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# Solution Properties of Poly(*n*-butyl isocyanate). 1. Characterization and Intrinsic Viscosity Behavior Over an Extended Molecular Weight Range

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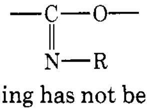
ABSTRACT: The intrinsic viscosity behavior of poly(*n*-butyl isocyanate) (PBIC) has been examined over the molecular weight ($\overline{M}_w$) range of $2.5 \times 10^4$ to $12.5 \times 10^6$ g mol$^{-1}$ in carbon tetrachloride, tetrahydrofuran, and chloroform. At low molecular weights ($<10^5$) PBIC exhibits rodlike behavior while at high molecular weight ($10^7$) the molecular posture of this polymer appears to be essentially that of a wormlike chain in tetrahydrofuran and chloroform. However, the $[\eta]$–$M$ characteristics of high molecular weight PBIC in $CCl_4$ do not support the wormlike chain model. The gel permeation chromatographic behavior of PBIC was examined. A nonlinear calibration was found, a reflection of the changing chain posture with increasing molecular weight.

Poly(*n*-butyl isocyanate) (PBIC) is a polymer which has been found to exhibit rodlike behavior[1] up to a molecular weight of about $10^5$. Its structure is similar to that of the polypeptides except for the absence of hydrogen bonding. Chain stiffness was first indicated by Shashoua, Sweeny, and Tietz[2,3] who found abnormally high intrinsic viscosities for relatively low molecular weight anionically synthesized polyisocyanates. Since then, chain stiffness has been observed by studying the dilute solution properties of PBIC and other poly(*n*-alkyl isocyanates). These measurements have examined both the dilute solution equilibrium and hydrodynamic properties of these polymers. All of these measurements, i.e., osmometry, light scattering, dielectric, electric dichroism, electric birefringence, rotatory diffusion, and intrinsic viscosity, have clearly demonstrated[1] the stiff-chain molecular posture possessed by the poly(*n*-alkyl isocyanates).

The origin of the chain stiffness of the poly(*n*-alkyl isocyanates) is at present not totally clear. The presence of the amide unit was considered by Schneider, Furusaki, and Lenz,[4] and they proposed the possibility of partial double bond character imposing coplanarity along the backbone. Troxell and Scheraga[5] later concluded from studies of the dichroism of PBIC solutions subjected to external electric fields that the double bond character of the backbone was too weak to explain the chain stiffness. Steric hindrance, however, is a strong argument in explaining chain stiffness. This is based, in part, on the similarity in structure between the poly(*n*-alkyl isocyanates) and the peptide poly-L-proline. Poly-L-proline exists predominantly in the rigid trans-helical conformation even though hydrogen bonding is absent due to the lack of hydrogens at the peptide nitrogens.[6] Recently, Tonelli[7] completed potential energy calculations which suggest that chain flexibility which accumulates as molecular weight increases is due to helix reversal sites along the chain. A chemical basis for this was suggested by Schneider, Furusaki, and Lenz[4] through a second possible repeat unit involving the flexible ether linkage, i.e.,



$$-\underset{\underset{\displaystyle N-R}{\|}}{C}-O-$$

Evidence for this grouping has not been found for polyisocyanates prepared from monoisocyanate monomers. However, this may be due to a lack of an analytical technique capable of detecting this group at low concentration levels, probably less than 0.1%. There is another possibility which could influence the solution properties in the same manner as induced flexibility. This could be branching in the polymer due to diisocyanate species present in the monoisocyanate monomer. As in the case of the ether linkage, no evidence for the presence of a diisocyanate monomer has been found.

Basically, the conformation of PBIC has been described by most authors as being helical and rigid at low molecular weight ($<10^5$), with a decrease in rigidity, but a retention of high elongation at higher molecular weights. The conformational model invoked to describe this trend is usually that of a rigid rod changing to a "wormlike" stiff chain. In this study, viscosity and light-scattering data for PBIC are presented over a molecular weight range ($2.5 \times 10^4$ to $1.25 \times 10^7$) which encompasses both the clearly defined rodlike and a possible wormlike chain region in which there are enough "persistence length" units so that the chain could appear in some properties to be a Gaussian chain.

## Experimental Section

The samples used were those used in previous studies.[8–12] Detailed discussions of the procedures used in their synthesis and characterization have been given.[8–12] The $\overline{M}_w$ values of two PBIC samples were determined with a low-angle light-scattering photometer operating at angles from 15 to 150°. The refractive index increment, d*n*/d*c*, was determined in tetrahydrofuran. Ultracentrifuge data were also obtained for $\overline{M}_w$ and $\overline{M}_z$ determinations. A specially designed[13] Zimm-type Couette low-shear viscometer was used in addition to commercial variable-shear capillary viscometers.

A gel permeation chromatograph was built by combining the Waters ALC/GPC 501 with its high-pressure 1000 psi pump, a 2.5 mL syphon, and a dual detector combining the UV (at 254 nm) and refractive index detectors. One each of the following 4-ft Styragel columns were used: $5 \times 10^6$ Å; $7 \times 10^5$ to $5 \times 10^6$ Å; $10^6$ Å; $1 \times 10^5$ to $7 \times 10^5$ Å; $3 \times 10^5$ Å; $10^5$ Å; $3 \times 10^4$ Å; $10^4$ Å; $10^3$ Å; and 250 to 100 Å. This column set provided a near-linear calibration for polystyrene from $2 \times 10^4$ to $10^7$ molecular weight. This column set had a plate count of 500 ppf at the flow rate of 1 mL min$^{-1}$. The solvent was chloroform at ambient temperature. Sample preparation and operating conditions were identical to those discussed previously.[14,15] Polystyrene standards used for column calibration were from this laboratory[13] and commercial sources.

