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Solution Properties of Poly(butene-1 sulfone)

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ABSTRACT

The viscosity-molecular weight relationships; $[\eta] = 0.043\overline{M}_v^{0.54}$ $cm^3\ g^{-1}$ in acetone, $[\eta] = 0.026\overline{M}_v^{0.55}$ $cm^3\ g^{-1}$ in methyl ethyl ketone, and $[\eta] = 0.0057\overline{M}_v^{0.72}$ $cm^3\ g^{-1}$ in cyclohexanone, all at 30°C, were obtained for poly(butene-1 sulfone).

INTRODUCTION

This paper reports an evaluation of the viscosity-molecular weight relationship for poly(butene-1 sulfone) made during an investigation of the effects of γ-irradiation on the polymer [1, 2]. It supplements measurements of the solution properties of poly(hexene-1 sulfone) [3, 4] and poly(2-methyl pentene-1 sulfone) [5] which have been reported by Ivin and co-workers, who studied the thermodynamics of the copolymerization [6, 7].

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EXPERIMENTAL

Poly(butene-1 sulfone) was prepared by UV irradiation of equimolar comonomer liquid mixtures at -78°C and dried in vacuum at 30°C. Microanalysis confirmed a 1:1 composition. The polymer was fractionated by addition of methanol to an acetone solution and cooling. Viscometric measurements in distilled acetone, methyl ethyl ketone, and cyclohexanone were made at 30°C using a Ubbelohde viscometer. The shear-rate dependence of high molecular weight polymer was considered [8]. $\overline{M}_n$ values were determined in cyclohexanone at 37°C using a Mechrolab 501 membrane osmometer (S and S 0.8 membranes). $\overline{M}_w$ values were obtained from light-scattering measurements in methyl ethyl ketone with a Brice-Phoenix photometer.

RESULTS AND DISCUSSION

The polymer sample was separated into 32 fractions which showed a continuous decrease in $[\eta]$ in acetone after fractions 1 and 2. The weighted-average $[\eta]$ for the fractions (58.4 $cm^3\ g^{-1}$) was less than $[\eta]$ for the unfractionated polymer (69.5 $cm^3\ g^{-1}$), indicating that some degradation occurred during fractionation. The refractive index increment for poly(butene-1 sulfone) in methyl ethyl ketone at 26°C was 0.1326 ± 0.0009 $cm^3\ g^{-1}$ at 436 nm and 0.1294 ± 0.0008 $cm^3\ g^{-1}$ at 546 nm.

$\overline{M}_w$ and $\overline{M}_n$ values, determined for 5 fractions, are given in Table 1 and show that the molecular weight distributions are broad, indicating an extremely polydisperse initial polymer and poorly-selective fractionation. Therefore, the constants K and a in the Mark-Houwink equation $[\eta] = K\overline{M}_v^{\,a}$ were determined by successive approximation [9] using $\overline{M}_v$ values for the fractions, derived from the Zimm-Schulz distribution function [Eq. (1)] using the measured values of $\overline{M}_w$ and $\overline{M}_n$:

$$W(M) = (y^{h+1}/h!)M^h \exp(-yM) \tag{1}$$

$$\overline{M}_v = (1/y)(\Gamma(h+a+1)/\Gamma(h+1))^{1/a} \tag{2}$$

where $\overline{M}_n = h/y$, $\overline{M}_w = (h+1)/y$, and $\Gamma(x)$ is the gamma function of x. Different values of $\overline{M}_v$ are obtained for the "good" and "poor" solvents.

TABLE 1. Light Scattering, Osmometry and Viscometry Results[a]

Fraction	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_v$ AC	$[\eta]_{AC}$
4	1,560,000	308,000	5.06	1,337,000	86.3
8	1,073,000	287,000	3.74	911,000	69.9
11	794,000	205,000	3.87	653,000	59.9
15	469,000	94,000	4.99	402,000	45.3
18	360,000	88,000	4.09	304,000	40.1
	$[\eta]_{AC}$	$[\eta]_{MEK}$	$[\eta]_{CH}$	$\overline{M}_v$ AC	
3	91.0	61.1	157.1	1,442,000	
5	83.5	56.6	139.5	1,227,000	
10	61.4	43.9	95.1	695,000	
13	48.4	35.5	69.1	446,000	
17	44.0	29.7	60.1	376,000	

[a] AC = acetone. MEK = methyl ethyl ketone. CH = cyclohexanone. All $[\eta]$ values in $cm^3\ g^{-1}$ for 30°C.

The log $[\eta]$ vs log $\overline{M}_v$ plots are shown in Fig. 1, and the K and a values are listed in Table 2.

The Stockmayer-Fixman equation [Eq. (3)] is frequently used to obtain the unperturbed dimensions of a polymer:

$$[\eta]M^{-1/2} = K_\theta + 0.51\phi_0 BM^{1/2} \tag{3}$$

$[\eta]\overline{M}_w^{-1/2}$ is plotted against $\overline{M}_w^{1/2}$ and the intercept at $\overline{M}_w^{1/2} = 0$ is K_θ, from which the unperturbed dimensions are calculated using the Flory-Fox equation [Eq. (4)]:

