Equilibrium Conformation and "Worm-Like Coil" Configuration of Poly(n-alkyl isocyanates)

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ABSTRACT: Osmotic pressure and light-scattering measurements of the polymers of n-butyl, n-hexyl, and n-octyl isocyanates are presented. The molecular weight dependence of the osmotic second virial coefficients and the radii of gyration is analyzed in terms of the worm-like-coil model of Kratky and Porod. The characterization of the n-butyl polymer, which has been studied most extensively, results in 500–600 Å for the persistence length and 1.8–2.1 Å for the monomeric projection along the contour direction of the chain. The dependence of the radii of gyration on the weight-average molecular weights for the n-hexyl and n-octyl polymers is found to be similar to that for the n-butyl polymer. Thus, although our analysis has focused on the n-butyl species, it appears that a similar set of Kratky–Porod parameters should be applicable to the other polymers with normal aliphatic side chains of moderate length.

Following an earlier study[2] of the hydrodynamic character of poly(n-butyl isocyanate) (PBIC), further attempts[3,4] to extend the evidence for the rodlike behavior of PBIC have shown that this polymer appears to be flexible above molecular weights of *ca.* 10^5. In the previous study, the molecular weight dependence of the dielectric relaxation times was interpreted in terms of the rigid-rod model. The observed rotatory diffusion constants had the correct dependence on the major molecular axis of the polymers, modeled as a prolate ellipsoid, in accordance with Perrin,[5] Burgers,[6] Kirkwood and Auer,[7] and Broersma.[8] The range of molecular weights of the polydisperse samples was sufficiently large, *i.e.*, 6×10^4–2×10^6, so that possible errors introduced by the small range of contour lengths in the analysis were ruled out. Thus, the hydrodynamic data were consistent with the rigid-rod model. However, the mean-square dipole moments were not consistent[2] with the rigid-rod model; that is, the mean-square dipole moments were not proportional to the square of chain length. In order to accommodate this apparent discrepancy, it was proposed that the addition sequence of repeating units was not uniform with respect to their dipolar senses, *i.e.*, while the chain configuration is rodlike, there are a number of dipole reversal sites within a chain. Hence, the two sets of data could be accommodated by the rigid-rod model.

Subsequently, Bur and Roberts[3] repeated the dielectric measurements with fractionated samples of PBIC to test this analysis of the chain configuration and to examine the effect of polydispersity on the earlier data. Their results[3] demonstrated the deviation from the rigid-rod model in the high molecular weight range. The molecular weight dependence of the dielectric relaxation time and the mean-square dipole moment deviates from the rigid-rod model as the degree of polymerization of PBIC exceeds 800. Thus, since these two sets of data were consistent with each other, the dipole-reversal model was discarded.

Hence, it was desirable to examine the configuration of PBIC by methods not based on hydrodynamic properties but on the equilibrium properties of polymers. Of such methods, we chose light scattering and osmometry. With the first method we were able to confirm the nonlinear dependence of the radii of gyration on molecular weight, and with the second the independence of the osmotic second virial coefficient on the molecular weights.[9]

This paper presents these measurements and their interpretation according to the worm-like-coil model of Kratky and Porod.[10,11] The two parameters introduced in our interpretation are the persistence length q and monomeric projection h on the chain axis instead of the customary contour length as in Benoit and Doty.[12] The projection of the monomeric unit along the chain axis enables us to infer the short-range conformation of PBIC, while the persistence length furnishes knowledge of the long-range configurational correlation. The translation along the molecular axis per monomeric unit is particularly interesting in view of the earlier value[2] of *ca.* 0.5 Å deduced from the dielectric relaxation times. As shown below, analysis of the present data yields 1.8–2.1 Å, which is in good agreement with a figure of 1.94 Å given by Shmueli, Traub and Rosenheck,[13] who studied oriented films of PBIC by X-ray diffraction and determined the unit-cell dimensions.

Methods and Results

(1) Preparation of Polymers. Commercially available monomers, n-butyl isocyanate and n-octyl isocyanate (Eastman Organic Chemicals), were purified by distillation after drying over calcium hydride dispersion for 1 week. The n-hexyl isocyanate was synthesized by the method of Shashoua, Sweeny, and Tietz.[14] The samples were synthesized with anionic initiators *in vacuo*. The n-butyl polymer was prepared in toluene solution at −78°, with n-butyllithium or fluorenyl sodium as the anionic initiator. Poly(n-hexyl isocyanate) and poly(n-octyl isocyanate) were synthesized in

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[2] H. Yu, A. J. Bur, and L. J. Fetters, *J. Chem. Phys.*, **44**, 2568 (1966).

