The Determination of the Addition Variation and Geometrical Isomerism of a Polybutadiene as a Function of Molecular Weight by Preparative Gel Permeation Chromatography and Infrared Analysis

FRANCIS M. MIRABELLA, JR., and EDWARD M. BARRALL II,*
Institute of Materials Science and Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268, and JULIAN F. JOHNSON,† *IBM Research Laboratory, San Jose, California 95193*

Synopsis

The addition variation, 1,2 and 1,4 units, and the geometrical isomerism, 1,4-*cis* and 1,4-*trans* units, of a fractionated polybutadiene were determined as a function of molecular weight using preparative gel permeation chromatography followed by infrared analysis of the fractions. Both the addition variation and geometrical isomerism remained essentially constant across the molecular weight distribution.

INTRODUCTION

The 1,4-*cis*, 1,4-*trans*, and 1,2 contents of olefinic linkages in polybutadienes are routinely determined. Although these configurational properties are determined on the bulk polymer, there appear to be no studies in which they were determined as a function of molecular weight. Several studies have been reported on the determination of the olefinic linkage content of polybutadienes as a function of molecular weight. In one such study,[1] preparative fractionation followed by unsaturation analysis of the fractions was employed while in another study,[2] a technique was reported using gel permeation chromatography (GPC) with UV and RI detectors.

In the present study, a polybutadiene sample was fractionated by GPC and the 1,2, 1,4-*cis*, and 1,4-*trans* content determined by infrared analysis of the fractions. The average molecular weight of the fractions was determined by calibration of the preparative column. Then the addition variation, 1,2 and 1,4 content, and the geometrical isomerism, 1,4-*cis* and 1,4-*trans* content, were plotted as a function of log molecular weight.

* On leave from IBM Research Laboratory, San Jose, California.
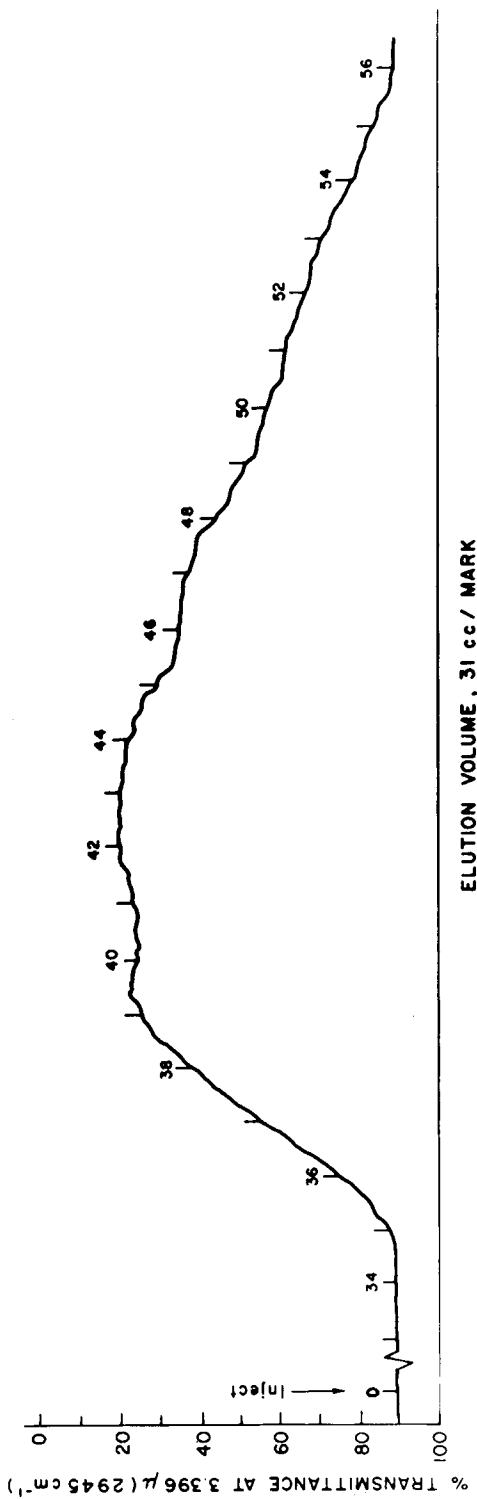† On leave from University of Connecticut.

