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Properties of Dilute Solutions of Polyurethanes. II. Branched Polymers

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Linear and branched polyurethanes, both of which contained polycaprolactone ($\overline{M}_n=1.80\times10^3$), were prepared. Each polymer was fractionated from a dimethyl acetamide solution by precipitation with a mixture of *n*-heptane and ethyl ether, and the fractions were characterized by viscosity and sedimentation. The degree of branching for the fractions of the branched polymer was estimated by using the relation between viscosity and branching, derived by Flory. The ratio of the concentration dependence of the sedimentation coefficient k_s to $[\eta]$ was about 1.7 for the linear polymer, but the $k_s/[\eta]$ value increased with an increase in the degree of branching for the branched polymer. The Huggins constant, k', seems to be independent of the degree of branching.

In a previous paper,$^{1)}$ the properties of dilute solutions of polyurethanes were investigated 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.

As linear polyurethane is usually prepared from a long chain diol, a diisocyanate, and a so-called chain-extender, such as diamine, a rather well-characterized branched polymer can easily be obtained by substituting triol for a part of the diol.

The purpose of the present paper is to estimate the degree of branching for branched polymers and to investigate the dependence of the properties of polymer solutions on the degree of branching.

The degree of branching can be estimated by several measurements, such as of the "*radius of gyration*" of the polymer chain,$^{2)}$ the osmotic second virial coefficient,$^{3)}$ the intrinsic viscosity, and the sedimentation.$^{4,5)}$ The methods used here consist of measuring the viscosity and the sedimentation, as these measurements are rather more accurate than the others.

Experimental

Polymer.—One mole of polycaprolactone (PCL), the number-average molecular weight of which was 1.80×10^3, was treated with 2 moles of 4, 4′-diphenylmethane diisocyanate (MDI) in bulk at 65°C for 2 hr. to form a prepolymer. The prepolymer thus obtained was then dissolved in dimethyl acetamide and extended into polyurethane by reaction with equivalent moles of ethylene diamine (ED) at 40°C for 1 hr.

The polyurethane obtained in this manner was designated as the linear polymer E.

The branched polymers were prepared as follows. A mixture of PCL ($\overline{M}_n=1.80\times10^3$) and a small amount of trimethylol ethane (TME) was treated with MDI in bulk at 65°C for 2 hr. to form a prepolymer, where the molar ratio of the isocyanate group to the hydroxyl group was 2. The prepolymer was extended into branched polyurethane with ED under the same conditions as in the case of the linear polymer. Thus, two kinds of branched polymers were obtained.

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1) H. Sato, This Bulletin, **39**, 2335 (1966).

2) C. D. Thurmond and B. H. Zimm, *J. Polymer Sci.*, **8**, 477 (1952).

3) W. R. Krigbaum and Q. A. Trementozzi, ibid., **28**, 295 (1958).

4) L. D. Moore, Jr., G. R. Greear and J. O. Sharp, ibid., **59**, 333 (1962).

5) J. Blachford and R. F. Robertson, ibid., **A3**, 1289 (1965).

Table I. Solution properties of fractions of linear polymer E

Fraction	Weight, g.	$[\eta]$	k'	$S_0\times10^{13}$	k_s	$k_s/[\eta]$	$\overline{M}\times10^{-4}$
UE-2	2.958	1.340	0.407	2.46	2.35	1.75	14.64
3	1.061	1.245	0.405	2.35	2.16	1.74	13.20
4	2.295	1.210	0.393	2.22	2.08	1.72	11.95
5	1.247	1.150	0.366	2.21	1.94	1.68	11.60
6	2.311	0.880	0.400	1.84	1.45	1.65	7.69
7	2.184	0.701	0.400	1.55	1.22	1.70	5.25
8	2.232	0.310	0.395	0.92	0.55	1.70	1.79

