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Conformation of Polyelectrolyte in Aqueous Solution

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ABSTRACT: The polyelectrolyte conformation in aqueous solution in the presence of an added neutral salt is studied by light scattering, using a poly(sodium acrylate) with a narrow molecular weight distribution. Comparing the experimental particle scattering function $P(\theta)$ with the theories for various conformations, it is confirmed that at the Θ state the conformation of polyelectrolyte is a Gaussian chain and at the non-Θ states the experimental $P(\theta)$ can be interpreted by the theory taking into account the excluded volume effect of segments rather than by the theory for the wormlike chain model.

It was clearly shown that the conformation of nonionic linear polymers is Gaussian at the Θ state and that, as the solvent becomes better, polymer chains expand into non-Gaussian ones on account of the so-called excluded volume effect.[2,3] It is also well-known that the conformation of the polymers having stiff backbones, for example, DNA,[4] polyisocyanate,[5] and polycrotonate,[6] deviates from the Gaussian chain and behaves like the wormlike chains. There is a clear difference between the molecular weight dependence of the expansions due to the excluded volume effect and those due to the stiffness of backbones. As the molecular weight increases, the conformation of linear flexible polymers more markedly deviates from the Gaussian chain if the expansion is due to the excluded volume effect. If the polymer is extended by the stiffness of the backbone, however, the polymer approaches the Gaussian chain as the molecular weight increases.

At low charge densities or at high ionic strengths, polyelectrolytes have more or less coiled conformations. As the ionic strength is decreased, the polyelectrolyte coil is expanded due to the electrostatic repulsion, which can be regarded as a kind of excluded volume effect. Consequently, the polyelectrolyte chains may become highly non-Gaussian ones. On the other hand, if there is no added salt, polyions are often assumed to be rods parallel to each other. If the concentration of added salt is finite but low, the polyelectrolytes are highly extended by the electrostatic interaction, and the bending force constant of polyelectrolyte chains must be much higher than that of the corresponding nonionic polymers. Therefore, it is understandable to assume that polyelectrolytes can be regarded as wormlike chains.

The polymer conformation, in general, can be observed in the overall behavior of polymers, for example, in the molecular weight dependence of the mean square radius of gyration $\langle s^2 \rangle$, frictional coefficient f, intrinsic viscosity $[\eta]$, etc. However, the conformation can be more directly studied by measurement of the particle scattering function $P(\theta)$ in light scattering, which reflects the local conformation as well as the overall conformation of polymers, that is by direct comparison of the experimental $P(\theta)$ with the values calculated for various conformations of the polymer such as a random coil, semiflexible chain, rod, etc.

In light scattering, however, it is important to use polymer samples having narrow molecular weight distributions, since $P(\theta)$ depends on the molecular weight distributions too. It is now possible to use poly(acrylic acid) having narrow molecular weight distributions and also a molecular weight high enough for light-scattering measurements.[7]

Deviation of the conformation from the Gaussian chain due to the excluded volume effect should be observed for nonionic polymers in good solvents too. However, the deviation is minor if the samples are nonionic polymers in organic solvents. The radius of gyration of polyelectrolytes can be changed to a much larger extent by the effect of charges than by the use of nonionic polymers.[8] It is interesting to investigate how the polyelectrolyte conformation does change with variation of the charge density of polyions or added salt concentrations.

Of course, the separation between short-range interaction and long-range interaction or between the effect of solvent on the stiffness of the backbone and the excluded volume of segments is merely practical. The extension of the polyelectrolyte chain by electrostatic repulsion must be caused more or less through both effects simultaneously. In this paper we simply discuss which effect is more predominant in the expansion of polyelectrolyte chains.

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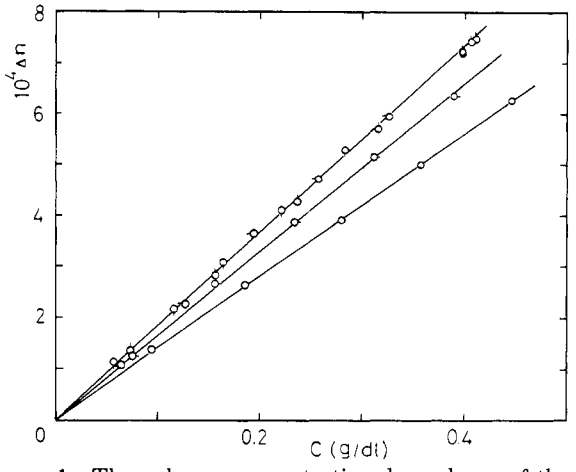

Figure 1. The polymer concentration dependence of the refractive index of poly(sodium acrylate) solutions. The degree of neutralization i = 1.0. The concentrations of NaBr, C_s, are: (ϕ) 0.01 N, (–o) 0.025 N, (φ) 0.1 N, (o–) 0.5 N at 25 °C and (o) 1.5 N at 15 °C.

Experimental Section

1. Sample. The poly(acrylic acid) sample having a narrow molecular weight distribution was prepared through acid hydrolysis of poly(*tert*-butyl acrylate), which was obtained by anionic polymerization of the *tert*-butyl acrylate monomer in tetrahydrofuran with *n*-butyllithium at −78 °C. The details of the preparation were reported in the previous paper.[7] To make the molecular weight distribution sharper, the poly(acrylic acid) thus obtained was further fractionated in dioxane by changing the temperature. The sedimentation pattern of poly(methyl acrylate) obtained by methylation of the present sample in a poor solvent, acetone, clearly shows that the molecular weight distribution of this sample is narrow. The fact that the sample has a molecular weight distribution narrow enough for the present purpose can be confirmed from the fact that $P(\theta)$ at the Θ state agrees with the theory of Debye, as shown later. The weight-average molecular weight, M_w, of poly(sodium acrylate) was found to be $1.5_0 \times 10^6$ by the light scattering measurements mentioned below. Poly(sodium acrylate) solutions were obtained by partial or complete neutralization of the poly(acrylic acid) solutions with sodium hydroxide solution. The degree of neutralization, i, was in the range 0.1–1.0.

