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

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

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

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

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

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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

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Table I
Molecular Characteristics of PTBC

sample code	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_z \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	in *n*-butyl chloride: $\langle s^2\rangle \times 10^{-4}$, Å^2	in *n*-butyl chloride: $A_2 \times 10^4$, mL/g^2	in ethyl acetate: $\langle s^2\rangle \times 10^{-4}$, Å^2	in ethyl acetate: $A_2 \times 10^4$, mL/g^2
TB7-3	$35._1$	$31._8$	$38._6$	1.1_1	$11._2$	5.8_1	$10._6$	1.4_6
TB4B-3	$20._4$	$19._5$	$21._9$	1.0_8	6.5_4	5.9_2	6.1_6	1.5_6
TB2-1-2	$16._1$	$12._8$	$19._4$	1.2_6	5.2_7	6.6_5	5.3_0	1.1_5
T-108	6.0_6	5.4_8	6.6_4	1.1_1	1.8_2	7.7_5	1.7_3	2.1_1

index increments of PTBC in *n*-butyl chloride and ethyl acetate at 25 °C at the wavelength 436 nm are 0.083 and 0.111 cm^3/g, respectively.

Results

A polymer which consists of segments with optical anisotropy exhibits stronger optical anisotropy as a whole as the chain becomes stiffer. In this work, therefore, the effect of optical anisotropy was examined first.

In light scattering with unpolarized incident light, the reduced intensity of scattered light, R_θ, of a wormlike chain with an optical anisotropy at infinite dilution is given by[4]

$$R_\theta = R_{V_v} + R_{H_v} + R_{V_h} + R_{H_h} \quad (1)$$

$$[R_{V_v}(u,\delta)/KMC]_{c=0} = (1 + \tfrac{4}{5}\delta^2) - \tfrac{1}{3}[1 - \tfrac{4}{5}f_1\delta + \tfrac{4}{7}(f_2\delta)^2]u + \mathcal{O}(u^2) \quad (1a)$$

$$[R_{H_v}(u,\delta)/KMC]_{c=0} = [R_{V_h}(u,\delta)/KMC]_{c=0} = \tfrac{3}{5}\delta^2 - \tfrac{1}{35}(f_3\delta)^2u + \mathcal{O}(u^2) \quad (1b)$$

$$[R_{H_h}(u,\delta)/KMC]_{c=0} = \tfrac{3}{5}\delta^2 + \cos^2\theta(1 + \tfrac{1}{5}\delta^2) - \{[\tfrac{2}{5}f_1\delta + \tfrac{13}{35}(f_4\delta)^2] + \tfrac{1}{3}\cos^2\theta[1 + \tfrac{2}{5}f_1\delta + \tfrac{1}{7}(f_2\delta)^2]\}u + \mathcal{O}(u^2) \quad (1c)$$

with $K = 4\pi^2n_0^2(dn/dC)^2/\lambda_0^4N_A$, $q = (4\pi n_0/\lambda_0)\sin(\theta/2)$, and $u = q^2\langle s^2\rangle$, where, for example, R_{H_v} denotes the reduced intensity of the horizontal component of light scattered from vertically polarized incident light, λ_0 is the wavelength of incident light, M, $\langle s^2\rangle^{1/2}$, and C are the molecular weight, mean-square radius of gyration, and concentration of polymer, respectively, n_0 is the refractive index, f_1, f_2, f_3 and f_4 are functions of chain stiffness which are equal to unity for rods and zero for flexible chains, and δ is experimentally obtained by the following relationship derived from eq 1a,b:

$$\delta^2 = 5\rho_V/(3 - 4\rho_V) \quad (2)$$

$$\rho_V = \lim_{\theta\to 0}(R_{H_v}/R_{V_v}) \quad (3)$$

Since the optical anisotropy of the present sample is of the order of 10^{-2} in *n*-butyl chloride as well as in ethyl acetate and its chain configuration is very different from a rod, the effect of anisotropy can be assumed to be negligible within experimental error. Hence, to determine the radius of gyration and the second virial coefficient, we may employ the well-known equation of light scattering with unpolarized light as follows:

$$(KC/R_\theta) = 1/[\bar{M}_wP(\theta)](1 + 2A_2\bar{M}_wC + \ldots) \quad (4)$$

where $\bar{M}_w$ is the weight-average molecular weight and A_2 is the second virial coefficient. An example of a Zimm plot according to eq 4 is shown in Figure 1. The mean-square radius of gyration and second virial coefficient are listed in Table I.

