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Investigation of Local Conformations of Polyelectrolytes in Aqueous Solution by Small-Angle X-ray Scattering. 2. Local Conformations of Stereoregular Poly(sodium methacrylates)

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ABSTRACT: Local conformations of isotactic and syndiotactic poly(sodium methacrylates) in aqueous sodium chloride solution were studied by small-angle X-ray scattering measurements, in comparison with those of the corresponding stereoregular poly(methyl methacrylates). It was observed that their local conformations are not much affected by the presence of charges.

Introduction

Stereoregular polymers often have locally characteristic conformations in solution, though their overall conformations can well be approximated by random coils. Typical examples may be syndiotactic and isotactic poly(methyl methacrylates) (PMMA), whose local conformations were well elucidated by Kirste,[1–3] and Yoon and Flory.[4–6] In the Kratky plots of small-angle X-ray and neutron scattering, syndiotactic PMMA shows a characteristic oscillation curve, whereas isotactic PMMA shows a monotonously changing curve.[1–3] On the basis of a realistic isomeric state model, Yoon and Flory[4–6] concluded that the maxima in the oscillation curve are due to the preference of racemic dyads of PMMA for the trans,trans conformation together with an inequality of the skeletal bond angles at $-CH_2-$ and at the double-substituted C^α and that the average length of sequence over which trans,trans states are perpetuated is about nine units for syndiotactic PMMA while it is only about three for isotactic PMMA. This conclusion implies that the syndiotactic PMMA chain has locally a preferred curvature, while the isotactic PMMA chain has a rather random conformation.

In our preceding paper,[7] the persistence lengths of an atactic polyelectrolyte, i.e. a conventional poly(acrylic acid), and its sodium salt were determined from small-angle X-ray scattering (SAXS) data according to the method of Kratky. It was concluded that the persistence lengths are almost equal to that of poly(*tert*-butyl acrylate) and depend neither on the charge density of poly(acrylic acid) nor on the ionic strength of the solution. That is, the local conformation of the polymer homologue, ester and acid, is almost fixed, probably because the local conformation is substantially determined by the strong steric hindrance between bulky side groups.

The purpose of the present work is to confirm this conclusion by comparing the small-angle X-ray scattering curves of stereoregular poly(sodium methacrylates) (PNaMA) with those of the corresponding stereoregular PMMA's. It was previously suggested by NMR[8] and potentiometric titration studies[9] that stereoregular poly(acrylic acids) may have locally characteristic conformations and, moreover, the characteristic local conformations are not changed by the presence of charges.

Experimental Section

1. Samples. Isotactic PMMA was prepared by polymerization of methyl methacrylate monomer with phenylmagnesium bromide in toluene at 20 °C.[10] Isotactic poly(methacrylic acid) (PMAA) was prepared by hydrolyzing the isotactic PMMA in concentrated sulfuric acid.[9] Its degree of hydrolysis was found to be ca. 100% from its ^{13}C NMR spectrum. Syndiotactic PMMA was purchased from Polymer Laboratories Ltd. Syndiotactic PMAA was prepared by polymerization of methacrylic acid in isopropyl alcohol with γ-irradiation at −78 °C.[11]

Table I
Molecular Characteristics of the Samples

samples	mol wt	DT
isotactic PMMA	2.4×10^4	$I = 0.80 \pm 0.05$
isotactic PMAA	1.4×10^4 [a]	$I = 0.89 \pm 0.05$
syndiotactic PMMA	4.7×10^5	$S = 0.79 \pm 0.05$
syndiotactic PMAA	9.3×10^3 [a]	$S = 0.88 \pm 0.05$

[a] These molecular weights are given in the Na salt form.

Approximate molecular weights of both stereoregular PMMA's were estimated from their GPC patterns, obtained with a high-speed gel chromatograph (TSK-HLC 801A, Toyo Soda Ltd.) and the use of a calibration curve determined with standard polystyrenes. Molecular weights (M) of both stereoregular PMAA's were estimated from their intrinsic viscosities in 2 M aqueous $NaNO_3$ solution at 25 °C using the equation[12]

$$[\eta] = 4.49 \times 10^{-4} M^{0.65}$$

which was determined for atactic PMAA.

The degrees of tacticity (DT) of PMMA and PMAA, expressed in triad content, were evaluated from the α-CH_3 peak in the proton NMR spectrum[13] and ^{13}C NMR spectrum,[11] respectively. The proton NMR spectra were recorded on a JEOL JNM-PMX 60 spectrometer and the ^{13}C NMR spectra on a Varian XL-100A spectrometer.

The molecular characteristics of the samples thus determined are listed in Table I.

