

## Chain Stiffness in Polyisocyanates\*

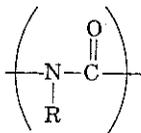
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### Synopsis

Light-scattering measurements of the molecular conformation of *n*-hexyl polyisocyanate (PIC) in tetrahydrofuran (THF) show that the ratio of the root-mean-square end-to-end distance to the maximum extension exceeds 25% even at a molecular weight of  $3 \times 10^5$  and that the effective bond length in the equivalent freely linked chain is 23 Å, corresponding to about 17 links per statistical segment. These results are at least twice as high as the values of cellulose trinitrate in acetone at a comparable degree of polymerization. Although a significant variation in intrinsic viscosity occurs in different solvents, the recently reported viscosity- and sedimentation coefficient-molecular weight exponents of 1.18 and 0.16 for *n*-butyl PIC in THF indicate that the polymer behavior lies outside the Gaussian region and must result from the short range structure rather than from strong interactions with the solvent. In fact, by using a form of the Kirkwood-Riseman theory, modified to take account of the expansion factor, a viscosity-molecular weight exponent of 0.9 is calculated for theta conditions. It is proposed that the chain is stiffened by restrictions to rotation imposed by resonance effects in the peptide bonds that make up the polymer backbone.

### INTRODUCTION

The low temperature anionic polymerization of a variety of *N*-substituted monoisocyanates to high molecular weight polyisocyanates (PIC) was reported by Shashoua and co-workers in 1960.<sup>1</sup> The polymerization system of choice was NaCN in *N,N*-dimethylformamide which gave polymer yields of about 70% with isocyanates carrying linear aliphatic substituents. Conceivably polymerization might take place either through the carbon-nitrogen double bond to yield the repeating structure I:

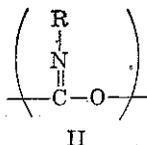


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\* Taken in part from the M.S. Thesis of S. Furusaki, Department of Chemical Engineering, Massachusetts Institute of Technology, January 1964.

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or through the carbon-oxygen double bond resulting in a polyacetalic structure II:



The intense carbonyl adsorption of  $5.9 \mu$  indicates that the first structure predominates, but this does not exclude the possibility that some addition occurs through the carbon-oxygen double bond. In a later study of the polymerization of *n*-butyl isocyanate with a variety of catalysts Natta's group<sup>2</sup> found that a polymer with a far higher degree of crystallinity could be obtained using the catalyst system, ethyllithium in benzene. As with the polymer of lower crystallinity from NaCN-DMF, this sample also showed the strong carbonyl adsorption typical of the substituted amide structure.

The properties of this class of polymers which are especially provocative are those which call attention to the possibility that the polyisocyanates possess an unusually extended chain structure. This was suggested by two items of the properties reported by Shashoua; first, an *n*-heptyl polymer of molecular weight 69,000 had an inherent viscosity in benzene of 2.4 dl./g., equivalent to the intrinsic viscosity of polystyrene of molecular weight  $1 \times 10^6$  in toluene and, second, in spite of the absence of hydrogen bonding the melting points of the polymers were unusually high, 250°C. for the *n*-ethyl and *n*-propyl homologs, which is comparable to the melting temperature of nylon 66. The more highly crystalline *n*-butyl PIC prepared by Natta's group also had an unusually high intrinsic viscosity. These inferences regarding chain extension have recently been substantiated by the results published by Buchard<sup>3</sup> on *n*-butyl PIC samples polymerized with the NaCN-DMF system to cover the molecular weight range of 18,000-210,000. His measurements on the solution properties of these samples showed that both the viscosity-molecular weight exponent and the sedimentation coefficient-molecular weight exponent appear to lie outside the range expected for Gaussian behavior.

This paper reports on a limited light scattering and viscosity study of a higher N-substituted homolog, the *n*-hexyl PIC, which furnishes additional information on the nature of the chain conformation in these polymers. When taken together with the work on the *n*-butyl polymer, the data suggest that the PIC molecules deviate from random-flight statistics as a result of inherent chain stiffness rather than strong interactions with the solvent and therefore, should exhibit partial draining even in a theta solvent. Many of the problems of interpretation that arise in the present work are similar to those which have been dealt with in the several extensive studies cellulose trinitrate (CTN),<sup>4-7</sup> and the behavior of the PIC may be viewed profitably by comparison with results obtained on this classical

stiff chain polymer. In the interests of brevity, concepts and equations found in the group of papers just cited will be used without full development. The papers by Holtzer, Benoit, and Doty,<sup>4</sup> and by Hunt, Newman, Scheraga, and Flory<sup>5</sup> are especially pertinent, while the recent review by Kurata and Stockmayer<sup>3</sup> was indispensable to the authors in preparation of this paper.

### EXPERIMENTAL

The sample was prepared following the directions given by Shashoua<sup>1</sup> as a single run performed to test the method of polymerization. Since only 5 g. of polymer was available a conservative approach to the experimental work was necessary. A number of measurements were first made to characterize the original sample. A little more than 1 g. of the sample was then fractionated from a 0.5% benzene solution by titration with acetone to the cloud point. The separation was poor with the fractions covering less than a threefold range of molecular weight. Since the ratio of the weight-average to number-average molecular weight in the sample was close to two, this limited resolution either reflects the poor choice and control of the fractionation conditions or the interference of some crystallization during phase separation. Consideration of the latter possibility raised the question as to whether association of molecules through polar interactions might occur in solution. As a check on possible aggregation a sample was dissolved with slow stirring in tetrahydrofuran and the viscosity first determined 30 min. after the addition of the solvent. No changes in viscosity were detected, either shortly after solution or over the following 96 hr. period. This suggests that aggregation does not occur in tetrahydrofuran and that the polymer in solution is stable at room temperature. Equivalent results were obtained in benzene.

