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 $1/2\lambda = 50\text{–}60$ 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 ($1/2\lambda = 50\text{–}60$ 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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$$[\eta] = 7.7 \times 10^{-5}\bar{M}_w^{0.82} \qquad (1)$$

in toluene and *n*-butyl chloride at 25 °C

$$D = 6.9 \times 10^{-4}\bar{M}_w^{-0.61} \qquad (2)$$

in *n*-butyl chloride at 25 °C

The relationships between M, $[\eta]M$, and the GPC retention volume V_R[6] are shown in Figures 5 and 6 together wiith the data for monodisperse polystyrenes from Pressure Chemical Co. Ltd. Using the relationship between $\bar{M}_n$ and V_R, we evaluated the ratio of molecular weights $\bar{M}_w/\bar{M}_n$ as listed in Table I.

Discussion

It was reported in the accompanying paper[2] that the expansion factors of PTBC in *n*-butyl chloride and ethyl acetate are close to unity. Therefore the present experimental data may be compared with hydrodynamic theories for the wormlike chain model, with neglect of the excluded-volume effect. Recently, Yamakawa and Fujii presented comprehensive theories for the hydrodynamic properties of wormlike chains.[7,8] According to these authors, the diffusion coefficient and the intrinsic viscosity of wormlike chains are given by

$$\frac{DM}{kT} = \frac{M_L}{3\pi\eta_0}[1.843(\lambda L)^{1/2} + A_2 + A_3(\lambda L)^{-1/2} + ...] \qquad (3a)$$

$$(\lambda L > 2.278)$$

$$\frac{DM}{kT} = \frac{M_L}{3\pi\eta_0}[C_1 \ln (L/d) + C_2 + C_3(\lambda L) + ...] \qquad (3b)$$

$$(\lambda L < 2.278)$$

and

$$[\eta] = \Phi(\lambda L,\lambda d)(\lambda M_L)^{-3/2}M^{1/2} \qquad (4)$$

with

$$L = M/M_L \qquad (5)$$

where L and M are the contour length and molecular weight of the polymer, respectively, M_L is the molecular weight per unit length, $1/2\lambda$ is the persistence length, d is the hydrodynamic diameter for a cross section of the chain, η_0 is the viscosity of the solvent, k is the Boltzmann constant, $A_2, A_3, ...$ and $C_1, C_2, C_3 ...$ are functions of λd, and Φ is a function of λL and λd. To calculate the theoretical values of $[\eta]$ and D from eq 3 and 4, one needs not only the values of $1/2\lambda$ but also those of M_L and d. Since the local conformation of PTBC is not yet known, M_L cannot definitely be determined; the theoretical values of $[\eta]$ and D were therefore evaluated for several combinations of $1/2\lambda$ and M_L determined in the accompanying paper,[2] assuming that d is an adjustable parameter.

Theoretical curves with $M_L = 60$ Å^{-1} are shown in Figures 3 and 4. The values $1/2\lambda$ and d are given in the figure captions. The experimental values of D are in good agreement with theory while the experimental values of $[\eta]$ agree with theory in the region of high molecular weight but deviate from theory in the region of low molecular weight. The same kind of theoretical curves were obtained for $M_L = 70$ and 80 Å^{-1} with different values of $1/2\lambda$. The deviations in the region of low molecular weight are understandable since the theory[8] is not very accurate for low values of $(\lambda L)^{1/2}/\lambda d$. From the comparison of the data with the theoretical values, we obtain $1/2\lambda$ = 50–60 Å, depending on M_L. This result is in good agreement with the light scattering data.[2]

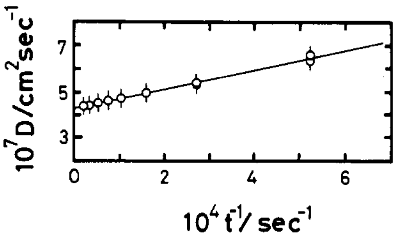

Figure 1. Example of a plot of apparent diffusion coefficient vs. inverse diffusion time, $1/t$, for PTBC (TB-2-1-2): (ό) Creeth method; (ϙ) Longsworth method.

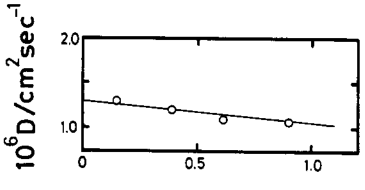

Figure 2. Example of the concentration dependence of the diffusion coefficient of PTBC (T107) in *n*-butyl chloride at 25 °C.