Sodium bromide of a special grade was used as an added salt without further purification. The concentration of NaBr in solvents, C_s, was changed from 0.01 to 1.5 N.

The polyelectrolyte solutions for the measurements of refractive index increments and light scattering were dialized against the solvent at 25 °C for 1 week. The dialysis was promoted by mixing the inside polyelectrolyte solution with glass beads placed in the dialysis cell. In this study, only the solution of the highest polyelectrolyte concentration at constant i and C_s was dialized against the solvent, and other sample solutions at lower concentrations were prepared by dilution of the dialized solution with the solvent.

2. Light-Scattering Measurement. A Fica 50 automatic light-scattering photometer was used with 436-nm natural light. The scattering angle was in the range 15–150°. The calibration constant of the photometer was determined with benzene at 25 °C.[9] The optical purification of the solution for light-scattering measurements was done by filtering the solution through a Millipore filter with a 0.45 μm pore size directly into a cylindrical cell. The cell was cleaned with acetone in an apparatus of the Thurmond-type immediately before use.[10] All measurements except those at the Θ state (15 °C) were done at 25 °C.

The refractive index increment $(dn/dC)_\mu$ of solution after dialysis was measured with a modified Shimadzu differential refractometer at the same conditions as those used in the light-scattering measurements. The cell constant of the refractometer was determined with an aqueous solution of potassium chloride at 25 °C.[11] Figure 1 shows some examples of refractive index differences, Δn, between the polyelectrolyte solutions and the solvent after dialysis. As shown in Figure 1, the slope of the Δn vs. C plot, $(dn/dC)_\mu$, is practically independent of the salt concentration C_s, if C_s is lower than 0.1 N. Moreover, $(dn/dC)\mu$ appears to be a linear function of the degree of neuralization i, as shown in Figure 2. At higher C_s, however, $(dn/dC)_\mu$ depends on the salt concentration C_s.

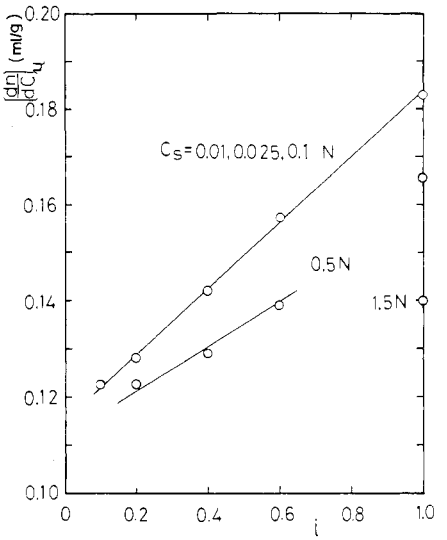

Figure 2. The variation of the refractive index increment $(dn/dC)_\mu$ with the degree of neutralization i.

Results

The analysis of light-scattering data in polyelectrolyte-added salt systems may be carried out in the same way as those in two-component systems if the sample solution is dialyzed against solvent.[12] That is,

$$(K^*C/R_\theta)_{\theta=0} = 1/M_w + 2A_2C + \ldots \quad (1)$$

$$(K^*C/R_\theta)_{C=0} = 1/[M_wP(\theta)] \quad (2)$$

where C is the concentration of polyelectrolyte (calculated as poly(sodium acrylate) in this paper), R_θ is the Rayleigh ratio at the scattering angle θ, and K^* is the optical constant defined by

$$K^* = 2\pi^2 n_0^2 (dn/dC)_\mu^2/(N_A\lambda_0^4) \quad (3)$$

where n_0 is the refractive index of solvent, N_A is Avogadro's number, λ_0 is the wavelength in vacuo, and A_2 is the second virial coefficient. $(K^*C/R_\theta)_{\theta=0}$ and $(K^*C/R_\theta)_{C=0}$ are the values of K^*C/R_θ extrapolated to zero angle at various concentrations and to infinite dilution at various angles, respectively. To make the extrapolation to the zero polymer concentration easier, the square root plot is often used for a nonionic polymer, such as

$$(K^*C/R_\theta)_{\theta=0}^{1/2} = (1/M_w)^{1/2}(1 + A_2M_wC) \quad (4)$$

We employed this method to obtain $(K^*C/R_\theta)_{C=0}$ at various θ, and the extrapolation appears to be satisfactory, as shown in Figure 3.

Examples of $P^{-1}(\theta)$ thus obtained at the Θ state, at a constant degree of neutralization and at a constant added salt concentration are shown in Figures 4–6, respectively. The molecular weight used for calculating $P(\theta)$ in eq 2 is the average value in the experiments at low degrees of neutralization and high ionic strengths ($M_w = 1.5_0 \times 10^6$).