Discussion

The radius of gyration of polymers is affected both by the stiffness of the polymer chain and by the excluded-volume effect. It is important to determine which gives

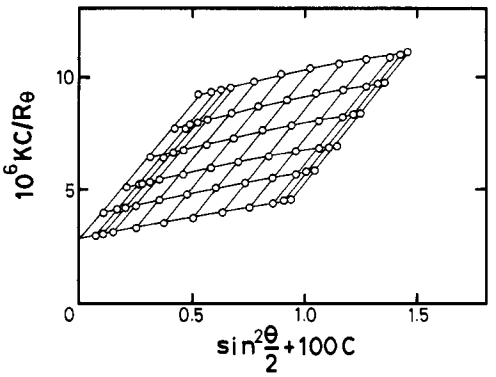

Figure 1. Example of a Zimm plot for PTBC (TB7-3) in *n*-butyl chloride at 25 °C.

the predominant effect on the radius of gyration of PTBC. The stiffness of polymer chains is expressed by the persistence length $1/2\lambda$ or the statistical length $1/\lambda$.

The dilute-solution properties of polymers may be expressed by two factors, the radius of gyration $\langle s^2\rangle^{1/2}$ and the second virial coefficient A_2 or the expansion factor α and penetration function Ψ, which are defined by

$$\alpha^2 = \langle s^2\rangle/\langle s^2\rangle_0 \quad (5)$$

$$\Psi = A_2M^2/4\pi^{3/2}N_A\langle s^2\rangle^{3/2} \quad (6)$$

where $\langle s^2\rangle_0$ is the unperturbed mean-square radius of gyration and N_A is Avogadro's number. According to Yamakawa and Stockmayer,[5] α and Ψ of wormlike chains are given in terms of the persistence length $1/2\lambda$ and the excluded-volume parameter z as

$$\alpha^5 - \alpha^3 = 1.276f_\alpha(\lambda L) \quad (7)$$

$$\Psi = \frac{\ln[1 + 5.73f_\Psi(\lambda L)\bar{z}]}{5.73f_\Psi(\lambda L)} \quad (8)$$

where

$$z = (3\lambda/2\pi)^{3/2}BL^{1/2} \quad (9)$$

$$\bar{z} = z/\alpha^3 \quad (10)$$

B is the excluded volume of a segment, the parameter of stiffness λL is the ratio of contour length L to the statistical length $1/\lambda$, and f_α and f_Ψ are functions of λL. If $\lambda L \gg 1$, that is, if the chain is flexible or if the molecular weight is high, eq 7 and 8 become the modified equations of Flory[6,7] and of Flory–Krigbaum–Orofino (FKO)[7,8] for flexible polymers, respectively. The theory of FKO for flexible polymers is in good agreement with experimental data[9] if z is small. If we assume $\lambda L \gg 1$ for PTBC, that is, $f_\alpha(\lambda L) = f_\Psi(\lambda L) = 1$, we can estimate $\bar{z}$ from the experimental values of Ψ using eq 8 and calculate α from eq 7. Since λL is not infinite for PTBC, however, it is to be noted that the values of α thus estimated should be upper limits for PTBC in these solvents. As shown in Table II, the expansion factors of PTBC thus estimated are around 1.02 and 1.1 in ethyl acetate and *n*-butyl chloride, respectively. Thus, it is concluded that the excluded-volume

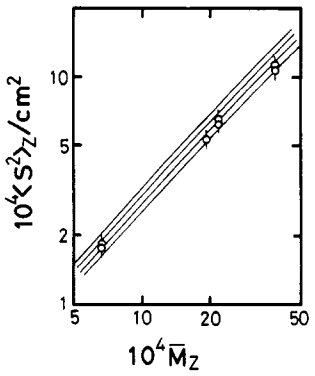

Figure 2. Relationship between $\langle s^2\rangle$ and $\bar{M}_z$ of PTBC in *n*-butyl chloride (○) and in ethyl acetate (○). The curves denote the theoretical values of a wormlike chain having $1/2\lambda$ = 65, 60, 55, and 50 Å from top to bottom, assuming M_L = 60 Å^{-1}.

Table II
Penetration Function and Expansion Factor of PTBC in *n*-Butyl Chloride and Ethyl Acetate at 25 °C

	in *n*-butyl chloride		in ethyl acetate	
sample code	Ψ	α	Ψ	α
TB7-3	0.17_2	1.1_7	0.047_0	1.0_3
TB4B-3	0.12_7	1.1_1	0.036_5	1.0_3
TB2-1-2	0.15_4	1.1_5	0.026_4	1.0_2
T-108	0.10_4	1.0_9	0.030_5	1.0_2

effect is essentially negligible in solutions of PTBC, particularly in ethyl acetate.

