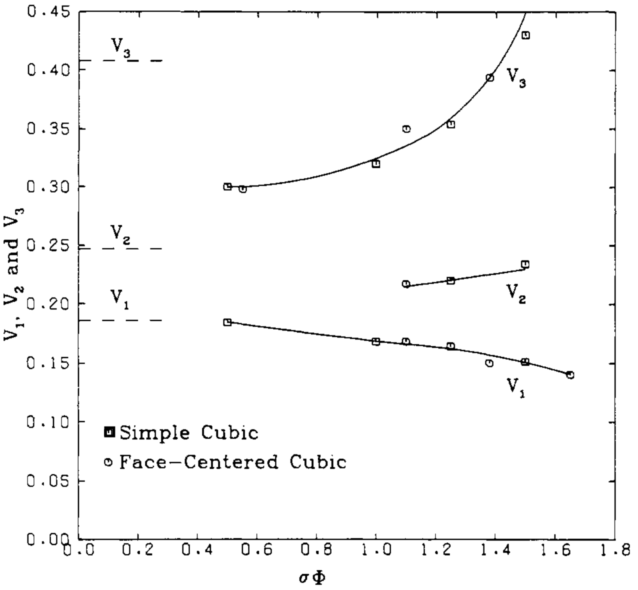

Figure 3. The relative variances of the principal moments for chains *vs.* $\sigma\Phi$.

Φ increases. These results say that the absolute variance along the long direction of the molecules is much greater than that along the other two directions.

In Figure 3 we have also noted by dashed lines the random-coil values of V_i as computed from the data of Šolc for five-choice chains of 200 segments.

Conclusions

The asymmetry of a random chain with excluded volume and attractive energies between segments was investigated for chains on the face-centered cubic and simple cubic lattices. The ratios of the ordered principal moments to the radius of gyration of the chains, the shape factors, differed greatly from the value of 1/3 for a symmetrical chain when viewed on their principal axes.

The shape factors have been found to be independent of the chain length in the range of N = 50-500. The shape factors are seen by Table I and Figure 1 to get slightly closer to the value 1/3 of a symmetrical polymer as Φ increases. Thus the chains become slightly more symmetrical with increasing attractive energies between segments. For Φ between 0.25 and 0.3 on the simple cubic lattice, the shape factors have the values for a random coil previously calculated by Stockmayer and Šolc.[2] This is the critical range of Φ in which other properties of the chain have been found in paper I to equal the random-coil values. The shape factors were also found to be independent of the lattice when plotted *vs.* $\sigma\Phi$. $\langle L_3{}^2\rangle/\langle S^2\rangle$ was found to have the value of a random coil at $\sigma\Phi = 1.29$, while $\langle S^2\rangle$ has the value of a random coil at $\sigma\Phi = 1.39$. However, the shape factors show much less variation with Φ than does $\langle S^2\rangle$ and do not deviate greatly from the random-coil values.

The relative variations (V_1, V_2, and V_3) among chain configurations of the principal moments have also been calculated. Some dependence on the chain length was found, so the variations of the moments were extrapolated to infinite chain lengths whenever possible. The variation V_3 of the largest principal moment is seen in Figure 3 to be much larger than the variations of the other principal moments, and to increase with increasing interaction parameter Φ. Also, the variations of the principal moments are independent of lattice when plotted *vs.* $\sigma\Phi$.

Intrinsic Viscosity Measurements on Rodlike Poly(*n*-butyl isocyanate) and Poly(*n*-octyl isocyanate)

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ABSTRACT: Previous calculations of the molecular length of rodlike poly(*n*-butyl isocyanate), $(\text{-CO-NC}_4\text{H}_9\text{-})_n$, from dielectric relaxation time measurements have not shown satisfactory agreement with the results from X-ray and light-scattering measurements. Here, we examine this conflict by extending our hydrodynamic experiments to include intrinsic viscosity measurements on well-characterized low molecular weight samples of poly(*n*-butyl isocyanate) (PBIC) and poly(*n*-octyl isocyanate) (POIC), $(\text{-CO-NC}_8\text{H}_{17}\text{-})_n$. Using the Kirkwood-Auer-Riseman equation relating intrinsic viscosity and rod dimensions, the intermonomer translation along the rod axis is calculated to be 1.66 ± 0.12 Å. This is lower than the 1.94-Å result from X-ray measurements, but higher than the 1.33 ± 0.12 Å result from dielectric relaxation time measurements. The root of the problem appears to be the application of hydrodynamic equations to a physical situation which does not satisfy the model assumptions.

