dipole moments. It should be stressed in this regard that the temperature coefficients are in general small quantities corresponding to changes of only a few tenths percent per degree, and consequently, serious errors may be involved in their determination.

Registry No. PVK (homopolymer), 25067-59-8.

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Intrinsic Viscosity of Poly(hexyl isocyanate) in Butyl Chloride

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ABSTRACT: Zero-shear-rate intrinsic viscosities $[\eta]$ of poly(hexyl isocyanate) (PHIC), a typical semiflexible polymer, in butyl chloride at 25 °C were determined for 31 fractions ranging in weight-average molecular weight from 4×10^3 to 7×10^6. The measured values of $[\eta]$ indicated the chain conformation of PHIC to change continuously from a short rod to a long coil with an increase in molecular weight and could be fitted accurately by the Yamakawa–Fujii–Yoshizaki theory for unperturbed wormlike cylinders (Kratky–Porod chains) provided that the values of 760 nm^{-1}, 35 nm, and 1.5 nm were assigned to the molar mass per unit contour length, persistence length, and diameter of the PHIC chain, respectively.

Introduction

Poly(hexyl isocyanate) (PHIC) is known as a typical semiflexible polymer.[2,3] In a previous paper,[4] it was shown that the dimensions and particle scattering function of this polymer in hexane can be described accurately by an unperturbed Kratky–Porod wormlike chain. Thus, PHIC should be useful as a model polymer for checking hydrodynamic theories on unperturbed wormlike chains.

In the present study, 31 PHIC fractions covering a wide range of molecular weight were examined by viscometry, with butyl chloride chosen as the solvent, and the zero-shear-rate intrinsic viscosities $[\eta]$ obtained were compared with the Yamakawa–Fujii–Yoshizaki theory[5,6] for unperturbed wormlike cylinders.

Experimental Section

Preparation of Low Molecular Weight Samples. Previous investigators[7-9] found that poly(alkyl isocyanates) in carbon tetrachloride (CCl_4) containing a small amount of a strong acid such as trifluoroacetic acid (TFA) undergo degradation. To take advantage of this finding to prepare samples of lower molecular weights, we examined the degradation of high molecular weight PHIC in mixtures of CCl_4 and TFA.

Figures 1 and 2 show the changes in $(\ln \eta_r)/c$ with time that occurred following the addition of TFA to CCl_4 solutions. Here, η_r is the relative viscosity and c, the polymer mass concentration. It can be seen from Figure 1 that 30% TFA rapidly fragments PHIC of different chain lengths to nearly equal shorter chains. In Figure 2, the rate of degradation for a sample (viscosity-average molecular weight $M_v = 1.7 \times 10^5$) is seen to depend strongly on TFA composition.

On the basis of these data, we chose the composition of TFA and the duration of exposure to the mixed solvent suitable for degrading high molecular weight PHIC samples ($10^5 \lesssim M_v \lesssim 5 \times 10^6$) and obtained seven shorter chain products. The degraded products were washed with methanol, water, and acetone and freeze-dried from benzene solutions. Elemental analysis showed no difference in chemical composition between the purified degraded and undegraded original samples.

Each of the degraded samples was divided into several parts by repeating fractional precipitation with CCl_4 as the solvent and methanol as the precipitant. Twelve fractions designated below as f-1, f-2, ..., f-12 were chosen, reprecipitated from CCl_4 solutions into methanol, and freeze-dried from benzene solutions. The high molecular weight fractions (F-1, F-2, ..., F-19) prepared in our previous work[4] were added to these fractions.

Sedimentation Equilibrium. The weight-average molecular weights M_w of fractions f-1, f-2, ..., f-12 were determined by sedimentation equilibrium in a Beckman Model E ultracentrifuge with butyl chloride at 25 °C as the solvent.[10] A Kel-F 12-mm double-sector cell was used, and the liquid column was adjusted to 1.5–2.0 mm. The rotor speed ranged from 15000 to 30000 rpm depending on the fraction studied.