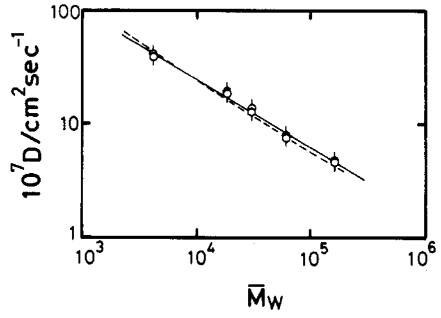

Figure 3. Double-logarithmic plots of diffusion coefficient vs. weight-average molecular weight: (ϙ) observed values in *n*-butyl chloride; (ό) values at a Θ state estimated by the procedure described in the text. The full and broken lines denote the experimental ($D = 6.9 \times 10^{-4}\bar{M}_w^{-0.61}$) and theoretical ($M_L$ = 60 Å^{-1}, $1/2\lambda$ = 55 Å, d = 5.5 Å) relationships, respectively.

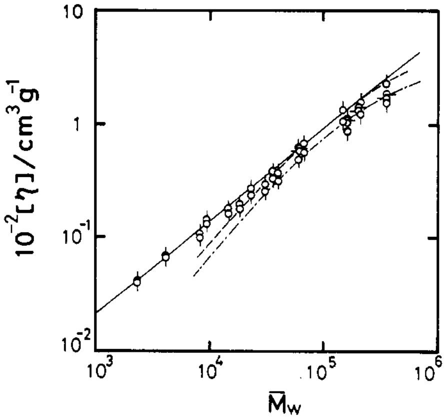

Figure 4. Double-logarithmic plots of intrinsic viscosity vs. weight-average molecular weight: (ό) observed values in toluene; (O-) observed values in ethyl acetate; (ϙ) values at a Θ state estimated from the data for toluene by the procedure described in the text; (-O) values at a Θ state estimated from the data for ethyl acetate by the procedure described in the text. The full, broken, and chain lines denote experimental ($[\eta] = 7.7 \times 10^{-5}\bar{M}_w^{0.82}$), theoretical ($M_L$ = 60 Å^{-1}, $1/2\lambda$ = 55 Å, d = 5.5 Å), and theoretical (M_L = 60 Å^{-1}, $1/2\lambda$ = 50 Å, d = 2 Å) relationships, respectively.

Strictly, however, the assumption of a negligible excluded-volume effect is not valid. If we assume that the

Table I
Molecular Weights, Diffusion Coefficients, and Intrinsic Viscosities of Poly(*tert*-butyl crotonate)

					$[\eta]$,[c] dL/g			
sample code	$\bar{M}_n \times 10^{-4}$ [a]	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$ [b]	$D \times 10^6$, cm^2/s	T	BC	THF	EA
T504	0.20 (v)		(1.1_4)		0.040_3			
T501	0.35_5 (v)		(1.1_5)	4.02	0.069_0			
T607	0.45_4 (v)							
T606	0.71_9 (v)		(1.1_4)		0.10_8			
T504	0.82_0 (v)		(1.1_4)		0.14_4			
T603	1.26 (g)		(1.1_5)		0.17_9			
T216	1.5_8		(1.1_4)	1.8_5	0.19_8			
T601	1.9_4 (g)		(1.1_8)		0.27_1			
T602	2.2_3 (g)							
T107	2.7_6			1.3_0	0.29_4			
T106	3.6_0				0.37_3			
TB1-3	3.2_0		(1.1_1)		0.39_2			
T108	5.4_8	6.06	1.1_1	0.75_0	0.60_2	0.68		0.62
T213	5.3_3		(1.1_9)		0.61_0			
T102	5.6_3				0.68_8			
TB2-1-2	12.8	16.1	1.26	0.45_5	1.12	1.11		1.10
T109	13.5				1.34			
TB3-2	19.2				1.56			
TB4B-3	19.5	20.4	1.0_8			1.59		1.43
TB4B-2	32.1				2.25		2.29	
TB7-3	31.6	35.1	1.1_1		2.30	2.20		1.86

[a] The letters v and g denote the number-average molecular weights obtained from vapor pressure osmometry and GPC, respectively. The other data were obtained by membrane osmometry. [b] The values in parentheses were obtained by GPC. [c] T, BC, THF, and EA denote data for toluene, *n*-butyl chloride, tetrahydrofuran, and ethyl acetate, respectively.

