Small-Angle Scattering of Random Coil Polymer Solutions

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ABSTRACT: Small-angle scattering functions of mixed solutions of two polymers (A and B) are calculated by using the radial distribution function of random coil polymers. It is assumed that the radiation is scattered by only part of the chain segment in the middle of each polymer A molecule but that the polymer B molecules and the solvent do not scatter the radiation. When the concentration of polymer A is low, the scattering function decreases monotonously with scattering angle, but when the concentration is high, the function has a peak which shifts to a higher scattering angle with increasing concentration. The qualitative form of the scattering curve almost agrees with those observed by neutron small-angle scattering of mixed solutions of partially deuterated polystyrene molecules and nondeutrated ones.

I. Introduction

In a previous paper[1] the small-angle scattering curve of a random coil polymer solution was calculated by use of the radial distribution function of the polymers.[2] The scattering curve of polymer solutions generally depends on both the intermolecular configuration and the intramolecular conformations of the polymer molecules. Therefore the radial distribution function of polymers in their solution cannot be directly determined from experimental scattering curves of this solution unless we set up some assumptions for the intramolecular conformation of the polymer or make some other alternative assumption.

However, when we consider certain cases where the scattering curves are more closely related to this radial distribution function, for example, when we suppose that each polymer molecule has a very small scattering element in the middle part of the chain and that the radiation is scattered by these elements only, there is no intramolecular interference of the scattered wave. Therefore the scattering curve of such a solution is directly determined from the radial distribution function of the middle points of these polymers.

In this paper the small-angle scattering curves of mixed solutions of two types of solute polymers A and B are calculated. Radiation is scattered at only part of a chain segment in the middle of polymer chain A, but polymer chain B does not scatter radiation.

II. Calculation of the Small-Angle Scattering Curve

For simplicity we assume that the two polymer chains A and B have the same random coil conformation and physical properties, except those for radiation scattering. The radiation is scattered at only part of a chain segment in the middle of each polymer chain A, but the polymer chain B does not scatter the radiation. Also assuming that the solvent molecules do not scatter the radiation, the scattered intensity $I(q)$ per unit volume of this polymer solution can be directly calculated from the general scattering theory of solution[3,4] as indicated in the previous case,[1] and the result can be written as (cf. Appendix A)

$$I(q) = C_{\mathrm{I}}\left[\langle i(q)^2\rangle + 4\pi n_{\mathrm{D}}\langle i(q)\rangle^2\int_0^\infty (g(R)-1)R^2\frac{\sin(qR)}{qR}\,\mathrm{d}R\right] \tag{1}$$

$$q = (4\pi/\lambda)\sin(\theta/2) \tag{2}$$

where $i(q)$ is the molecular scattering factor of polymer A, which is defined by the scattering wave vector $\mathbf{q}$, the coordinates of the ith scattering-active segment referred to the molecular center of gravity, $\mathbf{r}_i$, and the total number of these segments in a polymer, N_{D}

$$i(q) = N_{\mathrm{D}}^{-1}\sum_i \exp[-\mathrm{i}\mathbf{q}\cdot\mathbf{r}_i] \tag{3}$$

$g(R)$ is the radial distribution function of the centers of gravity of both polymers, n_{D} is the number density of polymers A, and C_{I} is a constant given by

$$C_{\mathrm{I}} = C_0 n_{\mathrm{D}} N_{\mathrm{D}}^2 = C_0 n_{\mathrm{D}}(Nf_{\mathrm{D}})^2 \tag{4}$$

where C_0 is a constant and f_{D} and N are defined in eq 8. λ and θ in eq 2 are the wavelength and the scattering angle of the radiation, respectively.

