ture of these peaks is different from the transverse peak that is expected to appear in the depolarized $c(b,c)a$ or $b(a,c)a$ spectra but does not appear because of small p_{44} and p_{55} photoelastic constants. The present sample is mechanically anisotropic and the two transverse peaks are not degenerate. The transverse peak that is not observed is associated with the elastic constant c_{44}, and the transverse peaks that appear in the $c(b,b)a$ and in the $b(a,a)c$ spectra are associated with negative sign in eq 4 and 5. These frequencies become degenerate only when $c_{11} = c_{22} = c_{33}$ and $c_{13} = c_{23} = c_{12}$, as in this case the Cauchy relation $c_{11} - c_{12} = 2c_{44}$ applies.

Discussion

The results of X-ray diffraction studies, scanning electron microscopy, and inelastic (Raman) and quasi-elastic (Brillouin) light scattering studies lead to a definitive picture of the structure of single-crystal-texture polyethylene. The extrusion process leads to the production of a material consisting of stacked sheets. These sheets are approximately 5000 Å thick and are *bc* planes, the thinnest dimensions being aligned with the *a* axis. Orientation is such that all axes are misaligned by at most 5°, and the orientation is generally better than that achievable in linear polyethylene obtained by more extreme methods. The sheets are composed of oriented lamellae with a peak lamellar thickness of 92 Å but there is a distribution of thicknesses ranging as high as 250 Å. Since the crystallinity is 80% the average amorphous thickness separating the lamellae is of the order of 20 Å. Brillouin scattering did not detect the presence of thicker lamellae outside the normal range of Raman LAM studies. Since this linear low-density polyethylene, which is a copolymer of ethylene with octene, is essentially a blend of linear and short-branched molecules, the possibility of fractionation at the high annealing pressures was a distinct possibility. Bassett[17] has reported very clear evidence for fractionation according to branching in similar materials when crystallized above 4 kbar. Here, however, the material was not crystallized at pressure. It was annealed at a temperature just a few degrees below its melting point at 4 kbar. Annealing on its own, therefore, does not provide for fractionation. Rejection of branched molecules during the crystallization process is essential. Unlike linear polyethylene in single-crystal-texture form the lamellar thickness remains low. It is therefore determined by the branching frequency. Since the branches are too long to be incorporated into the polyethylene crystal, they must remain outside the lamellae. The fact that no really thick lamellae were observed means that the polymer had behaved as a compatible blend producing cocrystallized species. If there had been a substantial amount of segregation then a bimodal distribution of lamellar thicknesses would have resulted.

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References and Notes

(1) I. L. Hay and A. Keller, *J. Mater. Sci.*, **1**, 41 (1966).
(2) I. L. Hay and A. Keller, *J. Mater. Sci.*, **2**, 538 (1967).
(3) R. J. Young and P. B. Bowden, *J. Mater. Sci.*, **8**, 1177 (1973).
(4) S. G. Burney and G. W. Groves, *J. Mater. Sci.*, **12**, 1139 (1977).
(5) J. Sandercock, in "Light Scattering in Solids", Flammanion, Paris, 1971, pp 9–12.
(6) D. B. Cavanaugh and C. H. Wang, *J. Appl. Phys.*, **52**, 5998 (1981).
(7) D. B. Cavanaugh and C. H. Wang, *J. Appl. Phys.*, **53**, 2793 (1982).
(8) D. B. Cavanaugh and C. H. Wang, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 1647 (1982).
(9) J. J. Hermans, P. J. Hermans, D. Vermaas, and Q. Weidinger, *Recl. Trav. Chim. Pays-Bas.* **65**, 427 (1946).
(10) R. W. Gray and R. J. Young, *J. Mater. Sci.*, **9**, 521 (1974).
(11) T. C. Damen, S. P. S. Porto, and B. Tell, *Phys. Rev.*, **142**, 570 (1966).
(12) R. G. Snyder, S. J. Krause, and J. Scherer, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1593 (1978).
(13) S. Mizushima and T. Shimanouchi, *J. Am. Chem. Soc.*, **71**, 1320 (1949).
(14) J. F. Rabolt and C. H. Wang, *Macromolecules*, **16**, 1698 (1983).
(15) J. L. Koenig and D. L. Tabb, *J. Macromol. Sci., Phys.*, **B9**, 141 (1974).
(16) G. Kanig, *Kolloid Z. Z. Polym.* **251**, 782 (1973).
(17) D. C. Bassett, "Principles of Polymer Morphology", Cambridge University Press, 1981.