[3] A. J. Bur and D. E. Roberts, *ibid.*, **51**, 406 (1969).

[4] J. B. Milstein and E. Charney, *Macromolecules*, **2**, 678 (1969).

[5] F. Perrin, *J. Phys. Radium*, **5**, 497 (1934).

[6] J. M. Burgers, "Second Report on Viscosity and Plasticity," Nordemann, New York, N. Y., 1938, p 127; *Verh. Kon. Ned. Acad. Wetensch. Afdel. Natuurk.*, [I] **16**, (4), 113 (1938).

[7] J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19**, 281 (1951).

[8] S. Broersma, *ibid.*, **32**, 1626 (1960).

[9] L. J. Fetters and H. Yu, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **7**, 443 (1966).

[10] O. Kratky and G. Porod, *Recl. Trav. Chim. Pays-Bas*, **68**, 1106 (1949).

[11] G. Porod, *Montash. Chem.*, **80**, 251 (1949).

[12] H. Benoit and P. Doty, *J. Phys. Chem.*, **57**, 958 (1953).

[13] U. Shmueli, W. Traub, and K. Rosenheck, *J. Polym. Sci., Part A-2*, **7**, 515 (1969).

[14] V. E. Shashoua, W. Sweeny, and R. F. Tietz, *J. Amer. Chem. Soc.*, **82**, 866 (1960).

Table I
Number-Average Molecular Weights and Second Virial Coefficients of Poly(n-alkyl isocyanates)

Sample[a]	No.	$\langle M_n\rangle \times 10^{-5}$, g mol^{-1}	$A_2 \times 10^3$, mol cm^3 g^{-2}	$\langle M_n\rangle A_2/\bar{v}_2$
PBIC	16	0.23	2.1	47
	4	0.52	2.0	101
	18	0.54	1.8	94
	28	0.63	2.4	141
	10	0.83	2.4	193
	31	0.90	1.9	166
	1	0.96	2.5	232
	27	1.02	1.9	188
	21	1.20	2.2	256
	35	1.25	1.9	231
	29	1.38	2.0	268
	100	1.40	2.2	300
	2	1.52	2.1	310
	19	1.70	2.1	347
	101	1.98	2.2	423
	3f	2.28	2.4	532
	10f	2.50	2.5	607
	12	2.55	1.8	447
	10′	2.72	2.2	581
	1′α	5.00	2.0	973
	3	5.23	2.1	1072
PHIC	1	0.61	2.2	130
	4	1.41	2.1	287
	6	6.06	1.8	1050
POIC	1	0.68	2.2	145
	2	0.82	1.9	151
	3	2.00	2.0	338

[a] PBIC, n-butyl polymer; PHIC, n-hexyl polymer; POIC, n-octyl polymer.

toluene at the same temperature. The details of the polymerization procedure have appeared elsewhere.[2,15]

(2) Osmometry. Solutions of polymers with different alkyl side groups were dissolved in toluene and osmotic pressures were measured. The instruments[16] were commercial membrane osmometers. All measurements were at 37°. Several types of commercially available membranes[17] were used. Table I contains the number-average molecular weights and second virial coefficients. The last column indicates the calculated axial ratios according to Zimm.[18] The precision of our measurements for $\langle M\rangle_n$ was about 5%, as judged from the calibration with NBS 705 polystyrene standard sample. Determination of the slope of the (π/c) *vs.* c plot to obtain the osmotic second virial coefficient was carried out with a simple least-squares progression technique. The independence of the second virial coefficients on molecular weight is clearly demonstrated. The arithmetic mean of A_2 for PBIC is 2.13×10^{-3} mol cm^3 g^{-2} and the standard deviation of the mean is 0.22×10^{-3}. Hence, we accept A_2 as being independent of $\langle M\rangle_n$. Furthermore, the precision of determining the slopes is roughly 10%, so that the observed standard deviation is consistent with our conclusion. The last two rows of PBIC data in Table I are for two samples with $\langle M\rangle_n \geq 5 \times 10^5$. Since that is at the limit of instrument capability, these data are of doubtful validity, although the A_2 values are consistent. They have appeared once before in the literature,[9] and we wish to retract our earlier comment that the osmotic second virial coefficients of PBIC show no dependence on the molecular weight for a 20-fold range. We claim only that such is the case for about a tenfold range of number-average molecular weight.