The rodlike molecular posture of low molecular weight poly(*n*-butyl isocyanate) (PBIC) in solution has been the object of measurement in many experiments. These measurements, dielectric,[2a,b,3] light scattering,[4] electric dichroism,[5,6] electric birefringence,[7,8] rotatory diffusion,[8] and intrinsic viscosity,[8] demonstrate the rigid rod conformation of the polymer molecule. However, the quantita-

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tive results of these experiments, particularly the calculation of the projected intermonomer distance L_0, are not in agreement. Experimental values of L_0 range from 1.1-1.3 Å (relaxation time measurements)[2a,3] to 2.0 Å (light scattering[4] and intrinsic viscosity[8]). The latter value agrees with X-ray measurements[9] on PBIC in the solid state from which L_0 = 1.94 Å. The difference in molecular dimensions between the liquid and solid state is not expected to be as large as 1.1 Å *vs.* 1.94 Å and, therefore, we have extended our measurements in order to isolate the source of the problem. The measurements which we report here are intrinsic viscosity measurements on well-characterized low molecular weight fractions of PBIC and poly(*n*-octyl isocyanate) (POIC). These measurements are compared with the dielectric relaxation time measurements. The applicability of the hydrodynamic equations is reviewed.

For a rigid rod molecule in solution, the relaxation time, τ, as a function of molecular dimensions was first calculated by Perrin[10] and subsequently by others.[11-13] For a rod of length L and radius b in a solvent of viscosity N_0

$$\tau = \frac{\pi N_0 L^3}{6KT(\ln L/b - \gamma)} \qquad L \gg b \qquad (1)$$

where γ is a constant or a slowly varying function of L and b which, as derived by different authors, takes on values between 0 and 1.6. The molecular weight M is proportional to L for a rod, so that in the range of L and b of interest here $\tau \propto M^{2.7}$. For the intrinsic viscosity of a rigid rod in solution[12]

$$[\eta] = \frac{4\pi N L^3}{9 \times 10^3 M \ \ln L/b} \qquad L \gg b \qquad (2)$$

where N is Avogadro's number. From this equation, the power dependence of $[\eta]$ on molecular weight M in the range of L and b of interest, is $[\eta] \propto M^{1.85}$. The criteria which we have used to demonstrate the rod conformation of the poly(*n*-alkyl isocyanates) are the 2.7 slope of the log τ *vs.* log M plot,[2a] and the 1.85 slope of the log $[\eta]$ *vs.* log M plot to be shown below.

In view of the disagreement arising from the use of eq 1 and 2, it will be useful to review the assumptions which underlie the derivation of these equations. Both the intrinsic viscosity and relaxation times are derived by assuming a macroscopic view of the solute molecule. This entails the following. (a) The dimensions of the solute molecule must be large relative to solvent molecule. For PBIC and POIC, the diameters[4,7-9] are in the range of 10-20 Å and may not be large enough (compared to 3.75 Å for CCl_4) to approximate the infinite size ratio assumption. (b) The molecule is a solid geometric body which the solvent molecules do not penetrate. For the main chain of the alkyl isocyanate polymer this is true. But, the alkyl side chains, which have some freedom of movement even in the solid state, bend and drift through the solvent. It is probable that the side groups produce hydrodynamic shielding different from that calculated using the Oseen tensor for a solid cylinder. A flexible side chain can affect more than just the apparent diameter of the molecule.

The different geometrical shapes which have been assumed in these calculations, an ellipsoid,[10] a rigid string of spherical beads,[12] and a cylinder,[11,13] give different values for γ in eq 1. Broersma's calculation ($\gamma \approx 1.55$) took into account the effect of the square ends of a cylinder and gives L_0 values 15-20% less than the Kirkwood-Auer-Riseman equation ($\gamma = 0$). The Broersma equation was specifically developed to deal with the hydrodynamic data on tobacco mosaic virus (TMV). This molecule is a closely packed helical protein which entwines an inner helix of RNA. TMV is aptly described as a solid cylinder since a molecular weight of 40×10^6 occupies a compact space 170 Å in diameter and 3000 Å in length.[14] A square-ended cylindrical view of the polypeptides and the poly(*n*-alkyl isocyanates) is probably inappropriate because of the much smaller diameter of the molecule and the somewhat flexible end groups. In several experiments with the polypeptides, a cylindrical model has been rejected in favor of an ellipsoid.[15,16]

Whether or not assumptions (a) and (b) are satisfied by a particular system can be ascertained by using eq 1 and 2 to calculate L and then comparing with the absolute results from other experiments such as light-scattering and X-ray measurements. At the present time these hydrodynamic equations cannot be used *a priori* to calculate molecular dimensions with reasonable accuracy until their application has been verified by other measurements. For the relaxation time and intrinsic viscosity measurements on PBIC and POIC we have chosen the Kirkwood-Auer-Riseman model ($\gamma = 0$) of a rigid string of beads because the calculated L_0 is the closest attainable agreement with X-ray data.[9] It is decided, as in the case with the polypeptides, that the Broersma model is not applicable here.