2. Measurements of Small-Angle X-ray Scattering and Numerical Computations. Details of measurements and numerical computations were described in our preceding paper.[7] The data are analyzed in the form of a Kratky plot, i.e., in the plot of Ih^2 vs. h. Here, I is the desmeared scattering intensity from a solute molecule and h is the magnitude of the scattering vector, defined by $(4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle. In the processing of data, the corrections for finite cross section of polymer chains and electron density fluctuation were bypassed for the same reasons as before.[7]

Results

Figure 1 shows Kratky plots of syndiotactic PNaMA with three different degrees of neutralization (i) obtained under the same experimental conditions. It can be pointed out that the plots for the samples having low degrees of neutralization (i = 0.15 and 0.3) are very much different from that for the sample with i = 1.0. This high dependence on i in the Kratky plots of PMMA is in contrast with the Kratky plots of atactic poly(sodium acrylates) reported in the preceding paper.[7]

In Figure 2 are compared the plots of isotactic and syndiotactic PNaMA's with i = 1.0 at an NaCl concentration (C_s) of 0.01 M. A marked difference is observed between those two plots; the scattering curve of syndiotactic PNaMA oscillates, whereas that of isotactic PNaMA changes monotonously. The Kratky plots of isotactic and syndiotactic PMMA in acetone, which were originally observed by Kirste,[1–3] are shown in Figure 3 for comparison

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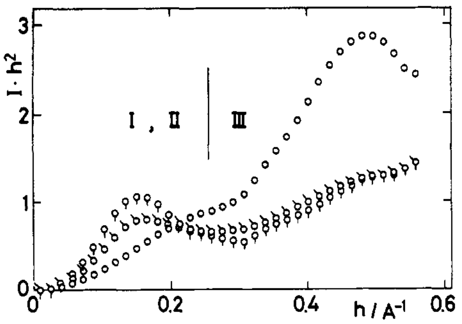

Figure 1. Kratky plots of syndiotactic PNaMA: i = 0.15 (ϙ), 0.30 (ɓ), and 1.0 (○) at C_s = 0.01 M and C_p = 20 g/dL.

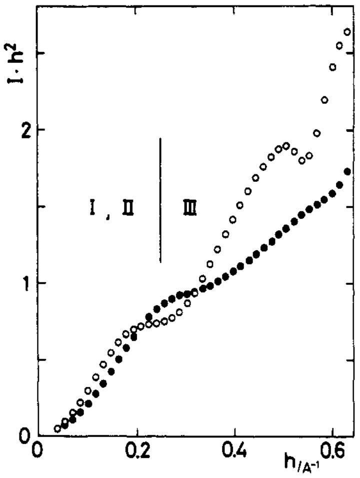

Figure 2. Kratky plots of isotactic (●) and syndiotactic (○) PNaMA. i = 1.0 at C_s = 0.01 M. C_p is 12 and 17 g/dL, respectively.

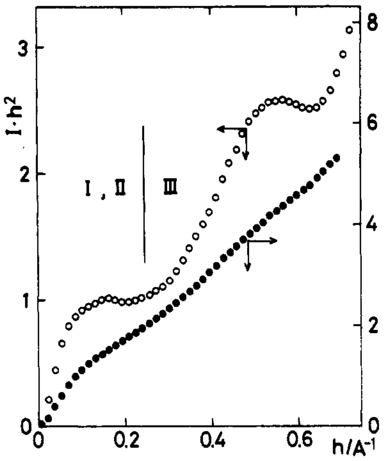

Figure 3. Kratky plots of isotactic (●) and syndiotactic (○) PMMA in acetone. C_p is 12 and 9 g/dL, respectively.

with the data in Figure 2. Comparison between Figures 2 and 3 shows that the characteristic features of isotactic and syndiotactic PMMA's are, respectively, well retained in the Kratky plots of the corresponding stereoregular PNaMA's. Moreover, it may be pointed out that the Kratky plot of isotactic PNaMA is very similar to that of atactic poly(sodium acrylate) as reported in the preceding paper.[7]

Discussion

It was previously confirmed[7] that the Kratky plots of atactic poly(sodium acrylate) consist of three regions, the Gunier (I), Debye (II), and rod (III) regions, as in the case of ordinary flexible polymers and, moreover, that the scattering curve in regions I and II is markedly affected by the excluded volume effect, but the curve in the higher region of h (region III) is free from the effect. That is, the scattering curves in regions I and II are affected by the conformation of a fairly large part of the polymer chain, whereas those in region III reflect the polymers local conformation only. Although it may not be proper to define the same three regions for stereoregular polymers, it is certain that the local conformation of stereoregular polymers can be observed in region III. Comparing the Kratky plots of PNaMA in Figure 1 with that of poly(sodium acrylate) in Figure 1 of the preceding paper,[7] we can see that region III for the present samples may be in the range of $h \gtrsim 0.25$, as indicated in Figure 1.

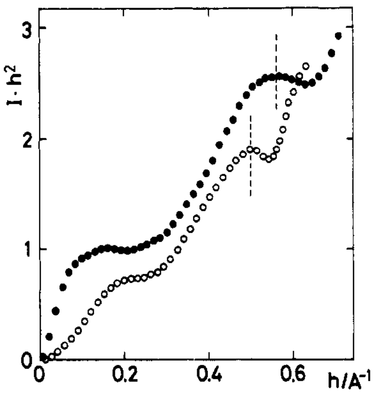

Figure 4. Comparison between the Kratky plots of syndiotactic PMMA in acetone (●) and PNaMA with i = 1.0 (○). C_p is 9 and 17 g/dL, respectively.

