

## Characterization of Polybutenes\*

WILLIAM F. HADDON, JR., ROGER S. PORTER, and JULIAN F. JOHNSON, *California Research Corporation, Richmond, California*

### Synopsis

To characterize butene polymers, rapid and precise small- and large-scale column fractionation techniques have been developed for low molecular weight pure polyisobutenes and for mixed butene polymers. Fractionation results have been used to determine molecular weight distribution curves of typical commercial butene polymers. Narrow distribution fractions obtained from fractionation have been used to investigate viscosity-molecular weight correlations for both pure polyisobutenes and for mixed butene polymers. Molecular weights were predominantly determined with the relatively new technique of vapor pressure osmometry. Molecular weights and distributions were also checked with cryoscopic and light scattering molecular weights. The chemical composition of several fractions was determined by high resolution nuclear magnetic resonance. The Huggins' constant was measured for several bulk polymers and established for low molecular weight butene polymers.

### Introduction

Butene polymers are of extensive commercial use; industry capacity is presently near 100 million pounds per year. In spite of this large volume production, published methods for molecular weight characterization of polybutenes are rare.<sup>1</sup> In this work, rapid and precise small- and large-scale column fractionation techniques have been developed for low molecular weight pure polyisobutenes and for mixed butene polymers. Fractionation results have been used to determine molecular weight distribution curves of typical commercial butene polymers. Narrow distribution fractions obtained from fractionation have been used to investigate viscosity-molecular weight correlations for both pure polyisobutenes and for mixed butene polymers. Molecular weights were predominantly determined with the relatively new technique of vapor pressure osmometry. Molecular weights and distributions were also checked with cryoscopic and light scattering molecular weights. The composition of several fractions was determined by high resolution nuclear magnetic resonance (NMR). The Huggins' constant was measured for several bulk polymers and established for low molecular weight polybutenes.

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### Experimental

Three butene polymers of different molecular weight were fractionated by using the solvent-thermal gradient method of Baker and Williams<sup>2</sup> as extended by Cantow et al.<sup>3,4</sup> The solvent-nonsolvent pair was benzene-methyl ethyl ketone, and the temperature gradient down the 1-m. fractionation column was from 50°C. to 18°C. All fractionations were performed with the use of logarithmic solvent gradients. Gradient speed and range were programmed according to known molecular weight-solvent composition relationships to give definitive separations over the relatively narrow molecular weight range encompassed by polybutenes. For the lowest molecular weight polybutenes, solvent composition limits were 0% and 50% of good solvent, and 0% and 75% for polybutenes of molecular weight about 3000. Instrumentation used to establish solvent gradients has been described in the literature.<sup>5</sup> Flow rates averaged 20 cc./hr., and total fractionation times were between three and five days.

Fractions from analytical separations, on 10-g. samples, were used to establish molecular weight distribution curves. These fractions were also used for NMR and intrinsic viscosity measurements. One large-scale fractionation of a low molecular weight pure polyisobutene was performed with the use of previously described multicolumn equipment;<sup>3</sup> 100 g. of polymer was charged. Large fractions were used for extended intrinsic viscosity studies. High molecular weight fractions used for light-scattering and intrinsic viscosity measurements were obtained from large-scale fractionations of a high molecular weight polyisobutene with a viscosity-average molecular weight,  $M_v$ , of 40,000.<sup>4</sup>

Chemical composition of selected polybutene fractions was determined qualitatively by high resolution NMR. The instrument employed was a Varian A-60 (Varian Associates, Palo Alto, California), polymer fractions being generally diluted to 12.5 wt.-% in  $\text{CCl}_4$ . Methods for assigning proton peaks present in typical butene and isobutene polymers have been previously reported.<sup>6</sup>

Light-scattering measurements were conducted on the SOFICA photogonio diffusometer, Model 40,000A (Societe Francaise D'Instruments de Control et D'Analysis, Strasbourg, France). This instrument was calibrated in absolute turbidity units at 436 and 576  $m\mu$  from measurements on colloidal silica solutions and on polymers of known turbidity and molecular weight.<sup>7</sup> Light intensity data were extrapolated to zero angle of observation, and measurements were conducted in a theta-solvent (ethyl octanoate at 23°C.) to eliminate concentration dependence of results.

Number-average molecular weights of narrow distribution fractions and bulk polymers were measured by vapor pressure osmometry. Two instruments were employed, a conventional Osmometer (Mechrolab, Inc., Mountain View, California) and a modified Osmometer, used for determining molecular weights above 6000.<sup>3</sup> Osmometer results show excellent agreement with cryoscopic data.

Intrinsic viscosities were obtained from a one-point determination of specific viscosity in standard cross-arm viscometers<sup>9</sup> by using the extrapolation method of Huggins.<sup>10</sup> Temperature regulation of viscosity baths was better than  $\pm 0.01^\circ\text{C}$ .

