

Diisocyanate-Linked Polymers. I. Dilute-Solution Properties of Toluene Diisocyanate-Extended Polypropylene Glycol*†

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I. INTRODUCTION

Although in recent years polyurethanes have been the subject of numerous publications (e.g., ref. 1), little information is available regarding the effect of chemical structure on the basic physico-chemical characteristics of these polymers. Therefore, the present investigation was carried out on extensively fractionated diisocyanate-extended polypropylene glycol to provide information about characteristics of a representative polyurethane system. Light scattering and dilute solution viscometric methods were used to characterize these polymers by establishing relationships between molecular weights, intrinsic viscosities, and second virial coefficients. Viscosities were determined in a theta solvent as well as in poor and good solvents to measure the effect of thermodynamic interactions on polymer configuration. The experimental results were used to investigate the applicability to polyurethanes of the theories of polymer interactions in dilute solutions. An estimate of the molecular weight distribution was secured from the fractionation data.

II. EXPERIMENTAL

A. Preparation of Polymer

The polymer was prepared by reacting in bulk polypropylene glycol 2025 (Union Carbide Chemicals Co., South Charleston, W. Va.) with a 5 mole-% excess of toluene-2,4-diisocyanate and by curing the reaction mixture for 50 hours at 60°C. Ferric acetylacetonate was used as curing catalyst as

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suggested by Petersen.² The intrinsic viscosity of the polymer mixture (in benzene at 25°C.) gradually increased as the reaction proceeded until it reached a constant value of 0.33 dl./g. after about 44 hours of curing. To avoid contamination with moisture and oxygen, mixing of the ingredients was done in a nitrogen (99.998% N₂) atmosphere in a dry box which had a dew point of less than -28°C. (1% relative humidity), and the curing was carried out under vacuum. Before use, the propylene glycol 2025 (hydroxyl 9.6×10^{-4} moles/g., carbonyl 1.1×10^{-5} moles/g.) was heated under vacuum for 4 hours at 150°C. to remove moisture and other volatiles, and the toluene-2,4-diisocyanate (Hylene T, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del., essentially all 2,4 isomer) was freshly distilled. The final product was stored under refrigeration.

B. Fractionation

The polymer was separated into fourteen fractions by fractional precipitation from a benzene solution with isooctane (2,2,4-trimethylpentane) as the precipitant. (The use of isooctane for fractionation was suggested by Dr. R. F. Landel of this laboratory.) To a 51-g. aliquot of the polymer dissolved in 510 ml. of benzene, 1450 ml. of isooctane were added. The resulting very turbid solution was warmed until, at 30°C., it turned clear; then it was allowed to cool over a 20-hour period to $25 \pm 0.02^\circ\text{C}$. This procedure permitted a good separation into two phases (a light phase and a more viscous, heavier phase) to be obtained. The light phase was siphoned off and called Solution 1, S-1. To the 34 g. of polymer which were recovered from the heavy phase and then redissolved in 575 ml. of benzene, 1220 ml. of isooctane were added, and the resulting two phases were allowed to separate in the above-described manner. The heavy phase was removed and called Fraction 1, and the same precipitation operation was re-

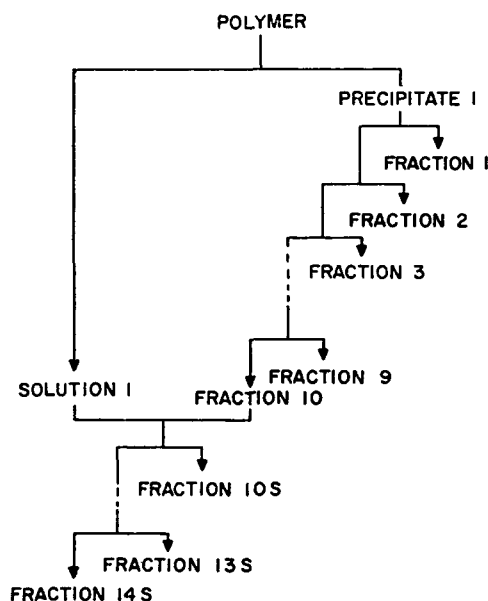


Fig. 1. Fractionation.

peated on the light phase. The procedure of precipitating and separating with progressively higher isooctane concentrations was continued until ten fractions (designated Fractions 1 to 10) were secured. The last fraction, Fraction 10, was then recombined with Solution 1; this mixture was then separated into five fractions called Fractions 10S to 14S. The fractionation of the polymer is summarized in Table I and Figure 1. The mixed solvent was evaporated from each fraction, and the fractions were then redissolved in benzene and stored in a refrigerator. When solutions in other solvents were needed, the polymer was recovered by freeze-drying or evaporation procedure under reduced pressure. The latter method was abandoned when it was observed that its use resulted in small amounts of methanol-insoluble polymer (0.2–0.3 wt.-%).

C. Light Scattering

Light-scattering measurements were made on the polyurethane solutions in methanol with the use of square 3-cm. cells in a Brice-Phoenix light scattering photometer (manufactured by Phoenix Precision Instrument Company, Philadelphia, Penna.). Measurements were made with unpolarized incident light at both the blue (4358 Å.) and the green (5461 Å.) mercury lines. The instrument was calibrated with a standard opal glass.³ To check the calibration, Rayleigh's ratios at 90° for unpolarized incident light were determined for both benzene and methanol;