In order to compare the experimental value of $P(\theta)$ with those of the other theories, it is necessary to know the mean square radius of gyration $\langle s^2 \rangle$ of the polymer. The reciprocal $P(\theta)$ can be, in general, expanded in terms of $\sin^2(\theta/2)$ without any assumption regarding the conformation of polymer, such as

$$P^{-1}(\theta) = 1 + (16\pi^2/3\lambda^2)\langle s^2 \rangle \sin^2(\theta/2) + \ldots \quad (5)$$

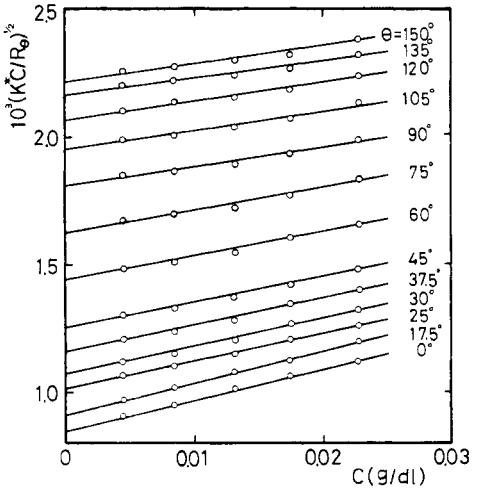

Figure 3. The square root plot of $(K^*C/R_\theta)^{1/2}$ at various scattering angles θ at $i = 0.6$ and $C_s = 0.1$ N.

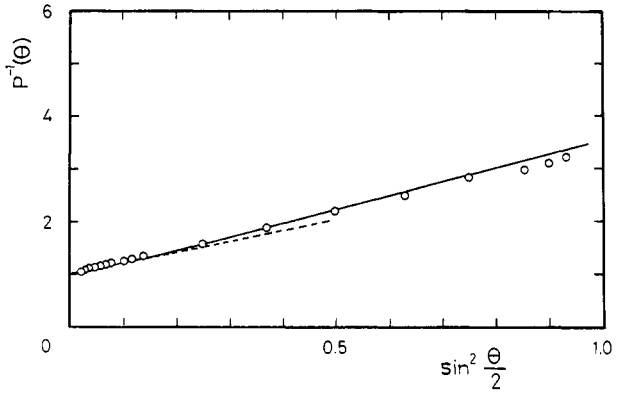

Figure 4. Comparison of the experimental $P(\theta)$, shown as open circles, with the theory of Debye at the Θ state ($i = 1.0$ in C_s = 1.5 N at 15 °C). The solid curve shows the calculated theoretical line of Debye, eq 13, using $\langle s^2\rangle_0^{1/2} = 630$ Å. The initial slope shown as the broken line is drawn using the value of $\langle s^2\rangle_0$.

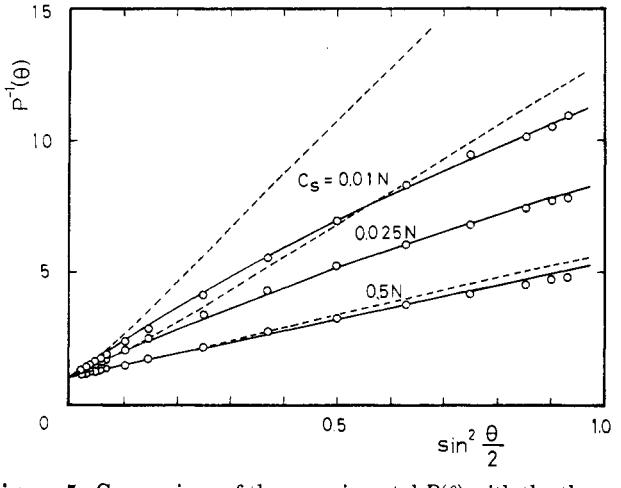

Figure 5. Comparison of the experimental $P(\theta)$ with the theory of Peterlin at different C_s and constant i (0.2). The solid lines are calculated from the theory of Peterlin, eq 22, using $\langle s^2\rangle^{1/2}$ = 1620 Å and $\epsilon = 0.30$ (0.28) in $C_s = 0.01$ N, $\langle s^2\rangle^{1/2}$ = 1300 Å and $\epsilon = 0.25$ (0.23) in $C_s = 0.025$ N, and $\langle s^2\rangle^{1/2}$ = 850 Å and $\epsilon = 0.05$ (0.02) in $C_s = 0.5$ N. The values of ϵ in parentheses are estimated from eq 25. Broken lines are calculated from the theory of Debye, eq 13, using the same values of $\langle s^2\rangle$ as were used for the theory of Peterlin.

where λ is the wavelength in the solvent. In practice, therefore, $\langle s^2\rangle$ can be determined from the initial slope of the $P^{-1}(\theta)$ vs. $\sin^2(\theta/2)$ plot, whatever conformation the polymer has. If $\langle s^2\rangle$ is large at high degrees of neutralization and low ionic strengths, however, it is difficult to determine $\langle s^2\rangle$ from the initial slope of this plot.

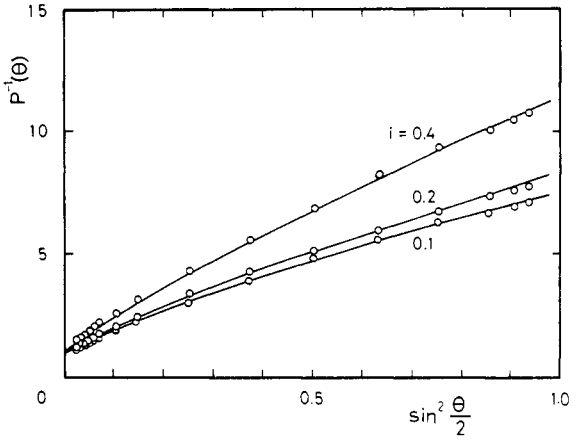

Figure 6. Comparison of the experimental $P(\theta)$ with the theory of Peterlin at different i and constant C_s (0.025 N). The solid lines are calculated from the theory of Peterlin, eq 22, using $\langle s^2\rangle^{1/2}$ = 1390 Å and $\epsilon = 0.30$ (0.28) at $i = 0.4$, $\langle s^2\rangle^{1/2}$ = 1300 Å and $\epsilon = 0.25$ (0.23) at $i = 0.2$, and $\langle s^2\rangle^{1/2}$ = 1230 Å and $\epsilon = 0.20$ (0.19) at $i = 0.1$. The values in parentheses are estimated in the same way as those in Figure 5.