Light-scattering determinations were made in cylindrical cells with plane entrance and exit windows at ambient temperature and at a wavelength of 436 Å. The Brice-Phoenix light-scattering photometer was calibrated against benzene, a value of  $48.9 \times 10^{-6} \text{ cm.}^{-1}$  being adopted for Rayleigh's ratio. The solutions were clarified by filtration through solvent-resistant microporous membranes of 0.45  $\mu$  pore diameter. Tetrahydrofuran was used as solvent, since it provided a relatively large refractive index increment  $dn/dc = 0.0978 \text{ cm.}^3/\text{g.}$ , in comparison to the value of 0.054  $\text{cm.}^3/\text{g.}$  in chloroform, the solvent used for this purpose by Shashoua.

Viscosity measurements were made in an Ubbelohde suspended-level viscometer on the three fractions  $f_1$ ,  $f_2$ , and  $f_3$  and on the reprecipitated but unfractionated sample 4, in tetrahydrofuran and in chloroform. In addition, a survey was made on the viscosity of the unfractionated sample in a number of other solvents as well. The intrinsic viscosity,  $[\eta]$ , was determined as the common intercept of linear plots of  $\eta_{sp}/c$  and  $\ln \eta_{rel}/c$  against concentration. No corrections were made for shear rate dependence, but judging from the results reported by Hunt<sup>4</sup> this would in-

crease values of the intrinsic viscosity above 8 by about 6%, with a smaller effect on the samples of lower viscosity.

### RESULTS

The Zimm plot for the lowest molecular weight fraction shown in Figure 1 has the appearance of a normal rectilinear grid. The plot for the unfractionated sample, shown in Figure 2, displays curvature in the zero angle line. There is also some evidence of curvature in the angular data at high angles but this was ignored, and the angular data at each concentration were fitted with a straight line. The graphs for the other two fractions showed no curvature in the angular data and the concentration dependence showed curvature only for the highest molecular weight fraction. Molecular weights and values of the second virial coefficient  $A_2$  were actually determined by plotting the data at zero angle according to the equation

$$Kc/R(\theta = 0^\circ, c)^{1/2} = Kc/R(\theta = 0^\circ, c = 0)^{1/2}(1 + \Gamma_2 c)$$

where  $\Gamma_2 = A_2 M$ . This is analogous to the recommended procedure for plotting osmotic pressure data, and was used for the light-scattering measurements as a result of the large values of  $\Gamma_2$ . Compared to the direct method of plotting the data, the molecular weights so determined for the PIC samples were lower by about 6% and the virial coefficients lower by about 10% for  $f_1$  and  $f_2$ , while for the two samples  $f_3$  and 4, where the zero angle line showed curvature, the differences were far less.

If the data were assumed to lie in the initial angular region of the particle-scattering factor, then, as is well known, the intercept determines the weight-average molecular weight:

$$Kc/R(0^\circ, 0) = 1/M_w$$

The  $z$ -average of the root-mean-square end-to-end distance,  $(\overline{R_z^2})^{1/2}$  is calculated from the initial slope of the zero concentration line:

$$(\overline{R_z^2})^{1/2} = [3\lambda'/2(2\pi)^{1/2}](SM_w)^{1/2}$$

where  $\lambda'$  is the wavelength of light in the medium and  $S$  is the slope. These values and the second virial coefficients from the implementation of the first equation are collected in Table I along with some derived parameters.

TABLE I  
Light-Scattering Results

Sample	$\overline{M}_w \times 10^{-5}$	$A_2 \times 10^4$	$A \times 10^{-3}$	$(\overline{R_w^2})^{1/2} / L_w$	$b = \left( \frac{\overline{R_w^2}}{2N_w} \right)^{1/2}, \text{ \AA.}$	$\Phi_0 \times 10^{21}$
$f_1$	1.46	7.6	1390	0.44	24	0.63
$f_2$	2.80	8.2	1800	0.29	22	0.97
$f_3$	3.20	7.8	1920	0.27	22	1.07
4	3.55	6.9	2040	0.26	23	0.92