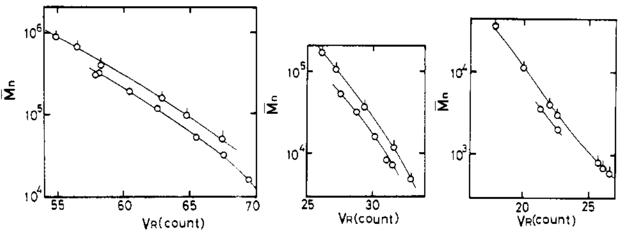

Figure 5. Relationships between molecular weight and retention volume V_R in GPC: (ó) polystyrene; (O) PTBC.

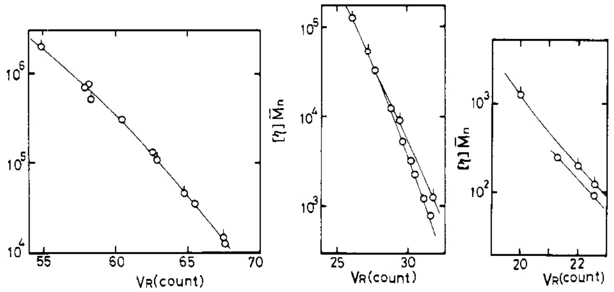

Figure 6. Universal calibration parameters $\bar{M}_n[\eta]$ vs. retention volume V_R in GPC. The symbols are the same as in Figure 5.

relationship between the radius of gyration and the hydrodynamic radius of PTBC is given by the same equation as that established for ordinary flexible polymers, the ratio of $[\eta]$ or D to that at the Θ state ($[\eta]_0$ or D_0) is, respectively, given by[9-11]

$$[\eta]/[\eta]_0 \equiv \alpha_\eta^3 \cong \alpha^{2.43} \qquad (6)$$

$$D_0/D \equiv \alpha_f \cong \alpha \qquad (7)$$

where α is the expansion factor defined by the ratio of the radius of gyration, $\langle s^2\rangle^{1/2}$, to that at the Θ state, $\langle s^2\rangle_0^{1/2}$.

$$\langle s^2\rangle/\langle s^2\rangle_0 = \alpha^2 \qquad (8)$$

As was discussed in the accompanying paper,[2] the maximum values of α allowed for wormlike chains may be estimated from experimental values of the interpenetration function Ψ if we assume that the theory of Yamakawa and Stockmayer[12] is correct. Moreover, eq 7 in the accompanying paper can be written as

$$\alpha^5 - \alpha^3 = KM^{1/2} \qquad (9)$$

The constant K can be determined by using the values of α estimated for PTBC in the accompanying paper,[2] and then the values of α of the other samples can be estimated from their molecular weights. The values of α thus determined are, therefore, upper limits of α for these samples. By introducing these values of α into eq 6 and 7, we can obtain $[\eta]_0$ and D_0 from $[\eta]$ in toluene and ethyl acetate and D in *n*-butyl chloride, where we assume that the expansion factor in toluene is equal to that in *n*-butyl chloride. The values of $[\eta]_0$ and D_0 thus estimated are shown in Figures 3 and 4, respectively. The difference between the values at 25 °C and at the Θ state is minor except for high molecular weights in toluene. Thus conclusions obtained by neglecting the excluded-volume effect need not be modified.

The relationship between M and V_R in GPC for PTBC is very different from that for polystyrenes, as shown in Figure 5. The relationship between $[\eta]M$ and V_R for PTBC is in good agreement with that for polystyrenes if the molecular weights are high but deviates in the region of low molecular weight. This fact can be understood since PTBC chains have extended forms in the region of low molecular weight. It is consistent with previous observations that stiff chain polymers show deviations from the universal calibration curve for flexible polymers[13,14] although the directions of these deviations are not always the same.

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Small-Angle X-ray Scattering Study of Perfluorinated Ionomer Membranes. 1. Origin of Two Scattering Maxima

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ABSTRACT: Small-angle X-ray scattering (SAXS) from perfluorinated ionomer membranes was studied in order to investigate their internal supermolecular structure. The SAXS curves generally exhibit scattering maxima at $s = (2 \sin \theta)/\lambda$ nearly equal to 0.07 and 0.3 nm^{-1} (θ and λ being one-half the scattering angle and the wavelength of the X-rays, respectively). Simultaneous investigation of wide-angle X-ray scattering indicated that the SAXS maximum at the smaller s is associated with crystallinity (the larger the crystallinity, the more distinct is the SAXS maximum) and is attributed to a long identity period in lamellar crystals. The maximum at the larger s is associated with the existence of ionic clusters whose size is a function of the number of perfluoroether side chains (with pendant sulfonic acid or carboxylic acid groups and their salts) per chain, the nature of the ionic sites (e.g., the electrostatic interaction energy released upon cluster formation), the temperature, and the amount of water absorbed by the membranes.