Fig. 1. GPC curve of a 10.0 mg/cc solution of a polybutadiene sample recorded at the conditions described in the text.
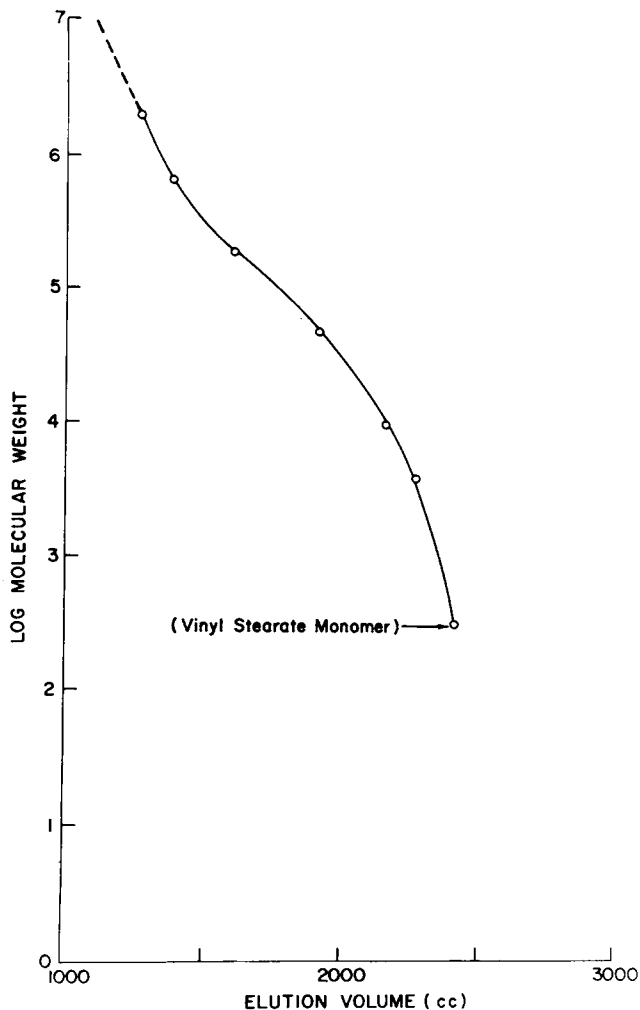
Fig. 2. Calibration curve for GPC system using polystyrene narrow MWD standards (Pressure Chemical Co.) and vinyl stearate monomer. The extrapolation was used for elution volumes outside the range of the standards, when observed.

EXPERIMENTAL

The polybutadiene sample which was prepared using a BuLi catalyst was dissolved at a concentration of 10.0 mg/cc in tetrachloroethylene by heating just below the boiling point for 30 min.

Gel permeation chromatography was done on a preparative scale system consisting of a high-capacity Milton-Roy pump with a six-port injection valve, 50.0-cc injection loop, and a 1.2-meter, $2\frac{1}{4}$-in. (I.D.) stainless steel column packed with 350 Å nominal exclusion limit, 200–400 mesh Bioglas porous glass beads. A 50.0-cc injection of the aforementioned polybutadiene was made at room temperature at a flow rate of 295 cc/hr.

The GPC eluent stream was detected as described previously[3] with a Perkin-Elmer (Norwalk, Conn.) 21 IR spectrometer fitted with a 3-mm-pathlength flow-through cell by monitoring the C—H absorption at 3.396 μ (2945
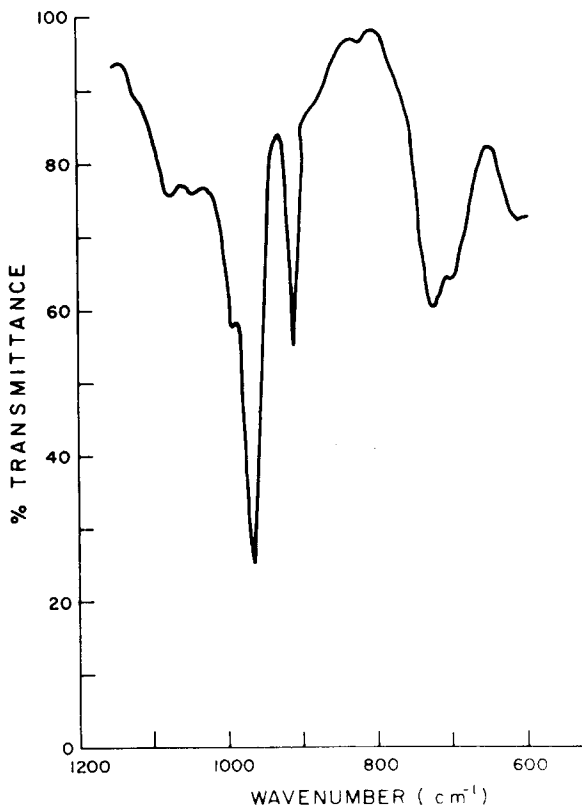
Fig. 3. Infrared spectrum of fraction 12 of a polybutadiene sample, showing the 1,4-*cis* peak at approximately 730 cm^{-1} (13.7 μ), the 1,4-*trans* peak at 967 cm^{-1} (10.34 μ), and the 1,2 peak at 910 cm^{-1} (10.98 μ).

cm^{-1}). A 3-mm-pathlength cell filled with pure tetrachloroethylene was used in the reference beam of the spectrometer to compensate for the solvent.