For our ideal random coil polymer model which consists of N molecular segments, the thermal averages $\langle i(q)^2\rangle$ and $\langle i(q)\rangle^2$ can be calculated as (cf. Appendix B)

$$\langle i(q)^2\rangle = \langle i(q)i(-q)\rangle = 2[f_{\mathrm{D}}Z - 1 + \exp(-f_{\mathrm{D}}Z)]/(f_{\mathrm{D}}Z)^2 \tag{5}$$

$$\langle i(q)\rangle^2 = (\pi/f_{\mathrm{D}}^2 Z)\exp(-Z/6)[\mathrm{erf}\,(f_{\mathrm{D}}Z^{1/2}/2)]^2 \tag{6}$$

$$Z = \langle R^2\rangle q^2 \tag{7}$$

$$f_{\mathrm{D}} = N_{\mathrm{D}}/N \tag{8}$$

$$\mathrm{erf}\,(x) = (2/\pi^{1/2})\int_0^x \exp(-t^2)\,\mathrm{d}t \tag{9}$$

where $\langle R^2\rangle$ is the thermal average of the square of the radius of gyration of the polymer and f_{D} is the ratio of the length of a scattering-active partial chain segment to the total length of a polymer.

Employing eq 5–9 and the previous calculation[2] of $g(R)$, curves of $I(q)/C_{\mathrm{I}}$ were calculated from eq 1.

III. Results

The results for the scattering function for various cases are shown in Figures 1–10. The calculation[2] of $g(R)$ assumed a Gaussian intermolecular potential between the polymers (cf. Appendix C)

$$U(R) = kTX_0\exp[-R^2/R_0^2]$$

$$R_0^2 \approx \langle R^2\rangle \tag{10}$$

where k and T are, respectively, the Boltzmann constant and the absolute temperature. Therefore $g(R)$ and hence $I(q)$ depend on the potential parameters X_0 and R_0 as well as on n_{D} and the total number density of polymer, n. The curves of the figures are calculated with the values

$$X_0 = 2.0 \tag{11}$$

$$R_0 = \langle R^2\rangle^{1/2} \tag{12}$$

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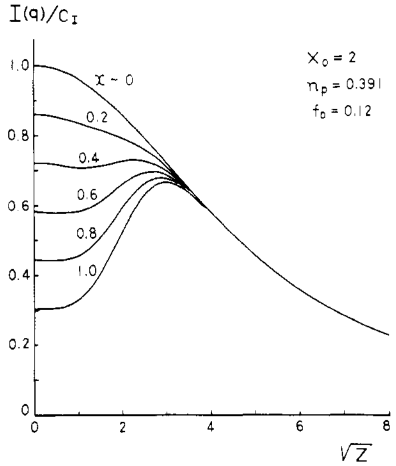

Figure 1. Scattering curves: $I(q)/C_I$ vs. $Z^{1/2}$ for $X_0 = 2$, $n_p = 0.391$, $f_D = 0.12$, and various proportions of A polymer, x.

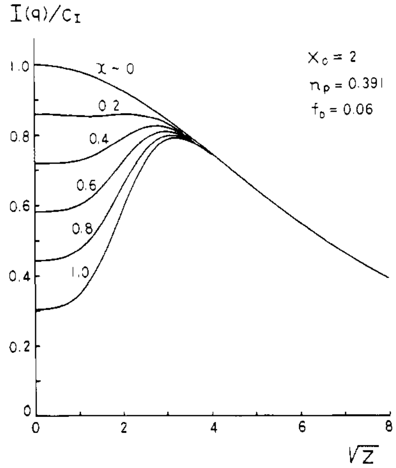

Figure 2. Scattering curves: $I(q)/C_I$ vs. $Z^{1/2}$ for $X_0 = 2$, $n_p = 0.391$, $f_D = 0.06$, and various proportions of A polymer, x.

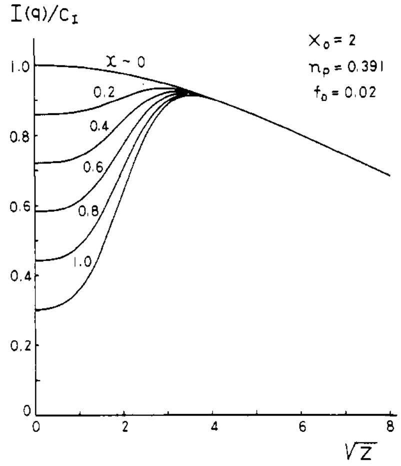

Figure 3. Scattering curves: $I(q)/C_I$ vs. $Z^{1/2}$ for $X_0 = 2$, $n_p = 0.391$, $f_D = 0.02$, and various proportions of A polymer, x.

