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Properties of Dilute Solutions of Polyurethanes. I. Linear Polymers

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Polyurethanes were prepared from polycaprolactone, 4, 4′-diphenylmethane diisocyanate, and ethylene diamine. Two kinds of polymers were used for the present experiments. One contained polycaprolactone with the number-average molecular weight, $\overline{M}_n$, of 1.30×10^3, while the other contained polycaprolactone with an $\overline{M}_n$ value of 2.80×10^3. Each polymer was fractionated from a dimethyl acetamide solution by progressive precipitation with a mixture of *n*-heptane and ethyl ether, and the fractions were characterized in terms of viscosity and sedimentation. The relations between the intrinsic viscosity and the molecular weight were found in DMF at 25°C to be:

$$[\eta] = 5.52 \times 10^{-4} M^{0.66}$$

for the polymer containing polycaprolactone ($\overline{M}_n=1.30\times10^3$) and

$$[\eta] = 7.71 \times 10^{-4} M^{0.62}$$

for the polymer containing polycaprolactone ($\overline{M}_n=2.80\times10^3$). The viscosities of the solutions of the polymers were measured in several solvents at different temperatures, and the polymer-solvent interaction parameters were obtained by using the Fixman theory for the expansion factor. The molecular-weight distribution of the polymer containing polycaprolactone ($\overline{M}_n=1.30\times10^3$) was obtained from the distribution of the sedimentation coefficient, while the value of $\overline{M}_w/\overline{M}_n$ was calculated from the distribution curve to be 1.95.

Recently a number of studies have reported on the elastic properties of polyurethanes. As is well known, the elastic properties of polymers depend on their polymer characteristics, such as their molecular weight and its distribution. As polyurethane used for fiber-forming has no cross-link in the molecule, the characteristics of the polymer exert a great influence on its behavior in the fiber-forming process and on the elastic properties of the fiber. Little information¹⁾ has,

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1) J. Moacanin, *J. Appl. Polymer Sci.*, **1**, 272 (1959); M. Nishide and M. Sera, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **63**, 189 (1960).

however, been found about the characteristics of the polymer.

On the other hand, it is of great interest from the point of view of physical chemistry to study polyurethane as a kind of block copolymer.

The present investigation has, therefore, been carried out in an attempt to establish the relation between the intrinsic viscosity and the molecular weight and to obtain knowledge of the molecular-weight distribution and the thermodynamic properties of solutions of polyurethane consisting of polycaprolactone, diphenylmethane diisocyanate, and ethylene diamine.

Experimental

Polymer.—One mole of polycaprolactone (PCL) was treated with 2 moles of 4, 4′-diphenylmethane diisocyanate (MDI) in bulk for 110 min. at 75°C in order to prepare the prepolymer. The prepolymer thus obtained was then dissolved in dimethyl acetamide and was extended into polyurethane by reaction with the equivalent moles of ethylene diamine (ED) at 40°C.

The solution thus obtained was spun into water in order to obtain the coagulated polymer, which was then dried in a vacuum at room temperature.

In this manner, two kinds of polyurethanes were prepared. One contained PCL with a number-average molecular weight, $\overline{M}_n$, of 1.30×10^3; it was designated as the polymer B. The other contained PCL with an $\overline{M}_n$ value of 2.80×10^3; it was designated as the polymer C.

The polymer may be symbolized as follows:

$$-(-\text{MDI}-\text{PCL}-\text{MDI}-\text{ED}-)_{\overline{n}}$$

Solvents.—Dimethyl formamide (DMF), dimethyl acetamide (DMAA), and dimethyl sulfoxide (DMSO) were purified by the usual method.

Fractionation.—Each polymer was fractionated from a 1% solution in DMAA by precipitation fractionation, using a mixture of *n*-heptane and ethyl ether as the precipitant at 25°C. The gel-like precipitate was then dissolved in a small amount of DMAA, and the resulting solution was added, drop by drop, into an excess of water. Thus, the polymer B was divided into 13 fractions, which were designated as UB(1300), and the polymer C, into 12 fractions, designated as UC(2800). Each fraction was dried in a vacuum at room temperature.

In the other runs of fractionation, both of the polymers B and C were divided into 3 fractions; the middle fractions were designated UB-T(1300) and UC-T(2800) respectively.

Viscosity.—A modified Ubellohde viscometer was used to measure the viscosity of polymer solutions.

Partial Specific Volume.—The density of solutions was determined over the concentration range from 0.5 to 3.0 wt. % by using a 10-cc. Ostwald picnometer at 25°C; the partial specific volume was then calculated from the density data.