Investigation of Local Conformations of Polyelectrolytes in Aqueous Solution by Small-Angle X-ray Scattering. 1. Local Conformations of Poly(sodium acrylates)

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ABSTRACT: Local conformations of poly(sodium acrylates) in aqueous solutions with an added salt were studied by small-angle X-ray scattering measurements. It is concluded that the chain stiffness of poly(sodium acrylates) is not much affected by the electrostatic repulsions.

Introduction

The conformation of a polymer chain in solution is in general discussed on an assumption that the conformation is determined by two independent factors: (i) the local chain stiffness due to the steric hindrance between adjacent segments and (ii) the excluded volume effect working between segments far apart along a chain.

Analysis of the conformation of polyelectrolytes has also been carried out on the two-parameter assumption. The electrostatic repulsion between charged groups surely causes an excluded volume effect between segments located far apart along a chain. From light scattering study of poly(sodium acrylates), Kitano et al.[1] concluded that the conformation of a polyelectrolyte in solution is determined mainly by the excluded volume effect.

However, this conclusion does not deny a possibility that the electrostatic repulsion increases the stiffness of the polymer chain, since the magnitude of the scattering vector

h in the light scattering is too small to observe a change in the local conformation of the polymer chain. In this work, therefore, we study the effect of electrostatic repulsion on the stiffness of the polymer chain by examining the change in the persistence length of poly(sodium acrylate), determined by applying the Kratky method to small-angle X-ray scattering (SAXS) data.

Experimental Section

1. Samples. Atactic poly(sodium acrylate) (PNaA), prepared by radical polymerization, was kindly provided by Toa Gosei Chemical Co. The sample was purified by the same process as in previous works.[2] The molecular weights of PNaA-I, -II, and -III in sodium salt form were 3.6×10^4, 15.2×10^4, and 84.5×10^4, respectively, if evaluated from their intrinsic viscosities using eq 1.[3] The PNaA-IV used for viscosity measurements was a commercial sample from Wako Chemical Industries Ltd. with $M_v = 33 \times 10^4$.

$$[\eta] = 1.45 \times 10^{-3} M_w^{1/2} \quad \text{(in 1.5 M NaBr solution at 15 °C)} \qquad (1)$$

PNaA was converted to poly(acrylic acid) (PAA) by passing it through a mixed-bed ion-exchange resin column of Amberlite IRB 120B and IRA 400 and then concentrating it with an ultrafiltration apparatus (Amicon ultrafiltration cell Model 202) if necessary. Sample solutions with the desired polymer concentration (C_p), added salt concentration (C_s), and degree of neutralization (i) were prepared by neutralizing the stock solutions of PAA with sodium hydroxide and adding calculated amounts of a concentrated solution of sodium bromide or sodium chloride. All solutions were prepared with deionized water.

Viscosity measurements were carried out with viscometers of the modified Ubbelohde type and of the Maron–Krieger–Sisko type.