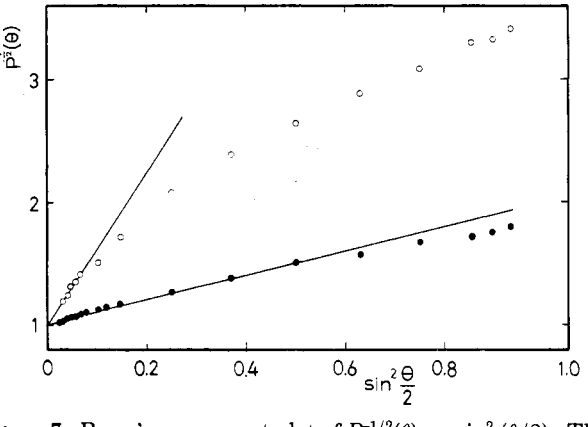

Figure 7. Berry's square root plot of $P^{-1/2}(\theta)$ vs. $\sin^2(\theta/2)$. The open circles show the data at $i = 0.6$ in $C_s = 0.025$ N at 25 °C, and the filled circles show the data at the Θ state, $i = 1.0$ in C_s = 1.5 N at 15 °C. The solid lines show the initial slopes.

If the polymer does not markedly deviate from the Gaussian chain, some devices such as Berry's square root plot,[13] eq 6, and Fujita's plot,[14] eq 7, have been proposed to estimate the initial slope more easily.

$$P^{-1/2}(\theta) = 1 + (8\pi^2/3\lambda^2)\langle s^2\rangle \sin^2(\theta/2) + \ldots \quad (6)$$

and

$$P^{-1}(\theta) = 1 + (32\pi^2/3\lambda^2)\langle s^2\rangle Z(v) \quad (7)$$

where

$$Z(v) = P^{-1}(\theta)v^{-4/3}\int_0^v P(\theta)v\,dv \quad (8)$$

and

$$v = \sin^3(\theta/2) \quad (9)$$

These methods, however, cannot be applied to the present experimental results due to their very high deviation from Gaussian chains except near the Θ state. Some examples of Berry's plot and Fujita's plot are shown in Figures 7 and 8, respectively.

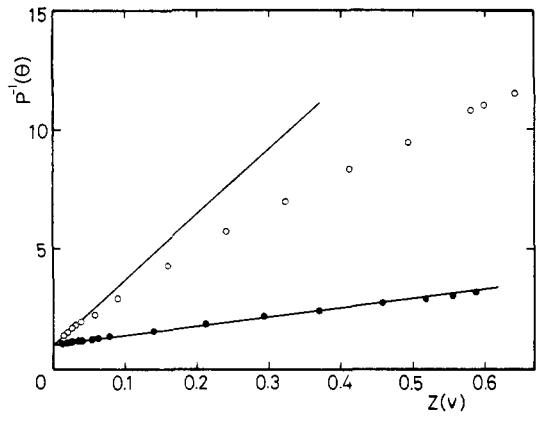

Figure 8. Fujita's plot of $P^{-1}(\theta)$ vs. $Z(v)$. See the caption for Figure 7.

In this work, therefore, $\langle s^2 \rangle$ is generally determined so as to have the best agreement between experimental and theoretical $P(\theta)$ in the respective comparison, where the values of $\langle s^2 \rangle$ thus determined are shown.

Discussion

The intrinsic viscosity $[\eta]$ of the polyelectrolyte in added salt solutions was discussed in terms of the excluded volume effect in the previous paper.[15] The same experimental results can be compared with those predicted by the theory for wormlike chains too. The $[\eta]$ for wormlike chains was given by Yamakawa and Fujii,[16] such as

$$[\eta] = \Phi L_r^{3/2}/(\lambda'^3 M) \tag{10}$$

where $1/2\lambda'$ is the persistence length, L_r is the reduced contour length defined by

$$L_r = \lambda' L \tag{11}$$

and

$$L = M/M_L \tag{12}$$

where M is the molecular weight of the polymer, M_L is the molecular weight per unit length, and, therefore, L is the contour length of the polymer. The constant Φ is a function of L_r and d_r which is the reduced diameter of the polymer defined by the ratio of the diameter of the polymer d to the Kuhn's statistical length $1/\lambda'$, such as

$$d_r = \lambda' d$$

The value of Φ was given numerically by Yamakawa and Fujii.[16] The comparison of the experimental $[\eta]$ of fractionated poly(sodium acrylate) in the previous paper[15] with eq 10 is shown in Figure 9, using the values of the parameters $1/2\lambda'$ and d chosen to have the best agreement between the theory and the experimental data. The agreement is as satisfactory as that found for a nonionic polymer, poly(*tert*-butyl crotonate), which has a semiflexible backbone and a narrow molecular weight distribution.[17] It will be reported in a separate paper that the solution behaviors of poly(*tert*-butyl crotonate) can be explained well by the theories for wormlike chains.[6,17] The persistence length $1/2\lambda'$ selected for poly(sodium acrylate) in Figure 9 is shown in the figure caption. If we plot $1/2\lambda'$ against the salt concentration C_s, we have a linear relationship between $1/2\lambda'$ and $C_s^{-1/2}$, as shown in Figure 10. Therefore, since we are concerned only with the viscosity behavior of polyelectrolytes, either theory, the theory for wormlike chains or the theory with the excluded volume effect, may be applicable to the expansion of polyelectrolyte chains.