Ultracentrifugation.—The sedimentation velocity was measured with a Hitachi analytical ultracentrifuge, Model UCA-1, equipped with Schlieren optics and a phase plate. The rotor temperature was maintained at 25°C, and the rotor speed was 55430 r. p. m. throughout the experiments.

TABLE I. PROPERTIES OF POLYMER B

Fraction	$[\eta]$	k'	$S_0\times10^{13}$	k_s	$k_s/[\eta]$	$\overline{M}\times10^{-4}$	N%
UB-1	1.262	0.406	2.41	1.94	1.54	12.8	4.63
3	1.650	0.406	2.79	2.85	1.72	18.4	4.50
5	1.478	0.397	2.55	2.45	1.66	15.1	4.46
7	1.243	0.421	2.28	2.11	1.70	11.8	4.47
9	1.031	0.417	2.05	1.76	1.71	9.39	4.32
10	0.875	0.420	1.91	1.45	1.66	7.16	
11	0.659	0.413	1.51	1.07	1.63	4.61	4.30
12	0.485	0.430	1.13	0.825	1.70	2.62	
Original	1.279	0.419	2.59	2.12	1.67	13.5	4.45*
UB-T	1.211					11.5	

* The calculated value is 4.52%.

TABLE II. PROPERTIES OF POLYMER C

Fraction	$[\eta]$	k'	$S_0\times10^{13}$	k_s	$k_s/[\eta]$	$\overline{M}\times10^{-4}$	N%
UC-1	1.190						2.74
3	1.748	0.395	3.08	3.08	1.76	26.6	2.46
4	1.215	0.390	2.29	2.05	1.69	14.2	
5	1.165	0.392	2.25	1.93	1.65	13.5	2.44
8	0.930	0.385	1.87	1.56	1.68	9.07	
9	0.820	0.400	1.74	1.37	1.67	7.71	2.40
10	0.652	0.408	1.51	1.14	1.74	5.56	
11	0.447	0.405	1.14	0.81	1.80	3.06	2.38
Original	1.244	0.390	2.66	2.19	1.76	18.3	1.43*
UC-T	1.177					13.8	

* The calculated value is 2.50%.

Results and Discussion

The Constitution of the Polymer. — The nitrogen content of the original polymer, as determined by the micro-Kjeldahl method, was less than the calculated value for both polymers B and C. This may mean that a small amount of water reacted with isocyanate groups in the polymerization process, resulting in the inhomogeniety in the composition (cf. Tables I and II).

The Relation between the Intrinsic Viscosity and the Molecular Weight.—From the plots of the reduced viscosity (η_{sp}/C) against the concentration (expressed in g./100 cc.), as is shown in Fig. 1, the intrinsic viscosity and the Huggins constant, k', were obtained by using the following equation:

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

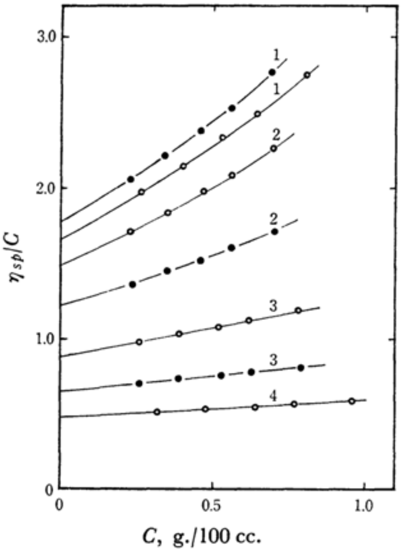

Fig. 1. (η_{sp}/C) vs. C of polymer fractions in DMF at 25°C.
Open circles, 1: UB-3, 2: UB-5, 3: UB-10, 4: UB-12
Solid circles, 1: UC-3, 2: UC-4, 3: UC-10

As the plots became curved in the higher-molecular weight fractions, the values of $[\eta]$ and k' for these fractions were estimated from the straight lines obtained from the plots of the inherent viscosity ($\ln \eta_r/C$) against the concentration by applying the following equation:

$$(\ln \eta_r/C) = [\eta] - (0.5 - k')[\eta]^2 C \qquad (2)$$

The results are given in Tables I and II for the UB(1300) and UC(2800) polymer fractions respectively.

The Huggins constant, k', slightly decreases with an increase in the molecular weight of PCL.