In the figures n_p denotes a reduced concentration of the polymers defined by

$$n_p = nR_0^3 \tag{13}$$

Also $x = n_D/n$ denotes the ratio of the quantity of polymer A to the total quantity of polymers in the solution.

Figures 1, 2, 3, and 5 show that $I(q)$ decreases monotonously with $Z^{1/2}$ ($\propto q$) for small x, that it has a maximum for large x (i.e., for a large proportion of polymer A), and that the maximum point shifts to a higher scattering angle as x increases. Figure 4 is the limiting case for $f_D \sim 0$, that is, a case where the scattering-active part in polymer A is an ideal point scatterer. In this case the curves have no peaks and $I(q)$ increases monotonously with $Z^{1/2}$ (when x is not zero).

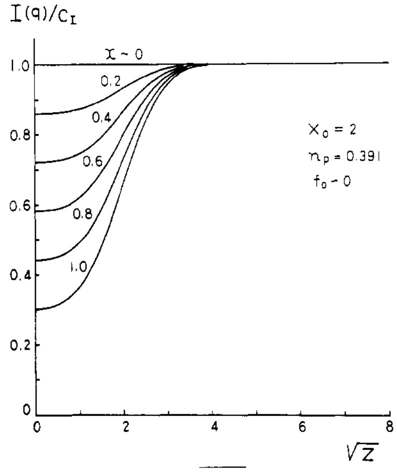

Figure 4. Scattering curves: $I(q)/C_I$ vs. $Z^{1/2}$ for $X_0 = 2$, $n_p = 0.391$, $f_D \sim 0$, and various proportions of A polymer, x.

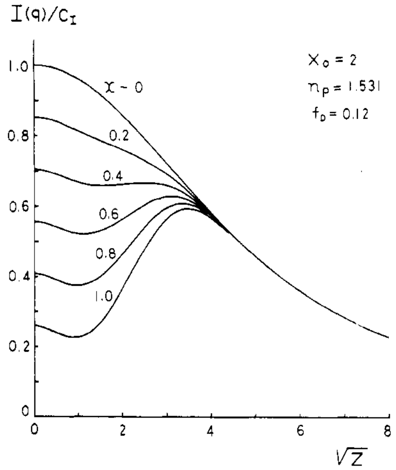

Figure 5. Scattering curves: $I(q)/C_I$ vs. $Z^{1/2}$ for $X_0 = 2$, $n_p = 1.531$, $f_D = 0.12$, and various proportions of A polymer, x.

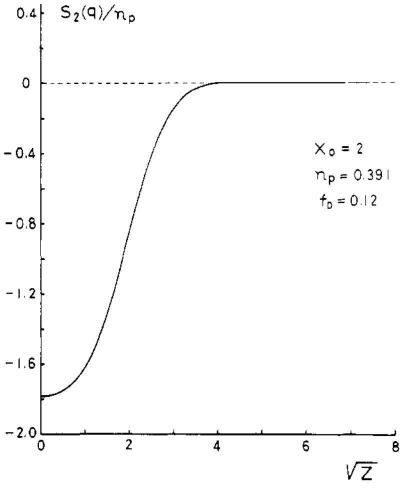

Figure 6. Intermolecular factor $S_2(q)/n_p$ vs. $Z^{1/2}$ for $X_0 = 2$, $n_p = 0.391$, and $f_D = 0.12$.