Table II. Solution properties of fractions for branched polymers F and G

Fraction	$[\eta]_b$	k'_b	$S_{0b}\times10^{13}$	k_{sb}	$k_{sb}/[\eta]_b$	$\overline{M}\times10^{-4}$	$[\eta]$
UF-4	1.505	0.387	2.91	2.92	1.94	20.0	1.647
UF-7	0.947	0.414	2.10	1.76	1.86	9.67	1.029
UG-3	1.120	0.413	2.50	2.43	2.17	13.7	1.292
UG-6	0.748	0.404	1.85	1.59	2.15	7.12	0.847

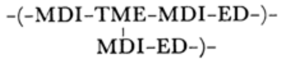
The molar ratios of PCL to the trifunctional component (TME) in the polymers were as follows:

Branched polymer F (PCL : TME=70 : 1)
Branched polymer G (PCL : TME=42 : 1)

The linear polymer E is symbolized as follows:

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

whereas the branched polymer contains trifunctional groups:



$$\text{-(-MDI-}\underset{\substack{|\\ \text{MDI-ED-)-}}}{\text{TME}}\text{-MDI-ED-)-}$$

Fractionation.—In the same manner as in the previous paper,[1] the linear polymer E was divided into 9 fractions, while the branched polymers F and G were divided into 8 fractions.

Viscosity and Sedimentation.—Viscosity and sedimentation measurements were carried out as in the previous paper.[1]

Results and Discussion

The UE-2-8, UF-4, UF-7, UG-3 and UG-6 fractions were selected from the fractions of the linear polymer E and the branched polymers F and G, because the Schlieren patterns for these fractions were narrow enough for an accurate determination of the sedimentation coefficient.

The data of viscosity in dimethyl formamide (DMF) at 25°C, shown in Figs. 1 and 2, were treated in accordance with the complementary relationships for intrinsic viscosity:

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

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

where η_r and η_{sp} are the relative and specific viscosities respectively, and where k' is the Huggins constant. The values of $[\eta]$ and k' derived therefrom are listed in Tables I and II.

The reciprocals of the sedimentation coefficients, $1/S$, are plotted against the concentration in Figs. 3—5; the sedimentation coefficients at an infinite dilution, S_0, were estimated from the intercepts of the straight lines, while the values of k_s were calculated from the relation:

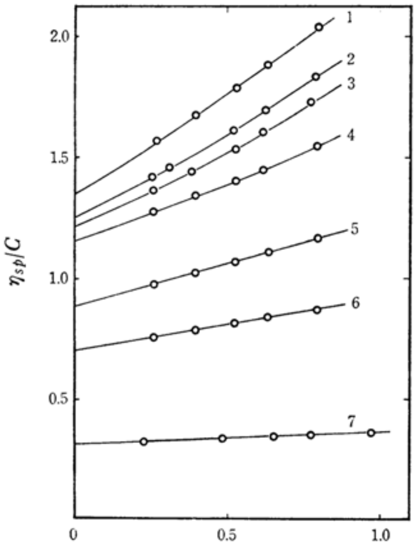


Fig. 1. (η_{sp}/C) vs. C of polymer fractions for linear polymer E in DMF at 25°C.
1: UE-2, 2: UE-3, 3: UE-4, 4: UE-5, 5: UE-6, 6: UE-7, 7: UE-8

$$1/S=(1/S_0)(1+k_sC) \tag{3}$$

Results are presented also in Tables I and II.

Figure 6 shows the plot of log S_0 against log $[\eta]$ for the fractions of the linear polymer E in DMF at 25°C, where the solid line through the points corresponds to the equation:

$$S_0=2.02\times10^{-13}[\eta]^{0.693} \tag{4}$$

In addition, the molecular weight, M, of each fraction was calculated according to the Mandelkern-Flory equation:[6]

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[6] L. Mandelkern, W. R. Krigbaum, H. A. Scheraga and P. J. Flory, *J. Chem. Phys.*, **20**, 1392 (1952).