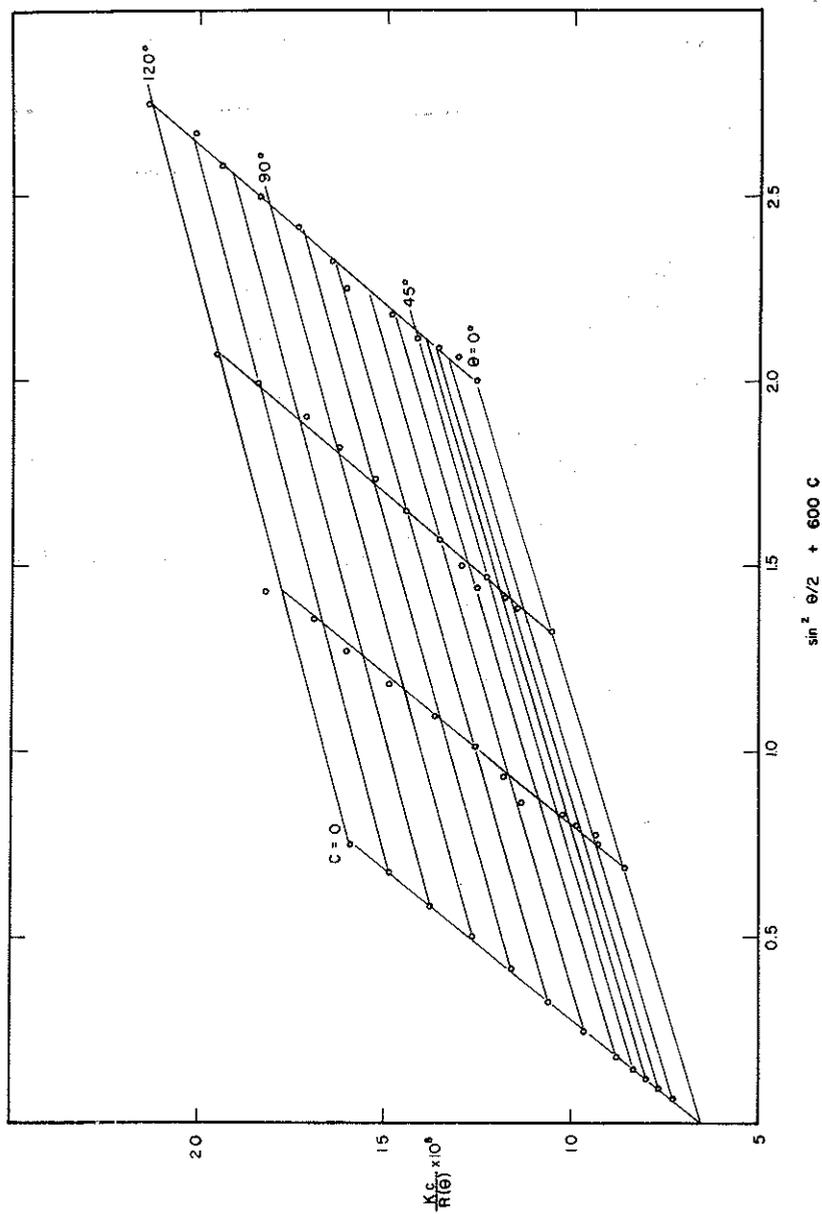


Fig. 1. Zimm plot for *n*-hexyl polyisocyanate,  $\bar{M}_w = 1.46 \times 10^5$ , in tetrahydrofuran.

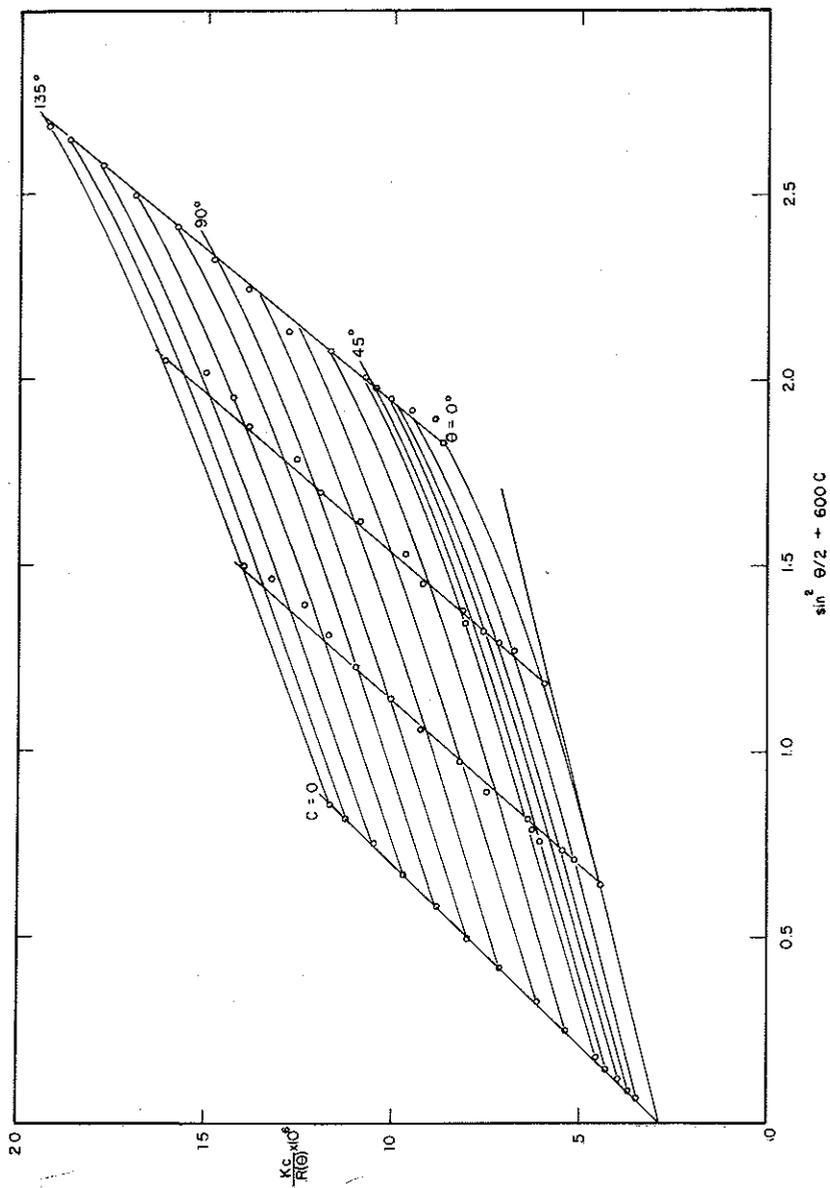


Fig. 2. Zimm plot for *n*-hexyl polyisocyanate,  $\bar{M}_w = 3.20 \times 10^5$ , in tetrahydrofuran.

