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Viscosity-Molecular Weight Relations for an Isotactic Polybutene-1

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Dilute solution studies of polymers in these laboratories have recently been extended to studies of some stereoregular polymers in solution. This paper reports results of an investigation of viscosity-molecular weight relations for an isotactic polybutene-1.

Experimental

The polybutene-1 was furnished by the Sun Oil Co. The material was soluble in pentane at room temperature. The x-ray pattern, using the powder technique, clearly indicated that the polymer is crystalline.

Fractionation

Fractionation was carried out by the fractional precipitation method from 1.5% solution in cyclohexanone at 115°C. A 3:1 (volume) mixture of cyclohexanol-glycol was used as the nonsolvent.

Melting Point Determination

Melting points of several of the fractions were determined with a Bausch and Lomb microscope equipped with a Kofler micromelting apparatus. The crystals were prepared by heating slowly to 165°C. on the hot stage, followed by slow cooling over a period of several hours. The spherulites thus formed were viewed through crossed prisms and the temperature was raised slowly until the field disappeared. This temperature was taken as the melting point of the polymer. Fraction 8 melted at 121.4°C. while fractions 5, 6, and 7 melted at 127°C.

Viscosity and Light Scattering

Intrinsic viscosities were determined in decalin at 115°C. and in heptane at 35 and at 60°C. An Ubbelohde dilution viscometer was used. Flow times for the reagent-grade solvents exceeded 100 sec. in all cases.

Refractive index increments (dn/dc) were determined with a Brice-Phoenix differential refractometer. For polybutene-1 in heptane at 60°C., dn/dc was found to be 0.115 cm.^{3}g.$^{-1}$ for λ = 5460 A. and 0.120 cm.^{3}g.$^{-1}$ for λ = 4360 A.

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Light-scattering measurements on solutions in heptane at 60°C. were made with a Brice-Phoenix light-scattering photometer. All solutions were clarified by centrifugation at 52,000 g. for 1 hr. in a Spinco preparative ultracentrifuge. Measurements were made on four or five concentrations of polymer at a series of angles between 32 and 135°. For fraction F-1 and the unfractionated material wavelengths 4360 and 5460 A. were used. In the other cases only 4360 A. was used.

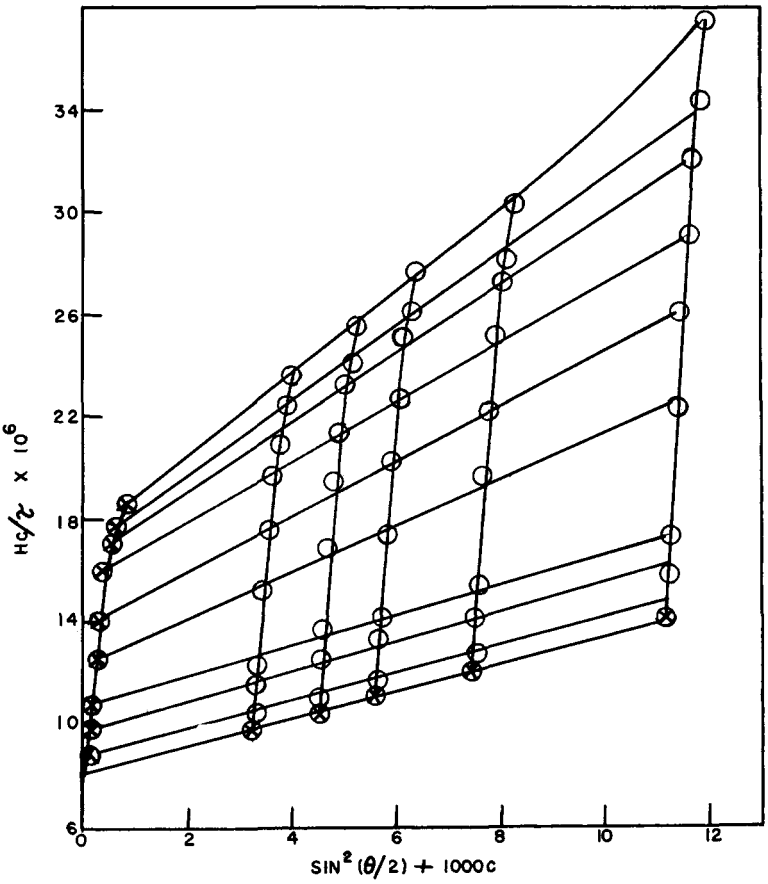

Fig. 1. Zimm plot for polybutene-1 F-4 in heptane at 60°C.