TABLE I
Fractionation of Polyurethanes

Fraction no.	Weight of polyurethanes, %	Approximate polyurethane concentration in fractionation mixture, g./dl.	Iso-octane concentration, vol.-%	Molecular weight ^a
Unfractionated polymer	100			36,500
Precipitate 1	66.2	2.6	74	
Solution 1	33.8			
1	8.28	1.7	61	73,000
2	3.39	1.5	62	66,000
3	6.27	1.4	63	61,000
4	3.40	1.3	63.5	56,000
5	11.00	1.2	64	52,000
6	4.08	1.0	64.5	46,000
7	6.64	0.85	65.0	41,000
8	4.66	0.67	67.0	37,000
9	8.09	0.50	76.0	31,000
10				
10S	5.70	1.5	76.0	35,000
11S	6.58	1.2	78.0	25,000
12S	6.67	0.89	81.5	22,000
13S	4.86	0.57	85.0	17,500
14S	20.38			7,700

^a From $[\eta]$ vs. M plots, except for unfractionated polymer for which the experimental M_w is given.

values of 46.8×10^{-6} for benzene for $\lambda = 4358$ Å. and 7.87×10^{-6} and 3.1×10^{-6} for methanol for $\lambda = 4358$ and 5461 Å. respectively, were obtained. These values are in good agreement with the currently accepted "high" values for these solvents.^{4,5} Refractive index differences were measured in a Brice-Phoenix differential refractometer.⁶

To remove dust, each master polymer solution was first pressure-filtered through a Corning sintered-glass "fine" filter at 3 to 4 psig. of pure nitrogen, and solutions of the desired concentration were then obtained by dilution of this filtered master solution with pure solvent. Absolute methanol ("Baker Analyzed," reagent grade) was used (acidity, 0.001 meq./ml.; Karl Fischer water content, 0.008%). Before use, all solutions were filtered through an "ultra-fine" filter directly into a clean light-scattering cell. Only solutions which appeared perfectly clear when visually observed at a low angle in a strong beam of light were accepted for light-scattering measurements. The cells and other glassware were kept scrupulously clean.

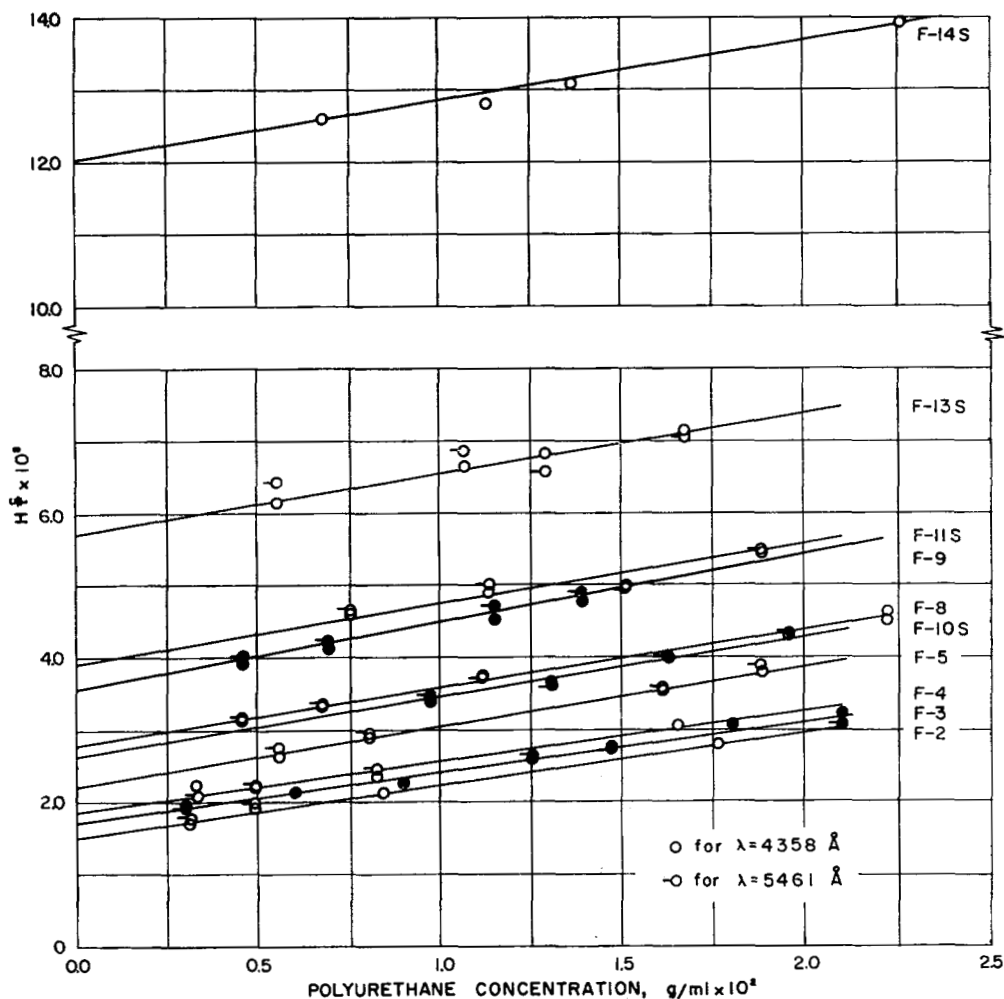


Fig. 2. Reciprocal turbidities vs. concentration for polyurethanes in methanol.

To determine turbidities, scattering ratios at the 90° angle were measured by the usual procedure.^{3,7} No corrections to the turbidities determined for these solutions were required, since depolarization, light absorption, and fluorescence effects were found to be negligible. The turbidity of methanol at room temperature (ca. 22°C .) was 0.132×10^{-3} and $0.051 \times 10^{-3} \text{ cm}^{-1}$. For the blue and the green light, respectively, the refractive index gradients dn/dc were 0.152 and 0.150 ml./g. for Fractions 10S to 14S, and 0.148 and 0.145 ml./g. for all the other polyurethanes. These differences in dn/dc are small, but probably significant.