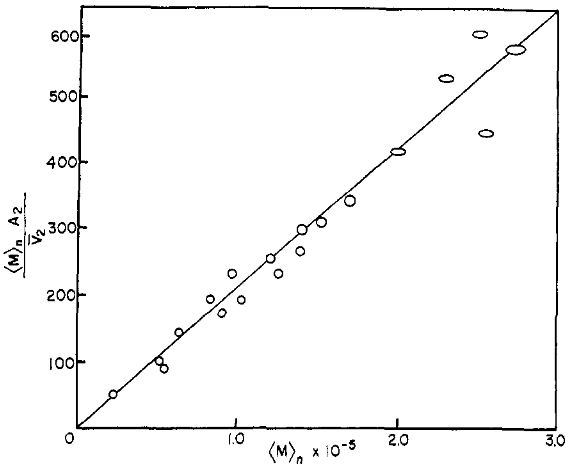

Figure 1. The number-average molecular weight of PBIC *vs.* the axial ratio.

For the moment, these data can be viewed as a demonstration of the rodlike character of poly(n-butyl isocyanate) as well as for the n-hexyl and n-octyl species, because of similar, although fewer, observations that were made pertaining to their second virial coefficients. In order to verify this presumption, we plot $(\langle M\rangle_n)A_2/\bar{v}_2$ against $\langle M\rangle_n$ in Figure 1. The straight line obtained passes through the origin. This is consistent with Zimm's theory[18] for rods of uniform diameter, with

$$\pi/c = RT/M(1 + A_2C + \ldots) \qquad (1)$$

and

$$A_2 = L\bar{v}_2/Md \qquad (2)$$

where L is the length of a rod whose diameter is d along the entire length and $\bar{v}_2$ is the partial specific volume of the rod. The value of $\bar{v}_2$ is taken[13] as 1.03 cm^3 gm^{-1}. With a value of 1.94 Å for the monomeric projection[13] and the data in Table I, the value of d is found to be *ca.* 10 Å for PBIC.

(3) Light Scattering. Polymer solutions in chloroform were twice filtered without applying pressure through 0.45-μ filters[19] prior to placement into the scattering cells. The light-scattering photometer[20] was a commercial instrument and was calibrated for absolute scattering intensity against benzene. The Rayleigh ratios[21] of benzene adopted for our measurements were 15.8×10^{-6} cm^{-1} at 546 nm and 45.6×10^{-6} cm^{-1} at 436 nm. Although the refractive index increment of 0.054 cm^3 g^{-1} in chloroform is small, the scattering intensities were strong enough to perform reasonably sensitive measurements. The refractive index increment in tetrahydrofuran for the PHIC and POIC samples was determined with a Rayleigh refractometer. These values at 435.8 and 546.1 nm were found to be 0.99 and 0.978 cm^3 g^{-1}, respectively, and agree with the values reported by Schneider,

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(15) L. J. Fetters, *J. Res. Nat. Bur. Stand., Sect. A*, **70**, 421 (1966).

(16) Hewlett-Packard Models 501, 502, and 503 and Dohrmann M-100 high-speed membrane servoosmometers.

(17) S and S-08 deacetylated acetylcelloulose and gel-celophane 450 membranes.

(18) B. H. Zimm, *J. Chem. Phys.*, **14**, 164 (1946).

(19) Millipore or Selas Flotronics filters.

(20) Bausch and Lomb PGD (the Sofica) light-scattering photometer.

(21) D. J. Coumou, *J. Colloid Interface Sci.*, **15**, 408 (1960).