Equation 1 can be written as

$$I(q) = C_{I0}[xS_1(q) + x^2S_2(q)] \tag{14}$$

$$C_{\mathrm{I}0} = C_0 n N_{\mathrm{D}}^2 \tag{15}$$

$$S_1(q) = \langle i(q)^2 \rangle \tag{16}$$

$$S_2(q) = 4\pi n \langle i(q) \rangle^2 \int_0^\infty (g(R) - 1)R^2 \frac{\sin (qR)}{qR}\, \mathrm{d}R \tag{17}$$

Figures 6 and 7 show the intermolecular term $S_2(q)$. $S_2(q)$ is negative and decays rapidly as q or the scattering angle increases.

Figures 8 and 9 show the results for the particular case $x = 1$, i.e., when the solute is of A-type polymer only. In this case the value of $I(q)/C_{\mathrm{I}}$ has a maximum, and Figure 9 displays that this maximum point, $Z_{\mathrm{m}}^{1/2}$, becomes large with increasing polymer concentration $n = n_{\mathrm{D}}$.

IV. Comparison with Experiments

Recently, neutron small-angle scattering experiments on solutions of polystyrene partially deuterated at the middle part mixed with nondeuterated polystyrene were carried out by Duplessix.[5] The solvent was chosen to have the same scattering length as the nondeuterated polymer chain, so only the neutron scattering by the deuterated parts of the chains was observed. This experimental scheme is identical with the present theoretical model. The experiment was done with 5% mixed solutions of polystyrene (of molecular weight 107 000) in which 12% of the middle part was deuterated and the same polymer (of molecular weight 103 000) nondeuterated. The observed scattering curves show rather similar forms to the curves of the present calculation. The mean radius of gyration of the deuterated part was found to be 57 Å, and so assuming that these polymers are ideal random coil molecules, their mean radius of gyration can be roughly estimated as

$$\langle R^2 \rangle^{1/2} = 57/0.12^{1/2} \approx 160 \text{ Å} \tag{18}$$

The density of a 5% solution is almost equal to that of the solvent; hence, using the value 1.26 of carbon disulfide as the density of the solution, the reduced concentration can be calculated as

$$n_{\mathrm{p}} = nR_0^3 \approx n\langle R^2 \rangle^{3/2} \approx 1.55 \sim 1.5 \tag{19}$$

This value corresponds to those of Figures 1 and 7. In Figure 1 the maximum value of $I(q)/C_{\mathrm{I}}$ can be seen at

$$Z^{1/2} = \langle R^2 \rangle^{1/2} q \approx 2.5\text{–}3.0 \tag{20}$$

Therefore with the value of eq 18, the maximum point q_{m} becomes

$$\begin{aligned} q_{\mathrm{m}} &= (1.56\text{–}1.88) \times 10^{-2} \text{ Å}^{-1} \\ &\approx 2 \times 10^{-2} \text{ Å}^{-1} \end{aligned} \tag{21}$$

This value approximately coincides with that seen in the experimental curve (Figure 1 of ref 5). Also the curves of $S_2(q)$ in Figures 6 and 7 have qualitative forms identical with those of the corresponding experimental curve [$S_2(q,c)$ in Figure 3 of ref 5].

Another neutron scattering experiment which used only a partially deuterated solute polymer was reported by Duplessix, Cotton, Benoit, and Picot.[6] The solute polymer was polystyrene molecules of molecular weight 107 000, each of which was deuterated at the middle part of molecular weight 13 000. As in the experiment described above, the solvent was carbon disulfide so that neutron scattering from only the deuterated polymer was observed. The observed scattering curve has a peak over a wide range of solute concentration from dilute to the bulk state, and it also shows that the peak value q_{m} shifts to a higher scattering angle as the concentration increases. These qualitative properties coincide with the curves in Figures 8 and 9.

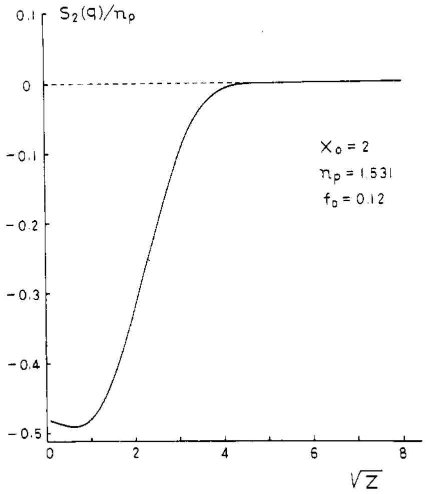

Figure 7. Intermolecular factor $S_2(q)/n_{\mathrm{p}}$ vs. $Z^{1/2}$ for $X_0 = 2$, $n_{\mathrm{p}} = 1.531$, and $f_{\mathrm{D}} = 0.12$.