TABLE II  
Viscosity Results

Sample	Tetrahydrofuran		Chloroform		$[\eta]_{\text{CHF}}$
	$[\eta]$	$k$	$[\eta]$	$k$	$[\eta]_{\text{CHCl}_3}$
f <sub>1</sub>	5.9	0.49	4.5	0.81	1.31
f <sub>2</sub>	10.3	0.60	7.0	0.61	1.47
f <sub>3</sub>	12.1	0.57	8.3	0.78	1.55
4	11.2	0.75	7.8	0.90	1.43

TABLE III  
Intrinsic Viscosity in Various Solvents<sup>a</sup>

Solvent	$[\eta]$	$k$	$[\eta]/[\eta]_{\text{CHCl}_3}$
Carbon tetrachloride	12.1	0.56	1.65
Benzene	11.5	0.51	1.57
Tetrahydrofuran	10.0	0.43	1.37
Tetrahydrofuran-dimethylformamide (4:1)	7.8	0.75	1.07
Chloroform	7.3	1.10	1.00

<sup>a</sup> Unfractionated sample.

Viscosities were determined over the concentration range of 0.01–0.06% and in some cases up to 0.08%. The values of  $\eta_{sp}/c$  or  $\ln \eta_{rel}/c$  followed a strictly linear dependence on concentration. Intrinsic viscosities in tetrahydrofuran and carbon tetrachloride are listed in Table II together with values of the Huggins constant  $k$  which occurs in the concentration dependence of  $\eta_{sp}/c$ . Results from the viscosity survey on the unfractionated sample appear in Table III.

## DISCUSSION OF RESULTS

### Light-Scattering Behavior

Application of the light-scattering results to the specification of chain conformation is complicated by a number of effects. Nonetheless, it will be shown that it is possible to develop a significant if qualitative measure of the magnitude of chain stiffness which provides a clear demonstration of the unique behavior of the polyisocyanates. To take account of the effects of polydispersity the corrections appropriate to the random distribution with  $\bar{M}_n:\bar{M}_w:\bar{M}_z = 1:2:3$  are invoked for the fractions as well as the unfractionated sample. If the fractions are significantly less polydispersed this procedure will underestimate the magnitude of the chain extension. On this basis the relative extension of the chain,  $(R_w^2)^{1/2}/L_w$ , equal to the ratio of the end-to-end distance to the length of the fully extended chain,  $L$ , and values of the effective bond length,  $b = (R_w^2/2N_w)^{1/2}$ , where  $N_w$  is the weight-average degree of polymerization, have been calculated and appear in columns 5 and 6 of Table I. In these calculations it was

assumed that  $(\overline{R^2})^{1/2}$  is proportional to  $M^{1/2}$  and that the projection of a PIC monomer unit in the direction of the chain is 2.27 Å. in accord with the structure to be discussed in the last section of the paper. The value of  $b$  signifies the bond length in the equivalent freely linked chain having the same number of bonds,  $2N_w$ , as the real chain.

Even after correction for heterogeneity the values of the relative extension and the effective bond length are enormous. The extraordinary nature of these values is even more apparent when the results for CTN are used as a yardstick. The difference in monomer molecular weight, 127 for PIC and 297 for CTN, must be taken into account so that the characteristic parameters are compared at the same degree of polymerization. For CTN the values of  $(\overline{R_w^2})^{1/2}/L_w$  drop rapidly in the appropriate molecular weight range from about 0.20 at  $M_w = 3.5 \times 10^5$  to 0.13 at  $M_w = 8 \times 10^5$ , according to values calculated on a weight-average basis from the results of Holtzer et al.<sup>4</sup> These are only one-half the corresponding values for PIC. The value of  $b$  is 34 Å. for CTN, about 40% larger than the values for PIC. However, the length of the projection of the rigid glucose unit in the chain direction is 5.15 Å. for CTN and the bond length is 1.32 Å. for PIC. Therefore, the respective values of  $b$  correspond to 6.6 links per statistical segment in the cellulose polymer compared to 17.4 links per statistical segment in the PIC chain. A comparison on this basis rather than in terms of the effective bond length appears to be a more satisfactory expression of chain stiffness since it relates directly to the rotational freedom above the bonds in the chain backbone.

The foregoing comparisons were based on values calculated under the assumption that the data for PIC lie in the initial angular region. Reference to Table I shows that the values of  $(\overline{R_z^2})^{1/2}$  are well above 800 Å., which is the approximate upper limit for the region in which the initial linear behavior of  $p^{-1}(\theta)$  can be observed for Gaussian coils,<sup>9</sup> and, therefore, the angular data for the highest molecular weight samples or possibly for all the samples may lie on the high angle asymptote of the reciprocal particle scattering factor,  $p^{-1}(\theta)$ . If this condition holds, the intercept  $Kc/R(0^\circ, 0) = 1/2M_n$ . In turn, the slope defines the number-average end-to-end distance,  $(\overline{R_n^2})^{1/2}$ , which would be lower than the tabulated values of  $(\overline{R_z^2})^{1/2}$  by a factor of  $(1/3)^{1/2}$ . This would leave the values for  $b$  unaltered but the values of  $(\overline{R_n^2})^{1/2}/L_n$  would be increased by 40%. It would then be necessary to make the comparison with values ranging from about 40 to 20 for CTN over the appropriate range of  $M_n$  values.