Turbidities of the polyurethanes were determined at several polymer concentrations. After being corrected for the solvent contribution, the data were converted into reciprocal specific turbidity and were plotted against concentration, as shown in Figure 2. From these data the weight-

TABLE II
Molecular Weight and Second Virial Coefficients

Fraction number	$\left(\frac{H}{\tau}\right)_{c \rightarrow 0} \times 10^5$	M_w	$A_2 \times 10^4$
2	1.50	67,000	3.6
3	1.70	59,000	3.4
4	1.85	54,000	3.5
5	2.20	45,500	4.1
8	2.78	36,000	4.0
9	3.55	28,200	4.6
10S	2.62	38,200	4.1
11S	3.90	25,600	4.2
13S	5.70	17,500	4.2
14S	12.05	8,300	4.2
Unfractionated polymer	2.74	36,500	5.1

average molecular weights M_w and the second virial coefficients A_2 were estimated by means of

the Debye equation⁷

$$H \frac{c}{\tau} = \frac{1}{M_w} + 2A_2c \quad (1)$$

where the constant H contains the refractive index gradient dn/dc , and the concentration c is expressed in grams/milliliter. The results are given in Table II. There was good agreement between results obtained with the blue and the green light.

D. Phase Equilibrium

The phase-separation temperatures T_p of solutions of three fractions ($M_w = 36,000, 54,000,$ and $67,000$) in toluene-isooctane (1:1.4 volume ratio) were determined at five polymer concentrations. These temperatures were plotted vs. $M^{-1/2}$ and points for each of the five concentrations were then extrapolated linearly to infinite molecular weight following a procedure used by Mandelkern and Flory⁸ in their work with mixed solvents. Data for infinite molecular weight were then extrapolated to infinite dilution to secure the critical miscibility temperature θ , which for the polyurethanes in the toluene-isooctane mixture was found to be at 39.5°C .

E. Viscosity

Viscosities of polyurethanes in dilute solutions were determined in three solvents: at the theta temperature of a toluene-isooctane (1:1.4 volume ratio) mixture ($T = \theta = 39.5^\circ\text{C}$), in methanol at 25°C ., and in benzene at 25 and 39.5°C . Measurements were carried out in Cannon-Ubbelohde dilution viscometers at several polymer concentrations. The efflux time for methanol in viscometers used for measurements on methanol solutions was about 85 seconds, and a small kinetic-energy correction had to be applied. In viscometers used for measurements on the theta and benzene solutions, however, the solvent efflux times were between 150 and 200 seconds, and the kinetic-energy correction was negligible. From observed viscosities the intrinsic viscosity $[\eta]$ and the slope constant k_1 were calculated by means of the Huggins equation:

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta - \eta_0}{\eta_0} \right) / c = [\eta] + k_1 [\eta]^2 c \quad (2)$$

where η is the viscosity of the solution, η_0 the viscosity of the solvent, and the concentration c is expressed in grams/deciliter. The results are given

TABLE III
Intrinsic Viscosities and Slope Constants k_1

Fraction Number	Toluene-isooctane mixture (1:1.4) at $T = \theta = 39.5^\circ\text{C}$.		Methanol at $T = 25^\circ\text{C}$.		Benzene			
					at $T = 25^\circ\text{C}$.		at $T = 39.5^\circ\text{C}$.	
	$[\eta]$, dl./g.	k_1	$[\eta]$, dl./g.	k_1	$[\eta]$, dl./g.	k_1	$[\eta]$, dl./g.	k_1
Unfractionated polymer			0.232	0.57	0.337	0.42		
P-1					0.402	0.41		
S-1					0.195	0.45		
1					0.556	0.40	0.598	0.33
2	0.268	0.74	0.352	0.53	0.520	0.36		
3			0.325	0.55	0.495	0.39	0.534	0.31
4	0.254	0.74	0.318	0.55	0.467	0.40		
5			0.294	0.56	0.447	0.37	0.454	0.38
6					0.412	0.37		
7	0.206	0.72	0.259	0.59	0.379	0.40	0.394	0.35
8	0.210	0.68	0.252	0.53	0.360	0.40		
9	0.188	0.79	0.220	0.59	0.320	0.39	0.327	0.38
10					0.212	0.43		
10S			0.242	0.54	0.350	0.40		
11S			0.197	0.72	0.286	0.38		
12S			0.180	0.59				
13S	0.144		0.164	0.59	0.218	0.42		
14S	0.100		0.105	0.68	0.138	0.42	0.141	0.40
Polypropylene glycol 1025			0.035		0.035			
Polypropylene glycol 2025	0.055		0.051		0.051			

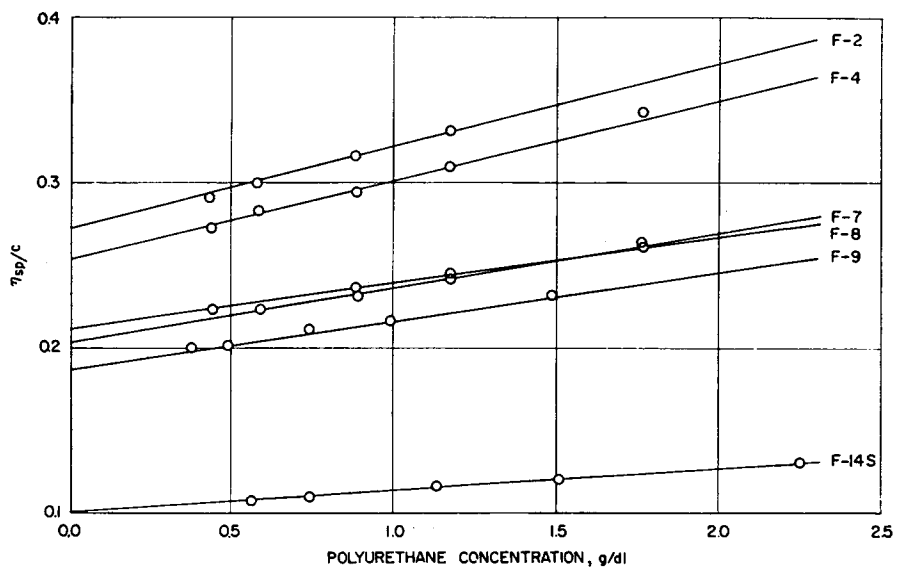


Fig. 3. Reduced viscosity vs. concentration for polyurethanes in toluene—iisooctane (1:1.4) at the theta temperature, 39.5°C.