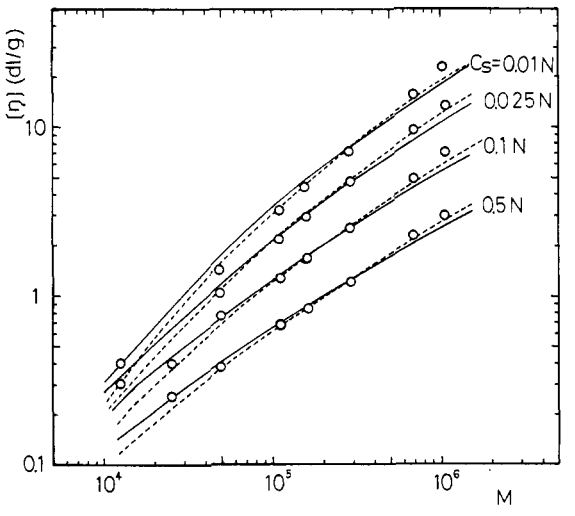

Figure 9. Molecular weight dependence of $[\eta]$ at $i = 1.0$ in different C_s. The data for poly(acrylic acid) in the previous paper, ref 15, are recalculated for poly(sodium acrylate). The theoretical curves for wormlike chains, eq 10, are shown using $M_L = 40$ Å^{-1} and $d = 2$ Å for the solid lines and $d = 5$ Å for the broken lines. The persistence lengths $1/2\lambda'$ used for calculations are 100 and 90 Å in $C_s = 0.01$ N, 70 and 60 Å in $C_s = 0.025$ N, 40 and 35 Å in $C_s = 0.1$ N, and 22 and 20 Å in 1.5 N, for $d = 2$ and 5 Å, respectively.

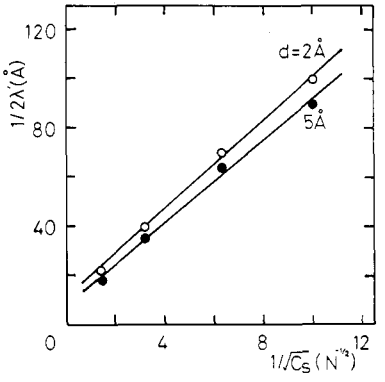

Figure 10. Added salt concentration dependence of the persistence length $1/2\lambda'$ at $i = 1.0$ (estimated from $[\eta]$ in Figure 9). The open circles and the filled circles are the values estimated, using $d = 2$ and 5 Å, respectively.

In Θ solvents, polymer coils generally have a Gaussian distribution of segments. $P(\theta)$ for the Gaussian chains was calculated by Debye[18] such as

$$P(\theta) = 2u^{-2}[\exp(-u) - 1 + u] \tag{13}$$

where

$$u = (16\pi^2/\lambda^2)\langle s^2 \rangle_0 \sin^2(\theta/2) \tag{14}$$

and $\langle s^2 \rangle_0$ is the unperturbed mean square radius of gyration of the polymer. It was confirmed that $P(\theta)$ for the Gaussian nonionic polymers having sharp molecular weight distribution in Θ states agrees with the value for the theory of Debye over the entire range of scattering angles θ.[19] According to Takahashi, Yamori, and Kagawa,[20] the Θ temperature for poly(sodium acrylate) is 15 °C in 1.5 N NaBr solution. Figure 4 shows the comparison between the experimental data and the data from the calculated curve of eq 13 at the Θ state. The value of $\langle s^2 \rangle_0$ agrees perfectly with the value determined from the initial slope. Therefore, it can be concluded that the conformation of the polyelectrolyte at the Θ state is Gaussian. Moreover, it is to be noted that the intrinsic viscosity $[\eta]$ of polyelectrolytes is proportional to the square root of the mo-

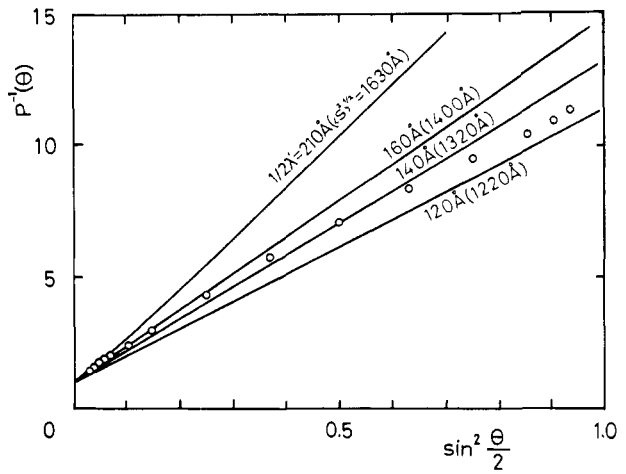

Figure 11. Comparison of the experimental $P(\theta)$ with the theory of Sharp and Bloomfield, eq 15, at $i = 0.6$ in $C_s = 0.025$ N, using $M_L = 40$ Å^{-1}. The values of $1/2\lambda'$ are shown in the figure. The values of $\langle s^2\rangle^{1/2}$ calculated from eq 17, using $1/2\lambda'$, are also shown in parentheses.