### Results

Table I defines and gives molecular weight data for three typical commercial butene polymers. Pyrolysis-gas chromatographic and NMR results for these specific polymers have been published previously.<sup>6</sup> New

TABLE I  
Characterization of Butene Polymers

Polymer	$[\eta]$ (CCl <sub>4</sub> , 30°C.)	$M_n$	$(M_w/M_n - 1)$
A	0.108	2700	0.76
B	0.066	1290	0.46
C	0.055	980	0.24

NMR results agree with published NMR and pyrolysis-gas chromatographic data showing decreasing isobutene content with decreasing molecular weight of polybutene fractions.<sup>6</sup> The lowest molecular weight fraction of the highest molecular weight polybutene (sample A) was shown to be a pure polyisobutene. Proton peaks attributable to chain units of 1- and 2-butene were totally absent from the NMR spectrum of this fraction. The three initial fractions obtained for polybutene C showed, however, by NMR appreciable and similar amounts of 1- and 2-butene. These

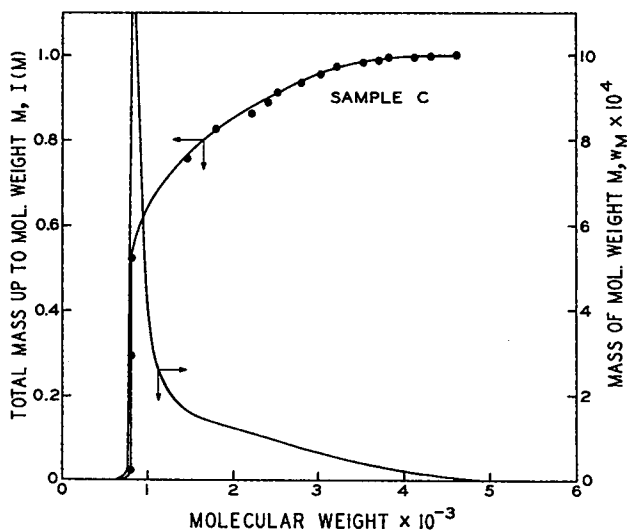


Fig. 1. Polybutene molecular weight distribution.

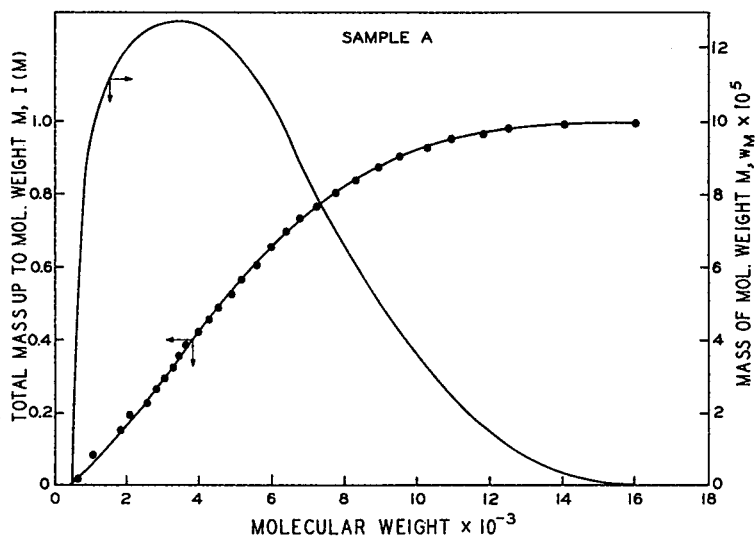


Fig. 2. Polyisobutene molecular weight distribution.

fractions were eluted with different column retention times and had nearly equal molecular weight (Fig. 1). These results indicate that fractionation under these conditions is dominantly based on molecular weight, with butene composition being of only minor influence.

Figure 1 shows integral and differential molecular weight distribution

TABLE II  
Fractionation Data on Polybutene B

Fraction no.	Weight, g.	Weight, %	$M_n$	$I(M)$
B-1	2.9757	32.170	900	0.1608
B-2	1.5330	16.573	1200	0.4046
B-3	0.8155	8.816	1670	0.5315
B-4	0.5294	5.723	2000	0.6042
B-5	0.4206	4.547	2400	0.6555
B-6	0.3448	3.728	2600	0.6989
B-7	0.2757	2.981	2800	0.7305
B-8	0.2323	2.511	3000	0.7579
B-9	0.2101	2.271	3150	0.7818
B-10	0.2018	2.182	3320	0.8041
B-11	0.1793	1.938	3500	0.8247
B-12	0.1263	1.365	3750	0.8412
B-13	0.1314	1.421	3900	0.8552
B-14	0.2423	2.570	4200	0.8851
B-15	0.1968	2.128	4650	0.8986
B-16	0.2198	2.376	5000	0.9211
B-17	0.2836	3.066	5800	0.9494
B-18	0.3314	3.582	6400	0.9826
	9.2498			

