Macromolecules 1984, 17, 1844-1847

Effect of β-Substitution on Chain Flexibility

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ABSTRACT: A Kratky small-angle X-ray scattering study of the chain flexibility of poly(*tert*-butyl crotonate) (PTBC) was made, and the chain flexibility of PTBC was compared with that of poly(*tert*-butyl acrylate), poly(*tert*-butyl methacrylate), and poly(sodium crotonate). From the comparison it was concluded that the substitution of the β-hydrogen in poly(*tert*-butyl acrylate) by a methyl group causes the semiflexibility of the chain because of the steric hindrance between the β-methyl group and the *tert*-butyl group.

Introduction

Polymer chain flexibility is reflected in the so-called σ-value, which is defined by $\sigma = (\langle r^2\rangle_0/\langle r^2\rangle_{0f})^{1/2}$, where $\langle r^2\rangle_0^{1/2}$ is the unperturbed dimension of the polymer and $\langle r^2\rangle_{0f}^{1/2}$ is that of the corresponding ideal chain whose rotation around C–C bonds of the backbone is not restricted. The σ-values of various polymers are well analyzed in the theory of Flory et al.[1] In poly(α-substituted, α,β-unsaturated carboxylate), the backbone chain is flexible and its flexibility is insensitive to the kind of α-substituent or alkyl ester group. For example, the backbone chains of poly(methyl methacrylate), poly(ethyl methacrylate), poly(dodecyl methacrylate), poly(methyl ethacrylate), and poly(methyl butacrylate) are all flexible and the difference in their flexibilities is negligibly small. Moreover, the difference between the flexibilities of polymethacrylates and polyacrylates is negligible also.

In the case of poly(β-substituted, α,β-unsaturated carboxylate), however, it can be speculated that the chain may be much stiffer due to the steric hindrance between β-substituent and alkyl carboxylate group. In practice, it was shown by light scattering[2] and intrinsic viscosity studies[3] that poly(*tert*-butyl crotonate) (PTBC) has a much more extended conformation than ordinary vinyl polymers. Moreover, the particle scattering function $P(\theta)$ of PTBC[2] in light scattering well agreed with the theory of Sharp and Bloomfield[4] for wormlike chains. The persistence length chosen to have the best agreement between the theory and experimental $P(\theta)$ was 50–60 Å, much larger than the values for flexible polymers.

In order to investigate a local structure of the polymer chain, however, small-angle X-ray scattering (SAXS) is a more suitable and direct method than light scattering, because of the available larger wave vector, **S**. The application of SAXS to the investigation on the local structure of polymers was suggested by Kratky and Porod[5] and has been carried out by numerous investigators.[6–15] In this work, we evaluate the persistence length of poly(*tert*-butyl crotonate) by the method of Kratky, assuming that the polymer is a flexible cylinder having uniform electron density. By comparing the data with those of poly(*tert*-butyl acrylate), poly(*tert*-butyl methacrylate), and poly(sodium crotonate), we attempt to clarify the cause of the semiflexibility of the poly(*tert*-butyl crotonate) chain. The rotational isomeric state analysis[16] is the most reasonable approach to the study on the local conformation. In this work, however, we are interested in evaluating the persistence length, characterizing the chain flexibility.

Experimental Section

(1) Samples. Poly(*tert*-butyl acrylate)[17] (PTBA), poly(*tert*-butyl methacrylate)[18] (PTBM), and poly(*tert*-butyl crotonate)[19] (PTBC) were prepared by anionic polymerization of the respective monomers with *n*-butyl- or (2-methylbutyl)lithium in THF at −78 °C. The number-average molecular weights M_n of PTBA, PTBM, and PTBC, determined with a Hewlett-Packard high-speed membrane osmometer, Type 502, in toluene at 20 °C, are 9.1×10^4, 52.9×10^4, and 13.5×10^4, respectively. PTBA was estimated from a proton NMR spectrum to have ca. 58% isotactic dyad content.[20] The carbon-13 and the proton NMR spectra showed that PTBM has ca. 50% isotactic triad content. The tacticity of PTBC estimated from the carbon-13 NMR spectrum is (mM) $\simeq$ 0.70 and (rR) + (mR) $\simeq$ 0.30, if expressed in the same terms as employed in the previous paper.[21]

Poly(sodium crotonate), PNaC(C-109), was obtained by hydrolysis of PTBC(T-109) with concentrated sulfuric acid at 50 °C. The degree of hydrolysis, determined by proton NMR, was ca. 100%. From osmotic pressure measurements in 0.1 N NaCl aqueous solution at 20 °C, M_n of PNaC was estimated to be 2.9×10^4. The tacticity of PNaC was assumed to be the same as the starting material, PTBC(T-109).