Interpretation of the asymptotic data in this form presumes that the sample is a polydisperse collection of Gaussian coils whereas deviations from Gaussian behavior can also decrease the slope of the asymptote. From the particle scattering factors calculated for stiff chains in terms of the Porod-Kratky wormlike chain model,<sup>9</sup> it can be shown that the values of  $(\overline{R_z^2})^{1/2}$  and of the relative extension should lead to some reduction in the slope of the asymptotic data. In view of the uncertainties about the angu-

lar region under observation and the polydispersity of the fractions it hardly seems worthwhile to attempt a more detailed examination of this effect at the present time.

The preceding discussion has sketched some of the issues that arise in any attempt to establish a definitive statement of the molecular conformation of the polyisocyanates on the basis of light-scattering data alone. However, the basic conclusion that the polyisocyanates are extraordinary stiff chain polymers appears to be clearly established by these results beyond the uncertainties in the precise values introduced by the various complications.

### Viscosity Results

In view of the evidence which has just been assembled to establish the unusual stiff chain nature of PIC one might be surprised in turning to the

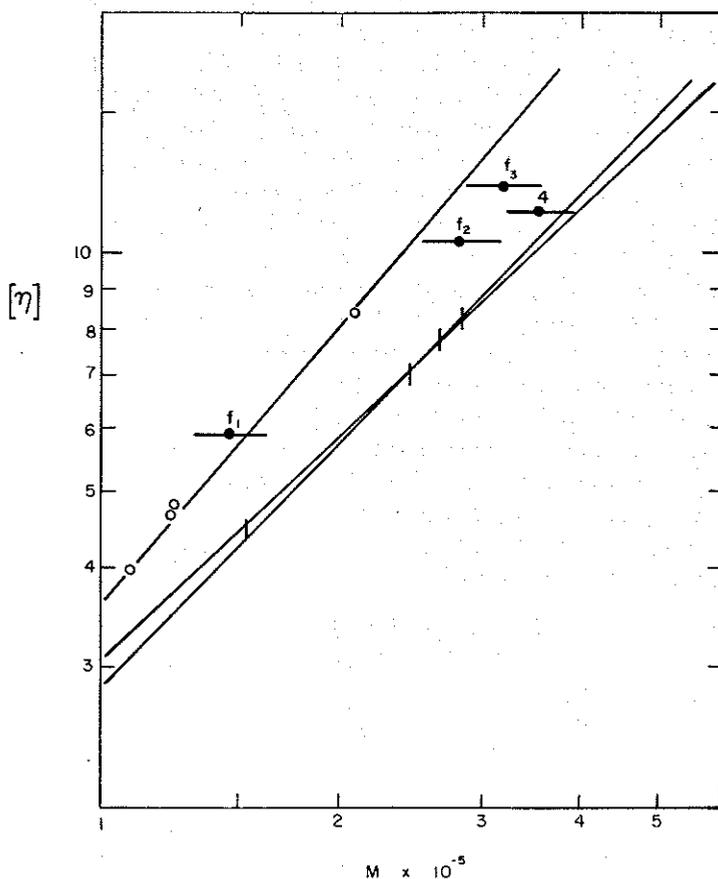


Fig. 3. Viscosity-molecular weight curve for *n*-hexyl polyisocyanate in chloroform (lower curves); vertical segments represent intrinsic viscosities in chloroform plotted at the molecular weights estimated from viscosities in THF using the calibration curve (upper line) based on Burchard's results<sup>3</sup> for *n*-butyl PIC in THF.

viscosity data in Table II to find that there is a difference of 30% to 50% for the viscosities in tetrahydrofuran and chloroform while a somewhat larger viscosity change can be observed by including other solvents as shown by the results on the unfractionated sample in Table III. These viscosity differences may arise from solvent effects on the short range interactions or from the resulting changes in the long range interactions. In general, the unperturbed dimensions of polymers are insensitive to the nature of the solvent except when there are strong polar interactions within the polymer chain. In the PIC molecule there is good reason to believe that the carbonyl oxygen and the amide nitrogen are strongly polarized (see the final section). However, there seems to be little interaction of these groups with the solvent since the polymer is soluble in liquids of low polarity. Therefore, it is tentatively suggested that the variation in viscosity is primarily the result of long range interactions.

On this assumption the viscosity changes provide a measure of the contribution of the excluded volume and it becomes of interest to test the viscosity-molecular weight exponent in chloroform, the solvent in which the polymer shows the lowest viscosity. To compensate for the limited molecular weight range covered by the samples and the uncertainties raised by the problems of molecular weight characterization discussed above, Burchard's viscosity data were used as a molecular weight calibration curve based on the viscosities in tetrahydrofuran. A portion of his data in the required range is plotted in Figure 3 as the open circles, and the solid line is drawn through the points with the slope of 1.18 deduced from the full set of data. When the present results are plotted against this curve (filled circles), the fractions can just be accommodated by horizontal lines representing an error of  $\pm 10\%$  in molecular weight, but the point for the unfractionated sample 4 deviates by a larger amount. With the use of the molecular weights estimated from the viscosities in tetrahydrofuran, the viscosities in chloroform have been plotted with vertical segments representing  $\pm 2\%$  error in viscosity. Two lines can be put through these data permitting a variation in slope from 0.96 to 1.04. Thus, the limited viscosity data in chloroform also appear to reside at the extreme limit of Gaussian behavior.