TABLE III  
Solution Viscosity Evaluation of Low Molecular Weight Polybutene Fractions

Fraction	$[\eta]$ ( $\text{CCl}_4$ , $30^\circ\text{C}.$ )	$\eta$ (Tetralin, $20^\circ\text{C}.$ ), cstokes <sup>a</sup>	$M_n$
C-3	0.0423		814
	0.0443		
C-4	0.0495		822
	0.0470		
112-3	0.0549	3.143	971
112-4	0.0542	3.150	1224
112-6	0.0625	3.211	1877
112-8	0.0795	3.332	4055
112-10	0.1035	3.428	4939

<sup>a</sup> At 2.76 wt.-% concentration.

curves for mixed polybutene C. Figure 2 shows comparable distribution curves for polyisobutene sample A. The type of data used to derive Figures 1 and 2 is shown in Table II, which contains fractionation data on the third polymer, polybutene B. Integral distribution curves were constructed and then differentiated graphically. The narrowness of individual fractions, as evidenced by the ratio of weight-average to number-average molecular weight,  $M_w/M_n \leq 1.03$ , has been demonstrated in previously published refractionation results.<sup>4</sup>

Table III shows intrinsic viscosity measurements on narrow distribution fractions of pure low molecular weight polyisobutenes and on several fractions of mixed butene polymer in carbon tetrachloride at  $30^\circ\text{C}$ . Intrinsic viscosities were calculated from one-point specific viscosity determinations using a Huggins' constant of 0.36. This Huggins' constant value is an average of three separate series of measurements, on polybutene

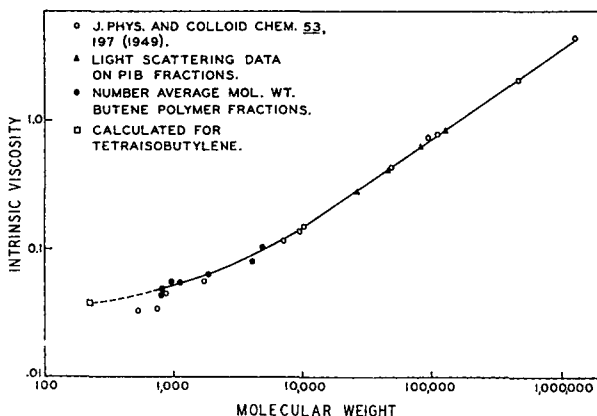


Fig. 3. Intrinsic viscosity-molecular weight relationship of polyisobutene in  $\text{CCl}_4$  at  $30^\circ\text{C}$ .

samples B and C, and on a high molecular weight pure polyisobutene,  $M_v = 40,000$ . Observed differences in  $k'$  between mixed and pure polybutenes were within experimental error.

Intrinsic viscosity data in Table II are compared with absolute number-average molecular weight measurements on these fractions by vapor pressure osmometry. Weight-average molecular weights of four pure polyisobutene fractions above 20,000 molecular weight were measured by light scattering (Table IV). In Fig. 3, intrinsic viscosity-molecular weight data are compared graphically with those of Fox.<sup>11</sup> Above 10,000 molecular weight, light-scattering data substantiate the linear log-log intrinsic viscosity-molecular weight relationship of Fox. Earlier published results

TABLE IV  
Light-Scattering Confirmation of Fox Equation

Fraction	$[\eta]$ (CCl <sub>4</sub> , 30°C.)	$M_w$	$M_w$ Light-scattering
A-G	0.277	25,200	26,800
A-J	0.411	45,300	46,000
A-L	0.628	82,000	83,600
A-O	0.834	125,000	127,000

$$[\eta] = 2.9 \times 10^{-4} M^{0.68} \quad (1)$$

gave an exponent of 0.64 which is thought to be low.<sup>12,13</sup>

At low molecular weights, the original data of Fox and Flory showed curvature in the log-log plot of intrinsic viscosity versus molecular weight. Present data on narrow distribution fractions define this region more explicitly and confirm the curvature indicated in Fox's results. Furthermore, this curvature is not a consequence of 1- and 2-butene components present in low molecular weight fractions of mixed butene polymers.

NMR and gas chromatographic analyses of mixed butene polymers from several sources indicate that the general method of synthesis yields a common and regular change of polymer composition with molecular weight. For fractions and for bulk polymers, the isobutylene content increases regularly with molecular weight, and at 4000 and above polybutenes are pure polyisobutene. This fact, along with intrinsic viscosity and additional NMR results discussed here, indicates that intrinsic determinations on mixed butene polymers will hold for samples derived from the principal commercial sources of polybutenes without modification of viscosity-molecular weight relationships. The graphical correlation in Figure 3 is thus a simple, useful, and general method for determining the molecular weight of both pure polyisobutenes and commercial polybutenes.