TABLE II

LIGHT-SCATTERING DATA OF POLY(*n*-ALKYL ISOCYANATES)

Sample	No.	Initiator[a]	$\langle M\rangle_w \times 10^{-5}$ [b]	$\frac{\langle M\rangle_w}{\langle M\rangle_n}$	$\langle S^2\rangle^{1/2}$, Å	$A_2 \times 10^3$ [c]
PBIC						
(546 nm, $CHCl_3$)	23	A	0.61		320	3.0
	1D″	B	1.03		420	1.5
	1	B	1.32	1.4	500	3.0
	21	A	1.33	1.1	525	2.5
	20	C	1.65		625	2.0
	29-4-A″	A	2.10		770	3.0
	10	C	2.26	2.7	760	2.5
	33	D	2.88	3.4	950	2.0
	10f	C	3.27	1.3	945	2.0
	1α	B	3.50		1010	2.0
	15	D	3.67		1180	2.5
	31	C	3.68	4.1	1110	3.5
	35[b]	C	3.87	3.1	1100	3.0
	35	C	3.80	3.0	1080	2.5
	12	D	4.46	1.7	1220	2.0
	3f	C	4.60	2.0	1200	2.0
	18	A	5.08	9.5	1210	2.7
	28	C	5.26	8.4	1330	3.5
	1′α	B	5.40	1.1	1250	2.5
	29	C	6.40	4.6	1500	3.3
	30	C	6.40	2.4	1450	2.0
	27	C	7.00	6.7	1530	3.5
	7	C	7.05		1480	3.0
	9	C	9.20		1650	2.0
	2	C	9.43	6.2	1660	2.5
	19	C	10.00	5.9	1690	2.5
	14-1	E	18.50		2400	2.5
	14	E	18.40		2400	2.5
	6	C	24.50		2800	2.4
	36-2	A	35.00		3000	2.0
	36-1	A	100.00		5200	2.1
PHIC						
(546 nm, $CHCl_3$)	1	C	2.07	3.4	870	2.5
(546 nm, THF)	1	C	1.97	3.2	890	1.7
(436 nm, THF)	1	C	2.05	3.4	910	1.3
(546 nm, $CHCl_3$)	3	C	2.97		925	3.0
(546 nm, $CHCl_3$)	4	C	3.43	2.4	1010	3.0
(546 nm, THF)	4	C	3.15	2.2	1080	1.2
(436 nm, THF)	4	C	3.25	2.3	1000	1.3
(546 nm, $CHCl_3$)	5	C	5.66		1360	2.5
POIC						
(546 nm, $CHCl_3$)	1	C	3.75	5.5	1180	3.0
(546 nm, THF)	2	C	4.00	4.9	1200	1.5

[a] A, fluorenyl sodium; B, sodium cyanide in dimethylformamide; C, *n*-butyllithium; D, diphenylhexyllithium; E, α-phenylethylpotassium. [b] g mol^{-1}. [c] mol cm^3 g^{-2}.

et al.,[22] for 435.8 nm and by Plummer and Jennings[23] for 435.8 and 546.1 nm.

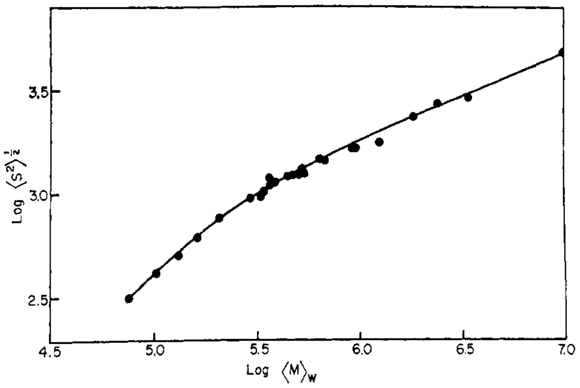

Figure 2. Log–log plot of the weight-average molecular weight of PBIC *vs.* the radius of gyration.

Unpolarized light was used for all measurements, while the scattered intensity was measured at 11 angles over the angular range of 30–150°. Optical alignment was verified by observing the scattering envelope for pure benzene at 22 (±0.5)° and by carrying out measurements on the NBS 705 and 706 polystyrene samples.

The data obtained from light scattering, namely weight-average molecular weight, radius of gyration, and second virial coefficient, were determined from a Zimm plot. The arithmetic mean of the light-scattering second virial coefficient, A_2, is 2.51×10^{-3} mole cm^3 g^{-2} and the standard deviation of the mean is 0.35×10^{-3}. The data in Table II show clearly that the radius of gyration does not increase linearly with molecular weight. This finding is not the one expected if the polyisocyanates are rodlike over the observed molecular weight range. Figure 2 is a double logarithmic plot of the radius of gyration, $\langle S^2\rangle^{1/2}$, *vs.* weight-average molecular weight, $\langle M\rangle_w$.