The solvent butyl chloride (Wako Pure Chemicals) was fractionally distilled over calcium chloride. The partial specific volume of PHIC in this solvent at 25 °C was determined to be 0.952 cm^3 g^{-1}, with fractions f-3, f-7, and f-8 used for the measurements. This value is very close to 0.950 cm^3 g^{-1} determined previously[4] for high molecular weight PHIC in hexane. The density of butyl chloride at 25 °C was 0.91272 g cm^{-3}.

The specific refractive index increment of PHIC in butyl chloride at 25 °C for 546-nm wavelength was 0.0916 cm^3 g^{-1}, independent of the molecular weight of the polymer.

Viscometry. Viscosities of high molecular weight fractions F-5, F-6, ..., F-19 in butyl chloride at 25 °C were measured at shear rates G lower than 1 s^{-1}, using a rotational viscometer of the Zimm–Crothers type.[11] The measured $(\ln \eta_r)/c$ were equated to the zero-shear-rate values, since they were independent of G.

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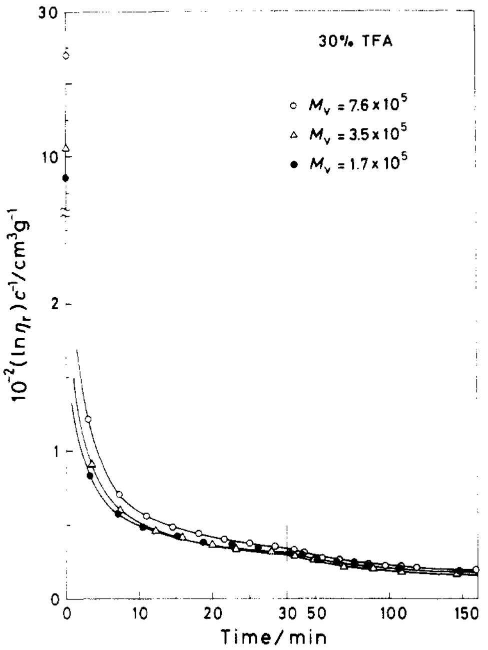

Figure 1. Changes in $(\ln \eta_r)/c$ with time at 25 °C following the addition of TFA to CCl_4 solutions of PHIC samples with different molecular weights. TFA composition, 30 vol %; c, 1.4 × 10^{-3} g cm^{-3}.

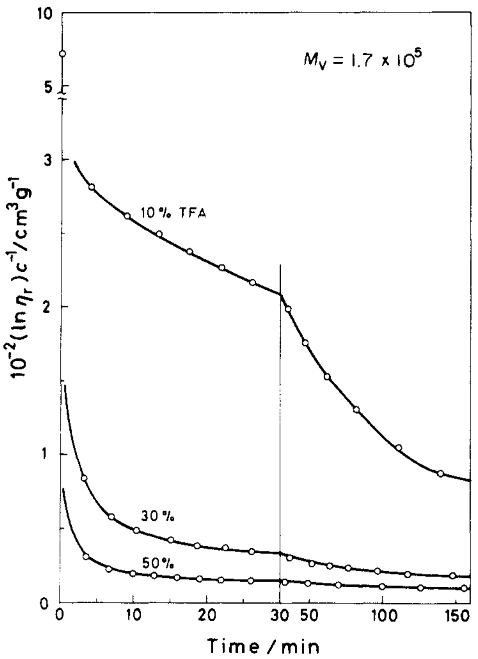

Figure 2. Changes in $(\ln \eta_r)/c$ with time at 25 °C following the addition of TFA to CCl_4 solutions of a PHIC sample (c = 1.4 × 10^{-3} g cm^{-3}).

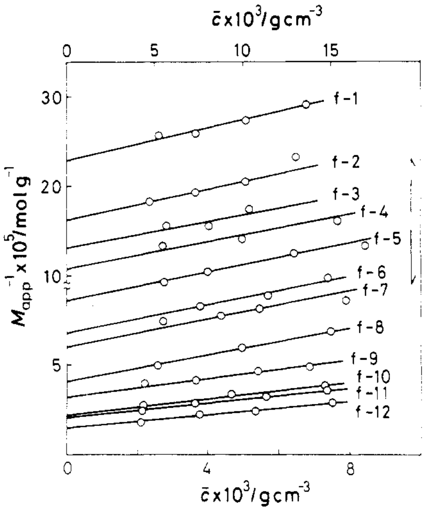

Figure 3. Sedimentation equilibrium data for acid-degraded PHIC samples in butyl chloride at 25 °C.