The radius of gyration of wormlike chain is given in terms of λL as[10]

$$\langle s^2\rangle = (1/\lambda^2)[\lambda L/6 - 1/4 + 1/4\lambda L - 1/8(\lambda L)^2(1 - e^{-2\lambda L})] \quad (11)$$

If the molecular weight per unit contour length $M_L = M/L$, which depends on the local conformation of the polymer, is given, eq 11 shows that $\langle s^2\rangle$ is expressed in terms of M and can be compared with the experimental relationship between $\langle s^2\rangle$ and M. If PTBC has the all-trans zigzag conformation, we have M_L = 57 Å^{-1}. If the molecular conformation is the 3_1 helical form, M_L is about 70 Å^{-1}. For comparison with experimental data, we calculated $\langle s^2\rangle$ as a function of M from eq 11 assuming M_L = 60, 70, and 80 Å^{-1}. In Figure 2, as an example, the theoretical curves with M_L = 60 Å^{-1} are compared with experimental data. From the comparison of the experimental data with the theoretical curves in Figure 2 and also in the corresponding figures with M_L = 70 and 80 Å^{-1} the persistence lengths were determined as shown in Table III.

The persistence length is also determined from the comparison between the experimental angular dependence of scattered light and the theoretical particle scattering factor $P(\theta)$ of wormlike chains calculated by Sharp and Bloomfield[11] and Yamakawa et al.[12] If $\lambda L \gg 10$, the factor $P(\theta)$ for a molecule having stiffness λL is given in terms of a parameter $x = Lq^2/6\lambda$ as

$$P(\theta) = \frac{2}{x}(x - 1 + e^{-x}) + \frac{4}{15\lambda L} + \frac{7}{15x\lambda L} + \left(\frac{11}{15\lambda L} + \frac{7}{15x\lambda L}\right)e^{-x} \quad (12)$$

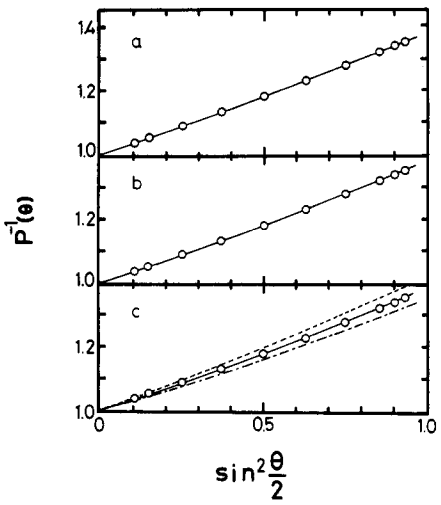

Figure 3. Comparison between the experimental and theoretical particle scattering factor. Sample, TB4B-3; solvent, *n*-butyl chloride. The curves denote the theoretical $P(\theta)$ of the wormlike chain. (a) M_L = 80 Å^{-1}, $1/2\lambda$ = 75 Å; (b) M_L = 70 Å^{-1}, $1/2\lambda$ = 65 Å; (c) M_L = 60 Å^{-1}, $1/2\lambda$ = 60, 55, and 50 Å from top to bottom.

In this case, too, the theoretical curves differ, depending on the value of M_L assumed. In Figure 3 an example of the comparison between experimental data and the theoretical curves is shown for M_L = 60. The agreement between theory and experiment appears to be almost perfect. From similar comparisons, the persistence length was determined, corresponding to the value of M_L shown in Table III.

The persistence lengths determined from the molecular weight dependences of $\langle s^2\rangle$ and the particle scattering factor agree with each other satisfactorily. However, the values in *n*-butyl chloride are always larger than those in ethyl acetate. Apparently this small difference is caused by the excluded-volume effect. Taking into account the ambiguities arising from the nonnegligible excluded-volume effect and also from the value of M_L, which cannot definitely be determined because the local conformation of the polymer is unknown, we can conclude that the persistence length of PTBC is about 50–60 Å. Thus the PTBC polymer chain is 5 or 6 times stiffer than other flexible-chain polymers, such as poly(α-methylstyrene)[9] or polystyrene. However, it is noted that the PTBC polymer behaves like an almost Gaussian chain in the present range

Table III
Persistence Length of PTBC

		$1/2\lambda$ from $\langle s^2\rangle$, Å			$1/2\lambda$ from $P(\theta)$, Å		
sample code	solvent[a]	M_L = 60	M_L = 70	M_L = 80	M_L = 60	M_L = 70	M_L = 80
TB7-3	B	55	65	75	50	60	70
	E	50	60	70	50	55	65
TB4B-3	B	55	70	80	55	65	75
	E	60	70	80	60	70	80
TB2-1-2	B	50	60	70	50	60	75
	E	45	55	65	50	60	70
T-108	B	60	70	80	55	70	85
	E	60	70	80	60	70	85

[a] The letters B and E denote the values of the persistence length in *n*-butyl chloride and in ethyl acetate, respectively.

of molecular weight since the contribution of terms other than the first term (which expresses Gaussian character) is small in eq 11 and 12 with $1/2\lambda$ = 50–60 Å. The relatively high stiffness of PTBC may be caused by steric hindrance of the β-CH_3 group and the large *tert*-butyl ester group at the α position.