(4) Infrared Measurements. Infrared spectral measurements[24] were performed with carbon tetrachloride solutions of PBIC, dimethylformamide, and polystyrene. Poly(γ-benzyl L-glutamate) (PBLG) solution was in chloroform as the solvent. The concentrations of the first three compounds were identical in order to facilitate the comparison of the carbonyl absorption peaks.

Discussion

The osmotic second virial coefficients of all three polymers are practically the same within the range of number-average molecular weights of 23,000–272,000. However, a more critical claim of the constancy of A_2 can be made only up to $\langle M\rangle_n$ 190,000 on the basis of the scatter of the data in Figure 1. It should be noted that the second virial coefficients are consistent with our choice of the worm-like-coil model with a certain persistence length.

A discussion of the light-scattering data is now in order. The applicability of the rigid-rod model throughout the observed molecular weight range is not borne out by the downward curvature of the double logarithmic plot in Figure 2. Hence, the Kratky–Porod[10] worm-like-coil model was chosen for the analysis as an alternative to the inapplicable rigid-rod model. The expression for the mean-square radius of gyration in the absence of excluded volume effects was derived by Benoit and Doty[12] as follows

$$\langle S^2\rangle_0 = q^2[(x/3) - 1 + (2/x) - (2/x^2)(1 - e^{-x})] \quad (3)$$

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[22] N. S. Schneider, S. Furusaki, and R. W. Lenz, *J. Polym. Sci., Part A*, **3**, 933 (1965).

[23] H. Plummer and B. R. Jennings, *Eur. Polym. J.*, **6**, 171 (1970).

[24] Perkin-Elmer 521.

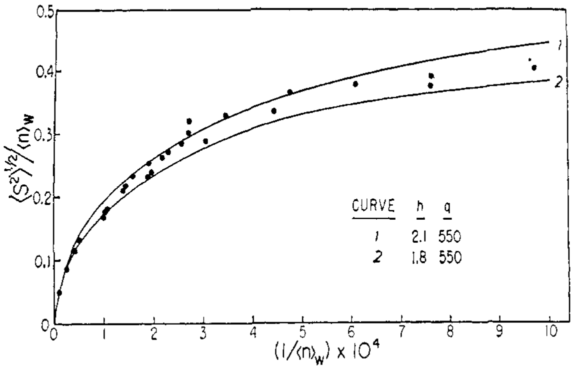

Figure 3. Plot of the observed ratio of the radius of gyration to the weight-average degree of polymerization against the reciprocal of the weight-average degree of polymerization.

with $x \equiv nh/q$, where q is the persistence length, n the degree of polymerization, and h the monomeric projection along the contour direction. The two adjustable parameters in eq 3 are q and h, whereas the experimentally accessible quantities are $\langle S^2\rangle_0$ and n, both obtainable from light scattering. The usual contour length L has been replaced by nh in eq 3. It should be noted that the limiting cases of eq 3 are

$$\lim_{x\to 0} (\langle S^2\rangle_0^{1/2}/n) = (h^2/12)^{1/2} \tag{4}$$

and

$$\lim_{x\to\infty} (\langle S^2\rangle_0/n) = hq/3 \tag{5}$$

These are both physically reasonable limits. When the contour length is small compared to the persistence length, we should expect a rodlike configuration, for which eq 4 gives the radius of gyration expression; if the contour length is much larger than the persistence length, we ought to have a random-coil configuration, such that $\langle S^2\rangle_0/nh^2$ must approach a constant value, as in eq 5. Hence, the characterization of PBIC could be easily accomplished by observing the limiting cases of chain-length dependence on $\langle S^2\rangle_0$, provided that the range of chain lengths is broad enough to reach either limit. Our data are unfortunately somewhat limited in the low molecular range. Hence, the ready determination of h is not possible from the observation of the asymptotic value of $\langle S^2\rangle_0/n^2$ at small n. Instead, $\langle S^2\rangle^{1/2}/\langle n\rangle_w$ is plotted against $(1/\langle n\rangle_w)$ in Figure 3, where the two parameters are selected to give the best fit to the data. As is apparent from Figure 3, the point where $\langle S^2\rangle^{1/2}/\langle n\rangle_w$ no longer depends on the reciprocal of chain length is not reached. Nonetheless, the range for the monomeric projection may be narrowed down to 1.8–2.1 Å, while the persistence length is chosen to be 550 Å. The solid curves are drawn with these parameters according to eq 3. It may be noted that both the ordinate and the abscissa of Figure 3 are experimental quantities, although no attempt is made to correct either for chain expansion beyond the unperturbed dimension or for polydispersity.