Although both the relaxation time and intrinsic viscosity equations are derived making the same assumptions, the phenomena differ. Whereas intrinsic viscosity is a property of the solution in the steady state, the relaxation time is a measure of the time of decay from a perturbed to an unperturbed state. Also, the relaxation times and intrinsic viscosities have a different functional dependence on molecular weight, so that for a sample with a distribution of molecular weights, the relaxation time and intrinsic viscosity correspond to different moments of distribution. These differences are reflected in the values of average L_0 which result from the two measurements. Our data show that the average L_0 from τ measurements is significantly less than the average L_0 from $[\eta]$ measurements.

Extensive measurements of both the relaxation time and intrinsic viscosity on rodlike polypeptides have also been beset with a lack of agreement regarding L_0. Measurements by Yang[15,17] on poly(benzyl L-glutamate) give satisfactory agreement but other measurements on PBLG and other biological molecules yield results which are less than satisfactory.[16,18-21] A review by Benoit and coworkers[21] points out these problems and discusses the use of eq 1 and 2.

By extending our measurements from PBIC to include POIC, we affect a change in molecular diameter while keeping the intermonomer length L_0 constant. Since the alkyl group is in the side chain, changing the length of the side group from *n*-butyl to *n*-octyl should not change the

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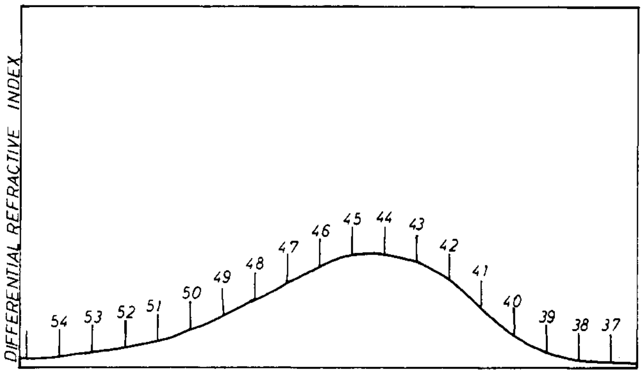

Figure 1. Gel permeation chromatogram of PBIC-2A.

C-N bond length in the main chain. X-Ray measurements verify that L_0 is the same in both polymers.[22] The question we pose is: Does the larger diameter POIC molecule behave in closer agreement with eq 1 and 2 than does PBIC? These results will show that no significant effect of the larger diameter is seen in the intrinsic viscosity and relaxation time measurements. Using the Kirkwood–Auer–Riseman[12] (KAR) equation, and the measured $[\eta]$ values, the resultant average value of $L_{0[\eta]}$ is 1.66 ± 0.12 Å, where 0.12 Å is an estimated standard deviation obtained from twelve $L_{0[\eta]}$ values. The average value of $L_{0\tau}$ calculated using the KAR equation and 17 τ measurements is 1.33 ± 0.12 Å, where 0.12 Å is again the estimated standard deviation.

In these experiments we have made an effort to make measurements of τ and $[\eta]$ on the same sample. Also we have taken all reasonable precautions with the samples to insure that we are working with well-characterized and uniformly narrow molecular weight fractions.

Experimental Section

Sample Preparation and Characterization. The synthesis,[23] fractionation[2a] and the characterization[2b,4] of the poly(*n*-alkyl isocyanates) (with the exception of PBIC-2A-9) have been described previously. The samples of PBIC and POIC which we have chosen for this study are fractions with weight-average degrees of polymerization, n_w, less than 1.4 × 10^3. Samples with higher degrees of polymerization (samples 14-3 and 37′-1a) cannot be considered in a quantitative manner since these polymers possess greater flexibility[2a,4,6] and are thus non-rodlike in behavior.

The PBIC samples 41, K1-2, 2A, and 21 were obtained with narrow molecular weight distributions directly from the polymerization. For sample K1-2, α-phenylethylpotassium was used as the initiator, while *n*-butyllithium was the initiator for the other three samples. As before,[23] toluene was the polymerization solvent. The change in the synthesis procedure which permitted the preparation of samples with narrow molecular weight distributions was a decrease in monomer concentration to about 1-2% (v/v) solutions. This lower concentration range resulted in polymerizations where the solution remained relatively fluid with no evidence of polymer insolubility. Previously, the polymerizations run at higher monomer concentrations, 5-10%, resulted in the formation of an opaque, highly viscous gel. The apparent partial insolubility of PBIC during polymerization prepared under these conditions was doubtlessly the cause of the broad molecular weight distributions found[23] for those samples.