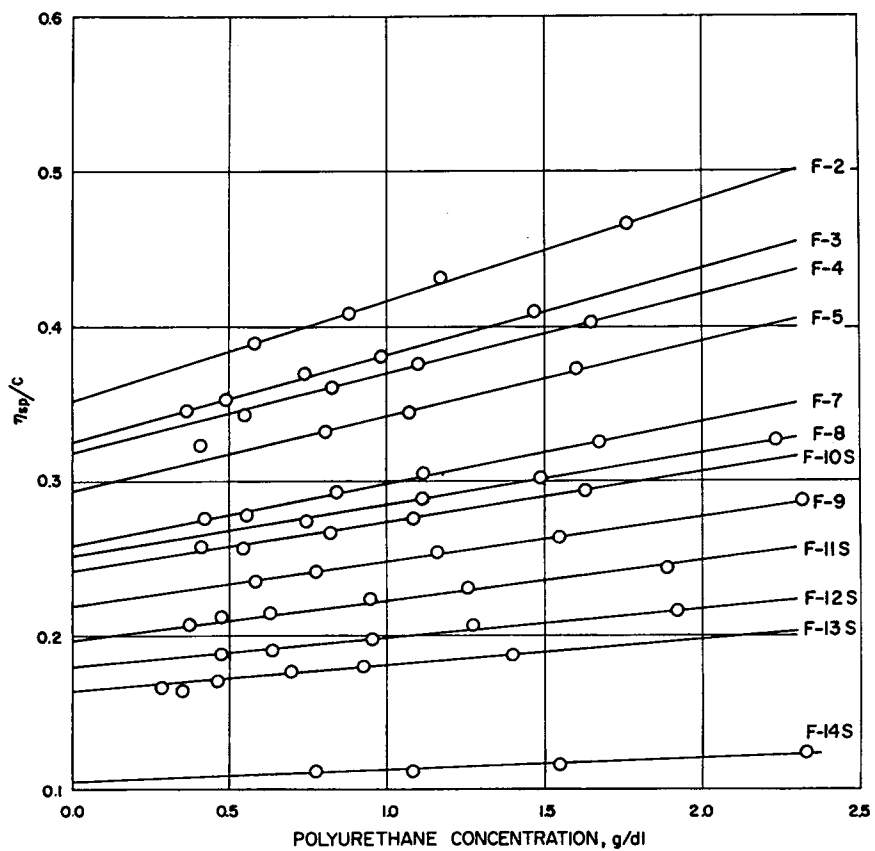


Fig. 4. Reduced viscosity vs. concentration for polyurethanes in methanol at 25°C.

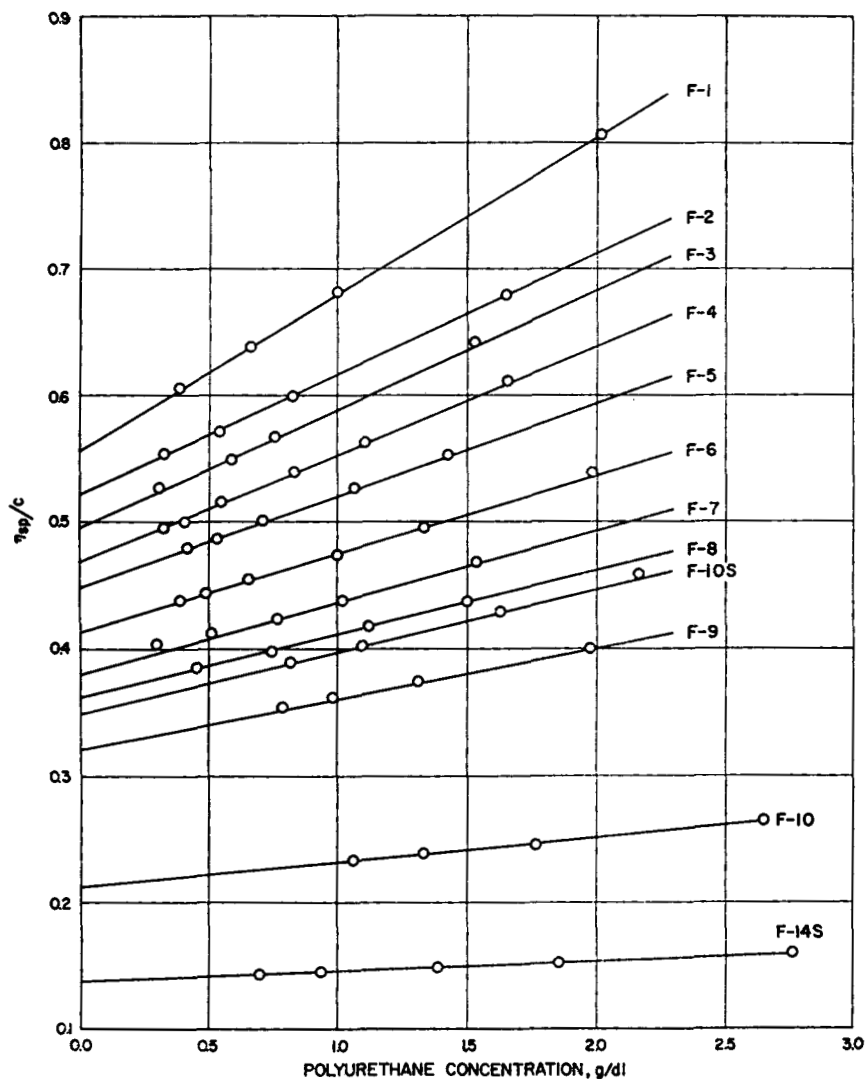


Fig. 5. Reduced viscosity vs. concentration for polyurethanes in benzene at 25°C.

in Table III and in Figures 3-6. Results from observations on polypropylene glycol 1025 and 2025 solutions (respective molecular weights about 1000 and 2000) are also included.