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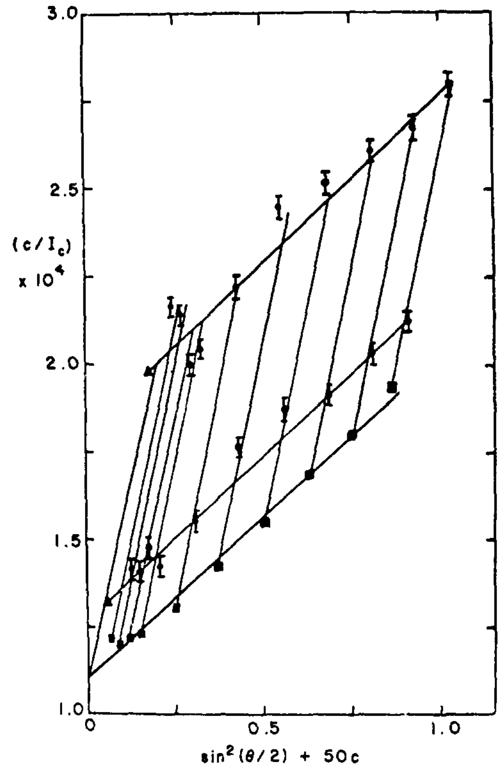

**Figure 1.** Zimm plot of PBIC-21R in tetrahydrofuran at 40 °C.

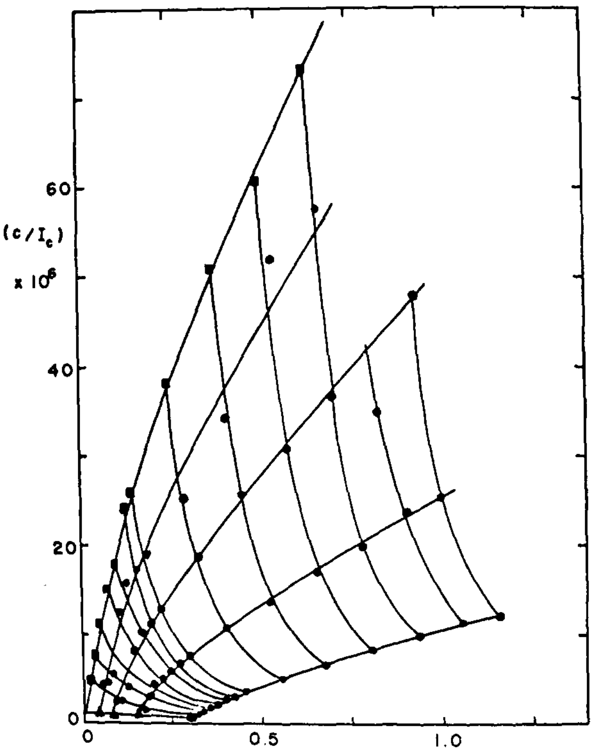

**Figure 2.** Zimm plot of PBIC-36-1 in tetrahydrofuran at 40 °C.

## Results and Discussion

Previous light-scattering work on these PBIC samples had been restricted to data obtained in chloroform.[10] Additional characterization work was done in tetrahydrofuran in order to use the scattering distribution function to study the conformation of PBIC in this solvent. Molecular weight data were obtained using both the Beckman analytical ultracentrifuge and the Phoenix low-angle light-scattering photometer in order to check the molecular weight data presented previously. Two samples were chosen: one relatively low molecular weight sample, PBIC-21R, was analyzed by both the ultracentrifuge and light scattering while one high molecular weight sample, PBIC-36-1, was analyzed by light scattering.

The sedimentation-equilibrium molecular weights were determined in tetrahydrofuran. A value of 1.03 for $\bar{v}$ was determined from the reported density of 0.97 g/cm$^3$ for PBIC measured by the flotation of crystals in $H_2O$/ethanol mixtures.[16] Two sedimentation-equilibrium runs were made. $1/\overline{M}_w$ and $1/\overline{M}_z$ were each plotted vs. $\bar{c}$ and extrapolated to $\bar{c} = 0$. The value for $\overline{M}_w$ for PBIC-21R was found to be $1.3 \times 10^5$, while $\overline{M}_z$ was found to be $1.75 \times 10^5$. The second virial coefficient, $A_2$, was calculated to be $8.1 \times 10^{-4}$ mol cm$^3$ g$^{-2}$. Analysis by gel permeation chromatography indicated an $\overline{M}_n$ of $7.6 \times 10^4$ g mol$^{-1}$.

A sample having a very broad distribution ($\overline{M}_z/\overline{M}_w = 3.7$, $\overline{M}_w/\overline{M}_n = 2.9$), PBIC 41-1, was used in the measurement of d$n$/d$c$, which was found to be 0.0838 (cm$^3$/g) at 40 °C. To see if there were any depolarization effects and/or differences with the PBIC samples, runs were made with unpolarized incident light, 546 nm, at 90° observation angle with appropriate horizontal and vertical analyzers before the photomultiplier tube. Measurements were made in tetrahydrofuran at 40 °C. Both the high molecular weight PBIC-36-1 and the low molecular weight PBIC had nonzero values of the depolarization ratios, $\rho_\mu$. The sample, PBIC-41-1, with pronounced low molecular weight tail (the molecular weights, from GPC analysis, are presented later in this paper) had a value of $\rho_\mu$ of 0.12. This was a result of the high degree of anisotropy possessed by the pronounced low molecular weight tail in this particular sample. All of these values of $\rho_\mu$ required the use of the Cabannes correction factor in the light-scattering calculations. No fluorescence occurred in these solutions.