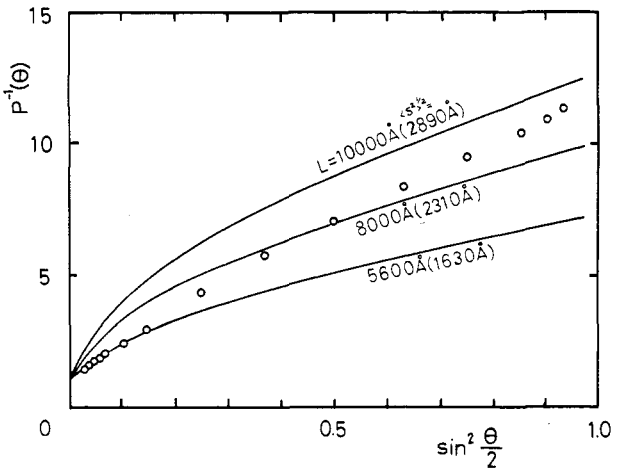

Figure 12. $P(\theta)$ for the rod, eq 18, at $i = 0.6$ in $C_s = 0.025$ N. The lengths of the rod, L, used for calculation are given in the figure.

lecular weight at the Θ states.[21,22]

Even in good solvents, $P(\theta)$ of monodisperse nonionic polymers is often approximated by eq 13 of Debye, using the value of $\langle s^2\rangle$ in good solvents in place of $\langle s^2\rangle_0$.[23] This trial, however, is not successful even qualitatively in the polyelectrolyte solutions. If we use the value $\langle s^2\rangle$ determined from the initial slope, the deviation from the value obtained with the Debye function is too large, as shown in Figure 5. It may be concluded that polyelectrolyte chains do not expand, keeping the segment distribution Gaussian.

As was discussed above, the deviation of the experimental $P(\theta)$ of polyelectrolytes from the Debye function may be explained either from the standpoint of the wormlike chain or from the standpoint of the excluded volume effect.

The calculation of $P(\theta)$ for wormlike chains was carried out by Sharp and Bloomfield[4] as follows:

$$P(\theta) = 2u^{-2}[\exp(-u) - 1 + u] + 4/(15L_r) + 7/(15L_r u) - [11/(15L_r) + 7/(15L_r u)]\exp(-u) \quad (15)$$

where

$$u = (16\pi^2/3\lambda^2)L(1/2\lambda')\sin^2(\theta/2) \quad (16)$$

and the persistence length $1/2\lambda'$ is related to $\langle s^2\rangle$ by

$$\langle s^2\rangle = (1/2\lambda')^2[2L_r/3 - 1 + 1/L_r - 1/(2L_r^2) + \exp(-2L_r)/(2L_r^2)] \quad (17)$$

The $P(\theta)$ value of Sharp and Bloomfield, eq 15, is valid for $L_r > 10$, while Yamakawa and Fujii[24] and Norisue, Murakama, and Fujita[25] calculated $P(\theta)$ for a wormlike chain with higher stiffness ($1 \leq L_r \leq 10$) and for the chain near the rod limit ($L_r \leq 1$), respectively. It will be reported in a separate paper that the $P(\theta)$ value of Sharp and Bloomfield, eq 15, agrees well with the experimental $P(\theta)$ value for poly(*tert*-butyl crotonate) with narrow molecular weight distributions.[6] Comparison of eq 15 with experimental results for poly(sodium acrylate) is shown in Figure 11, where M_L is assumed to be 40 Å^{-1}, corresponding to the stretched configuration of the trans zigzag form. Figure 11 shows that the theory for the wormlike chain deviates largely from the experimental values at lower θ and the value of $\langle s^2\rangle$ thus estimated is always smaller than the experimental values, as shown in Figure 11, when it is fitted to the experimental results at the higher θ by adjusting the value of $1/2\lambda'$. That is, it is not possible to have satisfactory agreement between the theory for wormlike chains and the present experimental $P(\theta)$ by adjusting the persistence length $1/2\lambda'$. Although it is not impossible to reproduce the experimental results, it is required to assume *unreasonably* large values for M_L and $1/2\lambda'$. Moreover, Figure 12 shows a comparison between the experimental value of $P(\theta)$ and the calculated values for a rod, for reference. $P(\theta)$ for a rod is given by[26]

$$P(\theta) = u^{-1}\int_0^{2u}(\sin x/x)\,dx - (\sin u/u)^2 \quad (18)$$

where

$$u = (2\pi/\lambda)L\sin(\theta/2) \quad (19)$$

and L is the length of a rod and is related to $\langle s^2\rangle$ as follows:

$$L^2 = 12\langle s^2\rangle \quad (20)$$

The calculated values of eq 18 in Figure 12 are obtained using the rod length L as a parameter. Apparently, neither the wormlike chain model nor the rod model is applicable to the polyelectrolyte solutions at higher C_s than 0.01 N. Thus, we conclude that both the initial slope of the plot of $P^{-1}(\theta)$ vs. $\sin^2(\theta/2)$, i.e., $\langle s^2\rangle$, and the entire shape of $P(\theta)$ cannot be consistently interpreted by the theoretical models containing a single parameter such as the chain stiffness.