III. DISCUSSION OF RESULTS

A linear polyurethane polymer (weight-average molecular weight 36,500) was prepared by extending a polyether chain (polypropylene glycol 2025, molecular weight 2000) with toluene-2,4-diisocyanate, under conditions such that side reactions which could lead to branching were minimized. The polymer was separated into fourteen fractions by fractional precipitation in a benzene-isooctane mixture because separation into two liquid phases occurred readily in this solvent system and thermodynamic equilibrium could

thus be approached. The balance and distribution of polyurethanes in the fractions were calculated on a weight basis (Table I) from determinations of total solids. The fractions were characterized by light-scattering and viscosity measurements.

Light-scattering measurements were carried out on methanol solutions because the polyurethanes had a higher refractive index gradient dn/dc in methanol than in any other common solvent. For example, dn/dc values of 0.031 and 0.094 ml./g. were found in benzene and butanone, respectively, as compared with 0.148 ml./g. in methanol for the same wavelength ($\lambda = 4358 \text{ \AA}$). The turbidities of one of the polyurethanes in 1.5% solutions in the same solvents were 0.13, 0.55, and 2.10 cm^{-1} , respectively, and the corrections for the contribution of the solvent were of the order of 0.15

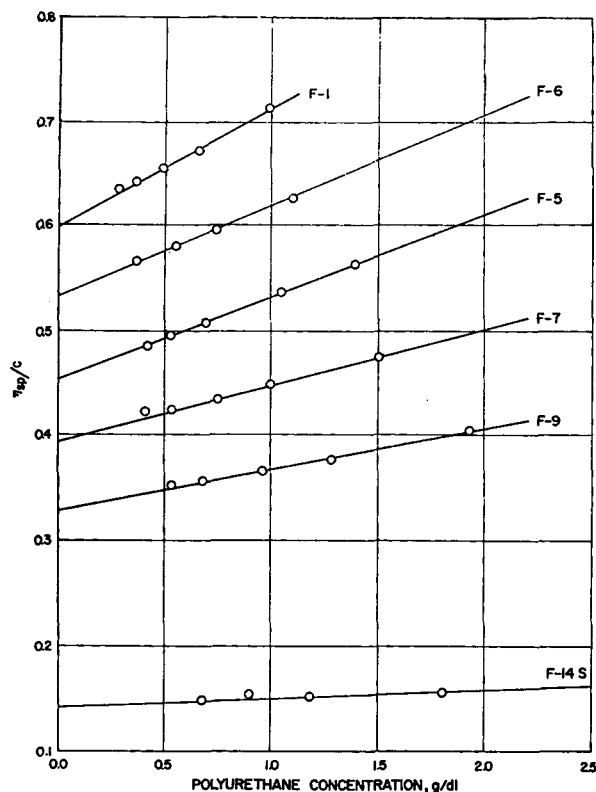


Fig. 6. Reduced viscosity vs. concentration for polyurethanes in benzene at 39.5°C.

cm.⁻¹. These results showed that only in methanol could reasonably accurate results be obtained with the polyurethanes of relatively low molecular weight which were available for this study.

To ascertain whether polyurethane solutions in methanol are stable enough to be used for light scattering or other experiments, changes in viscosity of a methanol solution heated at 70°C. in a sealed Cannon-Zhukov reversible viscometer were followed over a 20-day period. For the first five days the initial reduced viscosity, 0.35 dl./g., remained unchanged, and by the end of the experiment it had decreased to 0.32, which represents a total decrease in viscosity of less than 10%. This relatively small change in viscosity indicates fair stability at 70°C. and suggests that at room temperature polyurethanes in methanol should be reasonably stable. Also, no significant changes could be detected in the intrinsic viscosities in benzene of three of the polyurethane fractions for which viscosities were determined before and after they had been used in methanol solutions for light-scattering observations. After three or four months, however, small but significant decreases in intrinsic viscosities were detected, indicating some sensi-

tivity of these polymers toward repeated exposures to air and light over longer periods of time.

Molecular weights and second virial coefficients in methanol of the original polymer and of ten of the fractions were determined by a light-scattering method (Fig. 2 and Table II) described in the preceding section.

Intrinsic viscosities $[\eta]$ and slope constants k_1 (Table III) for the polyurethanes in three different solvents were secured from dilute solution viscosities [eq. (2), Figs. 3-6]. In a given solvent all the fractions may be characterized, within the experimental error at least, with the same k_1 value, about 0.74, 0.53, and 0.39 in the theta solvent, methanol, and benzene, respectively. This is in agreement with the work on polyvinyl acetates of Hobbs et al.,⁹ who have also found that linear polymers have a k_1 that is nearly independent of molecular weight, whereas for branched polymers they have found that k_1 varies strongly with molecular weight.