For the determination of the persistence length, eq 5 is rearranged into the familiar random-coil form.

$$\lim_{n\to\infty} (\langle S^2\rangle_0^{1/2}/nh^2) = q/3h \tag{6}$$

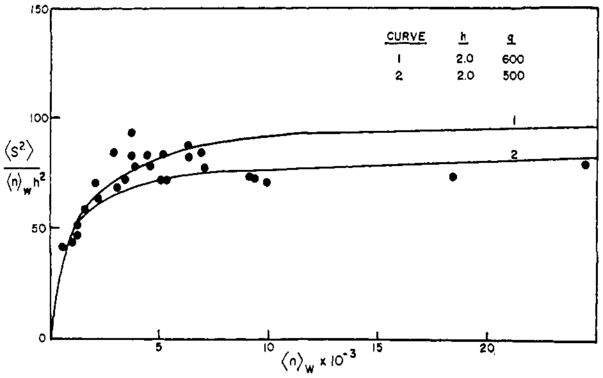

Figure 4. Plot of the observed characteristic ratio $\langle S^2\rangle/\langle n\rangle_w h^2$ *vs.* the weight-average degree of polymerization.

One purpose of recasting eq 5 in this fashion is to give a description of the PBIC chain configuration in terms of the characteristic ratio of Flory.[25] In Figure 4, a plot of $\langle S^2\rangle/\langle n\rangle_w h^2$ against $\langle n\rangle_w$ is given, with the solid curves drawn according to eq 3. The selection of a particular value for h is guided by the earlier choice in Figure 3. Thus, it can be concluded that the characteristic parameters for the PBIC chain configuration are h = 1.8–2.1 Å and q = 500–600 Å.

Other investigators' results[26–29] on the same polymer are shown in Table III. Other than the results of Bur and Roberts,[3] Jennings and Brown,[28] and us, the values for h and q were obtained from hydrodynamic methods for which the theoretical bases for the respective analyses[26,27,29] are not clear.

The results of Tsvetkov, *et al.*,[26,27] come from a reinterpretation of the data of Burchard[30] *via* Hearst and Stockmayer.[31] The dipole moment data of Bur and Roberts are equivalent to ours to the extent that they are direct measurements of the end-to-end distance. Furthermore, their results were obtained with fractionated samples, while ours are not. Bur and Roberts[3] determined a persistence moment of 900 D from the dipole moment dependence on the molecular weight. The monomeric projection of 1.1 Å, on the other hand, is calculated from the rotatory relaxation times in the low molecular weight region with the formula of Broersma.[8] They also give a value for the monomeric dipole moment of 1.13 D from a consideration of bond moments of the monomer.

Table III
Worm-Like-Coil Parameters of PBIC

h, Å	q, Å	Methods	Ref
2.1	1300	Viscosity sedimentation–diffusion	26, 27
1.1	880	Dielectric measurements	3
1.3	1000	Electric birefringence	28
0.6–1.1	>400	Dielectric and viscoelastic relaxation	29
1.8–2.1	500–600	Light scattering	This work

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[25] P. J. Flory, "Statistical Mechanics of Chain Molecules," Wiley, New York, N. Y., 1969, p 11.

[26] V. N. Tsvetkov, I. N. Shtennikova, Ye. I. Ryumtsev, L. N. Andreyeva, Yu. P. Getmanchuk, Yu. L. Spirin, and R. I. Dryagileva, *Vysokomol. Soedin., Ser. A*, **10**, 2132 (1968); *Polym. Sci. USSR*, **10**, 2482 (1968).

[27] V. N. Tsvetkov, *Eur. Polym. J., Suppl.*, 237 (1969).

[28] B. R. Jennings and B. L. Brown, *Brit. Polym. J.*, in press.

[29] S. B. Dev, R. Y. Lochhead, and A. M. North, *Discuss. Faraday Soc.*, **49**, 244 (1970).

[30] W. Burchard, *Makromol. Chem.*, **67**, 182 (1963).

[31] J. E. Hearst and W. H. Stockmayer, *J. Chem. Phys.*, **37**, 1425 (1962).