The characterization data for our fractions are listed in Table I. The weight-average molecular weights, $\langle M_w \rangle$, and the number-average molecular weights, $\langle M_n \rangle$, were determined from light-scattering and osmotic pressure measurements described elsewhere.[4] The half-width of the dielectric dispersion curve, $W/2$, is measured in decades of frequency. The half-width has been correlated[2b] with the ratio, $\langle M_w \rangle / \langle M_n \rangle$; if $W/2 < 2.10$, then $\langle M_w \rangle / \langle M_n \rangle < 1.20$. In Table I, the values of $\langle M_w \rangle / \langle M_n \rangle$ recorded have been obtained from $W/2$ measurements except where $\langle M_n \rangle$ has been measured.

Table I
Characterization Data of PBIC and POIC Fractions

Sample	$\langle M_w \rangle \times 10^{-4}$	$\langle M_n \rangle \times 10^{-4}$	$W/2$ Decades	$\langle M_w \rangle / \langle M_n \rangle$
		PBIC		
37′-2b	2.0		1.75	1.15
41	2.5	2.2	1.80	1.14
37-4	3.5		1.60	1.10
40-5	3.5		1.55	1.09
CN-6	3.5		1.50	1.07
37′-2a	5.1		1.70	1.12
K1-2	6.2	5.2	1.90	1.19
37-3	7.3		2.10	1.20
2A-9	9.5	8.5	1.80	1.12
1-d″	10.3		1.70	1.12
2A	12.5	11.1	1.90	1.13
21	13.3	12.0	2.05	1.11
1′f	14.0		2.00	1.19
14-3	28.0		2.10	1.20
37′-1a	38.0		1.65	1.10
		POIC		
02-5	5.9		1.50	1.07
02-4	10.0		1.45	1.05
02-3	14.0	13.1	1.50	1.07
02-2	20.0		1.70	1.12

The fact that our samples had symmetrical and narrow molecular weight distributions is fortified by the gel permeation chromatogram of PBIC-2A shown as Figure 1. The instrument used was the Waters Ana-Prep with tetrahydrofuran as the solvent at a temperature of 45°. A flow rate of 0.25 ml $\min^{-1}$ was used. A differential refractive index detector was used with the following columns of polystyrene gel: (2-5) × 10^3 Å, two columns with (5-15) × 10^3 Å, (1.5-5) × 10^4 Å, (5-15) × 10^4 Å, (1.5-7) × 10^5 Å, and 7 × 10^5 to 5 × 10^6 Å.

The weight to number-average molecular weight ratio calculated from the GPC trace was 1.3, which, within the limits of accuracy, is in agreement with the value listed in Table I. This ratio was determined with the aid of a calibration generated by the use of samples 21, 41, and K1-2. Over this molecular weight range a linear relation between peak elution count and $\langle M_w \rangle$ was observed. It should be noted that the seven column set used in this work when calibrated with standard polystyrene samples yielded a linear relationship between log M_w and peak elution volume over a molecular weight range of 4 × 10^3 to 2 × 10^6.

The PBIC sample 2A-9 was fractionated from the original 2A material by the use of a preparative column in the Waters Ana-Prep instrument. The column contained a 5 × 10^4 to 5 × 10^5 Å polystyrene gel. Benzene was the solvent and the flow rate was 5 ml $\min^{-1}$. Subsequent characterization demonstrated that the 2A-9 fraction was the lowest molecular weight fraction of the nine collected. The remaining eight fractions were combined to yield the 2A sample examined in this work since measurements of the relaxation times and $W/2$ revealed that these eight fractions possessed virtually identical molecular weights and distributions.

As were the dielectric dispersion measurements,[2a,b] the intrinsic viscosities were measured in carbon tetrachloride. Since the relaxation times of the PBIC and POIC polymers in solution are long (10^{-4}–10^{-3} sec), it is necessary to make the intrinsic viscosity measurements at low shear rates. Two Cannon-Ubbelohde four bulb variable shear rate viscometers were used. One had shear rates in the range of 43.8-202 $\sec^{-1}$, while the other had a range of 50-240 $\sec^{-1}$. Over this range our intrinsic viscosities were independent of shear rate. A cross-check between the viscometers was made with PBIC 21 and the results agreed within experimental error. POIC 02-3 was also examined with a Couette viscometer[24] with a specially designed drive. The shear rate employed was less than 0.1 $\sec^{-1}$. The intrinsic viscosity thus determined was in

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Table II
Molecular Constants of PBIC and POIC Fractions