2. Measurements of Small-Angle X-ray Scattering. Measurements were performed with a Kratky U-slit camera from Anton Parr Co. The X-ray source was a water-cooled copper anode tube operated at 45 kV and 30 mA and powered by a JEOL (Japan Electron Optics Laboratory Ltd.) X-ray generator Model DX-GE-2D. X-rays from the Cu Kα line with a 1.54-Å wavelength (λ) were employed. The width of the entrance and counter slits was 100 and 250 μm, respectively, and the distance between the sample and the plane of registration (L) was either 20 or 21 cm. The experimental conditions and procedure were almost the same as in our previous work.[4]

3. Numerical Computations. Numerical computations were carried out in almost the same manner as in our previous work.[4] The smeared net scattering intensity from solute molecules $\tilde{I}$ was obtained as the difference between the intensities scattered from the solvent (I_v) and solutions (I_n) with correction for the difference in their absorption coefficients and converted to a desmeared intensity I which would be obtained from a pinhole X-ray source, using Glatter's program.[5] The desmeared intensity, I, was further treated by the procedure described in our previous work[4] to obtain the scattering intensity (I_c) which the polymer would give if its cross section were negligible. I_c thus obtained was employed for the Kratky plot, i.e., for the plot of $I_c h^2$ vs. h. Here, h is the magnitude of the scattering vector, defined by $(4\pi/\lambda) \sin(\theta/2)$, where θ is the scattering angle.

The tail of the scattering curve at high angles may be affected by fluctuation in the electron density within the particles. The method of Luzzati et al.[6] was employed to estimate this effect. That is, Ih^4 was plotted against h^4 and the effect of electron density fluctuation was estimated from the slope of the plot.

Results

The Kratky plot for flexible polymers consists of three regions: the Guinier (I), Debye (II), and rod (III) regions, as shown in Figure 1. The plot is almost horizontal in region II since polymer chains are nearly Gaussian coils, while it is a straight line passing through the origin in region III. The value of h at the boundary between regions II and III gives the persistence length of the polymer. The overall conformation of the polyelectrolytes may be close to the Gaussian coil at high ionic strengths or if the polymer is uncharged. As the ionic strength is decreased or as the charge density of the polyelectrolyte is increased, however, the conformation should deviate from the Gaussian chain. Therefore, the $I_c h^2$ vs. h plot in region II for poly(sodium acrylate) should be markedly affected by changes in the degree of neutralization (charge density) and the concentration of added salt such as sodium chloride.

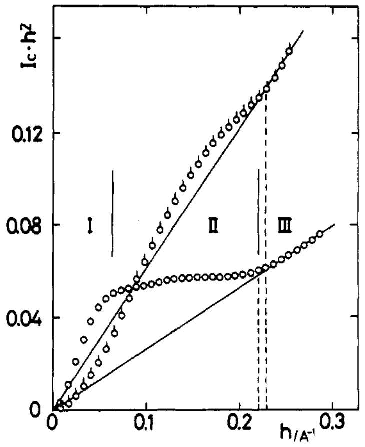

Figure 1. Comparison between the Kratky plots of poly(acrylic acid) and poly(sodium acrylate) sample PNaA-II: (○) degree of neutralization $i = 0$, NaCl concentration $C_s = 0$, polymer concentration $C_p = 3.7$ g/dL; (ȯ) $i = 0.8$, $C_s = 0.01$ M, $C_p = 2.5$ g/dL.