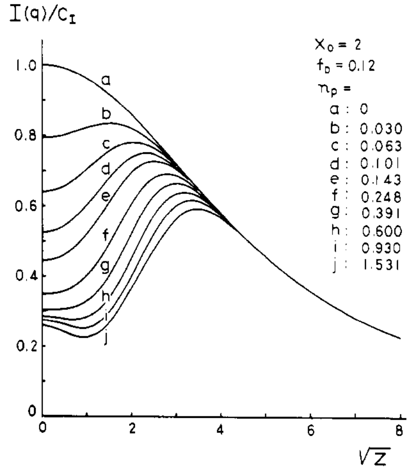

Figure 8. Scattering curves: $I(q)/C_{\mathrm{I}}$ vs. $Z^{1/2}$ for $X_0 = 2$, $f_{\mathrm{D}} = 0.12$, $x = 1$, and various n_{p} concentrations.

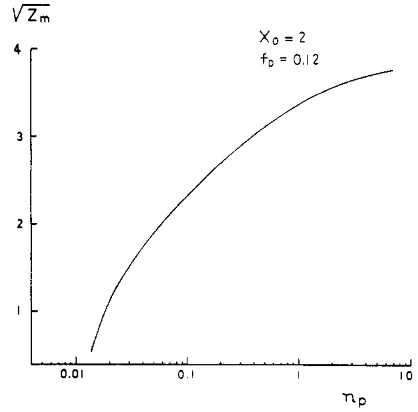

Figure 9. Dependence of peak point of $I(q)$ on concentration n_{p} in the case $X_0 = 2$, $f_{\mathrm{D}} = 0.12$, and $x = 1$.

V. Discussion

1. Scattering Curve and Radial Distribution Function of Polymers. According to eq 1, $I(q)$ depends on not only the intermolecular factor $g(R)$ but also the intramolecular factors $\langle i(q)^2 \rangle$ and $\langle i(q) \rangle^2$. When the scattering-active partial chain segment is very small, the dependence of the latter factors on q (or $Z^{1/2}$) is weak.

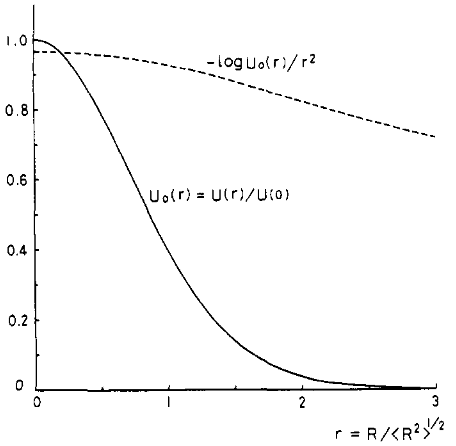

Figure 10. Assumed intermolecular potential $U(R)$ of random coil polymer.

Particularly in the limiting case of $f_D \sim 0$, we have from eq 4, 5, and 8

$$\langle i(q)^2\rangle = 1 \tag{22}$$

$$\langle i(q)\rangle^2 = \exp(-Z/6) \tag{23}$$

and the function $I(q)$ becomes the simple form

$$I(q)/C_I = 1 + 4\pi n_D \exp\left(-\frac{Z}{6}\right)\int_0^\infty (g(R) - 1)R^2\frac{\sin (qR)}{qR}\, dR \tag{24}$$

or

$$I(q)/C_I = 1 + n_D \exp[-\langle R^2\rangle q^2/6]\hat{G}(q) \tag{25}$$

where $\hat{G}(q)$ is the Fourier transform of the intermolecular correlation function $g(R) - 1$

$$\hat{G}(q) = \int_{-\infty}^{+\infty} (g(R) - 1) \exp[i\mathbf{q}\cdot\mathbf{R}]\, d\mathbf{R} \tag{26}$$

Hence there is a possibility of obtaining $g(R)$ from these equations and experimental curves of the polymer having a very small scattering-active partial segment.