The reciprocals of the sedimentation coefficients, $1/S$, were plotted against the concentration (expressed in g./100 cc.), as is shown in Fig. 2. The sedimentation coefficient at the infinite dilution, S_0, and the constant, k_s, were obtained from the empirical equation:

$$1/S = (1/S_0)(1 + k_s C) \qquad (3)$$

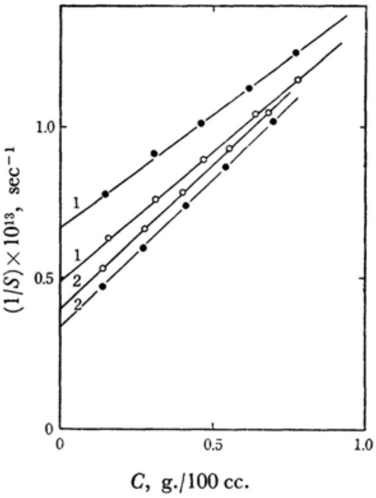

Fig. 2. ($1/S$) vs. C of polymer fractions in DMF at 25°C.
Open circles, 1: UB-9, 2: UB-5
Solid circles, 1: UC-10, 2: UB-5

Wales[2] has proposed this relation between the constant, k_s, and the intrinsic viscosity:

$$k_s/[\eta] = 1.66 \qquad (4)$$

Yamakawa[3] has theoretically estimated the ($k_s/[\eta]$) ratio to be about 1.7 in good solvent systems. The ratio obtained in the present study is also about 1.7, as may be seen in column 6 of Tables I and II. Wales' equation can, therefore, be applied to the case of these block copolymer solutions.

The molecular weight of each fraction, M, was calculated from the intrinsic viscosity and the sedimentation coefficient by using the Mandelkern-Flory equation[4]:

$$S_0[\eta]^{1/3}/M^{2/3} = (\boldsymbol{\Phi}^{1/3}\boldsymbol{P}^{-1})(1-\bar{v}\rho)/\eta_0 \boldsymbol{N}_A \qquad (5)$$

where $\boldsymbol{\Phi}$ and $\boldsymbol{P}$ are universal constants; ($\boldsymbol{\Phi}^{1/3}\boldsymbol{P}^{-1}$) takes the value of 2.5×10^6; $\bar{v}$ is the partial specific volume of the polymer in solution; ρ and η_0 are the density and the viscosity of solvent respectively, and $\boldsymbol{N}_A$ is Avogadro's number.

The partial specific volumes of the polymers in DMF at 25°C were calculated from the data of density to be as follows:

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[2] M. Wales and K. E. Van Holde, *J. Polymer Sci.*, **14**, 81 (1964).

[3] H. Yamakawa, *J. Chem. Phys.*, **36**, 2995 (1962).

[4] L. Mandelkern, W. R. Krigbaum, H. A. Scharaga and P. J. Flory, ibid., **20**, 1392 (1952).

$\bar{v} = 0.8480$ for the polymer B

$\bar{v} = 0.8745$ for the polymer C

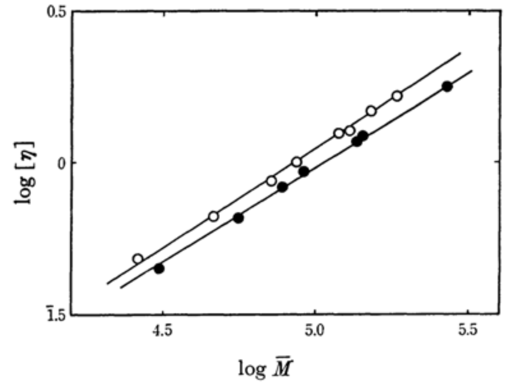

Fig. 3. Log [η] vs. log $\bar{M}$ of polymer fractions in DMF at 25°C.
Open circles: UB(1300), Solid circles: UC(2800)

The intrinsic viscosities are plotted logarithmically against the molecular weight in Fig. 3. From this figure, the following two equations, 6 and 7, are obtained for the UB(1300) and UC(2800) polymer fractions respectively in DMF at 25°C:

$$[\eta] = 5.52 \times 10^{-4} M^{0.66} \tag{6}$$

$$[\eta] = 7.71 \times 10^{-4} M^{0.62} \tag{7}$$

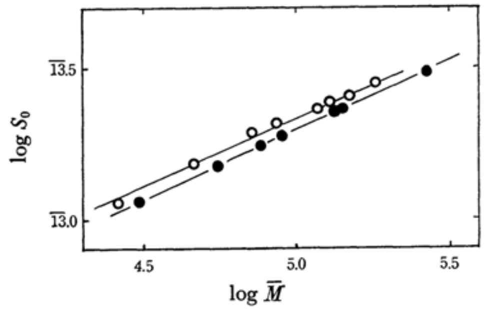

Fig. 4. Log S_0 vs. log $\bar{M}$ of polymer fractions in DMF at 25°C.
Open circles: UB(1300), Solid circles: UC(2300)

The relation between the sedimentation coefficient and the molecular weight was derived from the double logarithmic plots in Fig. 4; it was found in DMF at 25°C to be:

$$S_0 = 1.36 \times 10^{-15} M^{0.44} \tag{8}$$

for the UB(1300) polymer fractions and

$$S_0 = 9.86 \times 10^{-16} M^{0.46} \tag{9}$$

for the UC(2800) polymer fractions.