### Implications of the Viscosity- and Sedimentation-Coefficient Molecular Weight Exponents

The problem which remains to be considered is to what extent the highly extended conformation of PIC is due to intrinsic chain stiffness (perhaps involving short-range interactions with the solvent) or to favorable long-range solvent interactions which swell the chain. In the case of CTN it was long believed that the various results argued for departure from random-flight behavior even in the unperturbed conformation, since the expansion factor  $\alpha$  in ethyl acetate or acetone was estimated to be quite small and the parameters determined under these conditions were considered to differ little from the values in a theta solvent. However, it has recently been shown that these conclusions may be incorrect, and that

strong interactions with the solvent may account for the very large values of the expansion factor, as high as 2.7 in acetone and 3.0 in ethyl acetate at a molecular weight of  $3 \times 10^5$ , while under theta conditions the chain would deswell to the dimensions of a normal Gaussian coil.<sup>8</sup> In connection with the estimate of  $\alpha$ , we note that values of the quantity  $A_2M_w/[\eta]$  for PIC are in the range of 20–25, close to the values of 20–30 for CTN in ethyl acetate. In the case of CTN, interpretation of these values according to a theory for the second virial coefficient was responsible for the small estimated values of  $\alpha$ . However, Kurata and Stockmayer<sup>8</sup> have concluded that present theories of  $A_2$  are untrustworthy in the range of large  $\alpha$  or for polymers deviating from Gaussian statistics.

The viscosity–molecular weight and sedimentation–molecular weight exponents obtained by Burchard for the *n*-butyl PIC in tetrahydrofuran were  $\nu_v = 1.18$  and  $\nu_s = 0.16$ . Burchard pointed out that both of these molecular weight exponents fall beyond the limiting values expected for Gaussian behavior. The Flory theory<sup>10</sup> for the excluded volume effect predicts the limiting values  $\nu_v = 0.8$  and  $\nu_s = 0.4$  for a Gaussian chain swollen by strong interactions with solvent. The theory of Kurata, Stockmayer, and Roig<sup>11</sup> yields a stronger dependence of the expansion factor on molecular weight and leads to the limiting values  $\nu_v = 1.00$  and  $\nu_s = 0.33$  for nondraining molecules in a good solvent. While Burchard's conclusion was predicated on the limiting values  $\nu_v = 0.91$  and  $\nu_s = 0.40$  derived from still another theory, clearly the *n*-butyl PIC passes even the more stringent requirements posed by the Kurata-Stockmayer-Roig theory. Thus the values of the exponents constitute definitive evidence that the observed non-Gaussian behavior cannot arise solely from the swelling of the polymer chain by interactions with the solvent.

The trend of the viscosity data in Table III also suggests that the expanded coil dimensions are not the result of a large value for  $\alpha$ . Here the viscosity is seen to decrease in solvents of increasing polarity, and it has been found that the polymer is insoluble in ethyl acetate, methyl ethyl ketone, or in solvents such as dimethylformamide which are noted for their ability to solubilize polymers having strong polar interactions. The highest viscosities appear in carbon tetrachloride and benzene, where exothermic heats of mixing could hardly occur. The *n*-hexyl PIC is soluble even in aliphatic hydrocarbons such as cyclohexane and *n*-hexane, revealing a surprisingly non-polar character.

The plot of  $[\eta]^{2/3}/M^{1/3}$  versus  $M^{2/3}/[\eta]^{1/3}$  follows from the Kurata-Stockmayer-Roig theory as a means of extrapolating to an intercept on the ordinate which characterizes the unperturbed polymer chain dimensions. A necessary consequence of the fact that  $\nu_v$  exceeds unity for the *n*-butyl PIC is that this plot cannot make a positive intercept as it does for all polymers thus far examined, including CTN,<sup>8</sup> with but one exception, the polypeptides in the helical form. When Burchard's data are plotted in the recommended form (not shown) the line through the data strikes a negative intercept without any ambiguity. The fit of the data serves to demon-

strate the precision of Burchard's results and the reliability of the values for  $\nu_v$  and presumably also  $\nu_s$ .

From the pair of values,  $\nu_v$  and  $\nu_s$ , it is possible to estimate the level of polymer-solvent interactions and the molecular weight dependence of the viscosity and sedimentation coefficients in a theta solvent by application of the Kirkwood-Riseman relations for partially draining coils<sup>12</sup> in the form suggested by Kurata and Stockmayer.<sup>8</sup> Assuming an exponential form for the molecular weight dependence of the expansion factor,

$$\alpha = kM^{\nu_\alpha}$$

the draining parameter may be modified from  $X = \lambda_0 N^{1/2}$  to  $X = (\lambda_0 N^{1/2})/\alpha$  for nontheta conditions, where  $N$  is the degree of polymerization and  $\lambda_0$  the parameter defined by Kirkwood and Riseman. This leads to the following results:<sup>8</sup>