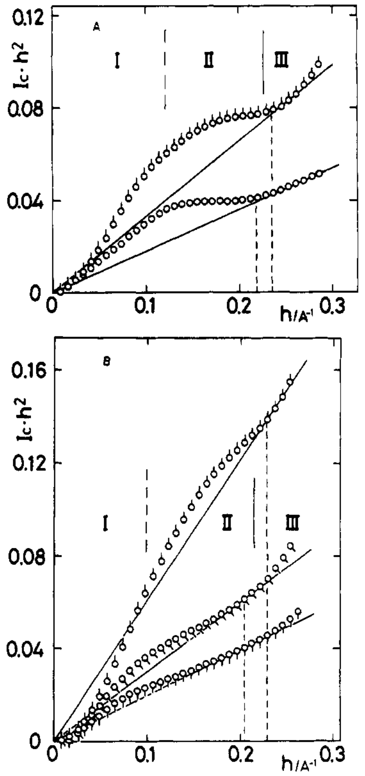

Figure 2. Kratky plots of poly(sodium acrylate) PNaA-II in solutions with (A) high ionic strengths ($i = 0.8$, $C_s = 0.1$ M, (○) $C_p = 1.6$ g/dL, (ȯ) $C_p = 3.2$ g/dL) and (B) low ionic strengths ((○) $i = 0.8$, $C_s = 0.01$ M, $C_p = 2.5$ g/dL; (ϙ) $i = 0.15$, $C_s = 0.01$ M, $C_p = 2.5$ g/dL; (ϙ) $i = 0.15$, $C_s = 0.01$ M, $C_p = 1.9$ g/dL).

Figure 1 shows a comparison between the Kratky plots of uncharged and charged polymers. In region II, the plot of the uncharged polymer ($i = 0$) is horizontal whereas that of PNaA with $i = 0.8$ has a positive slope. In parts A and B of Figure 2 are shown the Kratky plots at high and low concentrations of added salt, respectively. The data points

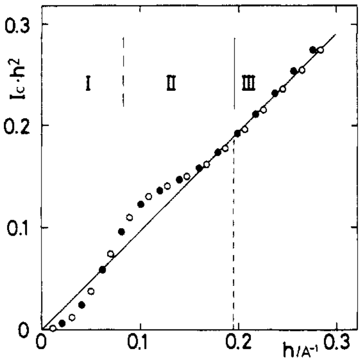

Figure 3. Comparison between the Kratky plots of poly(sodium acrylates) with different molecular weights at $i = 0.85$ and C_s = 0.01 M: (●) PNaA-I, C_p = 2.5 g/dL; (○) PNaA-III, C_p = 2.2 g/dL.

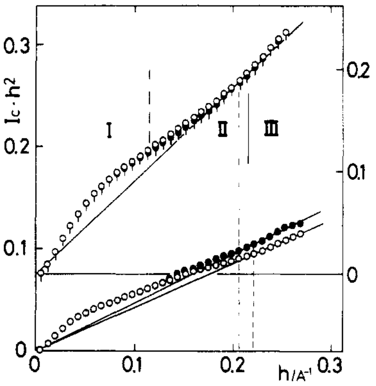

Figure 4. Effect of electron density fluctuation on the Kratky plots of PNaA-I. C_p = 2.2 g/dL (ϙ and ⧭) and 1.1 g/dL (○ and ●), i = 0.1, and C_s = 0.1 M. Filled and open circles are the data with and without the correction for electron density fluctuation.

at high ionic strength in Figure 2A form horizontal lines, whereas those at low ionic strength in Figure 2B fit lines with positive slopes.

Since only a part of the polymer chain is observed in regions II and III, there should be no detectable difference betweeen high and low molecular weight samples in those regions, unless the molecular weight is too low. Figure 3 shows a comparison between the scattering curves of two samples with different molecular weights, in which scattering intensity of a sample was multiplied by the ratio of their concentrations. Both plots are satisfactorily coincident with each other in regions II and III. In region I, too, the plot is almost independent of molecular weight. This is not unreasonable since the polymer coils overlap with each other in this range of polymer concentration.

The boundary between regions II and III, h^*, can unambiguously be determined if the plot in region II is horizontal. Since the conformation of polyelectrolytes is non-Gaussian such that the plot in region II is not horizontal, we assume that h^* is the point at which $I_c h^2$ begins to deviate from the straight line for region III, as shown in Figure 1 and 2B. This assumption is reasonable since the plot in region III is a straight line passing through the origin, which corresponds to the scattering function for a rod after all necessary corrections are made for the observed scattering intensity and, hence, it is certain that the straight line is free from the excluded volume effect of a polymer chain. Overall relative error in h^* thus evaluated may be about 5%.