2. Approximation Used in the Calculation. Equation 1 is derived as an approximation by assuming that the intramolecular conformations and the intermolecular configuration of the polymers are independent of each other (cf. eq A7 of Appendix A). However, the intramolecular factors $\langle i(q)^2\rangle$ and $\langle i(q)\rangle^2$ are calculated from the distribution functions of the scattering-active segments which are particularly in the middle part of the chain. Generally, such segments are positioned in the inner part of the polymer (namely, near the molecular center of gravity), so it can be considered that their distributions around the center of gravity of the polymer are affected less by the other polymers than those of segments on both end parts of the chain. Therefore this approximation may be better in the present case than the previous case,[1] where this was applied to the whole intramolecular conformation.

Appendix A

The scattering function of the type in eq 1 is given in several textbooks,[3,4] but to clarify the approximation used in this calculation the derivation is given as follows.

Let $\mathbf{R}_{i\lambda}$ be the coordinates of the ith segment in λth polymer molecule; the total amplitude scattered from the solution is

$$\sum_\lambda^{N_p}\sum_i \exp[i\mathbf{q}\cdot\mathbf{R}_{i\lambda}] \tag{A1}$$

so the total scattering intensity is given by

$$I(q) \propto \langle \sum_\lambda^{N_p}\sum_\mu^{N_p}\sum_i\sum_j \exp[i\mathbf{q}\cdot(\mathbf{R}_{i\lambda} - \mathbf{R}_{j\mu})]\rangle \tag{A2}$$

where N_p is the total number of polymer molecules having scattering-active segments in the solution and $\langle\ \rangle$ means the thermal average taken over the possible conformations and intermolecular configurations of the polymers in solution. Denoting by $\mathbf{R}_\lambda$ the coordinates of the center of gravity of λth polymer, we write $\mathbf{R}_{i\lambda}$ as

$$\mathbf{R}_{i\lambda} = \mathbf{R}_\lambda + \mathbf{r}_{i\lambda} \tag{A3}$$

where $\mathbf{r}_{i\lambda}$ are the relative coordinates of the ith segment referred to the center of gravity of the polymer λ. Then eq A2 can be written as

$$I(q) \propto \langle \sum_\lambda^{N_p}\sum_i\sum_j \exp[i\mathbf{q}\cdot(\mathbf{r}_{i\lambda} - \mathbf{r}_{j\mu})]\rangle + \langle \sum_\lambda^{N_p}\sum_\mu^{N_p} \exp[i\mathbf{q}\cdot(\mathbf{R}_\lambda - \mathbf{R}_\mu)]\sum_i\sum_j \exp[i\mathbf{q}\cdot(\mathbf{r}_{i\lambda} - \mathbf{r}_{j\mu})]\rangle \tag{A4}$$

By definition 3 the first term becomes

$$I_1 = N_p N_D^2\langle i(q)^2\rangle \tag{A5}$$

For the second term, first considering the average over intramolecular conformations of polymers, this can be written as

$$I_2 = \langle \sum_\lambda^{N_p}\sum_\mu^{N_p} \exp[i\mathbf{q}\cdot(\mathbf{R}_\lambda - \mathbf{R}_\mu)]\langle \sum_i^{N_D} \exp(i\mathbf{q}\cdot\mathbf{r}_{i\lambda})\sum_j^{N_D} \exp(i\mathbf{q}\cdot\mathbf{r}_{j\mu})\rangle\rangle \tag{A6}$$