Sample	$\langle M_w \rangle \times 10^{-4}$	log τ (sec)	L_0 (τ), Å	[η], dl/g	L_0 ([η]), Å	k
			PBIC			
37′-2b	2.0	−6.40	1.22			
41	2.5	−5.95	1.40	0.42	1.50	0.68
37-4	3.5	−5.70	1.24			
40-5	3.5	−5.75	1.19	0.86	1.54	
CN-6	3.5	−5.75	1.19	0.90	1.56	
37′-2a	5.1	−5.35	1.20			
K1-2	6.2	−4.75	1.49	3.80	1.80	0.39
37-3	7.3	−4.70	1.35			
2A-9	9.5	−4.40	1.31	6.60	1.66	0.27
1-d″	10.3	−4.35	1.27			
2A	12.5	−4.30	1.20	10.4	1.67	0.44
21	13.3	−3.90	1.41	11.5	1.67	0.72
1′f	14.0	−4.00	1.23	10.0	1.50	0.43
14-3	28.0	−3.40		21.3		0.57
37′-1a	38.0	−2.90		33.0		0.97
			POIC			
02-5	5.9	−5.30	1.48	0.76	1.60	0.0
02-4	10.0	−4.65	1.49	2.68	1.82	0.27
02-3	14.0	−4.25	1.51	5.10	1.80	0.27
02-2	20.0	−3.85	1.47	9.30	1.76	0.38

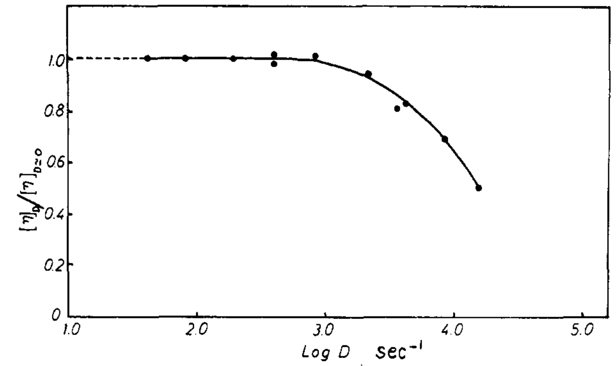

Figure 2. Intrinsic viscosity dependence on the rate of shear.

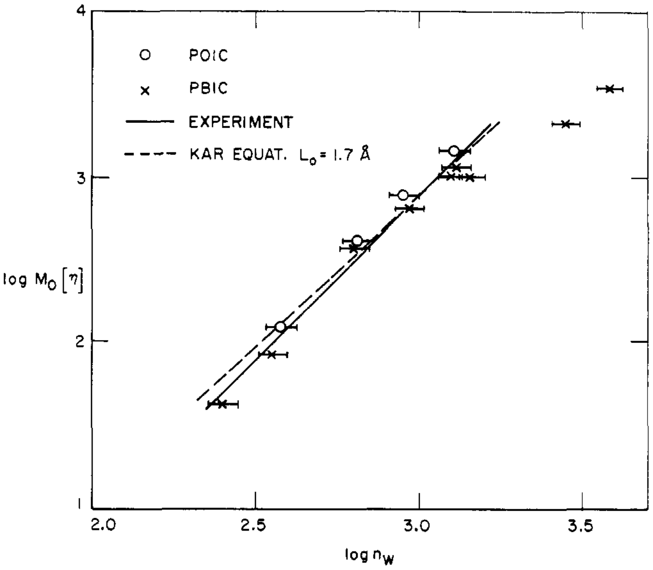

Figure 3. The dependence of log $M_0[\eta]$ on the log of the weight-average degree of polymerization, n_w.

agreement with those values determined from the Cannon-Ubbelohde viscometers. Thus the intrinsic viscosity values in Table II can be taken as identical with those which would be obtained at zero rate of shear. The uncertainty in the intrinsic viscosity measurements is ±3%. All measurements were made at 22.0 ± 0.5°.

The necessity of using viscometers with low rates of shear is shown in Figure 2. Here the intrinsic viscosities of a polydisperse PBIC sample ($\langle M_w \rangle = 7.4 \times 10^5$) were measured at various rates of shear (D). It is readily apparent that the intrinsic viscosity is quite dependent on shear rate. Thus, low rates of shear are necessary in order to obtain meaningful intrinsic viscosity values.

The estimated uncertainty in the other measured quantities considered here are: for molecular weight, ±10%; for τ, ±3%; and for concentration, ±1%.

Results and Discussion

In the analysis to follow, we confine our attention to the limiting behavior at low molecular weight. We know from other experiments[2a-8] that rigid rod conformation is present in the poly(*n*-alkyl isocyanates) at low molecular weight and, therefore, it is appropriate to consider the KAR theory of rigid rod hydrodynamic behavior. Only data for $n_w < 1.4 \times 10^3$ is treated in the analysis and data for samples 14-3 and 37′-1a are presented only to show that deviation from rodlike behavior does occur for $n_w > 2.0 \times 10^3$.