The Zimm plot for PBIC-21R in tetrahydrofuran at 40 °C is shown in Figure 1. Unpolarized light of 546-nm wavelength was employed in the Phoenix light-scattering photometer. Observation angles from 30 to 135° were plotted. Straight lines were drawn to best fit all the data. From the $y$ intercept and slopes, the following results were found: $\overline{M}_w = 1.32 \times 10^5$, $\langle S^2\rangle_z^{1/2}e = 492A$, $A_2 = 7.7 \times 10^{-4}$ mol cm$^3$/g$^{-2}$.

The Zimm plot for PBIC-36-1 in tetrahydrofuran at 40 °C is shown in Figure 2. Observation angles from 15 to 135° were plotted. Least-squares lines were drawn to fit all the data. From the $y$ intercept and slopes, the following results were found: $\overline{M}_w = 12.5 \times 10^6$, $\langle S^2\rangle_z^{1/2} = 6890A$, $A_2 = -0.6 \times 10^{-4}$ mol cm$^3$ g$^{-2}$. This sample had been found previously to have a $\overline{M}_w = 10 \times 10^6$, $\langle S^4\rangle_z^{1/2} = 5200A$, and $A_2 = 2.1 \times 10^{-3}$ mol cm g$^{-2}$ in chloroform.[10] Early experimental work[10] on this sample underestimated both $\overline{M}_w$ and $\langle S^2\rangle_z$ since the low angles needed to get accurate measurements at this large size were not available in the light-scattering instrument previously used.

The results of the analytical ultracentrifuge and light-scattering studies are listed in Table I.

**Table I**
**Results of Molecular Weight Analyses of PBIC Samples in Tetrahydrofuran**

| Sample | $\overline{M}_w$, g mol$^{-1}$ | $\langle S^2\rangle_z^{1/2}$, A | $A_2 \times 10^4$, mol cm$^3$ g$^{-2}$ |
|---|---|---|---|
| 21R[a] | $1.30 \times 10^5$ [b] | | 8.1[b] |
| | $1.32 \times 10^5$ [c] | 492 | 7.7[c] |
| 36-1 | $1.25 \times 10^7$ [c] | 6890 | −0.6[c] |

[a] Sample 21R is not sample 21 listed in ref 8, 10, 11, and 12. This sample is listed as PBIC-21 in ref 15 and as PBIC 1 in ref 10. [b] Analytical ultracentrifuge. [c] Light scattering.

**Table II**
**Molecular Parameters for PBIC Samples in Tetrahydrofuran at 40 °C**

| Sample | $\overline{M}_n \times 10^4$, g mol$^{-1}$ | $\overline{M}_w \times 10^4$, g mol$^{-1}$ | $\overline{M}_w/\overline{M}_n$ | $\langle S^2 \rangle_z^{1/2}$, A | $W/2$,[a] (decades) |
|---|---|---|---|---|---|
| 41 | 2.2 | 2.5 | $1.1_4$ | 103 | 1.80 |
| 2A | 11.1 | 12.5 | $1.1_3$ | 490 | 1.90 |
| 21R | | 13.2 | 1.6[b] | 494 | |
| 10f | 25.0 | 34.2 | $1.3_7$ | 1030 | 2.40 |
| 12 | 25.5 | 43.0 | $1.8_8$ | 1260 | 2.80 |
| 40-2 | | 90.0 | 1.2[c] | 1800 | 2.00 |
| 36-LE | | 150.0 | 1.2[c] | 2400 | 1.90 |
| 36-3 | | 307.0 | | 3450 | |
| 36-2 | | 420.0 | 1.2[c] | 4050 | 2.05 |
| 36-1 | | 1250.0 | 1.2[c] | 6900 | 2.10 |

[a] Half-width of the dielectric loss vs. log-frequency curve.[8,12,17] These data were obtained in $CCl_4$ at 22 °C. [b] Estimate from GPC. [c] Estimated from dielectric relaxation measurements.[17]

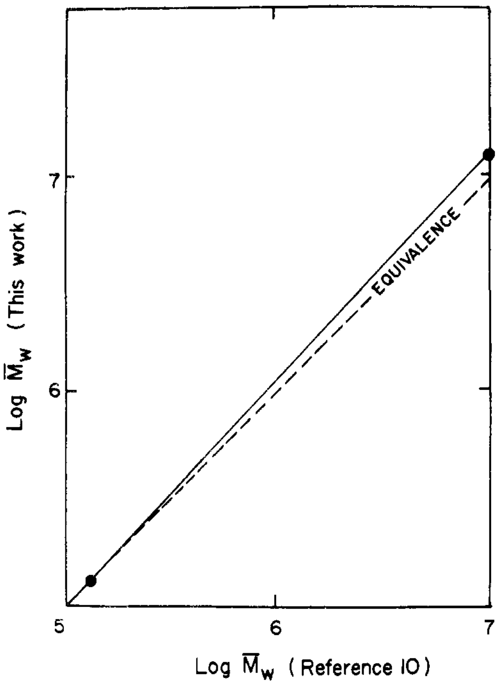

Figure 3. Correction of high molecular weight data of PBIC.

The second virial coefficient was found to decrease to a small negative value at this molecular weight. This is not indicative of true rigid rods, as $A_2$ should not change for rods. The change in $A_2$ was certainly more than the normal lowering of $A_2$ to be expected for Gaussian coils with increasing molecular weight. The low $A_2$ for PBIC-36-1 was suggestive of a drastic change in solvent power and excluded volume (analogous to a change in molecular shape) as molecular weight increased.