In SAXS measurements, the nonionic polymers PTBA, PTBM, and PTBC were dissolved in toluene of a special grade and the ionic polymer PNaC was dissolved in 0.01 N NaCl aqueous solution.

(2) Measurements of Small-Angle X-ray Scattering. The measurements were performed with an Anton Paar Co. Kratky U-slit camera. The X-ray source was a water-cooled copper-anode tube operated at 45 kV and 35 mA powered by a JEOL (Japan Electron Optics Laboratory Ltd.) X-ray generator, Model DX-GE-2D. In order to gain a stable X-ray intensity, the room temperature was kept at 25 ± 1 °C and the temperature of the cooling water was regulated near 24 °C to an accuracy of 1 °C. The widths of the entrance and counter slits were 100 and 250 μm, respectively, and the distance between a sample and the plane of registration was either 20 or 21 cm. The alignment procedure of the camera was carried out following the instruction manual offered from Anton Paar Co. The recipe of experimental conditions is almost the same as one employed in our previous paper.[22]

(3) Numerical Computations. Observed scattering intensities for solvents (I_v) and solutions (I_N) were corrected for the difference in their absorbance coefficients. The difference between those corrected intensities gives the net scattering intensity from solute molecules ($\tilde{I}$). The correction for finite slit width and length was carried out according to Glatter's program[23] to yield the desmeared scattering intensity I which would be obtained if a pinhole X-ray source were used. The calculation was carried out at the Nagoya University Computer Center, using a Facom 230-60/75 electronic computer.

Moreover, since our polymer model is a flexible cylinder with uniform electron density, as stated in the Introduction, we eliminate the effect of inhomogeneity in the electron density in the scattering particles by the method of Luzzati et al.,[24] using

$$I = K_1\mathbf{S}^{-4} + K_2 \tag{1}$$

where K_1 is a constant and K_2 is another constant showing a deviation from Porod's law.[25] The wave vector **S** is defined by

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

If we represent the distance between the center of gravity of the primary X-ray beam and a scattering point in the plane of registration by m and the distance between the sample and the plane of registration by L, $\sin(\theta/2)$ is equal to $m/(2L)$ and we have

$$I = K_1\left(\frac{2\pi}{\lambda}\frac{1}{L}\right)^{-4} m^{-4} + K_2 \tag{3}$$

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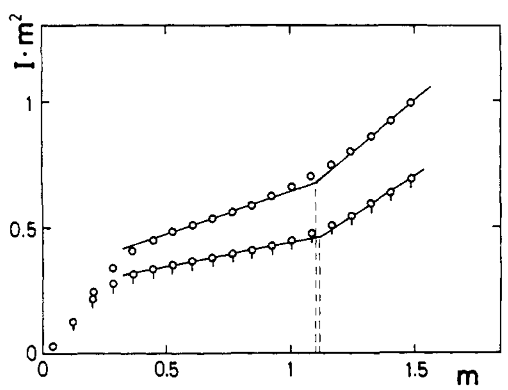

Figure 1. Original Kratky plots for PTBM in toluene. The scattering intensities were obtained with corrections for slit width and length but without corrections for inhomogeneity of electron density and finite cross section of the chain. The polymer concentrations are 5.0 (O) and 3.3% (w/v) (ϙ).

Consequently, the gradient of Im^4 vs. m^4 plots gives K_2, and subtraction of K_2 from I yields the scattering intensity which the polymer chain would give if it had a uniform electron density, I^0.

For a thick molecule, I^0 can be represented as a product of I^0_{thin} and I^0_{cs},[26,27] where I^0_{thin} is the scattering intensity from a hypothetical polymer coil with zero cross section and I^0_{cs} is that from the cross section. Since I^0_{cs} is theoretically expressed by[27]

$$I^0_{\text{cs}} \propto \exp\left\{-\frac{1}{2}\langle R_{\text{cs}}^2\rangle\left(\frac{2\pi}{\lambda}\right)^2\left(\frac{m}{L}\right)^2\right\} \tag{4}$$

where $\langle R_{\text{cs}}^2\rangle^{1/2}$ is the radius of gyration of the cross section, we have

$$I^0 \propto I^0_{\text{thin}} \exp\left\{-\frac{1}{2}\langle R_{\text{cs}}^2\rangle\left(\frac{2\pi}{\lambda}\right)^2\left(\frac{m}{L}\right)^2\right\} \tag{5}$$