$$\nu_v = \epsilon_v + (4 - 2\epsilon_v)\nu_\alpha$$

$$\nu_s = (1 - 2\nu_\alpha)\epsilon_s$$

Here  $\epsilon_v$  is the value of  $\nu_v$  for the free-draining case, tabulated by Kirkwood and Riseman, and  $\epsilon_s$  is the corresponding value of  $\nu_s$ , which may be calculated from their equation for the friction constant. Inserting the values for PIC leads to the following results:  $X = 0.28$ ,  $\nu_\alpha = 0.122$ ,  $\epsilon_v = 0.91$ , and  $\epsilon_s = 0.21$ . Thus tetrahydrofuran corresponds to a moderately good solvent, the limiting value of  $\nu_\alpha$  for an extremely good solvent being 0.167. The predicted viscosity-molecular weight exponent in a theta solvent,  $\epsilon_v = 0.91$ , indicates that the chain is abnormally expanded even in the absence of excluded volume effects. Further, from the value of  $X$ , the constant  $\Phi_0$  in the Flory-Fox equation:

$$[\eta] = \Phi_0(\overline{R_z^2})^{3/2}/M$$

is estimated to be  $0.42 \times 10^{21}$  under theta conditions. Values of  $\Phi_z$  calculated directly from the results  $(\overline{R_z^2})^{1/2}$ ,  $M_w$ ,  $[\eta]$ , in Tables I and II are in the range  $0.33 \times 10^{21}$ – $0.55 \times 10^{21}$ . When the correction for the assumed random distribution is applied,  $\Phi_0 = \Phi_z/0.51$ , the approximately twofold higher values listed in the final column of Table I are obtained.

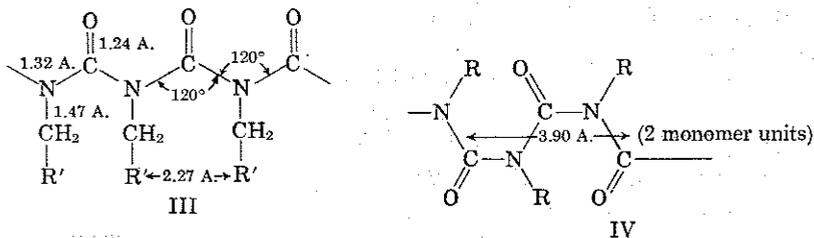
Consider the approximations involved in the data the correspondence between the calculated value of  $\Phi_0$  and that derived from the Kirkwood-Riseman relations is probably as good as could be expected and adds confidence to the conclusions on PIC conformation developed earlier from the light-scattering data. Thus we arrive at a reasonably consistent picture of the abnormally expanded conformation of the polyisocyanate chain. Further, it has been possible to show that the observed chain dimensions must be a consequence of short-range restrictions to rotation modified in only a secondary way by long-range excluded volume effects.

## STRUCTURE OF THE POLYISOCYANATES

In seeking an explanation for the abnormal chain stiffness of PIC the structural feature which immediately commands attention is the repeated peptide linkage which forms the chain backbone structure. It is well known that resonance between the nitrogen and carbonyl of the peptide group endows the carbon-nitrogen bond with partial double bond character, imposing rigorous coplanarity on the participating atoms: N, H, C, O, all lying in the same plane. In fact, coplanarity of the atoms in the peptide link represents one of the canonical principles observed in formulating the structure of crystalline proteins. In polypeptides an  $\alpha$ -methylene group separates each pair of peptide linkages. However in PIC there is the possibility of interaction between pairs of peptide groups involving resonance with the carbonyl groups on both sides of a given nitrogen in the fashion shown in eq. (1):



This would impose partial double bond character on all the atoms of the chain backbone and could furnish a simple explanation of the unique conformational behavior of PIC. There are two possible arrangements for such a regular planar structure, the *trans* conformation III, and the *cis* conformation IV:



Both planar structures suffer from severe steric crowding. In structure III the combined van der Waal's radii of the two carbonyl groups is 2.8 Å., which is not incompatible with the calculated 2.27 Å. separation, but the corresponding value for the two methylene groups is 4.0 Å., which exceeds the center-to-center distance of the methylene carbons by 1.73 Å. This is about 20% greater than the overlap of the substituents on the alternate carbons in polyisobutylene for which a strain energy of about 6 kcal./mole<sup>13</sup> has been estimated from the heat of polymerization. For the planar PIC conformation the strain energy should be somewhat higher due to the more severe crowding and the fact that the polyisobutylene chain spirals to relieve the steric interference. A further unfavorable aspect of structure III is the repulsive interaction between pairs of negatively polarized carbonyl groups and between the pairs of positively polarized nitrogens. In poly-

oxymethylene interaction between the oxygen atoms of the chain backbone favors the *gauche* over the *trans* conformation by about 1.8 kcal./mole.<sup>14</sup> The repulsive energy in the planar PIC conformation must be larger than twice this value owing to the doubling of the number of interacting groups, as well as the increase in polarity and the decrease in interatomic distances which results from resonance. While these estimates lead to a rather large increase in internal energy arising from steric and electronic interactions, it seems likely that the total remains below the value of 21 kcal./mole resonance energy of the peptide bond.<sup>15</sup> Values for the contour length of the chain,  $L_w$ , used in Table I are based on this *trans* structure.

Turning now to structure IV, the calculated center-to-center distance between the carbonyl oxygen and methylene carbon is 1.29 Å., which is 2.1 Å. less than the combined van der Waal's radii of these opposing groups. Thus, steric interference is greater than that operating between the pairs of methylene groups in the previous conformation. However, the present arrangement achieves a greater separation of the carbonyl groups virtually eliminating this contribution to the internal energy. Therefore, the *cis* conformation is probably not any less acceptable than the first model. Furthermore, shielding of the carbonyl group by the aliphatic substituent provides an explanation for the surprising lack of polar interactions that might have been expected on the basis of the *trans* structure.