The numerical values of the relaxation times and the intrinsic viscosities are listed in Table II along with the values of the Huggins constant, k, which occurs in the concentration dependence of n_{sp}/c. The values of τ and $[\eta]$ are used in eq 1 and 2 to calculate L_0 and the results are also shown in Table II. We have used $L = n_w L_0$. In applying eq 1 and 2 we take advantage of the fact that, for $L \gg b$, τ and $[\eta]$ are insensitive to changes in the factor ln L/b in the denominator. For the calculation we let $L/b = n_w L_0/b$ and the ratio L_0/b is assigned the value 0.30, *i.e.*, L_0 = 2 Å and $b \approx$ 7 Å. Here, $2b$ is the diameter of the molecule which, for PBIC, has been obtained from osmotic pressure,[4] and X-ray measurements.[9] A variation in the value of L_0/b by a factor of 20 will bring about a change in the resultant calculation of L_0 by only 20%.

The comparison of the values of L_0 in Table II with the 1.94-Å value from X-ray measurements[9] can be considered a test of the applicability of eq 1 and 2. If eq 1 and 2 are a valid description of the physical situation, the values of L_0 should differ from 1.94 Å by no more than 15%, our estimate of the uncertainty in L_0. All of the values obtained from dielectric relaxation measurements, $L_{0\tau}$, are less than 1.94 Å by more than 15% and therefore we conclude that good quantitative results cannot be obtained from eq 1 for this case. The average L from PBIC and POIC data is 1.33 ± 0.12 Å, where 0.12 Å is an estimated standard deviation. Using $[\eta]$ measurements, eq 2 yields six values of $L_{0[\eta]}$ which agree with 1.94 Å within 15%, but all twelve values of $L_{0[\eta]}$ are biased less than 1.94 Å. An average $L_{0[\eta]}$ from PBIC and POIC data is 1.66 ± 0.12 Å, where 0.12 Å is an estimated standard deviation. If one applies a t test to the $L_{0\,\eta}$ numbers, the probability is greater than 0.99 that $L_{0[\eta]}$ and $L_{0,\text{X-ray}}$, are significantly different.

For measurements on the *same* sample the relative precision of the values $L_{0[\eta]}$ and $L_{0\tau}$ should be less than 8% because the uncertainty in molecular weight measurement is not present. From the twelve samples for which both $[\eta]$ and τ were measured the average difference between $L_{0[\eta]}$ and $L_{0\tau}$ is 19%. Also, in all twelve cases, $L_{0\tau} < L_{0[\eta]}$. We conclude that the following order is observed: $L_{0\tau} < L_{0[\eta]} < L_{0,\text{X-ray}}$.

Any differences between the L_0 results for PBIC *vs.* L_0 results for POIC cannot be considered significant. Although we set out to observe the effect of the larger diameter of the POIC molecule, the data at hand indicate that there is no such effect. An increase in the precision of our measurement would help to clarify this point.

The Kirkwood–Auer–Riseman (KAR) equation[12] may be rewritten as

$$M_0[\eta] = \frac{4\pi N n_w{}^3 L_0{}^3}{9 \times 10^3 n_w \ \ln \ n_w L_0/b} \tag{3}$$

where M_0 is the monomer molecular weight. (For PBIC $M_0 = 99$, and for POIC $M_0 = 155$.) If L_0 is the same for all homologs of the poly(n-alkyl isocyanate) family and if we assume that $\ln L_0/b$ is a constant then the right-hand side of eq 3 is independent of the homolog and depends only on the weight-average degree of polymerization n_w. A plot of log $M_0[\eta]$ *vs.* log n_w, which is shown in Figure 3, shows that within the limits of experimental accuracy, the data for both PBIC and POIC polymers fall on the same straight line. Thus, $M_0[\eta]$ does not depend on the homolog being measured, and, on a log–log plot, is linear with respect to n_w in the low molecular weight limit.

For $n_w < 1.4 \times 10^3$, a least-squares fit of the data of Figure 3 yields the solid straight line with the following empirical form

$$\begin{gathered} M_0[\eta] = 7.58 \times 10^{-4} n_w{}^{2.0} \\ n_w < 1.4 \times 10^{-3} \\ n_w/n_n < 1.2 \end{gathered} \tag{4}$$

or

$$\begin{gathered} [\eta] = (7.58 \times 10^{-4}/M_0{}^{3.0}) M_w{}^{2.0} \\ n_w < 1.4 \times 10^{-3} \\ M_w/M_n < 1.2 \end{gathered} \tag{5}$$

Equation 5 is presented as a master equation which gives the intrinsic viscosity–molecular weight dependence for any fraction of poly(n-alkyl isocyanate) as long as $n_w < 1.4 \times 10^3$. The estimated standard deviation in the power dependence of M is ±0.13 or ±7%.

In Figure 3, the slope of the solid straight line, 2.0 ± 0.13 (by least-squares fit), is in reasonable agreement with the 1.85 slope of the KAR equation on such a plot. This agreement is a necessary and sufficient condition that the linear PBIC and POIC molecules are rigid rods over the molecular weight range examined. If L_0 is used as a parameter for fitting eq 3 (KAR) to the data plotted in Figure 3, we find the best fit to be the dashed line for which $L_0 = 1.7$ Å. The KAR slope, 1.85, is independent of the value of L_0.