This intramolecular average of the second factor depends generally on the intermolecular configuration ($\mathbf{R}_1$, $\mathbf{R}_2$, ..., $\mathbf{R}_{N_p}$). But with the assumption that the statistical intramolecular conformations of the polymers are independent of it, this is equal to $N_D^2\langle i(q)\rangle^2$ by eq 3, and eq A6 becomes

$$I_2 = \langle \sum_\lambda \sum_{\substack{\mu \\ (\lambda\neq\mu)}} \exp[i\mathbf{q}\cdot(\mathbf{R}_\lambda - \mathbf{R}_\mu)]\rangle N_D^2\langle i(q)\rangle^2 \tag{A7}$$

The average in this equation can be determined from only the intermolecular configurations. Therefore using the radial distribution function of the centers of gravity of the polymers, $g(R)$ (or the two-body distribution function $n_2(\mathbf{R}_1, \mathbf{R}_2) = n_D^2 g(R)$), we can be reduce this to

$$n_D^2\int\int g(R) \exp[i\mathbf{q}\cdot(\mathbf{R}_1 - \mathbf{R}_2)]\, d\mathbf{R}_1\, d\mathbf{R}_2 = n_D^2 V\left[\int_{-\infty}^{+\infty} (g(R) - 1) \exp(i\mathbf{q}\cdot\mathbf{R})\, d\mathbf{R} + \delta(\mathbf{q})\right] \tag{A8}$$

where V is the total volume of the solution. The last term on the δ function can be omitted in the scattering curve. By introducing eq A5, A7, and A8 into eq A4, we can deduce eq 1.

Appendix B

From eq 3 and 4 $\langle i(q)^2\rangle$ and $\langle i(q)\rangle^2$ can be written, respectively, as

$$\langle i(q)^2\rangle = N_D^{-2}\sum_{i,j=(N-N_D)/2}^{(N+N_D)/2}\sum \langle \exp[i\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_j)]\rangle \tag{B1}$$

$$\langle i(q)\rangle^2 = (N_D^{-1}\sum_{i=(N-N_D)/2}^{(N+N_D)/2}\langle \exp[-i\mathbf{q}\cdot\mathbf{r}_i]\rangle)^2 \tag{B2}$$

For an ideal random coil chain consisting of N segments the distribution functions of $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $\mathbf{r}_i$ are given, respectively, by[7]

$$f(r_{ij}) = (3/2\pi b^2|i-j|)^{3/2} \exp[-3r_{ij}^2/2b^2|i-j|] \quad \text{(B3)}$$

$$f(r_i) = (C_i^2/\pi)^{3/2} \exp[-C_i^2 r_i^2]$$

$$C_i^{-2} = (b^2/9N)[(N+1)(2N+1) - 6i(N+1) + 6i^2] \quad \text{(B4)}$$

The thermal averages of the quantities included in the angled brackets can be calculated by multiplying them by the respective distribution functions and integrating them over the entire spaces of $\mathbf{r}_{ij}$ and $\mathbf{r}_i$, respectively. Also the sums over i and j can be transformed into integrals for N_D, $N \gg 1$. Thus we can obtain directly eq 5–9.

Appendix C

The intermolecular potential between two polymers is defined by the product of the contact probability of their segments and their binary cluster integral as

$$U(R) = kT\beta\langle\sum_i^N\sum_j^N \delta(\mathbf{R}_{i1} - \mathbf{R}_{j2})\rangle_{\mathbf{R}_1\mathbf{R}_2} \quad \text{(C1)}$$

where the average is taken by fixing the coordinates of the centers of gravity of two polymers at $\mathbf{R}_1$ and $\mathbf{R}_2$. The average can be calculated by multiplying the δ functions by the distribution functions of segments around the molecular centers of gravity and integrating them over all possible conformations of the polymers. Assuming the polymers are of ideal random coil conformations, the distribution function B4 can be applied to the above calculation. The expression in double-integral form has already been given in a previous paper.[7] Figure 10 shows that the result can be represented approximately by a Gaussian function

$$U(R) = U(0) \exp[-R^2/\langle R^2\rangle] \quad \text{(C2)}$$

References and Notes

(1) Koyama, R. *Makromol. Chem.* **1980**, *181*, 1987.