The non-Gaussian character in the distribution of segments was taken into account in the calculation of $P(\theta)$ in terms of a parameter ϵ, such as

$$R_{ij}^2 = K'|i - j|^{1+\epsilon} \quad (21)$$

where R_{ij} is the distance between the ith and the jth segments and K' is a constant. That is,

$$P(\theta) = \int_0^1 2(1 - x)\exp(-ux^{1+\epsilon})\,dx \quad (22)$$

where

$$u = (8\pi^2/3\lambda^2)(2 + \epsilon)(3 + \epsilon)\langle s^2\rangle\sin^2(\theta/2) \quad (23)$$

$P(\theta)$ for non-Gaussian chains with the excluded volume effect, eq 22, was presented first by Peterlin.[27] The integration of eq 22 was given by Ptitsyn[28] and Benoit[29] analytically, using incomplete Γ functions, and by Hyde, Ryan, Wall, and Schatzky[30] numerically. If $\epsilon = 0$, eq 22 reduces to the Debye function, eq 13. The indirect estimation of ϵ is also possible from the intrinsic viscosity–molecular weight relationship,

$$[\eta] = KM^a \quad (24)$$

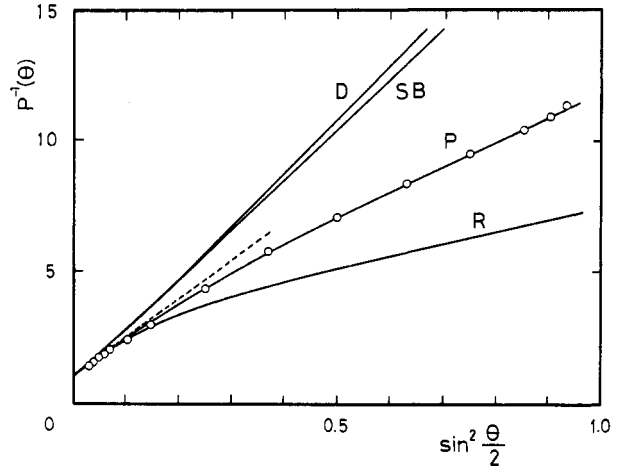

Figure 13. Comparison of $P(\theta)$ calculated for various conformations using the same value of $\langle s^2\rangle^{1/2}$ = 1630 Å at i = 0.6 in C_s = 0.025 N. The broken line shows the initial slope. The solid lines are calculated from the theories of Debye (D), eq 13, of Sharp and Bloomfield (SB), eq 15, using $1/2\lambda'$ = 210 Å, of Peterlin (P), eq 22, using ϵ = 0.30 (0.24), and of the rod (R), eq 18.

where K and a are constants. The ϵ may be related to a by[31]

$$\epsilon = (2a - 1)/3 \tag{25}$$

Assuming that the value of ϵ is nearly equal to the value calculated from the previous data of $[\eta]$ of poly(sodium acrylate),[15] the experimental $P(\theta)$ can be well fitted to the curves calculated by eq 22, and thus $\langle s^2\rangle$ can be determined as shown in Figures 5 and 6. The value of $\langle s^2\rangle$ thus obtained is found reasonable when compared with the one estimated from the initial slope. Moreover, it should be noted that a slight variation in the parameter ϵ does not have a serious effect on the evaluation of $\langle s^2\rangle$.

In addition, the theoretical particle scattering functions $P(\theta)$ calculated for the various models, with the same initial slope, are compared with each other as well as with the experimental $P(\theta)$ in Figure 13. It can be concluded from the figure that the deviation in the conformation of such a flexible polyelectrolyte as poly(sodium acrylate) from the Gaussian chain in aqueous solution with added salt is essentially due to the excluded volume effect rather than due to the effect of the stiffness of the backbone.

In the theory with the excluded volume effect, eq 22, it is assumed that the effective bond length is not disturbed by the electrostatic interaction but remains constant independent of either degree of neutralization of polyelectrolyte i or salt concentration C_s, while in the wormlike chain model used here, eq 15, the deviation from the Gaussian chain is attributed to the variation of the effective bond length, that is, the increase in the persistence length $1/2\lambda'$. Recently, Odijk[32] and Skolnick and Fixman[33] discussed the polyelectrolyte conformation by simultaneous consideration of both the local stiffness and the excluded volume of segments. As mentioned in the introduction, the effect of charges on the local stiffness of the polymer chain and that on the excluded volume effect cannot rigorously be separated. If we take into account the excluded volume effect in addition to the wormlike chain model effect, the experimental data could be well explained. In that case, however, the excluded volume effect, that is, a parameter corresponding to ϵ, would be as much as that in Figure 13 and would be much higher than the value of ϵ accepted for DNA.[4] On the contrary, it would also be possible to take into account the change in the effective bond length in addition to the excluded volume effect. Concerning the possibility of the minor variation of the effective bond length in addition to the major effect of the excluded volume, we would like to note that the assumption used in eq 22 appears to be acceptable if we take into account the previous studies on the molecular weight dependence of the intrinsic viscosity $[\eta]$ of polyelectrolytes.[15,34] Although the theory of Stockmayer and Fixman[35] on the expansion factor of nonionic polymers is not acceptable, we are now almost positive that the unperturbed mean square radius of gyration $\langle s^2\rangle_0$ can be obtained by using the following equation, if polymers having low molecular weights are employed,

$$[\eta]/M^{1/2} = K_0 + 0.51\Phi_0 BM^{1/2} \tag{26}$$

where

$$K_0 = \Phi_0[\langle s^2\rangle/(6M)]^{3/2} \tag{27}$$

Φ_0 is the Flory constant at the Θ temperature, and B is a constant related to the excluded volume effect. If the $[\eta]$ of polyelectrolytes is plotted in the same form as that of Stockmayer and Fixman, it is found that the intercept at $M^{1/2}$ = 0 does not markedly depend on C_s and i.[15,34] This implies that the assumption of the constant effective bond length during expansion may be a good approximation for linear flexible polyelectrolyte chains.