Table I
Results from Sedimentation Equilibrium and Viscosity Measurements on PHIC Fractions in Butyl Chloride at 25 °C

fraction	M_w × 10^{-4}	A_2 × 10^3/(cm^3 mol g^{-2})	[η] × 10^{-2}/(cm^3 g^{-1})	k'
f-1	0.439	2.2	0.0631	0.59
f-2	0.617	2.1	0.0828	0.52
f-3	0.758	1.8	0.116	0.52
f-4	0.926	1.8	0.144	0.49
f-5	1.16	2.0	0.181	0.49
f-6	1.47	2.0	0.228	0.45
f-7	1.66	1.9	0.303	0.43
f-8	2.38	1.7	0.436	0.40
f-9	3.00	1.2	0.703	0.39
f-10	4.52	1.2	1.19	0.38
f-11	4.78	1.0	1.27	0.39
f-12	6.76	0.92	2.06	0.38
F-1	6.80[a]		2.08	0.38
F-2	8.14[a]		2.61	0.38
F-3	11.2[a]		3.52	0.38
F-4	13.2[a]		4.47	0.38
F-5	18.0[a]		6.16	0.38
F-6	25.5[a]		8.76	0.37
F-7	31.1[a]		10.5	0.38
F-8	38.7[a]		12.9	0.39
F-9	50.5[a]		16.7	0.39
F-10	65.6[a]		21.8	0.39
F-11	94.7[a]		29.5	0.40
F-12	117[a]		34.7	0.39
F-13	149[a]		43.4	0.40
F-14	169[a]		48.1	0.40
F-15	241[a]		63.7	0.44
F-16	318[a]		74.3	0.42
F-17	334[a]		78.4	0.45
F-18	463[a]		106	0.46
F-19	724[a]		154	0.39

[a] From light scattering in hexane.

Those for fraction F-5 determined by the rotational viscometer and a capillary viscometer of the Ubbelohde type agreed with each other. Thus, the latter was used for lower molecular weight fractions f-1, f-2, ..., f-12 and F-1, ..., F-4.

Results

Figure 3 shows plots of M_{app}^{-1} (the reciprocal of an apparent molecular weight obtained by the sedimentation equilibrium measurements) vs. $\bar{c}$ (the mean polymer concentration) for acid-degraded PHIC samples in butyl chloride at 25 °C. The values of M_w and A_2 (the second virial coefficient) evaluated from the intercepts and slopes of the indicated straight lines are summarized in Table I, along with those of M_w for higher molecular weight fractions determined previously[4] by light scattering in hexane. This table also gives the values of [η] and k' (the Huggins constant) for all the PHIC fractions in butyl chloride.

The unfilled circles in Figure 4 show the molecular weight dependence of [η] in butyl chloride. The thick curve fitting them has an inflection point at $M_w \sim 2 \times 10^4$. Its slope is about 1.4 at this point and decreases to about 0.78 for M_w above 10^6. This decrease in slope suggests that the PHIC chain changes its shape from a weakly bent rod to a spherical coil with an increase in molecular weight. Below the inflection point, the slope decreases somewhat sharply with a decrease in M_w, as predicted theoretically

