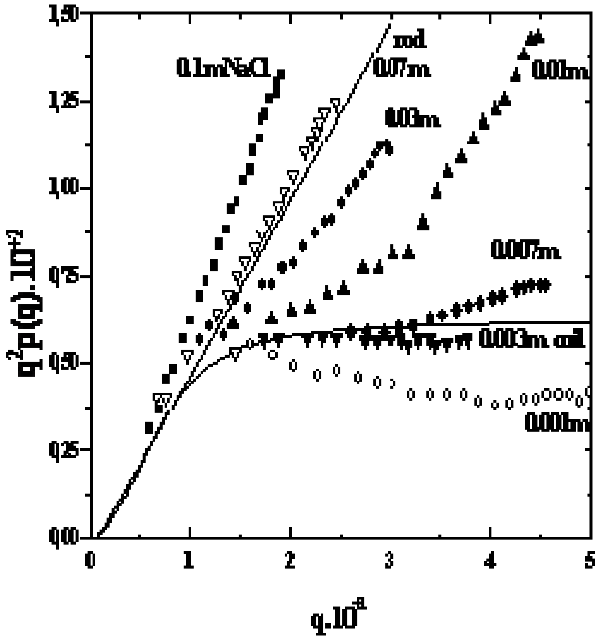

Figure 4 : Kratky plots for the derivative linear polyelectrolyte at various ionic strengths. The upper solid curve represent the behavior of thin rods where-as the lower solid one corresponds to monodisperse random coils.

Since the apparent degree of polymerization had not changed after derivatization, these findings indicate that the double helix of the non-substituted linear polyelectrolyte had been folded back after derivatization.

CONCLUSION

In order to collect some hints on the constraints due to branching, the starting point of this study was a quantitative comparison of the expansion behavior between branched and linear polyelectrolytes of the same chemical composition. Such an idealised comparison failed in the case of the starch polymers, because of structure stabilizing effects due to H-bonding that counteracted against the unspecific repulsion of charges. This unexpected experience turns out to be an instructive warning for taking care of particular caution when drawing conclusions on polyelectrolyte effects. The expansion behavior of the linear polyelectrolyte appeared to be very similar to that of the neutral polymer, but the analyzis of the structure revealed a far more complex behavior.

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