It was recognized that earlier characterization work[10] on the very high molecular weight samples may have been in error due to the limited angular range of the photometer used. The following method was used to correct the molecular weights and radii of gyration originally measured[10] and reported for the high molecular weight PBIC samples in chloroform. A double logarithmic plot was constructed of the molecular weights reported[10] for the samples vs. the values found in this work, as shown in Figure 3. From this graph the corrected molecular weights of all the PBIC samples were determined. To determine the relationship between $\langle S^2 \rangle^{1/2}_z$ and $\overline{M}_w$, a double logarithmic plot was constructed, as shown in Figure 4, from the two data points listed in Table I. The original data[10] were also plotted. This defined the general shape of the graph of our data. Figures 3 and 4 were constructed in light of the following. First of all, it was assumed that the errors in the reported values of $\overline{M}_w$ and $\langle S^2 \rangle_z^{1/2}$increased as the size of the molecules increased. Second, the $[\eta]$ data, to be discussed in a later section, were found to give $[\eta]$–$M$ plots in tetrahydrofuran and chloroform that were parallel, with the tetrahydrofuran values being higher than chloroform values. This suggested that the two $\langle S^2 \rangle_z^{1/2}$–$\overline{M}_w$ plots would also have the same general characteristics. Table II lists the final, molecular weight data for the PBIC samples used in this study with the $\langle S^2 \rangle_z^{1/2}$ data obtained from the smoothed curve. With the exception of the highest molecular weight samples ($>10^6$), these molecular weights are in good agreement with those presented elsewhere.[10]

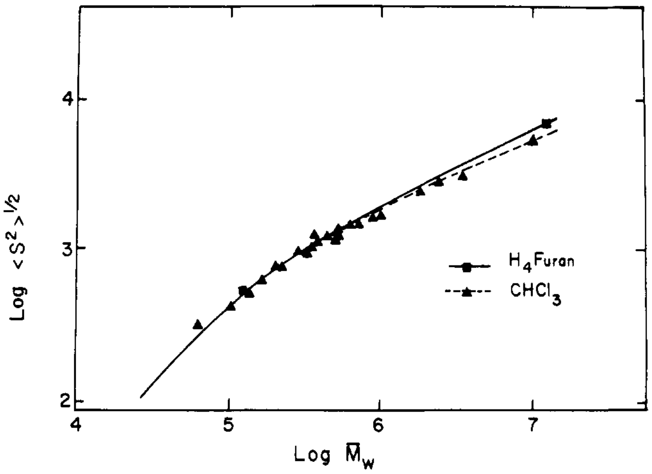

Figure 4. Radii of gyration vs. $\overline{M}_w$ for PBIC.

In order to check the characterization data, and especially to evaluate the distribution of the high molecular weight fractions, GPC data for six samples were obtained. The resultant molecular weight calibration curve, Figure 5, was developed[15] by curve fitting the chromatograms to $\overline{M}_w$ and then calculating $\overline{M}_n$ and $\overline{M}_z$ from the curve fitted calibration line. The results of the curve-fitting analyses are shown in Table III. Reasonably good agreement for the $\overline{M}_w$ values of the samples was found as is to be expected from the GPC calibration curve. The agreement of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ values in Tables II and III is not as good, but these values are deemed to be the best values for discussion. It is evident from Figure 5 that resolution in the GPC is satisfactory only up to about $3 \times 10^6$ molecular weight. Obviously this column set cannot resolve very high molecular weight PBIC even though it can resolve very high molecular weight ($10^7$) polystyrene.

The intrinsic viscosities at zero shear rate were calculated from the data obtained with a variable-shear capillary dilution viscometer using an extrapolation procedure discussed else-

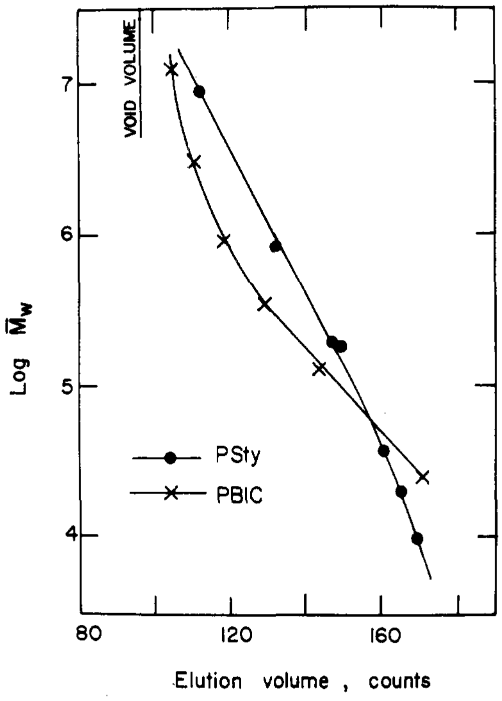

**Figure 5.** Gel permeation chromatography calibration curve for PBIC and polystyrene in chloroform.

**Table III**
**Molecular Weight Results of Curve-Fitting PBIC Chromatograms**

| Sample | $\overline{M}_z \times 10^4$, g mol$^{-1}$ | $\overline{M}_w \times 10^4$, g mol$^{-1}$ | $\overline{M}_n \times 10^4$, g mol$^{-1}$ |
|---|---|---|---|
| 41 | 3.03 | 2.95 | 2.17 |
| 21R | 19.1 | 12.3 | 7.63 |
| 41-1[a] | 62.0 | 16.6 | 5.78 |
| 10f | 67.0 | 40.3 | 23.6 |
| 40-2 | 119.0 | 88.3 | 66.2 |
| 36-3 | 607.0 | 299.9 | 180.0 |

[a] Molecular weights via absolute measurements were not determined for this sample.

where.[15] The $[\eta]$ values were determined in three solvents, carbon tetrachloride and chloroform at 30 °C and tetrahydrofuran at 40 °C. The $[\eta]$ values are given in dL g$^{-1}$. The constant $k'$ was determined from the data using the Huggins relation:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \qquad (1)$$

The Kraemer equation

$$\ln(\eta_{rel})/c = [\eta] - k''[\eta]^2c \qquad (2)$$

was also plotted. Due to the high values of $k'$, no attempt was made to force 1 and 2 to the same $y$ intercept. It was estimated that forcing eq 1 and 2 to agree would introduce at most a 3% error in $[\eta]$. Instead, only eq 1 was used to determine $[\eta]$.