If the sample is a rodlike molecule, I^0_{thin} should be inversely proportional to θ,[26,27] and therefore, the scattering intensity from the rodlike molecule I^0_{rod} should be

$$I^0_{\text{rod}} \propto \frac{1}{m} \exp\left\{-\frac{1}{2}\langle R_{\text{cs}}^2\rangle\left(\frac{2\pi}{\lambda}\right)^2\left(\frac{m}{L}\right)^2\right\} \tag{6}$$

If a polymer coil can be regarded as a rodlike molecule, the plot of ln (I^0m) vs. m^2 should be a straight line at high scattering angles. From the slope at high scattering angles we can calculate the radius of gyration of the cross section and, in turn, the scattering intensity which the polymer would give if its cross section were negligible, I^0_{thin}.

I^0_{thin} thus obtained was employed in the Kratky plot, i.e., in the plot of $I^0_{\text{thin}}m^2$ vs. m.

Results

Figure 1 shows examples of Kratky plots for PTBM, obtained with corrections for slit width and length but without corrections for inhomogeneity of electron density and finite cross section. Three regions,[5] that is, the coil part (region I), the Debye part (region II), and the rod part (region III), are roughly distinguished as can be seen in the figure. If m is higher than 1.1, we can speculate that the polymer chain may be regarded as a rodlike molecule. However, note that the plots in region III do not pass through the origin.

Figure 2 shows examples of Im^4 vs. m^4 plots to determine K_2 in eq 3. From the slope of the plot, we can determine K_2 and obtain I^0. I^0 values thus obtained are plotted in the form ln (I^0m) vs. m^2 in Figure 3. In the range $1.3 < m^2 < 2.4$, the plot may be regarded as a straight line with a negative slope. From the slope, we can obtain the radius of gyration of the cross section of the polymer, $\langle R_{\text{cs}}^2\rangle^{1/2}$. If the polymer chain has a circular cross section, the radius of the cross section, r, can be related to $\langle R_{\text{cs}}^2\rangle^{1/2}$ through the relation $\langle R_{\text{cs}}^2\rangle = {}^1/_2r^2$. The values of r thus obtained are 5 ± 2, 8 ± 2, 8 ± 2 Å for PTBA, PTBM, and PTBC, respectively. They appear to be reasonable, judging from their molecular models. From these cross sections and I^0, we can calculate the scattering intensities that the molecules would give if their cross sections were negligible, I^0_{thin}.

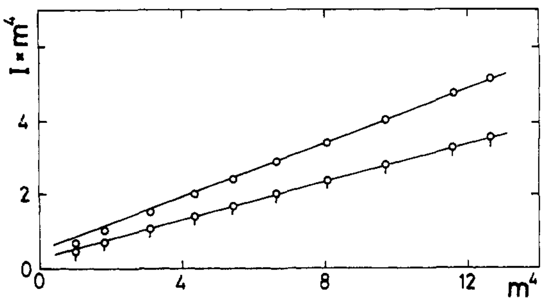

Figure 2. Plots according to Porod's law for PTBM in toluene. The data are the same as in Figure 1.

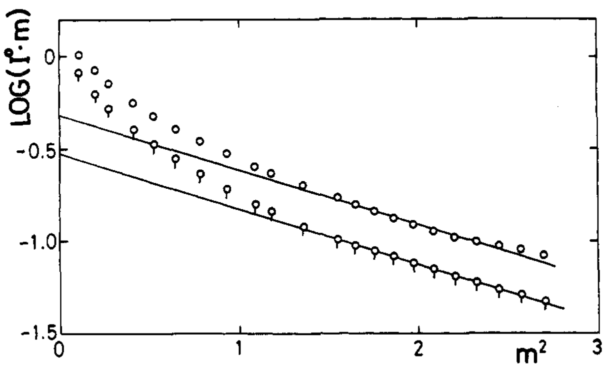

Figure 3. Plots of ln (I^0m) vs. m^2 for PTBM in toluene. The data were obtained by giving corrections for inhomogeneity of electron density to the data in Figure 1.

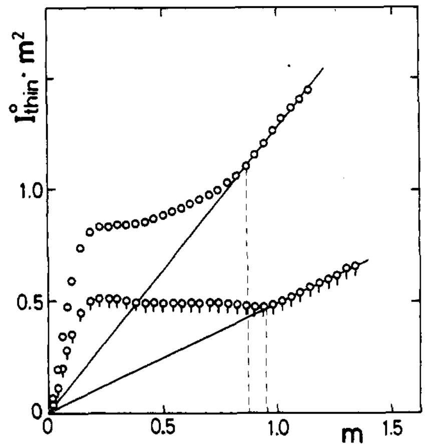

Figure 4. Kratky plots for PTBA in toluene. The polymer concentrations are 6.6 (O) and 2.2% (w/v) (ϙ).