The range of molecular weight, for which we observe rodlike behavior in these $[\eta]$ experiments, is up to PBIC $M_w = 140{,}000$. With increasing M_w, molecular flexibility is observed, and the next PBIC datum point at $M_w = 280{,}000$ is clearly outside the rodlike region. Considering the uncertainty in the molecular weight measurement, this observation agrees with the relaxation time data where we observed that non-rodlike behavior occurs in the vicinity of PBIC $M_w = 280{,}000$.[2a] These results from the dynamic τ and $[\eta]$ experiments contrast with the results from the static measurements of dipole moment,[2a] light scattering,[4] and electric dichroism.[5,6] The static measurements show that non-rodlike behavior begins at a somewhat lower range of molecular weights, 60,000–133,000 for PBIC. For the most part, the differences are attributed to differences in the sensitivity of the various experiments.

Even though the KAR equations for the relaxation times and the intrinsic viscosities are based on the same model and similar assumptions, the L_0 results from the two experiments are significantly different. But, as mentioned above, the two experiments differ especially in their dependence on molecular weight. Since the relaxation time is a more sensitive function of molecular weight than the intrinsic viscosity is, it is possible that the difference between the model and real physical picture is accentuated in the relaxation time measurement.

The experimental slope of the log τ–log M plot, which is 2.7 for both PBIC and POIC, and the slope of the log $M_0[\eta]$–log M plot, which is 2.0, are characteristic of the rigid rod conformation and these numbers agree well with the theory. It is the absolute value of the results which conflict with the X-ray data. A contradiction between the model assumptions, which were mentioned earlier, and the real physical situation is undoubtedly at the root of the problem. Since the slopes of the log τ–log M and log $M_0[\eta]$–log M plots do agree with the model, the source of the problem is probably at the local level, particularly with the form of the Oseen tensor describing near neighbor hydrodynamic interaction.

It should be mentioned that Tsvetkov and coworkers[8] have also made intrinsic viscosity measurements on PBIC as a function of molecular weight. Their results do not entirely agree with ours. They obtain $L_0 = 2$ Å but the uncertainty in their measurements is not given. The slope of their log $[\eta]$–log M plot is 1.2, markedly different from ours *and* from the theoretical value predicted by the KAR equation. We have no way of evaluating this difference since the experiments of Tsvetkov *et al.* are not well enough defined. In particular, the shear rates used in their viscosity measurements, the characterization data on their fractions and information on the distribution of molecular weights in each fraction were not given. Since the relaxation time and intrinsic viscosity are extremely sensitive functions of molecular weight and molecular weight distribution, it is obvious that only samples with a narrow distribution can be used in these experiments. We have confidence in the accuracy of our data because we have characterized our fractions not only by light-scattering and osmotic pressure measurements, but also by observing the envelope of the distribution of molecular weights using the dielectric dispersion and GPC measurements. In addition, the agreement of our data with the KAR equation fortifies this view. Thus, it is our conclusion that the results of Tsvetkov and coworkers[8] cannot be taken as an accurate reflection of the hydrodynamic behavior of PBIC of narrow molecular weight distribution.

The data which we have presented reflect the hydrodynamic behavior of the poly(n-alkyl isocyanates) in the limit of low molecular weight. We recognize that the flexibility of the molecule increases gradually as the molecular weight increases and, for $M_w > 10^6$ random-coil behavior is observed.[2a] If intrinsic viscosity data were available over a wider range of molecular weight including the limiting behavior at high molecular weight, it would be fruitful to consider a wormlike molecular model[25] in our analysis. Indeed, in previous work,[2a] the static dipole moment data of PBIC in CCl_4 solutions as a function of molecular weight has been analyzed in accordance with the wormlike model of Kratky–Porod. The persistence length was calculated to be 1600 Å, which is much higher than the 550-Å persistence length calculated using light-scattering data of PBIC in chloroform.[4] The difference can tentatively be attributed to a large solvent effect,[26,27] whereby the molecule shows a marked increase in flexibility in the presence of polar solvents. Troxell and Scheraga[5] have de-

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duced from their electric dichroism work on PBIC that the source of the rigidity is a combination of first, a high potential barrier to rotation from the planar amide configuration, and, second, steric interference of the *n*-alkyl side chain and the carbonyl group. In the presence of a polar solvent, we speculate that the potential barrier to rotation from a planar amide configuration is reduced. This solvent effect indicates that steric effects alone cannot account for the rigidity of the PBIC and POIC molecules.[28]

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Determination of the Thermodynamic Parameters of Selectivity on Polyelectrolytes by Potentiometry and Microcalorimetry

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ABSTRACT: The free energy of selectivity between different monovalent and divalent counterions is obtained by potentiometry between 14 and 65°; by microcalorimetry, the enthalpy is determined by exchange at 25°. From both sets of results, ΔH is confirmed and ΔS is given as a function of the nature of the counterions. The experiments were performed on a carboxymethylcellulose with a substitution degree $\overline{DS} = 2.49$.