Earlier work by Slagowski[13] has shown the ease with which high molecular weight polystyrene could be shear degraded in the usual shear stresses accompanying solution agitation and flow in capillary viscometers. No evidence of shear degradation was observed for PBIC in the viscometry work. This conclusion was based on three observations. First, for any given sample, during measurements with capillary viscometers, no problems were encountered in reproducing flow times during replicate runs. Second, after each viscosity determination, the solution was evaporated to dryness, and the same sample was re-used in another $[\eta]$ determination in a new solvent. The sequence of solvent and sample choice was random, and no unusual results related to shear degradation were encountered. Third, a high molecular weight polydisperse sample, PBIC-6 ($\overline{M}_w = 2.45 \times 10^6$)[10], was analyzed using both the capillary and the Zimm-type Couette viscometers. Separate portions of the sample were used. Virtually identical zero shear rate results were obtained using the capillary viscometer and by direct measurement with the low shear rate viscometer (see Table IV).

It has been found[3] that PBIC was susceptible to degradation by acids. In this work, PBIC was found to degrade in chloroform. For example, a sample of high molecular weight PBIC-6, which had been previously analyzed in $CCl_4$, was prepared in chloroform for analysis. The concentration, 0.04%, had been selected based on the $CCl_4$ run to give $\eta_{rel} \geq 1.8$. The solution was kept at 40 °C in a clear glass bottle for 1.5 days. Heat was provided by a light bulb. At the time the measurements were taken, the concentration was checked. It was found that the dry polymer retained in the tare pan now resembled a powder rather than the original tough, fibrous form. The flow time of the solution (157.4 s) was virtually the same as the solvent (155.6 s), indicating severe degradation. A lower molecular weight sample PBIC-2A also showed the same loss in viscosity.

This was undoubtedly due to the UV catalyzed reaction of chloroform producing phosgene and HCl. Ethanol inhibitor is added to chloroform, but its function is only to destroy phosgene. Consequently, the following precautions were used in all solution work: (1) only fresh chloroform stored in brown bottles was used, (2) dissolution was done in bottles wrapped in aluminum foil, (3) solutions were heated no higher than 60

**Table IV**
**Intrinsic Viscosities of PBIC Samples**

| Sample | $CCl_4$, 30 °C |  | Tetrahydrofuran, 40 °C |  | Chloroform, 30 °C |  |
|---|---|---|---|---|---|---|
|  | $[\eta]$, dL g$^{-1}$ | $k'$ | $[\eta]$, dL g$^{-1}$ | $k'$ | $[\eta]$, dL g$^{-1}$ | $k'$ |
| 41 | 0.376 ± 0.002 | 0.53 ± 0.02 | 0.294 ± 0.003 | 0.56 ± 0.06 | 0.272 ± 0.003 | 0.57 ± 0.05 |
| 21R | 5.72 ± 0.02 | 0.48 ± 0.01 | 4.35 ± 0.08 | 0.51 ± 0.07 | 3.64 ± 0.02 | 0.48 ± 0.01 |
| 2A[a] |  |  | 5.50 ± 0.18 | 0.55 ± 0.06 |  |  |
| 41-1 |  |  | 5.78 ± 0.04 | 0.51 ± 0.02 | 3.34 ± 0.09 | 0.47 ± 0.10 |
| 10f |  |  | 17.1 ± 0.0 | 0.33 ± 0.00 | 12.9 ± 0.0 | 0.57 ± 0.02 |
| 12 | 25.0 ± 0.1 | 0.68 ± 0.02 |  |  |  |  |
| 40-2 | 46.8 ± 0.2 | 0.58 ± 0.02 | 24.2 ± 0.3 | 0.63 ± 0.05 | 22.5 ± 0.3 | 0.54 ± 0.04 |
| 36-LE | 56.2 ± 1.3 | 0.72 ± 0.08 |  |  |  |  |
| 36-2 | 73.0 ± 0.9 | 0.90 ± 0.05 |  |  |  |  |
| 6[b] | 88.8 ± 0.1 | 0.70 ± 0.00 | 61.8 ± 0.6 | 0.75 ± 0.04 | 44.6 ± 0.5 | 0.86 ± 0.04 |
| 36-1 | 99.2 ± 1.2 | 0.79 ± 0.04 | 67.3 ± 1.0 | 0.73 ± 0.05 | 56.9 ± 0.4 | 0.71 ± 0.03 |

[a] $[\eta]_{25°C}{}^{\text{tetrahydrofuran}} = 9.12 \pm 0.14$, $k' = 0.73 \pm 0.05$. [b] $[\eta]_{30°C}{}^{CCl_4} = 91.8 \pm 2.3$, $k' = 0.52 \pm 0.08$ at $\gamma = 0.22$ s$^{-1}$; $\overline{M}_w = 2.45 \times 10^6$, ref 10, $\overline{M}_w/\overline{M}_n > 5$, ref 17.