Intrinsic viscosities $[\eta]$ were correlated with molecular weight M by means of the Mark-Houwink equation:

$$[\eta] = K'M^a \quad (3)$$

The parameters K' and a were secured from the intercepts and slopes of the straight lines representative of the plots of $\log [\eta]$ vs. $\log M$ for each solvent, as shown in Figure 7. To extend the molecular weight range covered by the polyurethane fractions, intrinsic viscosities of two polypropylene glycols are also included in Figure 7. The results are given in Table IV. Data secured at the θ temperature of the toluene-isooctane mixture may be represented quite accurately by assigning the theoretical value of 0.5 to the parameter a . The progressively increasing solvent power for polyurethanes of the theta solvent, methanol, and benzene is reflected in the progressively increasing values of a in these solvents. This increase in a accompanied by a decrease in the corresponding k_1 values (Table III) and is in qualitative agreement

TABLE IV
Intrinsic Viscosity Parameters

Solvent	Temp., °C.	$K' \times 10^4$	a	α^3
Theta solvent	39.5	10.75	0.50	1.00
Methanol	25	7.69	0.55	0.715 $M^{0.05}$
Benzene	25	4.13	0.64	0.384 $M^{0.14}$
Benzene	39.5	4.27	0.66	0.397 $M^{0.16}$

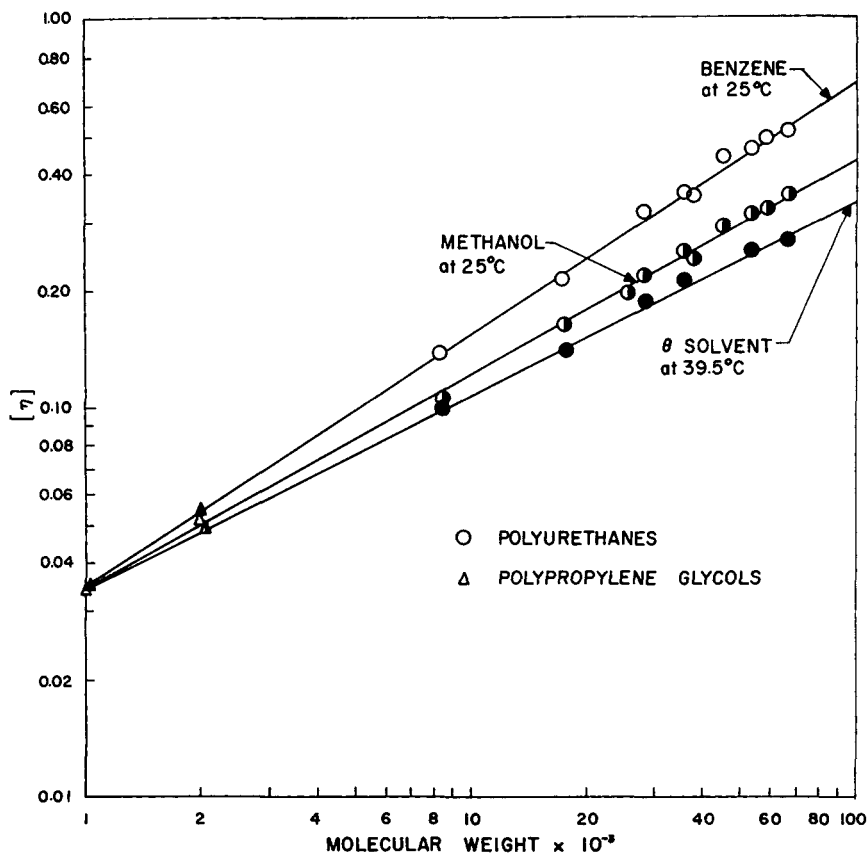


Fig. 7. Molecular weight—intrinsic viscosity relationships for polyurethanes and polypropylene glycols.

with the theories of the effect of the solvent on the concentration dependence of viscosities of dilute polymer solutions.¹⁰

The intrinsic viscosity depends on both the structure of the polymer and on the polymer-solvent interactions as made explicit in Flory's relationship for the intrinsic viscosity of flexible linear polymers¹¹:

$$[\eta] = \phi \left(\frac{\langle l_0^2 \rangle}{M} \right)^{3/2} M^{1/2} \alpha^3 = KM^{1/2} \alpha^3 \quad (4)$$

where ϕ is a constant, usually 2 and 2.6×10^{21} , $\langle l_0^2 \rangle$ the unperturbed mean-square end-to-end distance, and α the expansion coefficient which depends on the solvent and equals 1.0 in a theta solvent. The expressions for α^3 given in Table IV were secured by using the expressions for $[\eta]$ together with the relationship

$$[\eta]/[\eta]_\theta = \alpha^3 \quad (5)$$

In these calculations the assumption was made that the temperature dependence of $[\eta]_\theta$, i.e., of $\langle l_0^2 \rangle$, is negligible over the studied temperature range or

is at least very small, and this is usually the case. Unless the temperature dependence is large, which is unlikely, its effect on the conclusions of this discussion may not be significant.

A theoretical expression for the second virial coefficient has been derived recently by Orofino and Flory¹² by means of an approximation for the excluded volume integral for the interaction of a pair of randomly coiled polymer molecules. To test the applicability of this theory to the polyurethane polymers, experimental values of these second virial coefficients in methanol, as secured from light-scattering measurements, were compared with those calculated from intrinsic viscosity data by the following equation¹²:

$$A_2 = \frac{2^{5/2} \pi N}{3^3 \phi} \frac{[\eta]}{M} \ln \left[1 + \frac{\pi^{1/2}}{2} (\alpha^2 - 1) \right] \quad (6)$$

where N is Avogadro's number, α is the intramolecular expansion coefficient, and a value of 2.5×10^{21} is taken for the constant ϕ .¹¹ The results are shown in Figure 8 together with the relationship for A_2 proportional to $[\eta]/M$, as ex-