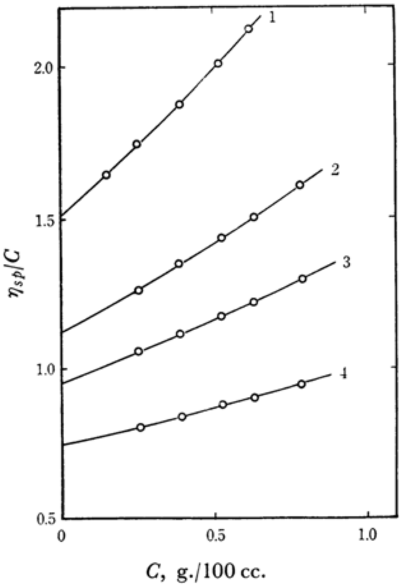

Fig. 2. (η_{sp}/C) vs. C of polymer fractions for branched polymers F and G in DMF at 25°C.
1: UF-4, 2: UG-3, 3: UF-7, 4: UG-6

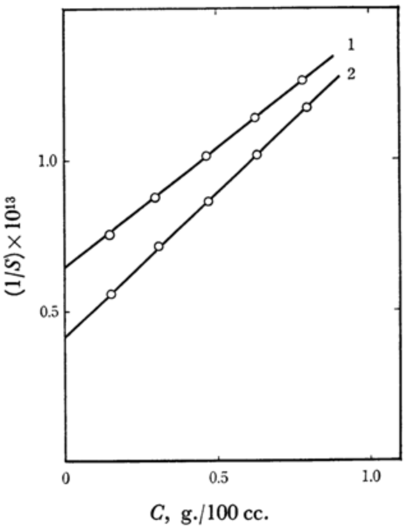

Fig. 3. $(1/S)$ vs. C of polymer fractions for linear polymer E in DMF at 25°C.
1: UE-7, 2: UE-2

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

where $\boldsymbol{\Phi}$ and $\boldsymbol{P}$ are constants, ρ and η_0 are the density and the viscosity of the solvent respectively, $\boldsymbol{N}_{\mathrm{A}}$ is Avogadro's number, and $\bar{v}$ is the partial specific volume, which was calculated from the data of density to be 0.8581 cc./g.

The relation between the intrinsic viscosity and the molecular weight and that between the sedimentation coefficient and the molecular weight

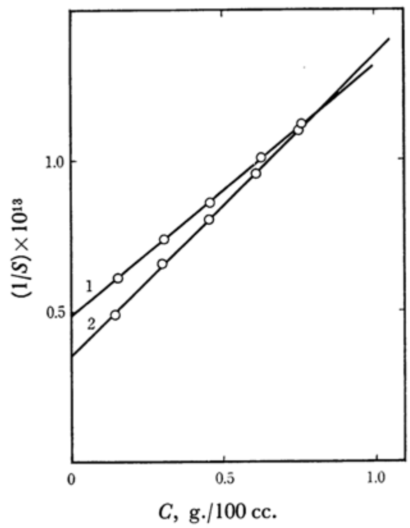

Fig. 4. $(1/S)$ vs. C of polymer fractions for branched polymer F in DMF at 25°C.
1: UF-7, 2: UF-4

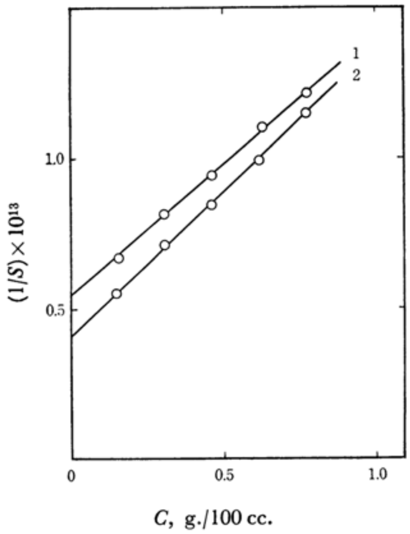

Fig. 5. $(1/S)$ vs. C of polymer fractions for branched polymer G in DMF at 25°C.
1: UG-6, 2: UG-3

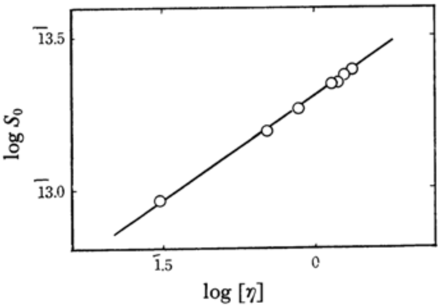

Fig. 6. Log S_0 vs. log $[\eta]$ of polymer fractions for linear polymer E in DMF at 25°C.