The intrinsic viscosity of tetraisobutene in carbon tetrachloride at 30°C. was calculated from estimated molecular dimensions by using the Einstein equation, extended for prolate ellipsoids by Simha.<sup>14,15</sup> The calculated value of  $0.038 \pm 0.003$  is shown in Figure 3. This point lies on the ex-

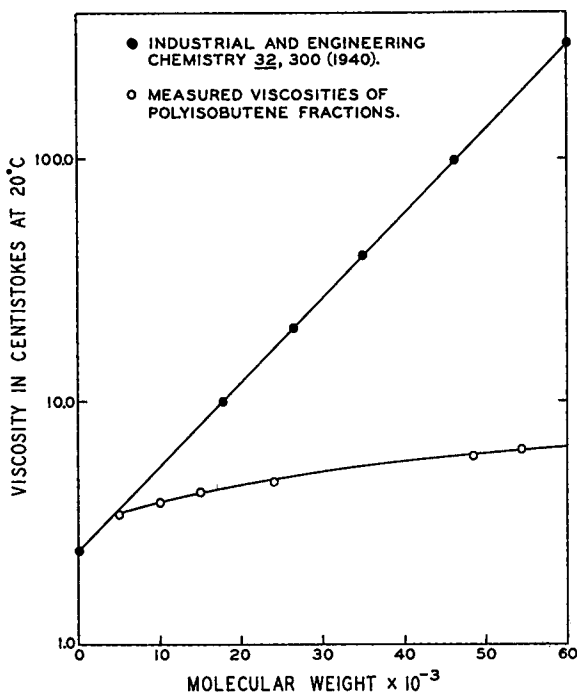


Fig. 4. Viscosity of polyisobutene in tetrahydronaphthalene (2.76 wt.-%).

tended portion of the curve developed for pure polyisobutene fractions. The measured intrinsic viscosity of a commercially available tetramer fell below this point, but sample purity was less than 50% tetraisobutene by gas chromatographic analysis.

Also in Table III are kinematic viscosity results in tetrahydronaphthalene (Tetralin), at 2.76 wt.-% concentration. Results on high molecular weight fractions are compared graphically with an earlier published Tetralin curve for butene polymers based on the Arrhenius equation.<sup>16</sup> Current results show that this equation specifically indicated for polybutenes is generally invalid, particularly at high molecular weights (Table III and Fig. 4).

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### Résumé

Des techniques rapides et précises de micro- et macrofractionnement sur colonne ont été développées pour caractériser des polymères de butène tant pour les polyisobutènes purs de faible poids moléculaire que pour des mélanges de polymères de butène. Les résultats du fractionnement ont été utilisés pour déterminer les courbes de distribution des poids moléculaires de polymères commerciaux de butène. Des fractions de distributions étroites obtenues par fractionnement ont servi à établir la relation entre la viscosité et le poids moléculaire pour les polyisobutènes purs et pour des mélanges. Les poids moléculaires ont été déterminés principalement par une technique assez récente d'osmométrie par pression de vapeur. Les poids moléculaires et les distributions sont aussi déterminées par cryoscopie et par diffusion lumineuse. La composition chimique de plusieurs fractions est déterminée par résonance magnétique nucléaire à haute résolution. La constante de Huggins est mesurée pour différents polymères en masse et établie pour des poids moléculaires faibles de polymères de butène.

### Zusammenfassung

Zur Charakterisierung von Butenpolymeren wurde eine rasche und genaue Säulenmethode zur Fraktionierung von reinen Polyisobutenen und gemischten Butenpolymeren in grossem und kleinem Massstab entwickelt. Die Fraktionierungsergebnisse wurden zur Bestimmung der Molekulargewichtsverteilungskurven typischer kommerzieller Butenpolymerer verwendet. Die durch Fraktionierung hergestellten Fraktionen mit enger Molekulargewichtsverteilung wurden zur Untersuchung der Viskositäts-Molekulargewichtsbeziehung sowohl reiner Polyisobutene als auch gemischter Butenpolymerer herangezogen. Das Molekulargewicht wurde hauptsächlich mittels der relative neuen Methode der Dampfdruckosmometrie bestimmt. Die Molekulargewichtsverteilung wurde ausserdem durch Bestimmung des Molekulargewichtes mittels Kryoskopie und Lichtstreuung kontrolliert. Die chemische Zusammensetzung der einzelnen Fraktionen wurde durch hochauflösende magnetische Kernresonanz bestimmt. Die Huggins-Konstante wurde für mehrere in Substanz hergestellte Polymere gemessen und für niedermolekulare Butenpolymere festgelegt.

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