At high angles the scattering curve may be affected by the fluctuation in the electron density within the scattering particles. To estimate this effect for the present samples, the data of two typical samples were corrected for the effect by the method of Luzzati et al.[6] and are represented in the form of the Kratky plot in Figure 4. Although slight differences are observed at high angles, the boundary value h^* between regions II and III is scarcely affected by the correction for density fluctuation. Therefore, we bypassed this correction for all other samples.

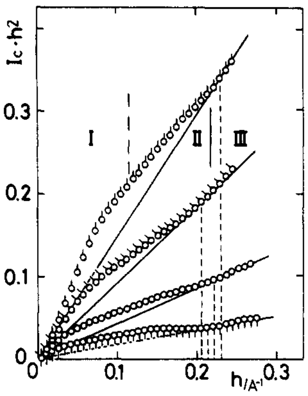

Figure 5. Effect of polymer concentration on the Kratky plots of PNaA-I at i = 0.1 and C_s = 0.1 M. The polymer concentrations C_p are 3.7 (⫰), 2.2 (ò), 1.1 (ϙ), and 0.54 g/dL (○), respectively.

Table I
Experimental Results

sample code	C_p, g/dL	C_s, M	i	y, Å	C_p*, g/dL
PNaA-I	2.5	0.01	0.85	9.8–14.5	0.21
PNaA-I	0.54	0.10	0.10	8.9–13.4	1.50
PNaA-I	1.12	0.10	0.10	8.6–13.0	
PNaA-I	2.24	0.10	0.10	9.3–13.9	
PNaA-I	3.73	0.10	0.10	8.3–12.4	
PNaA-II	1.92	0.01	0.15	9.4–14.1	0.16
PNaA-II	2.46	0.01	0.15	9.4–14.1	
PNaA-II	2.49	0.01	0.80	8.4–12.6	0.06
PNaA-II	1.64	0.10	0.80	8.7–13.1	0.16
PNaA-II	3.15	0.10	0.80	8.1–12.2	
PNaA-II	3.71	0	0	8.7–13.0	
PNaA-III	2.20	0.01	0.85	9.8–14.8	0.01
				8.9–13.4[a]	

[a] Mean.

The effect of polymer concentration on the scattering curve is shown in Figure 5 and is discussed in the Discussion. h^* is almost independent of polymer concentration.

The persistance length of the polymer chain, y, is inversely proportional to the boundary value between regions II and III, h^*, though the different proportionality constants are offered by various investigators.

$$y = k/h^* \tag{2}$$

The value of k is 1.91 according to Kratky[7] and Koyama[8] but is 2.87 according to Burchard and Kajiwara.[9] The values of y calculated from h^* using eq 2 with these k values are listed in Table I, where C_p of each sample is expressed in acid form. The values of h^* for PNaA are scarcely affected by C_s and i (Figures 2 and 3). Accordingly, it can be safely concluded that the local conformation of polyelectrolytes, which is reflected in the persistence length, is essentially fixed irrespectively of charge density and ionic strength in the present experimental ranges.

Here, it is to be noted the PNaA certainly has highly extended conformations due to the electrostatic repulsive force between segments under the present experimental conditions, that is, at i = 0.8, C_s = 0.01 M, and C_p = 1–3 g/dL, though we have no method of determining the radius of gyration of polyelectrolyte at finite polymer concentrations. The intrinsic viscosity $[\eta]$ of PNaA-IV with $i = 0.8$ in 0.01 M NaBr solution is 11.7 dL/g and its values of η_{rel} is 64.3, 36.7 or 17.4 at C_p = 2.84, 1.79, or 0.8 g/dL, respectively. The value of $[\eta]$ is about 10 times higher than the intrinsic viscosity of nonionic polymers with the same molecular weight in good solvents, such as that of poly(α-methylstyrene) in toluene.[10] The values of η_{rel} at C_p = 1–3 g/dL are also about 5 times higher than those of poly(α-methylstyrene) in toluene[11] if compared at the same polymer concentrations.