(2) Koyama, R. *J. Chem. Phys.* **1980**, *72*, 247. *J. Phys. Soc. Jpn.* **1977**, *43*, 287.

(3) Guinier, A.; Fournet, G. "Small-Angle Scattering of X-rays"; Wiley: New York, 1955.

(4) Beeman, W. W.; Kaesberg, P.; Andereg, J. W.; Webb, M. B. *Handb. Phys.* **1957**, *32*, 341.

(5) Duplessix, R. IUPAC International Symposium on Macromolecules, Mainz, Sept 1979; Preprints, Vol. II, p 870.

(6) Duplessix, R.; Cotton, J. P.; Benoit, H.; Picot, C. *Polymer* **1979**, *20*, 1181.

(7) Koyama, R. *J. Chem. Phys.* **1957**, *27*, 234.

Solution Properties of Poly(*tert*-butyl crotonate) with a Semiflexible Backbone and Sharp Molecular Weight Distributions. 1. Light Scattering

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ABSTRACT: Measurements of light scattering from poly(*tert*-butyl crotonate) with a narrow molecular weight distribution were carried out in *n*-butyl chloride and ethyl acetate at 25 °C. We conclude that the persistence length of the polymer is about 50–60 Å, based on the molecular weight dependence of the radius of gyration and also from comparison of the experimental particle scattering factor with the theory of Sharp and Bloomfield. The expansion factor was estimated from the second virial coefficient by means of the theory of Yamakawa and Stockmayer and was found to be close to unity.

Introduction

In a previous paper[1] we reported that the poly(*tert*-butyl crotonates) (PTBC) prepared by an anionic polymerization technique have narrow molecular weight distributions and suggested that PTBC is a semiflexible chain from the fact that the exponent in the Mark–Houwink–Sakurada viscosity relation for PTBC in toluene at 25 °C is close to unity.[1] In the present work we carried out the measurements of light scattering of PTBC to determine the stiffness of the chain quantitatively.

Experimental Section

Materials. The samples used here are poly(*tert*-butyl crotonates) which were prepared by an anionic polymerization technique and fractionated three or four times by successive precipitational fractionation, with toluene or tetrahydrofuran as the solvent and methyl alcohol as the nonsolvent. Their molecular characteristics are shown in Table I. The ratio of the weight-average molecular weight to the number-average molecular weight, $\bar{M}_w/\bar{M}_n$, is around 1.1. The z-average molecular weight, $\bar{M}_z$, in Table I was estimated by the assuming the relationship between various average molecular weights in the Schulz–Zimm distribution to be $\bar{M}_n/h = \bar{M}_w/(h+1) = \bar{M}_z/(h+2)$. It appears from ^{13}C NMR spectra that the samples have an atactic structure with respect to both the α and β substitutions.[2]

n-Butyl chloride and ethyl acetate were used for light scattering measurements. *n*-Butyl chloride of special grade was shaken with concentrated H_2SO_4 until the H_2SO_4 layer became colorless, washed with water, dried with $CaCl_2$, and fractionally distilled. Ethyl acetate of special grade was distilled over K_2CO_3, and the second fraction was further purified by fractional distillation.

Osmotic Pressure Measurements. Osmotic pressure measurements were carried out in toluene at 25 °C to determine the number-average molecular weight, using a high-speed Hewlett-Packard Type 502 membrane osmometer.

Light Scattering Measurements. The light scattering measurements were carried out in *n*-butyl chloride and ethyl acetate at 25 °C with a Fica 50 automatic light scattering photometer. The incident beams were polarized and unpolarized light of 436 nm. The scattering angle ranged from 15 to 150°. Optical purification was carried out by filtering the solvent and solution through Millipore filters with 0.45- and 0.25-μm pore sizes. The instrument was calibrated by using Merck special grade benzene as an optical standard. The reduced intensity value of light scattering from the benzene is[3] 45.6×10^{-6} cm^{-6}.

Refractive index increments (dn/dC) were measured with a modified Shimadzu differential refractometer. The refractive