Results and Discussion

In the early stages of this work attempts were made to make light-scattering measurements in heptane at 35°C. Reproducible results could not be obtained. Indeed after a few days the polymer slowly separated from solution. The high and erratic molecular weights from light scattering indicated a considerable degree of association even for freshly made solutions. This difficulty was avoided by raising the temperature to 60°C.

Molecular weight and viscosity data are reported in Table I. The

TABLE I
Molecular Weight and Viscosity Data for Isotactic Polybutene-1

Sample	$M_w \times 10^{-6}$	$[\eta]$, dl./g.			$A_2 \times 10^4$	
		Heptane at 60°C.	Heptane at 35°C.	Decalin at 115°C.	λ = 4360 A.	λ = 5460 A.
F-1	0.90	1.98	2.63	1.87	5.0	5.1
Unfractionated	0.27	0.88	1.25	0.98	7.6	6.6
F-2	0.25	0.80	1.20	0.90	5.0	
F-3	0.13	0.52	0.55	0.55	7.4	
F-4	0.12	0.43	0.48	0.45	2.7	
F-5	0.10	0.38	0.38	—	6.8	
F-6	0.045	0.27	0.26	0.22	8.0	

molecular weights were obtained from extrapolation of Zimm plots in the usual way. For illustrative purposes a Zimm plot is shown in Figure 1. Some curvature in the angular lines was observed, especially for the lower molecular weight fractions. The plot of F-2 was somewhat distorted but satisfactory linear extrapolation to zero concentration at each angle could be carried out, followed by extrapolation to zero angle. The molecular

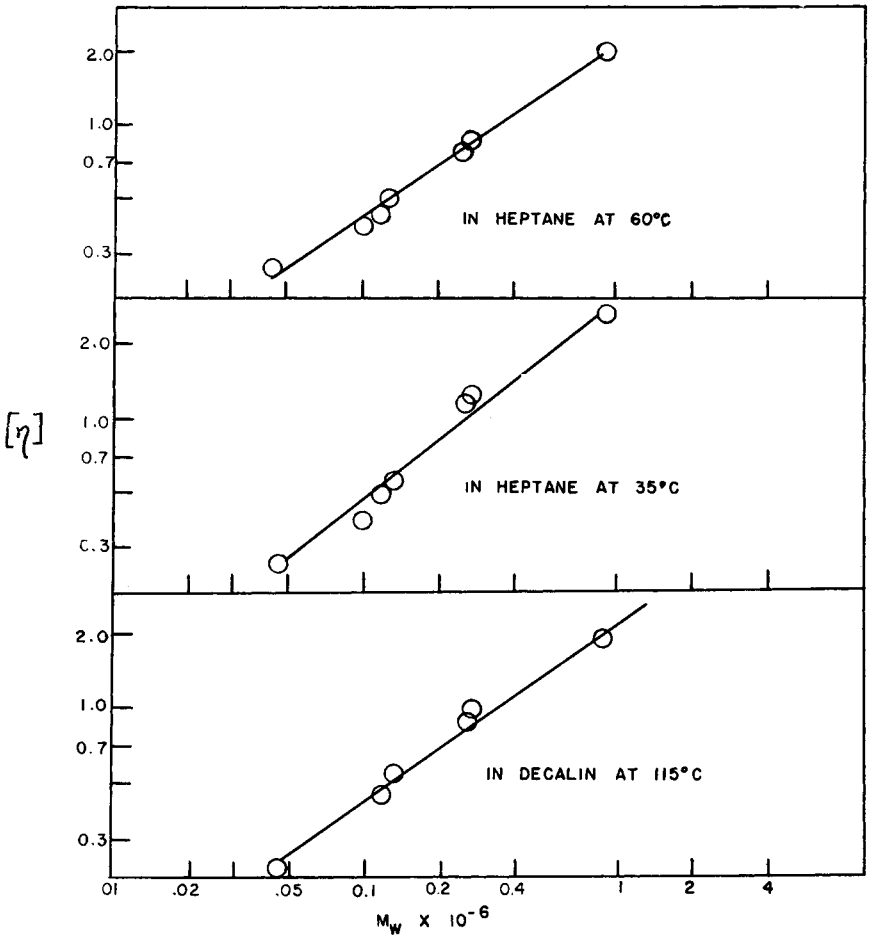

Fig. 2. Relation between intrinsic viscosity and molecular weight for polybutene-1.

weight for F-6 was obtained by extrapolation of 90° scattering to zero concentration.