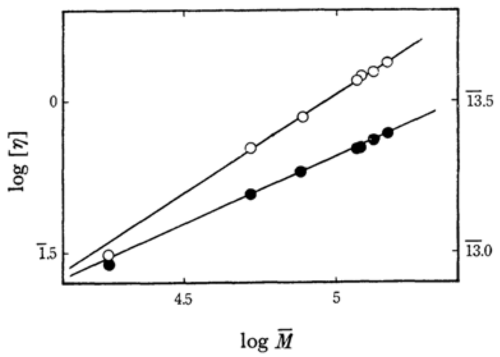

Fig. 7. Log [η] vs. log $\bar{M}$ (open circles) and log S_0 vs. log $\bar{M}$ (solid circles) of polymer fraction for linear polymer E in DMF at 25°C.

for the linear polymer E were derived from double logarithmic plots, shown in Fig. 7, as follows:

$$[\eta] = 5.90\times 10^{-4}M^{0.65} \qquad (6)$$

$$S_0 = 1.18\times 10^{-15}M^{0.45} \qquad (7)$$

in DMF at 25°C.

The ratio of the mean-square radius of gyration of a branched molecule, $\bar{r}_b^2$, to that of a linear molecule, $\bar{r}^2$, of the same molecular weght is defined by g:

$$g = \bar{r}_b^2 \,/\, \bar{r}^2 \qquad (8)$$

where g is related to the number of branches per molecule, m, according to Zimm and Stockmayer's theory.7)

For a branched molecule, the intrinsic viscosity, $[\eta]_b$, and the sedimentation coefficient, S_{0b}, are expressed by the following equations:

$$[\eta]_b = g'[\eta] = g'\boldsymbol{\Phi}6^{3/2}(\bar{r}^2)^{3/2}/M \qquad (9)$$

$$S_{0b} = M(1-\bar{v}\rho)/\boldsymbol{N}_A\eta_0 h\boldsymbol{P}6^{1/2}(\bar{r}^2)^{1/2} \qquad (10)$$

where $[\eta]$ is the intrinsic viscosity of a linear molecule having the same molecular weight as the branched polymer and where the g' and h factors are a function of g.

Several theories8−10) have been proposed to relate g' to g. According to the Flory theory, g' and h are related to g as follows:

$$g' = g^{3/2} \qquad (11)$$

$$h = g^{1/2} \qquad (12)$$

The combination of Eqs. 9—12 leads us to the following equation:

$$S_{0b}[\eta]_b^{1/3}/M^{2/3} = \boldsymbol{\Phi}^{1/3}\boldsymbol{P}^{-1}(1-\bar{v}\rho)/\eta_0\boldsymbol{N}_A \qquad (13)$$

For the calculation of the g factor, intrinsic viscosities measured at Θ-temperature should be used in principle, as the g factor in the Zimm-Stockmayer theory7) is defined for unperturbed quantities. Many experimental results2,11,12) show, however, that the value of g' is nearly the same for both good and Θ-solvents. Consequently, the estimation of the value of g' from intrinsic viscosities measured at non-Θ-temperature is permissible.

When the value of M is the same in Eq. 5 for the linear molecule and in Eq. 13 for the branched molecule, the following equation can be derived:

$$S_{0b}[\eta]_b^{1/3} = S_0[\eta]^{1/3} \qquad (14)$$

The substitution of Eq. 4 for the linear polymer into Eq. 14 then gives:

$$S_{0b}[\eta]_b^{1/3} = 2.02\times 10^{-13}[\eta]^{1.03} \qquad (15)$$

Thus, the value of $[\eta]$ for a linear polymer having the same molecular weight as a branched polymer can be evaluated with $[\eta]_b$ and S_{0b} in accordance with Eq. 15.