Discussion

Strictly speaking, the Kratky plot should be applied only to dilute solutions below a critical concentration C_p^*, where two isolated polymer chains begin to overlap with each other. The C_p^* for polyelectrolytes may be particularly low and can be evaluated from intrinsic viscosity by using eq 3 and 4, where N_A is Avogadro's number, Φ is the Flory

$$C_p^* = \frac{3M}{4\pi\langle s^2\rangle^{3/2}N_A} \tag{3}$$

$$[\eta] = 6^{3/2}\Phi\langle s^2\rangle^{3/2}M \tag{4}$$

viscosity coefficient, and M and $\langle s^2\rangle$ are the molecular weight and the mean square radius of gyration of polymer, respectively. The numerical value of Φ for polyelectrolytes is not well established but is reported to be much lower than the value for nonionic polymers.[12] Here, therefore, we simply assume $6^{3/2}\Phi = 1 \times 10^{22}$. The C_p^* values evaluated for the present samples are listed in Table I. It can be pointed out that almost all experiments were carried out at polymer concentrations higher than C_p^*, since such higher concentrations were required to obtain scattering intensities strong enough for analysis of the data.

However, it was pointed out in a previous paper[4] that the value of h^* may be related to the persistence length of the polymer chain y if the polymer concentration is not so high that the distance between two entanglement points, that is, the correlation length ξ, becomes shorter than the persistence length. The values of 30–40 Å were obtained for the correlation length ξ in the present sample solutions with 0.1 M NaCl when we employ the same procedure as in the previous work.[4] The persistence length obtained in 0.1 M NaCl is much shorter than these correlation lengths.

If the concentration of added salt becomes lower, moreover, a miximum generally appears in the range of low h in the scattering curves of polyelectrolyte solutions.[13-20] Since the maximum is due to a combination of intra- and intermolecular interferences as was proved in a small-angle neutron scattering experiment[18] and h^* appears in a range of h much higher than the maximum, it is certain that h^* is the value for a single chain. Moreover, it is found in Figure 5 that h^* is practically independent of polymer concentration.

The persistence length y can also be evaluated by using the relationship between the unperturbed dimension and molecular weight obtained from intrinsic viscosity, such as in eq 5, where M_L is the molecular weight of a polymer

$$y = (M_L/2)(K_0/\Phi_0)^{2/3} \tag{5}$$

per unit length, Φ_0 is the Flory viscosity constant at an unperturbed state, which is 2.5×10^{21} for ordinary fractionated polymers,[21] and K_0 is the constant in the Mark–Houwink–Sakurada equation at an unperturbed state, and $[\eta] = K_0M^{1/2}$. The experimental value of K_0 for PNaA is 1.45×10^{-3} as shown in eq 1. M_L is assumed to be 37 Å^{-1} for the trans zigzag form. Substitution of these values into eq 5 gives y = 13 Å, which agrees with the values in Table I. Moreover, y = 8–14 Å for PNaA (Table I) agrees with the value obtained for poly(*tert*-butyl acrylate) (PTBA), which has a bulky side group (10–15 Å).[4]

Thus, if the ionic strength is not too low and, hence, the assumption of two-parameter theory is valid, it can be concluded that the persistence length, i.e., the local conformation of poly(sodium acrylate) in the presence of added salt, is almost fixed probably because of the strong steric hindrance between side groups and because the polyelectrolyte coils are expanded by a kind of excluded volume effect. This conclusion is in good agreement with the experimental results obtained by NMR[22] that isotactic PNaA has a fixed local conformation independent of ionic strnegth and charge density. However, this conclusion does not necessarily mean that the wormlike chain model, in which the persistence length is assumed to vary with charge density and ionic strength,[23,24] should not be applied to polyelectrolytes. The wormlike chain model may be acceptable and useful for some purposes.[25]

Moreover, it has not yet been studied whether the persistence length of polyelectrolyte chains is affected by the electrostatic force when the ionic strength is too low. In this case the two-parameter theory may not be applicable to polyelectrolytes.