Some relief from steric interference in either structure could be achieved by slight departures from coplanarity, or by the distortion of bond angles. In the accepted structure for the *trans* polypeptide conformation the C—N—C bond angle in the chain backbone is opened to 123° and the O—C—N angle to 125° to provide greater separation between the carbonyl oxygen and the substituent on the  $\alpha$ -carbon. Either or both types of modifications could be applied to structure IV and the first type to structure III. Further, it is possible that there is a distribution of monomer units between the two conformations. The infrared spectra for the polymer sample used in this study was virtually identical with that shown by Natta for the more crystalline polymer, the only strong difference being the presence of an adsorption peak of medium intensity at 1000  $\text{cm.}^{-1}$  which was not present in Natta's sample. The similarity of the spectra indicates that the primary structure of the two samples are essentially identical. Since there are also no asymmetric centers in the molecule the only remaining cause for the difference in crystallinity would appear to be configurational differences such as that between *cis* and *trans* arrangement or, possibly, an increased number of units enchainned through the carbon-oxygen bond in the polymer prepared with NaCN-DMF system.

The preceding suggestions about the chain structure are clearly provisional. A more detailed study of the properties of polymers prepared from the two catalyst systems would hold much interest while, hopefully, x-ray diffraction studies could provide a test of the proposed planar structures.

**Note added in proof:** Measurements of the dielectric relaxation which are being carried out on solutions of *n*-butyl PIC at the National Bureau of Standards provide further information about PIC structure. There is observed only a single loss peak which occurs at a low and strongly molecular weight dependent frequency. Both the values and the molecular weight dependence of these long relaxation times are consistent with virtually rod like behavior of the molecule involving rotation about an axis transverse to the rod length. The absence of dispersion peaks at higher frequencies indicates that no flexible chain bonds are present. Furthermore, the large magnitude of the dielectric increment and the fact that it increases almost in proportion to molecular weight, indicates that there is an additive dipole moment along the chain. This suggests that the dominant configuration is the *cis* arrangement of units in Model IV.

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### Résumé

Des mesures de diffusion de lumière sur la conformation moléculaire du polyisocyanate (PIC) de *n*-hexyle dans le tétrahydrofurane (THF) montrent que le rapport entre la distance quadratique moyenne entre extrémités de chaînes et celle de l'extension maximale, dépasse 25% même pour un poids moléculaire de  $3 \times 10^6$  et que la distance effective d'une liaison dans la chaîne équivalente liée librement est de 23 Å, ce qui correspond à environ 17 liaisons par segment statistique. Ces résultats sont au moins deux fois aussi élevés que les valeurs pour le trinitrate de cellulose dans l'acétone à un degré de polymérisation comparable. Bien qu'il y ait une variation importante de viscosité intrinsèque dans différents solvants, les exposants du poids moléculaire déterminés récemment par viscosité et sédimentation, de valeur 1.18 et 0.16 pour le PIC de *n*-butyle dans le THF montrent que le comportement du polymère est situé en dehors de la région gaussienne et doit résulter de la structure à courte distance plutôt que de fortes interactions avec le solvant. En fait, en se basant sur la théorie de Kirkwood-Riseman, modifiée pour tenir compte du facteur d'expansion, on a calculé dans des conditions  $\theta$  un exposant viscosimétrique du poids moléculaire de 0.9. On propose que la chaîne est rendue moins

mobile à cause des empêchements de rotation imposées par des effets de résonance dans les liaisons peptidiques qui constituent le squelette du polymère.

### Zusammenfassung

Lichtstreuungsmessungen der Molekülkonformation von *n*-Hexylpolyisocyanat (PIC) in Tetrahydrofuran (THF) zeigen, dass das Verhältnis der Wurzel aus den mittleren End-zu-End Abstandsquadrat zur maximalen Ausdehnung sogar bei einem Molekulargewicht von  $3 \times 10^6$  25% übersteigt und dass die effektive Bindungslänge in der äquivalenten frei verknüpften Kette 23Å beträgt, was etwa 17 Gliedern pro statistischem Segment entspricht. Diese Ergebnisse liegen mindestens doppelt so hoch als die Werte für Zellosetrinitrat in Aceton bei einem vergleichbaren Polymerisationsgrad. Obgleich eine signifikante Änderung der Viskositätszahl in verschiedenen Lösungsmitteln auftritt, zeigen die neuerdings mitgeteilten Viskositäts- und Sedimentationskoeffizienten und Molekulargewichtsexponenten von 1,18 und 0,16 für *n*-Butyl PIC in THF, dass das Polymerverhalten ausserhalb des Gauss- Bereiches liegt und durch die Nahstruktur und nicht durch starke Wechselwirkung mit dem Lösungsmittel bedingt sein muss. Tatsächlich kann mit Hilfe der zur Berücksichtigung des Expansionsfaktors modifizierten Kirkwood- Riseman-Theorie für Theta- Bedingungen ein Viskosität- Molekulargewichtsexponent von 0,9 berechnet werden. Es wird angenommen, dass die Kette durch Rotationsbewegungen welche durch Resonanzeffekte in den die Polymerkette bildenden Peptidbindungen bedingt sind, versteift wird.

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