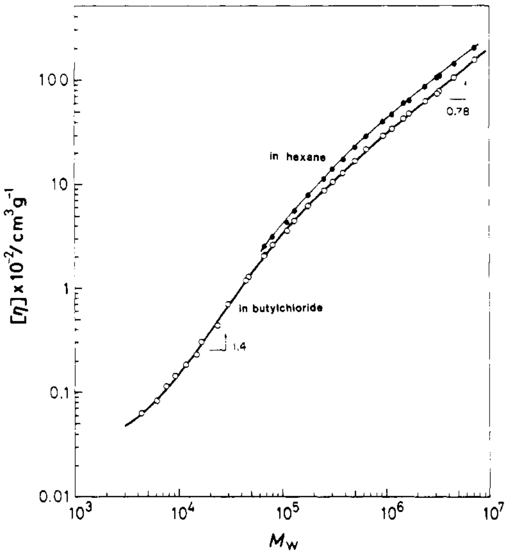

Figure 4. Molecular weight dependence of $[\eta]$ for PHIC in butyl chloride at 25 °C. Filled circles, previous data[4] in hexane at 25 °C.

by Yamakawa and Yoshizaki[6,12] for short rodlike molecules.

The filled circles in Figure 4, representing our previous data[4] for PHIC in hexane, appear systematically above the curve for butyl chloride. This difference indicates that the dimensions of PHIC in dilute solution are appreciably affected by the kind of solvent.

Discussion

Determination of Wormlike Chain Parameters. The Yamakawa–Fujii–Yoshizaki theory[5,6] for $[\eta]$ of an unperturbed wormlike cylinder capped with two hemispheres at its ends contains three parameters, M_L (the molar mass per unit contour length), q (the persistence length), and d (the cylinder diameter). Bushin et al.[13] and Bohdanecký[14] independently showed that this theory can be replaced approximately by

$$(M^2/[\eta])^{1/3} = A + BM^{1/2} \quad (1)$$

with

$$A = 1.516 \times 10^{-8} A_0 M_L \quad (\mathrm{g}^{1/3}\ \mathrm{cm}^{-1}) \quad (2)$$

$$B = 1.516 \times 10^{-8} B_0 (M_L/2q)^{1/2} \quad (\mathrm{g}^{1/3}\ \mathrm{cm}^{-1}) \quad (3)$$

where M is the molecular weight of the cylinder and A_0 and B_0 are certain known functions of $d/2q$.[15] It should be noted that for $d/2q \sim 10^{-2}$ (typical semiflexible chains) eq 1 is applicable to as wide a range of the Kuhn statistical segment number n_K ($\equiv M/2qM_L$) as from 0.4 to 300.[14]

Figure 5 shows the plot of $(M_w^2/[\eta])^{1/3}$ vs. $M_w^{1/2}$ constructed from the present data. The data points for $250 < M_w^{1/2} < 2000$ are fitted accurately by a straight line whose intercept and slope are equal to 156 and 0.528 $\mathrm{g}^{1/3}\ \mathrm{cm}^{-1}$, respectively. For $M_w^{1/2} < 250$, the data points deviate progressively from this line with decreasing $M_w^{1/2}$. This deviation, along with the intercept and slope values, may be used for determining the three unknown parameters, q, M_L, and d.

The inset of Figure 5 shows the $[\eta]$ values for $M_w^{1/2} < 250$ plotted double logarithmically against M_w. The solid curves have been calculated from the Yamakawa–Fujii–Yoshizaki theory[6] for the indicated d values with $A = 156$ $\mathrm{g}^{1/3}\ \mathrm{cm}^{-1}$ and $B = 0.528$ $\mathrm{g}^{1/3}\ \mathrm{cm}^{-1}$. When combined, the two relations $A_0 M_L = 1.03 \times 10^{10}\ \mathrm{cm}^{-1}$ and $B_0(M_L/2q)^{1/2} = 3.48 \times 10^7\ \mathrm{cm}^{-1}$ yield $M_L = 790\ \mathrm{nm}^{-1}$ and $q = 36$ nm, $M_L = 760\ \mathrm{nm}^{-1}$ and $q = 35$ nm, and $M_L = 720\ \mathrm{nm}^{-1}$ and $q = 33$ nm for $d = 2.0$, 1.5, and 1.0 nm, respectively. It appears that the curve for $d = 1.5$ nm gives the best fit to the data points, and hence it may be concluded that M_L, q, and d for PHIC in butyl chloride are 760 nm^{-1}, 35 nm, and 1.5 nm, respectively.