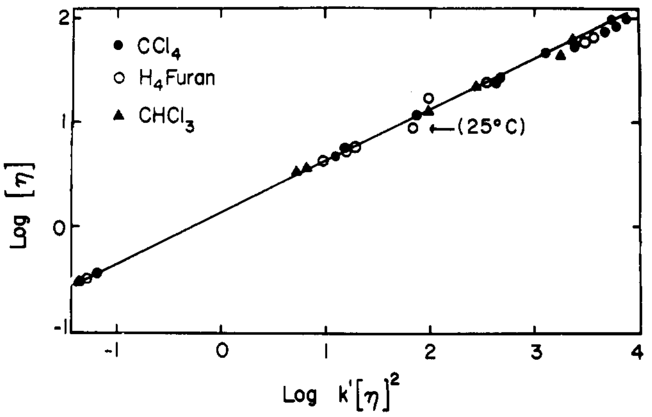

**Figure 6.** Intrinsic viscosity $[\eta]$ vs. concentration dependence of $\eta_{sp}/c$ $(k'[\eta]^2)$, in eq 1. This figure contains data from Table IV and ref 11, 12, and 15.

°C (this was done with all solvents to avoid thermal degradation) for the shortest time possible, (4) viscosity measurements were taken as soon as possible. After the analyses were completed, the chloroform was always evaporated to almost dryness and the polymer precipitated with a large excess of methanol before final drying. The chloroform/methanol mixture was then evaporated to dryness to ensure all polymer had precipitated. (Recovery was required because of the small quantities of sample available.) In all cases, precipitation was found to be complete.

All reduced specific viscosity values at zero shear rate were found to be linear with concentration. The final results of the $[\eta]$ determinations are tabulated in Table IV. Sample PBIC-6 was analyzed in $CCl_4$ in both the capillary and Zimm type Couette viscometers to establish the accuracy of the extrapolation procedure. The results show that the extrapolation procedure gave the same results, within about 3%, as an actual measurement under zero shear rate conditions.

Several trends were immediately obvious from the viscosity data. First, the intrinsic viscosity of a given sample decreased with solvent in the order $CCl_4$ > tetrahydrofuran > chloroform, although the Huggins constant $k'$ did not change. Second, for each solvent $k'$ increased from around 0.50 to 0.90 with molecular weight. This has been suggested by Eirich and Riseman[19] to be due to an increase in chain compactness brought about by a decrease in solvent power. These results were in qualitative agreement with the $A_2$ data which suggested for tetrahydrofuran a decrease in solvent power with increasing molecular weight. They were in keeping with the experimentally determined changes of $k'$ of a flexible coil with solvent power[20] but were not in good agreement with the current theories of $k'$.[21] The value of $k'$ at low molecular weight where PBIC was suspected to be a rigid rod, 0.50, was far below that predicted for rigid rods (>2) and rigid spheres (1.7–2.2),[19] but was in good agreement with those experimentally determined by Doty, Bradbury, and Holzer[22] for rodlike PBLG.

The change in $k'$ and $[\eta]$ with solvent was explored further. In Figure 6 $[\eta]$ is plotted vs. the viscosity slope, $k'[\eta]^2$. It was obvious there were no abnormalities in $k'[\eta]^2$ between the three solvents. Since there was no preferential increase in $k'$ as the $[\eta]$ increased for any one solvent, the solvents must have similar concentration behavior. This apparently ruled out agglomeration as the cause of the increase in $[\eta]$ with solvent, as was suspected for PBLG in chloroform.[22]

It was found that with the solvent and temperatures used in the previous section, no agglomeration problems were encountered. However, at other temperatures evidence of agglomeration was found. For example, it was observed that a concentrated solution of high molecular weight PBIC in toluene, upon standing at ambient temperature, phase separated over a period of months into a compact crystalline phase and a clear supernatant liquid. It also has been found that in tetrahydrofuran, dissolution of the sample would not occur with any reasonable speed unless the mixture was heated for a time at 60 °C and then dissolution occurred within an hour or less. It was also noted that tetrahydrofuran solutions, if cooled to 20–25 °C, occasionally showed turbidity and/or precipitation of the polymer. The analytical ultracentrifuge runs for PBIC were used to monitor aggregation. After equilibrium had been achieved at 40 °C in tetrahydrofuran, the temperature was lowered, equilibrium was reestablished, and the fringe shift was redetermined. The data are not listed here, but it was found that at 30 °C the change in fringe shift from that of 40 °C was only that to be expected from the change in temperature. However, when the temperature was lowered to 20 °C, there was evidence of coagulation at the bottom of the cell and an abnormally large decrease in fringe shift. For the high molecular weight sample PBIC-36-1 light scattering was used. At 30 °C in tetrahydrofuran the Zimm plot showed that for all the concentrations $(c/I_c)$ went almost straight down at the low angles. The Zimm plot could not be properly constructed. This enhanced scattering at low angles was that expected if large aggregates were present. The viscosity data in tetrahydrofuran at 25 °C also indicated aggregation. At 40 °C in tetrahydrofuran sample PBIC-2A had values of $[\eta]$ almost half those at 25 °C and $k'$ decreased to 0.55 from 0.73. (This decrease in $[\eta]$ with temperature was even more than that expected in good solvents.[23]) The $[\eta]$ changes could also reflect a change in rigidity. It appears that tetrahydrofuran at ambient temperature is not a very good solvent for PBIC. This is also the case for PBIC[1] and poly($n$-hexyl isocyanate)[24] in toluene. This finding casts some doubt on Burchard' studies[25] of the solution properties of PIBC in tetrahydrofuran at 20 °C.