From Table I it appears that the second virial coefficients show no significant trend with molecular weight.

The relation between molecular weight and intrinsic viscosity is shown in Figure 2 for the isotactic polybutene-1 in heptane at 35 and 60°C. and

in decalin at 115°C. The appropriate relations over the molecular weight range covered are:

$$\text{In heptane at } 35°\text{C. } [\eta] = 4.73 \times 10^{-5} M_w^{0.80}$$

$$\text{In heptane at } 60°\text{C. } [\eta] = 1.50 \times 10^{-4} M_w^{0.69}$$

$$\text{In decalin at } 115°\text{C. } [\eta] = 9.49 \times 10^{-5} M_w^{0.73}$$

It is noted that in all cases the values of the exponent a in the Mark-Houwink equation fall within the range 0.5 to 0.8. This is to be expected for randomly coiled polymers.[1]

Except for fraction F-1 the molecular weights were rather low, so that dissymmetries were not high enough for accurate calculation of the polymer dimensions. In the case of F-1, the z-average root-mean-square end-to-end length, $(\bar{r}^2)^{1/2}$, was estimated to be 1050 A. For this fraction the value of Φ was obtained by[2]

$$\Phi = \frac{[\eta]M_w}{\gamma(\bar{r}^2)^{3/2}}$$

In order to get the appropriate factor γ, an assumption had to be made as to the polydispersity. The method of Cleland[2] was used to obtain γ, using $v = 4$ as suggested by Zimm[3] for crude fractions from one precipitation. For F-1 Φ was found to be 2.2×10^{21} which is in agreement with the currently accepted value for randomly coiled polymers.[4]

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References

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Synopsis

An isotactic polybutene-1 was fractionated, and melting points of several fractions were determined. The fractions were studied by light-scattering and viscosity techniques. The parameters in the Mark-Houwink equation are $[\eta] = 4.73 \times 10^{-5} M_w^{0.80}$ in heptane at 35°C., $[\eta] = 1.50 \times 10^{-4} M_w^{0.69}$ in heptane at 60°C., and $[\eta] = 9.49 \times 10^{-5} M_w^{0.73}$ in decalin at 115°C. The molecular weight range studied was 0.45×10^5 to 0.9×10^6.

Résumé

Un polybutène-1 isotactique a été fractionné et les points de fusion de plusieurs fractions ont été déterminés. Les fractions ont été étudiées par diffusion lumineuse et par viscosimétrie. Les paramètres de l'équation de Mark-Huowink sont: $(\eta) = 4.73 \times 10^{-5} M_w^{0.80}$ dans l'heptane à 35°C, $(\eta) = 1.50 \times 10^{-4} M_w^{0.69}$ dans l'heptane à 60°C, $(\eta) = 9.49 \times 10^{-5} M_w^{0.73}$ dans la décaline à 115°C. Le domaine de poids moléculaire étudié était de 0.45×10^5 à 0.9×10^6.

Zusammenfassung

Ein isotaktisches Polybuten-1 wurde fraktioniert und die Schmelzpunkte einiger Fraktionen bestimmt. An den Fraktionen wurden Lichtstreuungsmessungen und Viskositätsmessungen ausgeführt. Die Parameter der Mark-Houwink-Gleichung sind in Heptan bei 35°C, $[\eta] = 4{,}73 \times 10^{-5} M_w^{0.80}$, in Heptan bei 60°C, $[\eta] = 1{,}50 \times 10^{-4} M_w^{0.69}$ und in Dekalin bei 115°C $[\eta] = 9{,}49 \times 10^{-5} M_w^{0.73}$. Die untersuchten Molekulargewichte lagen im Bereich von $0{,}45 \times 10^6$ bis $0{,}9 \times 10^6$.

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