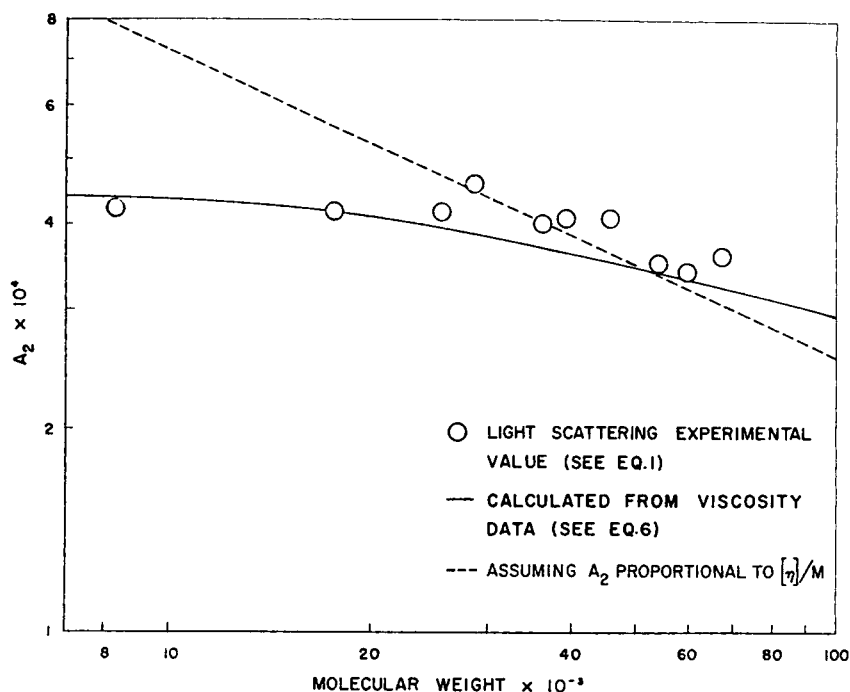


Fig. 8. Experimental and calculated second virial coefficients in methanol at 25°C.

pected from the crude approximation to the A_2 which disregards the effect of the thermodynamic interaction between polymer and solvent on the excluded volume.¹¹ The agreement between the experimental results and the theory of Orfino and Flory is very good and appears to be somewhat better than that with the crude treatment, although a more significant comparison could be made if data over a wider molecular-weight range were available. From light scattering measurements in benzene, a value for A_2 of approximately 12×10^{-4} was obtained for a polyurethane with a molecular weight of 40,000, and the value calculated from eq. (6) was 18×10^{-4} . In view of the unreliability of light scattering data in benzene (caused by the low refractive index gradient for the polyurethane), one should not expect more than a qualitative agreement between the two values. It appears, however, that by applying the Orfino-Flory theory, reasonably good estimates of the second virial coefficients can be made from viscosity data in poor solvents as well as in good solvents.

The ratio of the mean-square end-to-end distance to the molecular weight, $\langle l_0^2 \rangle / M$, for the polyurethanes was secured from the expression for $[\eta]_0$ [eq. (4)] and was found to be 0.57×10^{-16} . With the assumption of free rotation, the ratio $\langle l_0^2 \rangle / M$ was calculated to be 0.24×10^{-16} .

For this calculation only bond lengths and bond angles in the polyether part of the polymer molecule were considered, the contributions of the urethane linkages and the benzene rings, being neglected. In first approximation, this should be permissible, since the bulk of the polymer chain consists of polyether segments. A measure of the flexibility of the molecular chain can now be obtained by taking the ratio $(\langle l_0^2 \rangle / l_0 r^2)^{1/2}$, which is 1.54. This value indicates a flexibility comparable to that of natural rubber with the ratio of 1.71 and is considerably greater than many other polymers. For example, polystyrene and polyisobutylene have ratios of 2.4 and 1.9, respectively.¹¹ The considerable flexibility of the polyurethanes is undoubtedly due to the rather free rotation about ether oxygens.

The molecular weight distribution was estimated from fractionation data on the two sets of fractions: (1) fractions 10S to 14S, and (2) fractions 1 to 9 (Fig. 1). The distribution in each of the two sets was first evaluated; then, by combining the results, the distribution representative of the whole polymer was constructed, as shown in Figure 9. The distribution covers a molecular-weight range from a few thousand to about 100,000.

The weight-average molecular weights used in these calculations were the smoothed values secured from the $[\eta]$ vs. M plots (Fig. 7). The