Polymer-Solvent Interaction Parameters.—The intrinsic viscosity depends on the molecular weight of the polymer in accordance with the relationship:

$$[\eta] = KM^{1/2}\alpha^3 \tag{10}$$

where $K = \Phi(\bar{r}_0^2/M)^{3/2}$, $\bar{r}_0^2$ is the mean square end-to-end distance for an unperturbed chain and α, the viscosity expansion factor.

Stockmayer and Fixman⁵⁾ have proposed the simple relation:

$$[\eta] = KM^{1/2} + 0.66\Phi BM \tag{11}$$

by combining Eq. 10 with the following Fixman equation⁶⁾ for the excluded volume effect:

$$\alpha^3 = 1 + 2z \tag{12}$$

where $z = (3/2\pi)^{3/2}(\bar{r}_0^2/M)^{-3/2}BM^{1/2}$; $B = 2(\bar{v}^2/V_1 \boldsymbol{N}_A)\psi_1(1-\Theta/T)$; V_1 is the molar volume of the solvent; ψ_1, the entropy term of Flory's polymer-solvent interaction parameter, and Θ, Flory's temperature.

Hence, a plot of $[\eta]/M^{1/2}$ vs. $M^{1/2}$ will be linear in a given solvent at a particular temperature. The value of K is determined by the intercept. Thus, the value of α^3 can be evaluated by putting the value of K into Eq. 10. $(\alpha^3-1)M^{-1/2}$ should give a straight line when plotted against $1/T$, and both Θ and ψ_1 for any given solvent can be evaluated.

The values of K were obtained by using Eq. 11 in DMF at 25° and 70°C for UB(1300) and UC(2800) fractions respectively; a small decrease in K with an increase in the temperature was observed for both polymers. The decrease in K with the temperature was, then, assumed to be linear between 25°C and 70°C, and the α for each polymer-solvent-temperature combination was calculated from the intrinsic viscosity by using Eq. 10 and the interpolated value of K at the temperature, T.

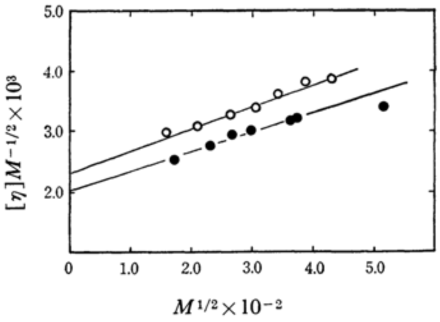

Fig. 5. ($[\eta]/M^{1/2}$) vs. $M^{1/2}$ of polymer fractions in DMF at 25°C.
Open circles: UB(1300), Solid circles: UC(2800)

Figure 5 shows the Stockmayer-Fixman plots. The relations obtained from the straight lines are as follows:

$$[\eta] = 2.29 \times 10^{-3} M^{1/2} + 3.64 \times 10^{-6} M \tag{13}$$

for UB(1300), and

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5) W. H. Stockmayer and M. Fixman, *J. Polymer Sci.*, Part C, No. 1, 137 (1963).

6) M. Fixman, *J. Chem. Phys.*, **36**, 3123 (1962).

$$[\eta] = 2.02 \times 10^{-3} M^{1/2} + 3.20 \times 10^{-6} M \quad (14)$$

for UC(2800), both being measured in DMF at 25°C.

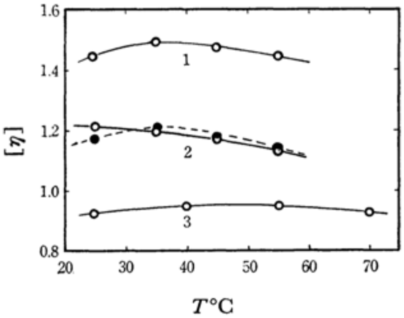

Fig. 6. Dependence of $[\eta]$ on temperature in various solvents.
Open circles: UB-T (solvent 1: DMAA, 2: DMF, 3: DMSO)
Solid circles: UC-T (solvent: DMF)

Figure 6 shows the temperature dependence of the intrinsic viscosities of the UB-T(1300) and UC-T(2800) polymers plotted against the temperature in several solvents.