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Registry No. PNaA, 9003-04-7.

References and Notes

(1) Kitano, T.; Taguchi, A.; Noda, I.; Nagasawa, M. *Macromolecules* **1980**, *13*, 57.
(2) Noda, I.; Tsuge, T.; Nagasawa, M. *J. Phys. Chem.* **1970**, *74*, 710.
(3) Kato, T.; Tokuya, T.; Takahashi, A. *Polymer* **1984**, *25*, 218.
(4) Muroga, Y.; Sakuragi, I.; Noda, I.; Nagasawa, M. *Macromolecules* **1984**, *17*, 1844.
(5) Glatter, O. *J. Appl. Crystallogr.* **1974**, *7*, 147.
(6) Luzzati, V.; Witz, J.; Nicolaieff, A. *J. Mol. Biol.* **1961**, *3*, 367.
(7) Kratky, O. *Kolloid-Z.* **1962**, *182*, 7.
(8) Koyama, R. *J. Phys. Soc. Jpn.* **1973**, *34*, 1029.
(9) Burchard, W.; Kajiwara, K. *Proc. R. Soc. London, A* **1970**, *316*, 185.
(10) Noda, I.; Mizutani, K.; Kato, T.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1970**, *3*, 787.
(11) Takahashi, Y.; Isono, Y.; Noda, I.; Nagasawa, M. *Macromolecules*, in press.
(12) Takahashi, A.; Kato, T.; Nagasawa, M. *J. Phys. Chem.* **1970**, *74*, 944.
(13) Cotton, J. P.; Moan, M. *J. Phys., Lett.* **1976**, *37*, L75.
(14) Moan, M.; Wolff, C.; Cotton, J. P.; Ober, R. *J. Polym. Sci., Polym. Symp.* **1977**, *No. 61*, 1.
(15) Moan, M. *J. Appl. Crystallogr.* **1978**, *11*, 519
(16) Nierlich, M.; Williams, C.; Boué, F.; Cotton, J. P.; Daoud, M.; Farnoux, M.; Jannink, G. *J. Appl. Crystallogr.* **1978**, *11*, 504.
(17) Nierlich, M.; Williams, C.; Boué, F.; Cotton, J. P.; Daoud, M.; Farnoux, F.; Jannink, G.; Picot, C.; Moan, M.; Wolff, C.; Rinaudo, M.; de Gennes, P.-G. *J. Phys. Lett.* **1979**, *40*, 701.
(18) Williams, C. E.; Nierlich, M.; Cotton, J. P.; Jannink, G.; Boué, F.; Daoud, M.; Farnoux, B.; Picot, C.; de Gennes, P.-G.; Rinaudo, M.; Moan, M.; Wolff, C. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 379.
(19) Ise, N.; Okubo, T.; Hiragi, Y.; Kawai, H.; Hashimoto, T.; Fujimura, M.; Nakajima, A.; Hayashi, H. *J. Am. Chem. Soc.* **1979**, *101*, 5836.
(20) Ise, N.; Okubo, T.; Yamamoto, K.; Kawai, H.; Hashimoto, T.; Fujimura, M.; Hiragi, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7901.
(21) Brandrup, J.; Immergut, E. H., Eds. "Polymer Handbook", 2nd ed.; Wiley-Interscience: New York, 1975; p IV-1.
(22) Muroga, Y.; Noda, I.; Nagasawa, M. *J. Phys. Chem.* **1969**, *73*, 667.
(23) Skolnick, J.; Fixman, M. *Macromolecules* **1977**, *10*, 944.
(24) Odijk, T. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 477; *Polymer* **1978**, *19*, 989.
(25) Nagasawa, M.; Kitano, T.; Noda, I. "Dynamic Aspects of Biopolyelectrolytes and Biomembranes"; Oosawa, F., Ed.; Kodansha: Tokyo, 1982; p 43.