The value of *h* was obtained by extrapolating to zero molecular weight the ratio of the weight-average degree of polymerization to the mean-square dipole moment. From these three numbers, one can calculate a persistence length of 880 Å. In view of the discrepancy between 600 and 880 Å, we are easily tempted to attribute our value to the polydispersity of our samples. However, since the radius of gyration is a measure of a higher moment of the molecular weight distribution than the weight-average molecular weight,[32] the ratio of these two quantities should overweight the higher molecular weight components in a polydisperse system. Thus, a larger ratio for the radius of gyration to the weight-average molecular weight would be observed with a polydisperse sample than with a monodisperse sample. Our value, however, is smaller than theirs. Thus, we cannot readily dismiss our range of 500–600 Å on the basis of polydispersity.

We now come to the discussion of the origin of the chain rigidity. From the infrared spectral data for the polyisocyanates, we propose that the chain rigidity of poly(*n*-alkyl isocyanates) can be attributed to both the side-chain interactions and the partial-double-bond character of the backbone carbon–nitrogen bond. A comparison of our PBIC spectrum to that of Iwakura, *et al.*,[33] reveals no difference for the carbonyl stretching band at 1700 cm^{-1}. Moreover, the latter authors show that the carbonyl stretching band does not shift in either direction when the *n*-butyl side chain is replaced with an ethyl, *n*-pentyl, benzyl, or cyclohexyl group.

On the other hand, if the side chain is a *p*-chlorophenyl, *p*-tolyl, or *p*-methoxyphenyl group, the band shifts to *ca.* 1730 cm^{-1}. Hence, this shift can be taken as evidence for delocalization of the carbonyl bond in polymers with aliphatic side chains. If such a delocalization is contrasted to that of a helical synthetic polypeptide, PBLG, the PBIC carbonyl band at 1700 cm^{-1} differs substantially from that of the "amide I" structure of polypeptides. We show the spectrum of PBLG and PBIC in chloroform together with that of dimethylformamide in carbon tetrachloride in Figure 5 for comparison. The amide I band of PBLG is at 1650 cm^{-1}, while that of N,N-disubstituted amide, DMF, in dilute solution, is close to 1680 cm^{-1}. Thus, there is indirect spectroscopic evidence for the partial-double-bond character of the carbon–nitrogen bonds arising from the delocalization of carbonyl bonds. However, total coplanarity of the disubstituted amide structure of PBIC may be precluded on the basis of arguments for the side-chain interaction.[13,22] One further interesting point with regard to the origin of the chain stiffness is the observation by Tsvetkov, *et al.*,[26] for the *p*-tolyl polymer. They concluded that poly(*p*-tolyl isocyanate) possesses a random-coil configuration in bromoform, which is consistent with the view that the partial-double-bond character of carbon–nitrogen bonds in the *n*-alkyl polymers may be responsible for the chain stiffness whereas such may not be the case with those polyisocyanates possessing aromatic groups attached to the nitrogen.[34]

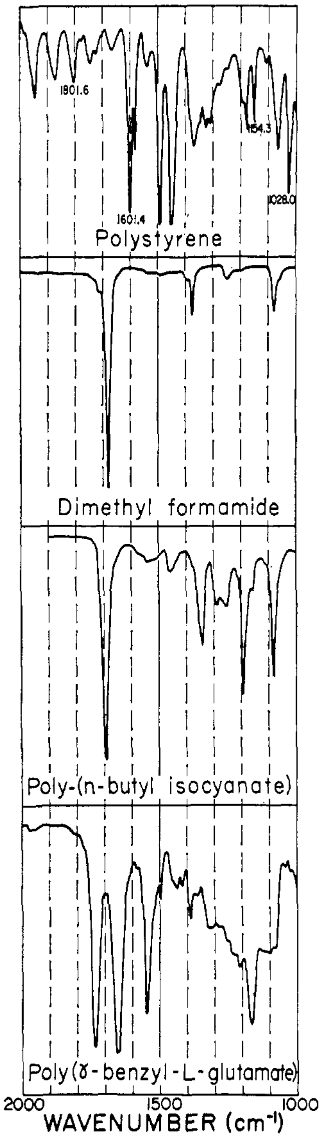

Figure 5. The ir spectra of DMF, PBIC, and PBLG with the spectrum of polystyrene as the reference between 1000 and 2000 wave numbers.

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[34] Certain commercial equipment and materials are identified in this paper in order to adequately specify experimental procedures. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.