It is well-known that PMAA undergoes a conformational transition a globule–coil transition, when it is neutralized with NaOH.[14] PMAA becomes a compact globule if $i < 0.2$ and a random coil if $i > 0.4$. A transition from the compact globule to he random coil takes place in the range $0.2 < i < 0.4$.[9] Therefore, it is expected that the transition would manifest itself in the Kratky plot. As expected, it is observed in Figure 1 that there is a marked difference between the Kratky plots at i = 0.15 and 0.3 and that at i = 1.0. In regions I and II, the scattering curve of the sample with high charge density (i = 1.0) is similar to that of atactic poly(sodium acrylate) in Figure 1 of the preceding paper,[7] whereas big bumps are observed if i is low (i = 0.15 and 0.3). In region III, too, the behavior of PMAA at i = 0.15 and 0.3 is quite different from that at i = 1.0. However, discussion of the anomalous behavior of PMAA with low charge densities, which may be caused by their compact globular conformations, is beyond the scope of the present paper.

Comparison between Figures 2 and 3 shows that there is a close similarity between the scattering curves of stereoregular PNaMA's and those of the corresponding stereoregular PMMA's. The similarity suggests that the characteristic features in the local conformations of stereoregular PMMA's are essentially retained in those of the corresponding PNaMA's. In particular, not only syndiotactic PMMA but also syndiotactic PNaMA appears to have a characteristic conformation with a preferred curvature, which was well elucidated by Kirste and by Yoon and Flory. In Figure 4 the position of the second peak in the scattering curve of syndiotactic PNaMA is compared with that of syndiotactic PMMA. The peak position of PNaMA is closer to the origin than that of PMMA.

In the theory of Kirste,[3] in which a model chain with persistence of curvature is employed, the peak position is inversely proportional to the radius of the preferred cur-

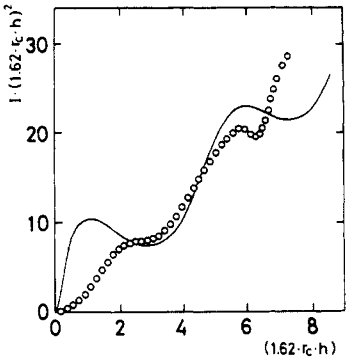

Figure 5. Comparison between the observed Kratky plot for syndiotactic PNaMA and the theoretical curve of Kirste with $r_c = 7.2$ Å. The experimental datum is the same as in Figure 2.

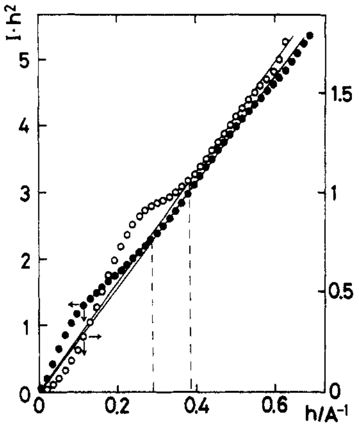

Figure 6. Comparison between the Kratky plots of isotactic PMMA in acetone (●) and PNaMA with $i = 1.0$ (○). The data are the same as in Figures 3 and 2, respectively.

vature of the polymer chain, r_c. The scattering curve of syndiotactic PNaMA calculated from the theory of Kirste using $r_c = 7.2$ Å, which was determined by fitting the second peak position characterizing the local structure, is compared with the observed one in Figure 5. The theoretical curve appears to reproduce the qualitative feature of the observed one. This value of r_c is slightly larger than that of PMMA reported by Kirste (6.7 Å).[3]

The Kratky plots of isotactic PNaMA as well as that of isotactic PMMA show normal behavior as flexible linear polymers, as shown in Figure 6. If the conformations of these polymers may be approximated by random coils, their local conformations may be represented by a persistence length, which can be determined from the following equation of Kratky and Porod[15,16]

$$y = k/h^* \tag{1}$$

where k is 1.9 or 2.87 and h^* is the value of h at the boundary between regions II and III.[7] Applying this method to the data in Figure 6, we obtain y = 5.0–7.5 and 6.6–10.0 Å for isotactic PNaMA and PMMA, respectively. The persistence length of isotactic PMMA is in good agreement with the values reported by Kirste[3] and with those calculated from the viscosity–molecular weight relationship at unperturbed states.[17] It is interesting to see that the persistence length of isotactic PNaMA is smaller than that of atactic PNaA reported previously (8.9–13.4 Å),[7] while the persistence length of isotactic PMMA is comparable to that of atactic poly(methyl acrylate).[17]

From the above experimental results, it can be concluded that the local conformations of polyelectrolytes are so tightly fixed probably due to the strong steric hindrance between side groups that the local conformation is not much affected by the presence of charges on the polymer chain. This conclusion is consistent with our previous conclusion[7] that the persistence length of poly(sodium acrylate) is comparable to that of poly(*tert*-butyl acrylate) and is not much affected by the presence of charges if the ionic strength is not too low.

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