The values of $[\eta]$ thus calculated are listed in column 2 of Table III, while calculated values of g' are given in column 3 of that table.

The values of g were calculated in accordance with Eq. 11, they are presented in column 4 of Table III.

TABLE III. DEGREE OF BRANCHING

Fraction	[η]	g'	g	m
UF-4	1.647	0.914	0.942	0.58
UF-7	1.029	0.921	0.947	0.52
UG-3	1.292	0.868	0.910	0.90
UG-6	0.847	0.883	0.920	0.78

The value of m in Table III is the number of branches per molecule which are estimated to be trifunctional branches of random lengths by Zimm and Stockmayer.7)

Many investigators have discussed the dependence of the Huggins constant, k', of a branched polymer on the degree of branching. Orofino11) has shown that k' in a good solvent is not affected by branching, but in a Θ-solvent the k' value for a branched polymer is slightly larger than that for the corresponding linear polymer. Morton12) has observed, however, that for a branched polymer the values of k' are slightly larger than that for a linear polymer in both good and Θ-solvents. In Pollock's work,13) there is no evidence for such a difference in k' due to branching. Blachford et al.5) have observed that the value of k' for a branched polymer increases with the increase in the degree of branching in a good solvent.

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7) B. H. Zimm and W. H. Stockmayer, ibid., **17**, 1301 (1949).

8) W. H. Stockmayer and M. Fixman, *Ann. N. Y. Acad. Sci.*, **57**, 334 (1953).

9) B. H. Zimm and R. W. Kilb, *J. Polymer Sci.*, **37**, 19 (1959).

10) K. Katsuura, *J. Phys. Soc. Japan*, **15**, 2310 (1960).

11) T. A. Orofino and F. Wenger, *J. Phys. Chem.*, **67**, 566 (1963).

12) M. Morton, T. E. Helminiak, S. D. Gadkary and F. Bueche, *J. Polymer Sci.*, **57**, 471 (1962).

13) D. J. Pollock, L. J. Elyash and T. W. DeWitt, ibid., **15**, 335 (1955).

In the present work, the viscosity data on branched polymers in a rather poor solvent give values of k' experimentally indistinguishable from those obtained for the linear polymers. As many factors, such as the molecular weight distribution, may affect k', it is difficult to determine whether the value of k' depends on the degree of branching or not.

Wales[14] has proposed the following relation between k_s and $[\eta]$:

$$k_s/[\eta] = 1.66 \tag{16}$$

This relation has been supported by many investigations for linear polymers. For branched polymers, however, a larger $k_s/[\eta]$ value has been reported.[6]

For the fractions of the linear polymer E, the values of $(k_s/[\eta])$ were about 1.7, but the values for the branched polymer, as may be seen in column 6 of Table II, are higher than that for the linear polymer and it seems that the ratio of k_s to $[\eta]$ increases with the increase in the degree of branching. The larger values of $(k_s/[\eta])$ may suggest that the dependence of k_s on the degree of branching is less than that of $[\eta]$.

The degrees of polymerization of the fractions for the branched polymers are about 85, 41, 62 and 30 for UF-4, UF-7, UG-3 and UG-6 respectively. If the polymer molecules contain trifunctional groups (TME) in proportion to the molar ratio of TME to PCL, then the numbers of branches per molecule may be 1.21, 0.59, 1.47 and 0.71 for UF-4, UF-7, UG-3 and UG-6 respectively. The initial two fractions obtained by precipitation fractionation, however, contained many micro gel particles for both of the branched polymers, F and G. This might mean that the trifunctional groups are localized upon the initial few fractions having high molecular weights. It may be reasonable, therefore, that the degrees of branching for the fractions measured in this study were less than the above-calculated values.

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[14] M. Wales and K. E. VanHold, *J. Polymer Sci.* **14**, 81 (1954).