The selectivity of a polyanion is directly related to its charge density and to the nature of the ionic site (-COOH or -SO$_3$H) and that of the counterions. By potentiometric titration, the affinity sequence is clearly described and is found to be Li > Na > K > Cs > TEA (tetraethylammonium) for monovalent counterions on carboxymethylcellulose.[1] The enthalpy change (obtained by microcalorimetry) accompanying the exchange of two counterions depends on the counterions and is directly related to the charge density.[2] A theoretical treatment may be proposed with the Lifson-Katchalsky rodlike model to interpret the electrostatic contribution[3,4] but no theory explains the selectivity.

In this communication, the results obtained by both techniques are given and used to calculate the thermodynamic parameters which characterize the selectivity of a carboxymethylcellulose (CMC) with a charge parameter $\lambda = 3.44$; λ is defined by the relation $\lambda = \alpha\epsilon^2/DbkT$, with ϵ protonic charge, α number of ionic sites per monomeric unit, b length of a monomeric unit, D dielectric constant, and kT Boltzmann term.

Experimental Section

The potentiometric titrations are followed with a Sargent S 30,000 potentiometer using a combination electrode S 300-72-15 (Sargent) for pH determinations at 14, 25, 35, 45, 55, and 65 ± 0.1°.

The titration experiments with monovalent counterions were all performed by titrating solutions 5×10^{-3} N in H-CMC with 0.1 N base XOH ($X^+ = TEA^+, Li^+, K^+$) there being no added salt. With divalent counterions the titrations are carried out with 0.04 N base $X(OH)_2$ ($X^{2+} = Ca^{2+}, Ba^{2+}, Sr^{2+}$). The acidic form H-CMC is obtained by passage of the sodium salt solution through an ion-exchange column (Amberlite IR 120 H$^+$).

The free energy of exchange $\Delta G(T)$ is given by the potentiometric area between the both neutralization curves concerned ($TEA^+ \rightarrow Li^+$; $TEA^+ \rightarrow K^+$; $K^+ \rightarrow Li^+$; $Na^+ \rightarrow Ca^{2+}$; $Na^+ \rightarrow Sr^{2+}$; $Na^+ \rightarrow Ba^{2+}$); experimentally, the ΔG values are found to be independent on the polymer concentration. During titration of a polyacid, the pH values are related to the change of the electrostatic free energy ΔG_{el} by the following expression

$$\mathrm{pH} = \mathrm{p}K_0 - \log\,[(1-\alpha)/\alpha] + 0.434\Delta G_{el}/kT$$

in which K_0 is the intrinsic constant of ionization and α the degree of neutralization. The electrostatic free energy per ionizable site at the degree of ionization α is given by

$$G_{el}(\alpha) = 2.3kT\int_0^{\alpha}\{\mathrm{pH} + \log\,[(1-\alpha)/\alpha] - \mathrm{p}K_0\}\mathrm{d}\alpha$$

corresponding to the area under the graph $\{\mathrm{pH} + \log\,[(1-\alpha)/\alpha] - \mathrm{p}K_0\}$ *vs.* α.[5] As a consequence, the area between two curves of neutralization gives directly the free energy (per charged carboxyl) of transfer of fully charged polymer from a solution in which it has one counterion to a solution in which it has another counterion.

Microcalorimetric measurements were performed at 25° with a Calvet microcalorimeter standard model manufactured by D.A.M. Lyon (France). To eliminate the dilution effects, a differential technique is employed in which same additions of reactant are made at the same time in two identical cells, one of which contains the polyelectrolyte solution and the second one pure water.

The ΔH of exchange is obtained with monovalent counterions by addition of 1 N XCl to 40 ml of a 10^{-2} N TEA-CMC solution. With divalent counterions, addition of 0.5 N XCl$_2$ solution are made to 40 ml of a 5×10^{-3} N Na-CMC solution. The ΔH by monomeric unit is found experimentally to be independent on the polymer concentration.

The ΔH of exchange is also obtained by a second method which consists of adding 1 N HCl solution at the same time in two identical cells one of which contains a 10^{-2} N TEA-CMC solution and the second a 10^{-2} N X-CMC solution;[2] these experimental conditions correspond directly to those used in potentiometry.

The ΔH values obtained in both ways are in good concordance. The results are expressed in calories per equivalent ionic site.

Experimental Results and Discussion

The data obtained by potentiometry are given in Table I as a function of the temperature; experimental curves are presented on Figures 1 and 2 for monovalent and divalent counterions.

For monovalent cations, one can directly observe that

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