I. Introduction

The electrochemical behavior of perfluorinated ionomers as ion-exchange membranes[1] as well as their mechanical properties[2,3] should be closely related to their internal structure, especially the spatial distribution of ionic sites, e.g., structure and size of ionic clusters, if these exist. In this series of reports we will analyze the structure of perfluorinated membranes in the absence of any applied external electric field by means of the small-angle X-ray scattering (SAXS) technique.

We studied the molecular organization of Nafion (registered trademark of E. I. du Pont de Nemours and Co., Inc., for its perfluorinated sulfonic acid products) and their salts with Na$^+$, Cs$^+$, and propanediamine (SO_2NHR, R = $(CH_2)_3NH_2$) derivatives as well as that of the perfluorinated carboxylic acid and carboxylates which are obtained by chemical modification of the Nafion membranes.[21] The molecular organization of the ionic species as assessed in our studies can be compared with that obtained for other hydrocarbon-based carboxylated ionomer membranes, such as polyethylene, polystyrene, and polybutadiene.[4] Especially, the structure of the carboxylated perfluorinated ionomers should bear a close similarity to that of the ethylene ionomers with the following differences: (i) fluorocarbon chains are replaced by hydrocarbon chains and (ii) the number of carboxylic acid groups of typical perfluorinated ionomers is larger than that of the usual ethylene ionomers.

As in the hydrocarbon-based ionomers, the carboxylated and the sulfonated perfluorinated ionomers show clustering of ionic groups.[4] The ion clusters give rise to a SAXS maximum at $s = (2 \sin \theta)/\lambda$ (λ and 2θ being the wavelength of the X-rays and the scattering angle, respectively) approximately equal to the inverse of the cluster size. We show in this paper that, as in the case of the hydrocarbon-based ionomers, we can interpret this scattering maximum in terms of two models: (1) core–shell models, as proposed by MacKnight, Stein, and co-workers[5,6] (the scattering maximum being attributed to intraparticle interference of the core–shell-type clusters) and (2) a two-phase model proposed by Marx, Caulfield, and Cooper[7] (the maximum being attributed to interparticle interference between the ionic clusters). The origin of this "ionic scattering maximum" will be discussed in detail in a forthcoming paper.[8] In addition to the scattering maximum associated with the ionic clusters, the perfluorinated ionomer membranes generally exhibit another scattering maximum at an even smaller scattering angle. The origin of this maximum is here shown to be due to a regularity of the interlamellar spacing (section III-I).

In a recent publication, Roche et al.[23] reported results on small-angle neutron scattering (SANS) and SAXS from sulfonic acid and sodium sulfonate Nafion membranes having an equivalent weight (EW, i.e., weight of polymer which will neutralize 1 equiv of base) of 1200. They showed that there exist in general two types of small-angle scattering maxima of different origin: (i) the scattering maximum at small angles, which can be assigned to interference between crystalline structures, and (ii) the scattering maximum at larger angles, which can be assigned to the ionic clusters. Their conclusions are generally confirmed and further reinforced by the present studies, which extend the SAXS studies to a series of perfluorinated ionomer membranes having different equivalent weights, different cations (H$^+$, Na$^+$, Cs$^+$, etc.), and different anions (COO$^-$ and SO_3^-) (section V).

II. Experimental Section

1. Chemical Modifications and Test Specimens. A series of Nafion membranes with different equivalent weights (1100, 1150, 1200, 1400, and 1500) are chemically modified to prepare a series of sulfonic acid and carboxylic acid perfluorinated ionomer membranes having equivalent weights corresponding to the original Nafion membranes. For a given equivalent weight (1100), membranes in the form of sulfonic acid, sodium and cesium sulfonates, sulfonyl chloride (SO_2Cl), and sulfonamide (SO_2NHR, R = $(CH_2)_3NH_2$) as well as carboxylic acid and sodium carboxylate were prepared.

First we describe a procedure to prepare the carboxylic acid form (designated as Nf-COOH for convenience). The Nafion membrane was first treated with 2 N HCl for 3 h at 80 °C to prepare the sulfonic acid form, Nf-SO_3H. In this way we obtained a series of sulfonic acid forms. The membrane was then washed with water for 3 h, followed by reaction with 5% NH_4OH for 16 h at room temperature to obtain Nf-SO_2NH_4. The membrane was again washed with water for 4.5 h, dried under vacuum, and

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