Finally, what we want to stress here is that the excluded volume effect is predominant rather than the change of local stiffness in the expansion of polyelectrolyte chains due to the electrostatic repulsion. Moreover, we do not deny the possibility that the overall behaviors of polyelectrolyte chains such as mean square radius of gyration $\langle s^2\rangle$ and intrinsic viscosity $[\eta]$ can be well explained by using the wormlike chain model. It is a future problem how much effect the non-Gaussian character of the segmental distribution in polyelectrolyte chains would have on the overall behavior of polyelectrolytes.

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Reactivity of Benzyl Cation and of Benzhydryl Cation with Alkenes in Solution: Initiation Step in Cationic Polymerization[1]

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ABSTRACT: The pulse radiolysis technique has been used to determine rate constants for the initiation step in cationic polymerization. The reactivity of the benzyl cation and of the benzhydryl cation toward some 13 alkenes in dichloroethane solution has been determined. The rate constants vary over four orders of magnitude with the molecular structure of the nucleophiles. The reactivity–molecular structure dependence is discussed.

Pulse radiolysis studies of the reactivity of phenylcarbenium ions in solution[2-5] have provided new information about a class of reaction of importance in the field of polymer chemistry. We refer to the process of cationic polymerization[6-10] and specifically to the initiation step of this process. We have generated the benzyl cation and the benzhydryl cation on a submicrosecond time scale[5] in 1,2-dichloroethane solution and have determined rate constants for reactions of these ions with some 13 different alkenes. These phenylcarbenium ions, generated by an electron pulse,[2,11] are free of complexities such as ion pairing and cation aggregation which may be encountered when cationic polymerization is induced chemically, as with strong acid,[12-14] with iodine,[15] with Friedel–Crafts reagents,[16,17] or with carbocation salts.[18,19] The reaction observed here is the single-step condensation reaction of cation with alkene exclusive of any propagation reaction. The reactivity–molecular structure relationship is of interest not only from the point of view of polymer chemistry, but also with respect to carbenium ion reactivity, for the alkenes are a class of nucleophile for which carbocation reactivity has not, heretofore, been determined directly.

Experimental Section

As previously described,[20,21] the source of the electron pulse was a Varian V-7715A electron linear accelerator, delivering 3–4 MeV electrons at a pulse current of about 300 mA for pulses of 100–400 ns duration and about 600 mA for pulses of 80 ns duration or less. The 80 ns pulses were used in most of the following experiments. The concentration of transients produced was on the order of 10^{-6} M or lower. All of the runs were done at 24 ± 1 °C. The transient absorptions were observed with either an RCA 1P28 or RCA 7200 photomultiplier as the detector. A Bausch and Lomb grating monochromator, type 33-86-25, f/3.4, was used.

Our standard 20-mm reaction cells with high purity silica windows were used in all experiments with, generally, a double pass of the analyzing light beam. A detailed description of the optical arrangement and the detection system has been presented.[20,21]

1,2-Dichlorethane (DCE) was 99+% gold label obtained from Aldrich Chemical. Dibenzylmercury was obtained from Alfa Inorganics; diphenylmethyl bromide, technical grade, was from Chemical Samples Co. The method of purification of these compounds has been described.[2,4] Anhydrous ammonia, 99.99% purity, ethylene, c.p. grade, 99.5% purity, propylene, c.p. grade, 99.5% purity, and 1,3-butadiene, instrument purity, 99.5% minimum purity, were all obtained from Matheson and used without further purification. Research grade isobutylene, 99.93% purity, was obtained from Phillips Petroleum Co. and was also used as obtained. The foregoing compounds were all stored under vacuum in the dark.

The following compounds, all obtained from Aldrich Chemical, were subjected to vacuum distillation and stored under vacuum and refrigerated: 3,3-dimethyl-1-butene (neohexene) 99%, cyclohexene 99%, 1,3-cyclohexadiene 99%, 2-methyl-1,3-butadiene (isoprene, MBD) 99+% gold label, 2,3-dimethyl-1,3-butadiene (DMPD) 98%, 4-methyl-1,3-pentadiene (MPD) 98%, and 2,4-dimethyl-1,3-pentadiene (DMPD) 98%. Allylbenzene and 1-phenylcyclohexene, 99%, from Aldrich, were purified by partial freezing.

In order to obtain the concentration of the gaseous alkenes in 1,2-DCE, the solubilities of ethylene, isobutylene, and 1,3-butadiene in DCE were measured. The results are ethylene, 0.95 mol % at 927.8 torr, isobutylene, 1.07 mol % at 131 torr, and 1,3-butadiene, 1.08 mol % at 90.2 torr. For the experiments with

Table I
Rate Constants for the Reactions of the Benzyl Cation and of the Benzhydryl Cation with Alkenes in 1,2-DCE at 24 °C[a]

alkene	$PhCH_2^+$	Ph_2CH^+
ethylene	$<10^5$	
propylene	1.9×10^6	$<10^5$
isobutylene	1.9×10^7	9.5×10^6
3,3-dimethyl-1-butene	2.2×10^6	
allyl benzene	1.5×10^6	
cyclohexene	9.4×10^6	
1,3-cyclohexadiene	2.7×10^7	1.5×10^7
1-phenylcyclohexene		7.4×10^7
1,3-butadiene	8.7×10^5	$<10^5$
2-methyl-1,3-butadiene		7.1×10^6
2,3-dimethyl-1,3-butadiene		2.7×10^7
4-methyl-1,3-pentadiene		2.5×10^8
2,4-dimethyl-1,3-pentadiene		1.0×10^9

[a] Units are M^{-1} s^{-1}. All of the rate constants, save two, have an experimental uncertainty of ±15%. The uncertainty is ±25% for the rate constants for the benzyl cation with 1,3-butadiene and for the benzhydryl cation with 1,3-cyclohexadiene.

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