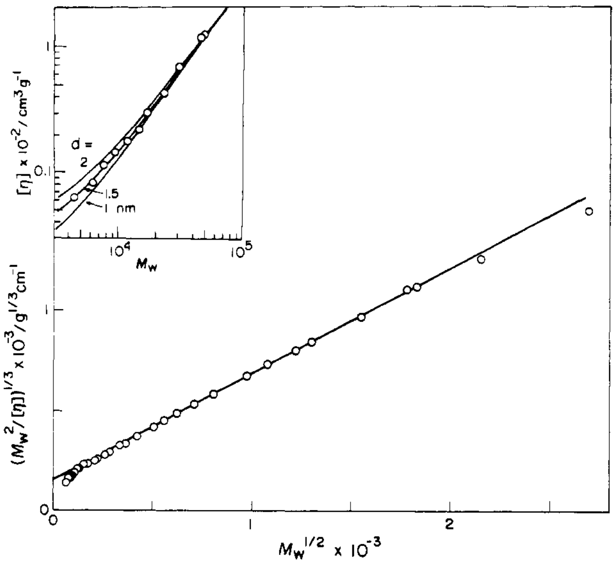

Figure 5. Plot of $(M_w^2/[\eta])^{1/3}$ vs. $M_w^{1/2}$ for PHIC in butyl chloride. The circles and the curves in the insert represent, respectively, the measured $[\eta]$ for $M_w^{1/2} < 250$ and the theoretical $[\eta]$ calculated from the Yamakawa–Fujii–Yoshizaki theory[6] for the indicated d values (see text).

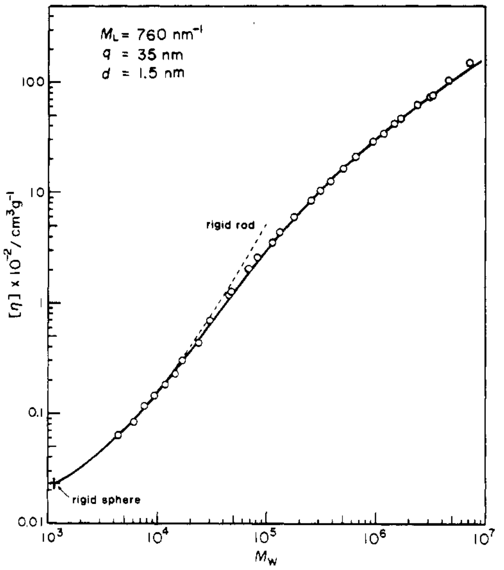

Figure 6. Comparison between the measured $[\eta]$ for PHIC in butyl chloride and the Yamakawa–Fujii–Yoshizaki theoretical values (the solid line) for $M_L = 760\ \mathrm{nm}^{-1}$, $q = 35$ nm, and $d = 1.5$ nm. Dashed line, theoretical values for rigid cylinders ($M_L = 760\ \mathrm{nm}^{-1}$ and $d = 1.5$ nm); cross, theoretical value for a rigid sphere ($d = 1.5$ nm).

These M_L and d values may be compared favorably with 715 nm^{-1} and 1.6 nm determined previously[4] from radius of gyration and $[\eta]$ data for PHIC in hexane, while the q value is distinctly smaller than the previous value[4] of 42 nm in hexane. Thus, the difference in $[\eta]$ between butyl chloride and hexane observed in Figure 4 may be ascribed primarily to the difference in q between the two solvents.

Comparison between Theory and Experiment. Figure 6 compares our $[\eta]$ data in butyl chloride with the Yamakawa–Fujii–Yoshizaki theoretical values calculated for $M_L = 760\ \mathrm{nm}^{-1}$, $q = 35$ nm, and $d = 1.5$ nm. Except for the highest molecular weight fraction, the agreement between theory and experiment is very satisfactory. It is to be noted that the Yamakawa–Fujii–Yoshizaki theory predicts correctly the S-shaped experimental log $[\eta]$ vs. log M_w relation. The data point for the highest molecular weight fraction may be expected to depart from the theoretical curve because of an excluded-volume effect. In fact, the n_K value of 136 for this sample exceeds the critical n_K ($\sim$50) previously estimated[16] for the onset of volume effect on the average dimensions of a linear polymer chain.