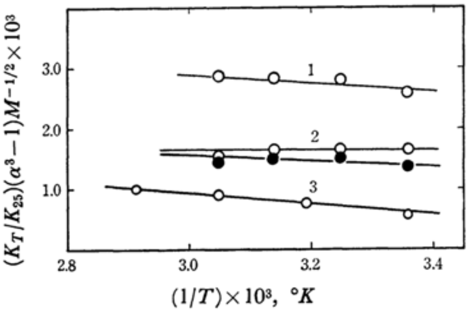

Fig. 7. Plots of $(K_T/K_{25})(\alpha^3-1)M^{-1/2}$ vs. $(1/T)$ for polymer fractions in various solvents.
Open circles: UB-T (solvent 1: DMAA, 2: DMF, 3: DMSO)
Solid circles: UC-T (solvent: DMF)

The plots of $(K_T/K_{25})(\alpha^3-1)M^{-1/2}$ against $1/T$ are given in Fig. 7. K_T/K_{25}, the ratio of K at T to K at the reference temperature, 25°C, was introduced in view of the temperature dependence of $(\bar{r}_0^2/M)^{3/2}$.

The results are given in Table III, where the heat term, κ_1, at 25°C was calculated by the relation:

$$\kappa_1 = \psi_1 \Theta / T \quad (15)$$

and where the polymer-solvent interaction parameter, χ_1, at 25°C was evaluated from the following relation:

$$(1/2) - \chi_1 = \psi_1 - \kappa_1 \quad (16)$$

Table III. Thermodynamic parameters

Polymer	Solvent	ψ_1	Θ°K	κ_1^{25}	χ_1^{25}
UB-T(1300)	DMAA	0.35	141	0.17	0.32
UB-T(1300)	DMF	0.10	0	0	0.40
UB-T(1300)	DMSO	0.21	235	0.16	0.45
UC-T(2800)	DMF	0.17	158	0.09	0.42

For the solutions of UB-T(1300), the heat of dilution behaves athermally in DMF and endothermally in DMAA and DMSO. The cohesive energy densities (CED) of these solvents are 123, 147 and 170 cal./cc. for DMAA, DMF and DMSO respectively. The value of κ_1 is related to the solubility parameter, δ, which is the square root of CED, through the following Hildebrand equation:

$$\kappa_1 = (V_1/\boldsymbol{R}T)(\delta_1-\delta_2)^2 \quad (17)$$

where $\boldsymbol{R}$ is the gas constant and where the suffixes 1 and 2 represent the solvent and the polymer respectively. Consequently, the value of CED for the polymer B lies between those for DMAA and DMSO, and is nearly the same as that for DMF.

The constant, a, of the Mark-Houwink equation and the long-range interaction term of the Stockmayer-Fixman equation decrease in DMF solutions with an increase in the molecular weight of PCL, as has been shown above. When the long-range interaction term is separated into two terms, the heat and the entropy of dilution, the heat term, κ_1, increases with the molecular weight of PCL.

These results lead us to the conclusion that the PCL segments may mix endothermally with such a polar solvent as DMF, although the value of CED for the copolymer may be obtained as the average of the values of two sorts of segments and although the values of CED have not been obtained for each segment of the polymers used in the present study.

Molecular-weight Distribution.—The distribution of the limiting sedimentation coefficient, S_0, for the polymer B was evaluated by making corrections for both diffusion and concentration, and the transformation from the distribution of the sedimentation coefficient to the molecular-weight distribution was made by using Eq. 8. The results are given in Fig. 8.

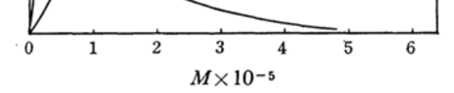

Fig. 8. Molecular weight distribution of polymer B.

The ratio of the weight-average molecular weight, $\overline{M}_w$, to the number-average, $\overline{M}_n$, was calculated from the distribution curve. The value of 1.95 for the $\overline{M}_w/\overline{M}_n$ ratio agrees fairly well with the value of 2.0 for the "*most probable distribution*" which can be expected in the addition polymerization.

On the other hand, the distribution estimated from the data of precipitation fractionation seems to be narrower than that obtained by the sedimentation method. This may be caused by insufficient effectiveness of fractionation.

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