In Figure 4 is shown the Kratky plot for PTBA in toluene at two polymer concentrations C, 6.6 and 2.2% (w/v), using I^0_{thin} thus calibrated. At larger angles, data points form straight lines passing through the origin, showing region III clearly. In region II, however, data points do not follow a horizontal straight line, but a line with a certain slope, showing a deviation from the Debye function. The boundary between regions II and III, m^*, can be clearly defined.

In Figure 5 are shown Kratky plots for PTBM and PTBC in toluene at various polymer concentrations. The plots for PTBC are apparently different from those of PTBM and PTBA in that the values of m^* are a few times smaller than for PTBM and PTBA.

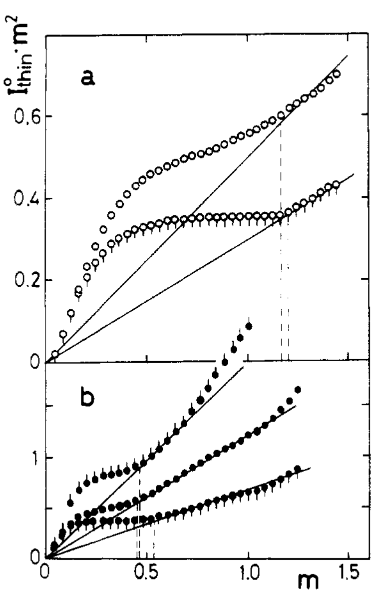

Figure 5. Kratky plots for (a) PTBM and (b) PTBC in toluene. The polymer concentrations are 5.0 (○) and 3.3% (w/v) (ϙ) for PTBM and 4.8 (●), 2.4 (●), and 1.2% (w/v) (●) for PTBC.

In the absence of the excluded volume effect, the value of m^* is inversely proportional to the persistence length of the polymer chain, as was shown by several investigators.[6-8,13,14] Even in good solvents, in which the present experiments were carried out, the excluded volume effect on m^* is minor if the expansion factor is not very high.[28] As was pointed out by Kirste et al.,[29] the excluded volume effect of segments affects the scattering functions in regions I and II but not in region III. Since the molecular weights of the polymers used in SAXS are generally small, the expansion factors of polymers do not become so high. The expansion factor α of PTBC in toluene was estimated to be 1.1 in previous papers.[2,3] Therefore, the difference of m^* in Figure 5b from that in Figure 4 and Figure 5a shows that the persistence length of PTBC is about 2–2.5 times longer than that of PTBA or PTBM. That is, the following conclusions may be derived: Substitution of an α-hydrogen in PTBA by an α-methyl group does not modify the polymer chain flexibility to such an extent that its persistence length is affected. However, exchange of a β-hydrogen with a β-methyl group brings about a remarkable change in the polymer chain flexibility. These conclusions are consistent with the conclusion from light scattering[2] and viscosity studies.[3]

The numerical value of the persistence length for each polymer chain, y, however, cannot be definitely determined, because different relationships between y and θ^* are offered by different investigators. Therefore, we estimated a possible range of y by using the eq 7 and 8. Equation 7 was given by Porod[6] and Koyama,[14] while eq 8 was given by Burchard and Kajiwara.[13]

$$y = \frac{1}{3.29}\frac{\lambda}{\theta^*} \tag{7}$$

$$y = \frac{1}{2.19}\frac{\lambda}{\theta^*} \tag{8}$$

The obtained ranges of y are listed in Table I.

To see whether the polymer chain rigidity of PTBC is retained even after hydrolysis, SAXS measurements were carried out for PNaC in 0.01 N NaCl solution. The Kratky plot of the data is shown in Figure 6. Estimated values of y are 11 ± 2 Å at degrees of neutralization 100, 50, and 25%. This fact seems to verify that the interaction between the β-methyl group and the *tert*-butyl group plays an essential role in producing the polymer chain rigidity of PTBC, rather than between the β-methyl group and the carbonyl group.