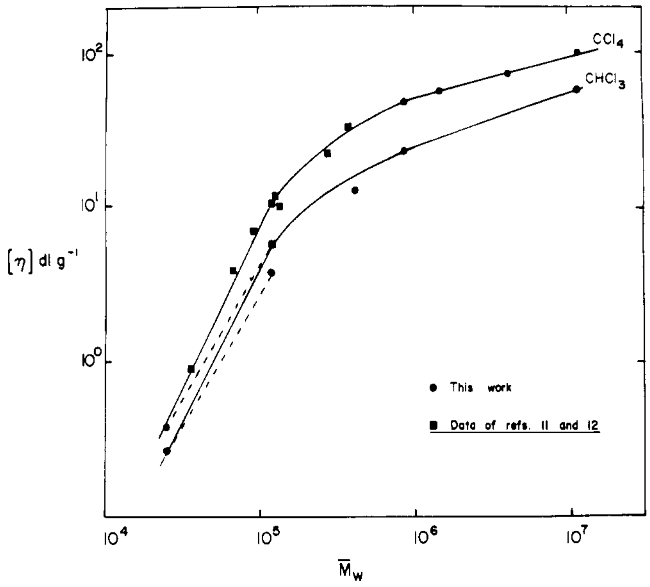

**Figure 7.** Intrinsic viscosity vs. $\overline{M}_w$ for PBIC over an extended molecular weight range. (See discussion for explanation of full and dashed lines.)

In Figure 7 is a plot of log $[\eta]$ vs. log $\overline{M}_w$ for PBIC in $CCl_4$ and chloroform. The intrinsic viscosity data for the full line were taken from Table IV and the $\overline{M}_w$ data from Table II along with earlier data from ref 11 and 12, excluding sample PBIC-21R. (The dotted line is discussed later.) Although the data appear to fit a continuous curve, the $[\eta]$–$\overline{M}_w$ plot could also somewhat arbitrarily be divided into two straight line

**Table V**
**Slope Value $a$ as a Function of Molecular Weight for PBIC in Various Solvents**

| $\overline{M}_w$, g mol$^{-1}$ | $CCl_4$ | $a$, THF | Chloroform |
|---|---|---|---|
| $10^5$ | 2.0 | 1.83 | 1.83 |
| $10^7$ | 0.26 | 0.37 | 0.37 |

**Table VI**
**Slopes of the $\langle S^2\rangle_z^{1/2}$– $\overline{M}_w$ Plot at Several Values of $\overline{M}_w$**

| $\overline{M}_w$, g mol$^{-1}$ | Slope | $\overline{M}_w$, g mol$^{-1}$ | Slope |
|---|---|---|---|
| $2.5 \times 10^4$ | 1.00 | $1.0 \times 10^5$ | 0.86 |
| $6.0 \times 10^4$ | 1.00 | $1.0 \times 10^7$ | 0.49 |

regions at the low and high molecular weight extremes. Slopes for the three solvents are listed in Table V.

For all three solvents, slope values of 2.0 to 1.83 were found for low molecular weight PBIC; values in the range of 1.85 are expected for chains possessing the rodlike posture. The slopes at high molecular weight differed for the three solvents. For chloroform and tetrahydrofuran the value of $a$ was 0.37, slightly less than that expected for wormlike chains at high molecular weight.[26] Along this line Milstein and Charney[27] have concluded from electric dichroism studies that high molecular weight PBIC ($\overline{M}_w = 1.7 \times 10^6$ g mol$^{-1}$) in chloroform seems to adopt a "folded" conformation. Also, consideration of the data in Table V shows that the wormlike nature of PBIC does not persist in $CCl_4$ in the high molecular weight region because (1) $a$ in $CCl_4$ is less than anticipated for a wormlike structure and (2) the decrease of $[\eta]$ for $CCl_4$ is larger than for tetrahydrofuran and chloroform. This behavior demonstrates pronounced deviation from the wormlike coil model. A spectroscopic, UV and IR, examination of PBIC in $CCl_4$ has seemingly revealed the presence of intramolecular attraction between the nitrogens and the carbonyl carbons, whereas no such bonding is present in the more polar solvents tetrahydrofuran and chloroform. The presence of this intramolecular bonding could, of course, lead to distortion of the wormlike chain conformation.

Parenthetically, it can be mentioned that the highest molecular weight sample discussed here, PBIC-36-1, does not represent the highest molecular weight sample in our laboratory. An additional PBIC sample was found to have an $[\eta]$ in $CCl_4$ and $2.5 \times 10^2$ dL g$^{-1}$. This indicates that this material may have a molecular weight in excess of $10^8$ g mol$^{-1}$. However, this sample is not included in our analysis due to the difficulty of determining its molecular weight and the breadth of the molecular weight distribution. The markedly high molecular weight of this sample is attested to by the fact that Bur[17] was unable to determine its relaxation time from dielectric measurements. The bridge used by Bur had a frequency range of $10^{-1}$ to $2 \times 10^6$ Hz[17].

Increasing polydispersity with increasing molecular weight for the high molecular weight samples may, in part, be to blame for the slight disagreement in slope values in the wormlike region. The GPC study indicated that for these samples polydispersity increased as the molecular weight increased from about 1.1 at low molecular weight to about 1.3 at the highest molecular level that resolution was possible ($\sim 10^6$). Taking $\overline{M}_w/\overline{M}_n$ equal to 1.3 would make $\overline{M}_w \simeq 1.15\overline{M}_v$ for the highest molecular weight sample. Considering that the plotted parameter $\overline{M}_w$ in Figure 7 was greater than $\overline{M}_v$, the corresponding shift in the $x$ axis could add about 0.1 unit to the slope values at high molecular weight for the situation where $\overline{M}_w/\overline{M}_v$ is increasing with increasing molecular weight. This would make the $a$ exponent about 0.47 in tetrahydrofuran and chloroform very close to the value expected for the wormlike model. This correction is based on the assumption that these high molecular weight samples possess symmetrical distributions, as indicated by dielectric relaxation methods.[17]

A correction to the $[\eta]$ values using the equation of Bianchi and Peterlin,[29]

$$[\eta]_{\text{cor}} = [\eta]_0 + [\eta]_n$$

where $[\eta]_0$ is the intrinsic viscosity of the smallest unit ($\overline{M}_w \simeq 10^5$) and $[\eta]_n$ is the conventional value for the Kirkwood–Riseman necklace model, provided only minimal changes to the data at high molecular weights and did not alter the slopes.