The dashed line in Figure 6 represents the theoretical values calculated from the Yoshizaki–Yamakawa equation[12] for rigid cylinders capped with hemispheres, with $M_L = 760\ \text{nm}^{-1}$ and $d = 1.5$ nm. It substantiates that the PHIC chain in butyl chloride is almost completely rigid for M_w below 10^4. The cross mark in Figure 6 indicates the limit where the axial ratio becomes unity, i.e., a rigid sphere of 1.5 nm in diameter. The theoretical value of $[\eta]$ (2.33 $\text{cm}^3\ \text{g}^{-1}$) for this sphere happens to be very close to 2.38 $\text{cm}^3\ \text{g}^{-1}$ calculated from the Einstein equation for a compact sphere whose density is equal to the inverse of the partial specific volume (0.952 $\text{cm}^3\ \text{g}^{-1}$) of PHIC in butyl chloride.

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Molecular Weight Dependence of Preferential Adsorption

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ABSTRACT: The dependence of preferential adsorption coefficient (λ) on molecular weight (M), or on segment density, is usually expressed empirically by the equations $\lambda = \lambda_\infty + AM^{-1/2}$ or $\lambda = \lambda_\infty + K[\eta]^{-1}$ ($[\eta]$, intrinsic viscosity; A and K, constants). No attempt has been made until now to predict theoretically the magnitude of such dependence (to calculate K or A). Using just general thermodynamic relationships, we derive an equation which allows the calculation of these constants from other experimental properties of the system such as the second virial coefficient or the intrinsic viscosity. This equation predicts that the M dependence of λ should be large in solvent + precipitant mixtures and should vanish when the total sorption potential of the coil is at a maximum. These predictions are in agreement with experimental data from the literature. In order to provide experimental data of K on systems representing different combinations of solvent power, we have determined λ and $[\eta]$, as functions of M, for PMMA samples in three solvent mixtures: good solvent + precipitant (benzene + 1-butanol), a cosolvent pair (CCl_4 + butyl chloride), and two good solvents (1,2-dichloroethane + ethyl acetate). The experimental results for these systems are qualitatively well described by our theoretical equation. Quantitative agreement is also possible if the single-liquid approximation is used for the total sorption.

Introduction

Experimental results of preferential sorption by polymers in mixed solvents have shown that the coefficient of preferential adsorption, λ, for a given polymer in a solvent mixture of fixed composition, depends on the molecular weight of the polymer sample, M.[1-11] However, this dependence of λ on M has not always been detected. According to Dondos and Benoit,[2] it is detectable only for molecular weights lower than a certain value.

The empirical dependence of λ with M was originally described by means of the law[1]

$$\lambda = \lambda_\infty + AM^{-1/2} \tag{1}$$

where λ_∞ is the value of λ extrapolated to $M \rightarrow \infty$, and A is a constant for each solvent composition. The variation of λ with M has been attributed to the influence of the coil segment density on preferential adsorption.[1]

Theoretical expressions from which the molecular weight dependence of λ could be deduced have been derived by Shultz and Flory,[12] by Read,[13] and by Pouchlý, Živný, and Šolc.[14,15] Dondos and Benoit[1] have calculated explicitly the theoretical dependence of λ on M with the result

$$\lambda = \lambda_\infty + A'M^{-1/2}\alpha^{-3} \tag{2}$$

where α is the coil expansion factor and A' a constant. As a measure of coil expansion, Dondos[16] and also Katime[17] have taken the intrinsic viscosity, $[\eta]$. By writing

$$\alpha^3 = [\eta]/K_\Theta M^{1/2} \tag{3}$$

where K_Θ means unperturbed dimensions, they arrive at equations of the form

$$\lambda = \lambda_\infty + K[\eta]^{-1} \tag{4}$$

with K again a constant for each mixed-solvent compo-

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