Table I

sample	C, g/dL	C^*, g/dL	y, Å	ξ_{obsd}, Å
PTBA	2.2	4.2	10–15	
	6.6		11–16	50 ± 10
PTBM	3.3	1.4	8–12	
	5.0		8–13	
PTBC	1.2	1.0	19–28	
	2.4		21–31	75 ± 10
	4.8		20–30	50 ± 10

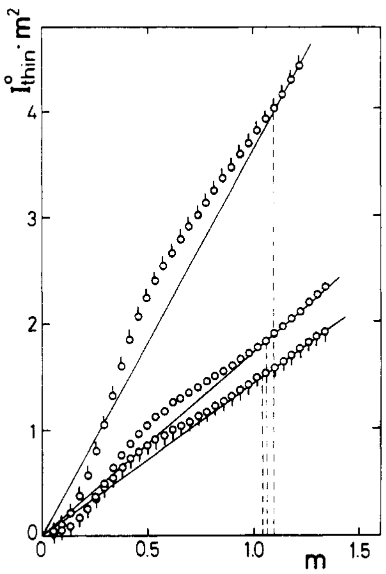

Figure 6. Kratky plots for PNaC in 0.01 N NaCl aqueous solution. The degree of neutralization is 100 (δ), 50 (○) and 25% (ϙ), and the polymer concentration is 2% (w/v) for all samples.

Discussion

In the present investigation, the measurements were carried out at fairly high polymer concentrations, C, because of low scattering intensity. It is certain that the concentrations are higher than the critical polymer concentration, C^*, where polymer coils begin to overlap. However, it seems reasonable to assume that the polymer concentration effect on y is negligible if y is sufficiently small compared with the distance between two entanglement points, i.e., the correlation length, ξ. The correlation length can be estimated from the scattering intensities at the scattering angles in the range $1/\xi > \mathbf{S} > 1/R$, where R is the radius of gyration of a polymer chain, such as[30]

$$I^0_{thin} \propto C\xi/(\mathbf{S}^2 + \xi^{-2}) \tag{9}$$

It can be observed that the plot of $1/I^0_{thin}$ vs. $\mathbf{S}^2$ is linear, from which we can determine ξ. The values of ξ estimated are listed in Table I. Since the values of y are smaller than ξ and also since they are almost independent of polymer concentration, it may be concluded that the values of y obtained in this work are the values at infinite dilution.

The persistence length of PTBC determined in this work (20–30 Å) is small compared with the values determined from light scattering (50–60 Å)[2] and intrinsic viscosity–molecular weight relationship (50–60 Å).[3] The reason for the difference is not fully clear at present. As was discussed in the Results, the persistence length determined by the Kratky method is substantially free from the excluded volume effect, whereas the values determined from light scattering and viscosity studies may be affected by the excluded volume effect. However, this is not the main reason for the difference. It was already discussed in previous papers that the excluded volume effect of segments is minor in the extension of PTBC. Moreover, if we calculate the unperturbed radius of gyration $\langle R^2 \rangle_0^{1/2}$ of PTBC assuming y = 20–30 Å and estimate the expansion factor from the ratio of the experimental radius of gyration in light scattering to $\langle R^2 \rangle_0^{1/2}$, the expansion factor becomes too high to be accepted as reasonable.

Another conceivable reason for the difference may be difficulty in eliminating the effects of background and cross section of a polymer chain, as was pointed out by Kirste.[15] Since the persistence length (20–30 Å) is not sufficiently larger than the radius of gyration of the cross section (4–6 Å) in PTBC, the transition region from coil to rod in the calibrated profile is considerably influenced by the value chosen for the cross section.[31] However, this reason does not seem to be a main one because ambiguities arising from the effect of background and cross section considerably affect the shape of the scattering curve, but the position of the transition point m^* only slightly, as is clear from the comparison between Figures 1 and 5a.

Both in the light scattering and in the X-ray scattering, the polymer chains are assumed to be smeared chains with uniform electron density. However, in the study on the local conformation by the Kratky plot, the fine structure of the chain should be more seriously taken into account than in light scattering.[32–34] A better approach to the local conformation may be the rotational isomeric state analysis, as was carried out for polyisobutylene by Hayashi et al.[35] It was shown in our previous paper[21] that the configuration of PTBC is determined by a propagation mechanism of a reversible double-Markovian process and 16 stereochemical species should be taken into account. Since occurrence of various conformations of a given stereochemical species is determined by the same rotational potentials as those affecting the stereochemical equilibrium, three- and five-bond interactions of β-methyl (β-CH_3) with β-CH_3 and of *tert*-butyl carboxylate (COO-*t*-Bu) with COO-*t*-Bu and four-bond interactions of β-CH_3 with COO-*t*-Bu should be taken into consideration in the calculation of the conformation of atactic PTBC. The reason for the difference in the persistence lengths determined by light scattering and the present method can not be clarified until these problems are solved. However, the comparison among the data of PTBC, PTBA, and PTBM suggests that the β-substitution increases the rigidity of polymer chain.

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