The slopes of the plot of the log $\langle S^2\rangle_z^{1/2}$ vs. log $\overline{M}_w$ in Figure 4 for PBIC in tetrahydrofuran at 40 °C are listed in Table VI. At low molecular weights, the slope of $\langle S^2\rangle_z^{1/2}$–$\overline{M}_w$ was 1, as expected for rigid rods, and decreased at high molecular weights, as anticipated for wormlike chains.

The intrinsic viscosity and radius of gyration data support the previous findings that low molecular weight PBIC exists as a true rigid rod in all three solvents while at high molecular weight flexibility accumulates. The transition region from rodlike to wormlike chain appears at a molecular weight of about $10^5$ g mol$^{-1}$, a result in agreement with conclusions obtained from dichroism data.[5,27] However, the $[\eta]$–$M$ characteristics of these data for high molecular weight PBIC in $CCl_4$ do not support the wormlike chain model.

The finite (and unknown) molecular weight distributions of samples must be considered when evaluating other publications[30-36] on the solution properties of PBIC. The nature and breadth of the distributions of the "fractions" used in most of the studies of PBIC published to date are probably the cause of the disagreement between the slope values and also the values of $[\eta]$ at various molecular weights that are reported in the literature. For example, Tsvetkov and co-workers[33] have reported $[\eta]$–M characteristics for PBIC in $CCl_4$ which differ markedly from these results. Although Tsvetkov and co-workers have claimed[30-36] that their studies were carried out on PBIC "fractions", these authors have not given a numerical estimate of the breadth of the molecular weight distributions of their "fractions". It is clear that a poly($n$-alkyl isocyanate) can contain a distribution of both molecular weights and molecular conformations. Hence, well-characterized fractions with reasonably narrow molecular weight distributions must be used if a simple molecular interpretation of the hydrodynamic data is to be obtained.

The effects of polydispersity on the intrinsic viscosity of rodlike PBIC can be seen in the data of Table IV and ref 12. The polydisperse PBIC-21R of Table IV has an $[\eta]$ of 5.72 dL g$^{-1}$ in $CCl_4$ while the near-monodisperse PBIC-21 exhibits an $[\eta]$ of 11 dL g$^{-1}$. These two samples possess virtually identical values for $\overline{M}_w$. In the plot of $[\eta]$–$\overline{M}_w$ in Figure 7 the dashed lines represented the smoothed data that would be found if PBIC-21R were used, whereas the full line represents the curve when the more monodisperse PBIC-21 is used. The slope of the dashed curve is 1.60 in contrast to the value of 2.0 for $CCl_4$ discussed earlier.

It can also be noted that the polydisperse PBIC-6 (which possessed an extended high molecular weight tail[17]) has an intrinsic viscosity close to that of PBIC 36-1, even though the latter has an $\overline{M}_w$ of about five times that of the former. The $[\eta]$–$\overline{M}_w$ characteristics of the PBIC-6 sample are in good agreement with the results of Tsvetkov and co-workers.[33]

Much effort was spent in characterization of these PBIC samples. Future articles will present additional aspects of the solution properties and conformation of PBIC in $CCl_4$, tetrahydrofuran, and chloroform.

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# Structure and Rigidity of Molecules of Aromatic Polyamides in Solutions

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ABSTRACT: Possibilities of using dynamooptical data (flow birefringence) for the analysis of conformations and equilibrium rigidity of aromatic polyamides in solutions have been shown. It has been proved experimentally and theoretically that molecules of para-aromatic polyamides are characterized by tremendously high equilibrium rigidity. Hence, they can be used to obtain ultrahigh modulus fibers. Aromatic polyamides responsible for these properties exhibit the following structural features: the trans conformation of their amide groups and the para position of aromatic rings in their chain which imparts the "crankshaft" shape to this chain.

In recent years rigid-chain polymers have attracted great attention of research workers in the field of physicochemistry and technology of macromolecular compounds. The reason for this is the fact that up-to-date polymer materials with very valuable thermomechanical properties may be obtained on the basis of macromolecular compounds characterized by a limited chain flexibility and usually called rigid-chain polymers. Aromatic polyamides are some of the most important among these polymers.

## Conjugation in Chain and Rigidity of Molecules of Aliphatic Polyamides

High thermomechanical properties of polyamide materials, such as "nylon 6" (polycaprolactam) and other aliphatic polyamides, are related primarily to their high crystallinity and ability to form intermolecular hydrogen bonds. These properties are determined in turn by the peculiar structure of their molecules containing amide groups (the source of hydrogen bonds) separated along the chain by links of five or more methylene groups $CH_2$ ensuring the "tactic" chain order and thus facilitating its packing in the polymer crystal.

At the same time investigations of conformational properties of molecules of aliphatic polyamides (nylon 6 and nylon 66) in dilute solutions have shown[1] that in the absence of intermolecular interactions they are typical flexible-chain polymers similar, for instance, to polyethylene. This seems quite natural since over four-fifths of nylon 6 molecule consists of the polymethylene chain, the high flexibility of which (just as for other carbochain polymers) is ensured by a considerable freedom of intrachain molecular rotations about the C–C bonds.

The situation changes greatly when the amide groups in aliphatic polyamide are very close to each other along the chain. This is the case with poly(alkyl isocyanates) (nylon 1, –CONR–), the molecules of which consist entirely of amide groups incorporated in the chain one after another in a

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