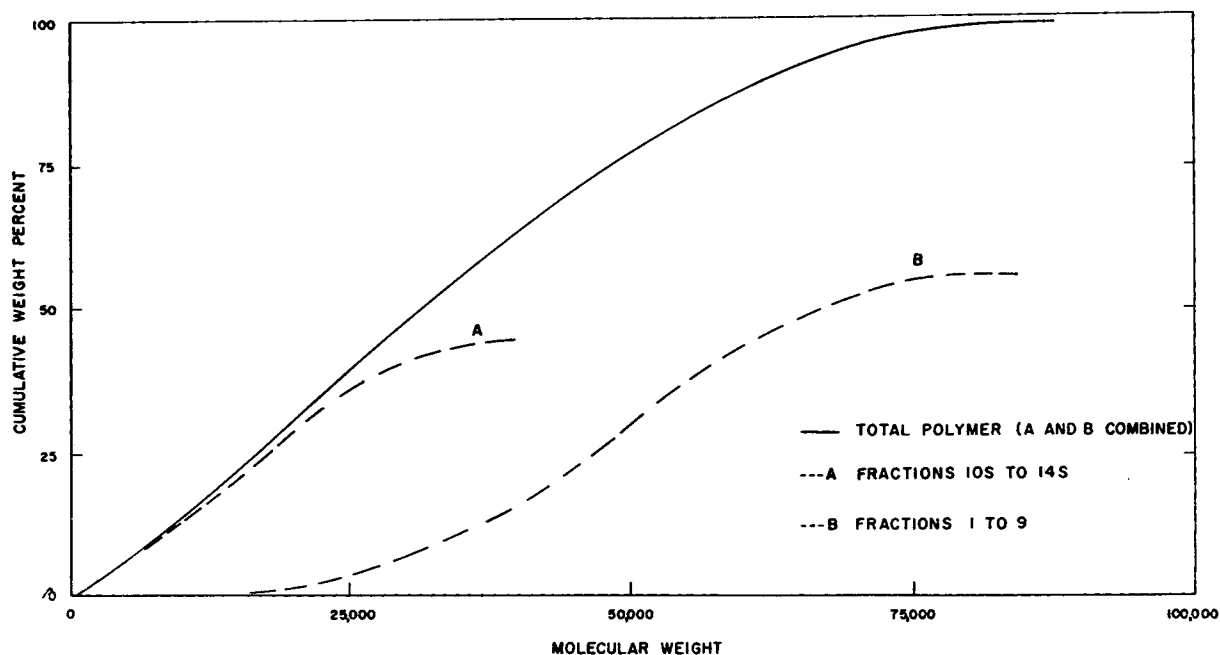


Fig. 9. Molecular weight distribution.

weight-average molecular weight for the whole polymer, obtained by taking the weighted sum of the values for each of the fractions, is 36,900, which is in good agreement with the value of 36,500 obtained directly from light scattering observations on the unfractionated polymer. The number-average molecular weight was estimated from the relationship

$$M_n = \left(\sum_i \frac{w_i}{M_i} \right)^{-1} \quad (7)$$

where the summation is carried over all fractions, and was found to be 21,600. Thus the value of 1.7 for the ratio M_w/M_n , which is a measure of the standard deviation of the distribution, is fairly high but is lower than the value of 2.0 for the "most probable distribution" usually expected for polycondensation-type polymers, although the estimate of 1.7 would be raised if polydispersities in the fractions were considered. There are, however, several factors that may affect the distribution: (1) the molecular-weight distribution in the polypropylene glycol, (2) differences in reactivities between the primary and secondary hydroxyls on the polypropylene glycol molecule, and (3) differences in reactivities of the ortho- and para-isocyanates on the toluene-2,4-isocyanate. The importance of these factors is not known.

In conclusion, it has been shown that the experimental results can be interpreted in terms of the

behavior expected of flexible linear polymers. In view of the results and the care taken to prepare the polymer, the assumption that a linear polymer consisting of a diisocyanate extended polypropylene glycol was obtained is believed to be substantially correct. It should be pointed out, however, that due to the complexity of isocyanate reactions and the not well-defined composition of a commercial polypropylene glycol preparation,¹³ the possibility of deviations from a simple linear structure cannot be ignored. To clarify some of the problems of fine structure in these polymers, further experiments are being conducted at this laboratory.¹⁴

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Synopsis

A study was made of the dilute solution properties and the molecular weight distribution of a polyurethane polymer prepared from polypropylene glycol 2025 and toluene-2,4-diisocyanate by a bulk polymerization under anhydrous conditions at 60°C. Such conditions were chosen to minimize possible side reactions which could produce branching. The polymer, which had a weight-average molecular weight of 36,500, was separated into fourteen fractions by fractional precipitation from a benzene solution with isooctane as precipitant. The fractions were characterized by light scattering measurements on methanol solutions and by dilute solution viscosities in methanol, benzene, and a theta-solvent. The molecular weight distribution of the unfractionated polymer and the relations between molecular weight and intrinsic viscosity in the various solvents were determined. Polymer configurations and interaction parameters are discussed.

Résumé

On a étudié les propriétés de dissolution et la distribution de poids moléculaire d'un polymère de polyuréthane préparé à partir de polypropylène glycol 2025 et de toluène-2,4-diisocyanate par une polymérisation en bloc en milieu an-

hydre à 60°C. De telles conditions opératoires ont été choisies pour minimiser la possibilité de réactions concurrentes qui pouvaient donner des ramifications. Le polymère, qui avait un poids moléculaire moyen en poids de 36.500, a été séparé en 14 fractions par précipitation fractionnée à partir d'une solution benzénique en employant l'isooctane comme précipitant. Ces fractions ont été caractérisées par diffusion de lumière, en solution dans le méthanol et par des viscosités en solution diluée dans le méthanol, le benzène et dans un solvant theta. La distribution de poids moléculaire du polymère non fractionné et les rapports entre la viscosité intrinsèque et les poids moléculaires dans différents solvants ont été déterminés. On a discuté les configuration du polymère et les paramètres d'interaction.

Zusammenfassung

Eine Untersuchung der Eigenschaften eines Polyurethanpolymeren, das aus Polypropylenglykol 2025 und Toluol-2,4-diisocyanat durch Polymerisation in Masse unter Wasserausschluss bei 60° dargestellt worden war, in verdünnter Lösung sowie seiner Molekulargewichtsverteilung wurde durchgeführt. Es wurden Reaktionsbedingungen gewählt, bei welchen Nebenreaktionen, die zu Verzweigungen führen könnten, möglichst ausgeschaltet waren. Das Polymere, das einen Gewichtsmittelwert des Molekulargewichts von 36500 besass, wurde durch fraktionierte Fällung aus Benzollösung mit Isooktan als Fällungsmittel in vierzehn Fraktionen zerlegt. Die Fraktionen wurden durch Lichtstreuungsmessungen an Methanollösungen sowie durch die Viskosität in verdünnter Lösung in Methanol, Benzol und einem Theta-Lösungsmittel charakterisiert. Die Molekulargewichtsverteilung des unfraktionierten Polymeren und die Beziehung zwischen Molekulargewicht und Viskositätszahl in den verschiedenen Lösungsmitteln wurde bestimmt. Die Konfiguration der Polymeren und die Wechselwirkungsparameter werden diskutiert.

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