$$K_\theta = \phi_0(\overline{r_0^2}/M)^{3/2} \tag{4}$$

Equation (3) is applicable for poor solvents, but for good solvents

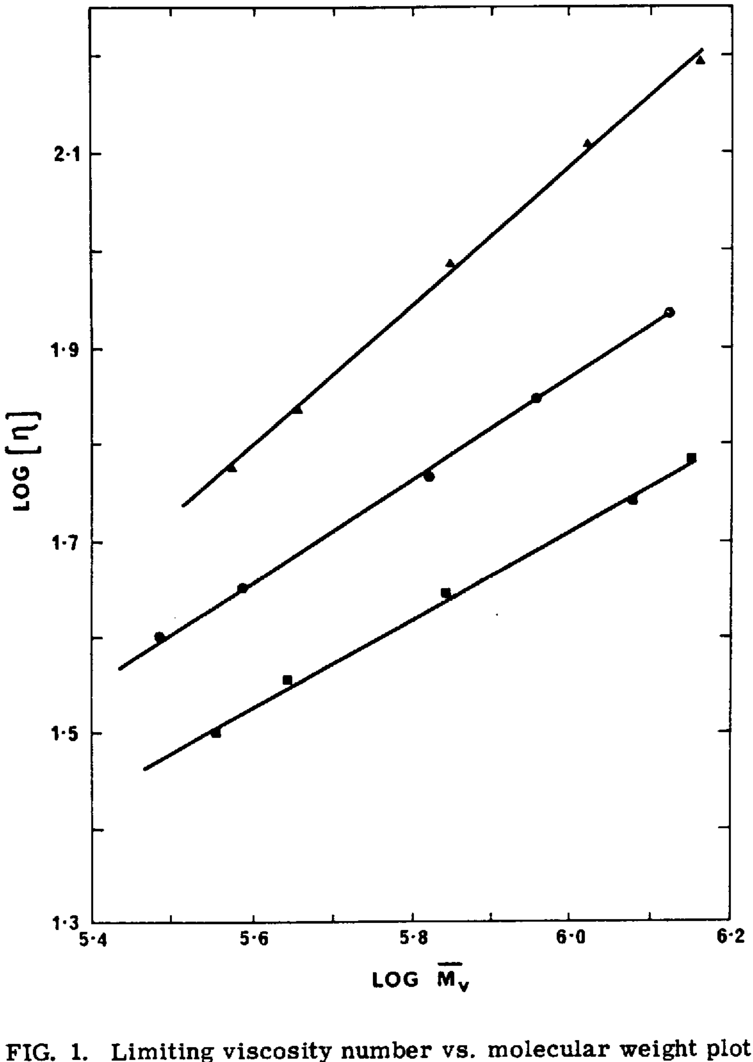

FIG. 1. Limiting viscosity number vs. molecular weight plots for evaluation of K and a in Mark-Houwink equation for acetone (●), methyl ethyl ketone (■), and cyclohexanone (▲).

the plot is frequently curved [10]. Booth and co-workers [11, 12] have shown that for broad fractions, K_θ is obtained when $[\eta]\overline{M}_v^{-1/2}$ is plotted against $\overline{M}_v^{1/2}$. Beech and Booth [10] have shown that this

TABLE 2. Mark-Houwink Parameters for Poly(butene-1 sulfone) at 30 °C

Solvent	a	K (cm^3 g^{-1})
Acetone	0.54	0.043
Methyl ethyl ketone	0.55	0.026
Cyclohexanone	0.72	0.0057

heterogeneity correction applied to broad molecular weight distribution poly(ethylene oxide) samples in a poor solvent gave a value of K_θ in agreement with the value determined with narrow fractions.

Acetone and methyl ethyl ketone are poor solvents for poly-(butene-1 sulfone) and plots of $[\eta]\overline{M}_v^{-1/2}$ vs $\overline{M}_v^{1/2}$ were near horizontal and gave K_θ = 0.067 and 0.053, respectively. Cyclohexanone is a good solvent and gave a steeply sloping curve. ϕ_0 was taken as 2.87×10^{23} for $[\eta]$ in cm^3 g^{-1} [14], and $(\overline{r_0^2}/N)^{1/2}$ values, where N is the number of mainchain bonds in $\overline{M}_w$, were 0.39 in acetone and 0.36 in methyl ethyl ketone. No correction for polydispersity is required since $\overline{M}_v^{1/2} = (\overline{M^{1/2}})_w$ is used in the evaluation of K_θ [12].

The effect of diminished free rotation due to steric hindrance, given by $\sigma = (\overline{r_0^2}/N)^{1/2}/(\overline{r_{of}^2}/N)^{1/2}$, using $(\overline{r_{of}^2}/N)^{1/2} = 0.2324$ nm from the calculations of Huglin and Stepto [13], gives $\sigma = 1.68$ in acetone and 1.54 in methyl ethyl ketone The reason for the low value of $(\overline{r_0^2}/N)^{1/2}$ in methyl ethyl ketone is unknown. Bates and Ivin [4] observed a similar effect in poly(hexene-1 sulfone), their viscosity measurements giving $\sigma = 1.93$ in dioxane-n-hexane and benzene-cyclohexane mixtures and in hexyl chloride, and $\sigma = 1.80$ in methyl ethyl ketone—n-hexane and methyl ethyl ketone-isopropanol mixtures. These values are calculated using revised $\overline{r_{of}^2}$ values [13] and are now 5% higher. There is apparently an expansion in the unperturbed dimension from poly(butene-1 sulfone) to poly(hexene-1 sulfone). Bates, Biggins, and Ivin [5] observed a further expansion from poly(hexene-1 sulfone) to poly(2-methyl pentene-1 sulfone) using narrow fractions ($\overline{M}_w/\overline{M}_n = 1.1$).

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