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Solution Properties of Poly(*tert*-butyl crotonate) with a Semiflexible Backbone and Sharp Molecular Weight Distributions. 2. Intrinsic Viscosity and Diffusion Coefficient

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ABSTRACT: Intrinsic viscosities and diffusion coefficients of poly(*tert*-butyl crotonates) with a semiflexible backbone and sharp molecular weight distributions were measured in *n*-butyl chloride, toluene, and ethyl acetate at 25 °C. The data are well explained by the theory of Yamakawa and Fujii for the hydrodynamic properties of wormlike chains, except for polymers of low molecular weight, and with the same persistence length estimated by light scattering measurements ($1/2\lambda$ = 50–60 Å). The effect of chain stiffness on the universal calibration curve in GPC was also examined.

Introduction

Poly(*tert*-butyl crotonates) (PTBC), polymerized with an anionic initiator,[1] have a stiff chain backbone because of the steric hindrance between β-methyl and carboxylate groups and have sharp molecular weight distributions.[1] In the accompanying paper, the persistence length was found from light scattering measurements[2] to be 50–60 Å. In the present work, we report on the hydrodynamic properties (intrinsic viscosity and diffusion coefficient) of the polymer in solution, to be compared with theories for the hydrodynamic properties of wormlike chains. Moreover, the GPC universal calibration curve is studied with the present semiflexible polymers.

Experimental Section

Materials. Some samples used here are the same ones described in the accompanying paper[2] but additional samples with low molecular weights were prepared in this work. Their molecular characteristics are shown in Table I.

Solvents used here are toluene, *n*-butyl chloride, tetrahydrofuran, and ethyl acetate. Purification methods for the solvents were reported in the accompanying paper.[2]

Vapor Pressure Osmometry. A Hitachi Perkin-Elmer 115 vapor pressure osmometer was used to determine the number-average molecular weights of the samples having low molecular weights. The measurements were carried out in benzene at 35 °C.

Viscosity Measurements. Measurements of intrinsic viscosity were carried out in toluene, *n*-butyl chloride, tetrahydrofuran, and ethyl acetate at 25 °C with a modified Ubbelohde-type viscometer. The shear rate dependence of $[\eta]$ was negligible.

Diffusion Measurements. Measurements of the diffusion coefficient were carried out in a Beckman Spinco Model H electrophoresis–diffusion apparatus with a Rayleigh interference optical system in *n*-butyl chloride at 25 °C. The quartz cell was made for the interference method in organic solvents.[3] To minimize the error arising from the concentration dependence of the diffusion coefficient, the difference between the concentrations of the two solutions at the diffusion boundary was made as small as possible. The Rayleigh fringe was analyzed by the method of Longsworth[4] as well as by the method of Creeth.[5] The latter gives correct results if the diffusion coefficient varies linearly between two solutions. The apparent diffusion coefficient thus obtained was plotted against inverse diffusion time, $1/t$, and extrapolated to $1/t = 0$ to obtain the diffusion coefficient at a nonvanishing concentration which is an arithmetic average of the concentrations of the two solutions. An example of the plot is shown in Figure 1. The diffusion coefficient thus determined at finite concentrations was extrapolated to zero concentration to find the limiting diffusion coefficient at infinite dilution, as shown in Figure 2.

GPC Measurements. GPC measurements were carried out with a high-speed gel chromatograph (TSK-HLC 801A, Toyo Soda Co. Ltd). The columns used were chosen from TSK-G3000H × 3, TSK-G Mix × 3, and G6000H × 3 (Toyo Soda Co. Ltd.), depending on the molecular weight of the sample. The solvent for the GPC measurements was tetrahydrofuran, and the temperature was 30 °C.

Results

All data for intrinsic viscosity $[\eta]$ and diffusion coefficient D are listed in Table I. It can be seen from the table that the intrinsic viscosities in toluene, *n*-butyl chloride, and tetrahydrofuran coincide to within experimental error. However, the intrinsic viscosities of high molecular weight PTBC in ethyl acetate are smaller than those in the other solvents. This result is consistent with the light scattering data.[2] The molecular weight dependences of D and $[\eta]$ are shown in Figures 3 and 4, respectively. From these figures we have the following experimental relationships:

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