The GPC chromatogram is shown in Figure 1. Twenty 31-cc fractions were collected over the molecular weight distribution.

Average "working" molecular weights of the fractions were calculated by using the polystyrene calibration curve in Figure 2 which was determined for the same GPC system. The polystyrene molecular weights were corrected for the difference in the molecular weights of the styrene and butadiene units by using the formula

$$M_P = \frac{M_B}{M_S} M_C \tag{1}$$

where M_P = "working" MW of polybutadiene, M_B = MW of a butadiene mer unit (54.06), M_S = MW of a styrene mer unit (104.15), and M_C = MW from polystyrene calibration curve (Fig. 2). The $\bar{M}_w$ of the whole polymer was measured by light scattering (Brice Phoenix, Philadelphia, Pa.) in CS$_2$ solution.

The fractions were analyzed by infrared spectroscopy. A Beckman (Fullerton, Cal.) IR-7 infrared spectrometer was used. The polybutadiene was

cast as a film by evaporating the tetrachloroethylene solutions on a salt plate heated to 90° to 100°C in a nitrogen atmosphere. The spectrometer was warmed up for 1 hr, and the following settings were used: scan speed, 20 cm^{-1}/min; glower current, 0.6 amp; scale, 0–100 T; double beam operation; fine gain, 350; coarse gain, 10; period, 8 and slits on select program for 2.25 mm at 960 cm^{-1}. The pen was set at 95% T at 850 cm^{-1} by adjusting a comb in the reference beam before scanning each spectrum. Figure 3 shows a typical spectrum.

The baseline absorbances were calculated using the following equations:

$$\text{baseline } A_{10.34\,\mu} = A_{10.34\,\mu} - \frac{A_{9.68\,\mu} + (2A_{10.70\,\mu})}{3} \tag{2}$$

$$\text{baseline } A_{10.98\,\mu} = A_{10.98\,\mu} - (0.5A_{10.70\,\mu} + 0.5A_{11.26\,\mu}) \tag{3}$$

"Integrated" absorbance of
$$13.7\ \mu \text{ peak} = [A_{13.10\,\mu} + A_{13.20\,\mu} + A_{13.30\,\mu} + \ldots A_{14.00\,\mu}]$$
$$- 5\,[A_{13.00\,\mu} + A_{14.00\,\mu}]. \tag{4}$$

Then, the response due to each type of unit was determined as follows:

$$1,4\text{-}trans \text{ response} = \text{baseline } A_{10.34\,\mu} \times 0.084 \tag{5}$$

$$1,4\text{-}cis \text{ response} = \text{"integrated" absorbance} \times 0.096 \tag{6}$$

$$1,2 \text{ response} = \text{baseline } A_{10.98\,\mu} \times 0.059 \tag{7}$$

TABLE I
Polybutadiene Microstructure as a Function of "Working" Molecular Weight

| Sample	Average elution volume, cc	Average "working" MW M_p	Log M_p	1,4 Content, %	1,2 Content, %	1,4trans content %	1,4-cis content, %
Bulk Poly-butadiene	—	—	—	82.41	17.59	41.05	41.36
Fraction 1	1100.5	4.84(10^6)	6.68	86.51	13.49	45.31	41.20
Fraction 2	1131.5	3.77(10^6)	6.58	84.99	15.01	42.87	44.12
Fraction 3	1162.5	2.86(10^6)	6.46	83.28	16.72	48.09	35.19
Fraction 4	1193.5	2.12(10^6)	6.32	85.98	14.02	42.58	43.40
Fraction 5	1224.5	1.57(10^6)	6.20	84.05	15.95	43.45	40.60
Fraction 6	1255.5	1.16(10^6)	6.06	86.42	13.58	42.48	43.94
Fraction 7	1286.5	9.02(10^5)	5.96	84.76	15.24	46.22	38.54
Fraction 8	1317.5	5.96(10^5)	5.78	83.29	16.71	30.04	53.25
Fraction 9	1348.5	4.53(10^5)	5.66	84.23	15.77	45.57	38.66
Fraction 10	1379.5	3.52(10^5).	5.55	86.04	13.96	37.99	48.05
Fraction 11	1410.5	2.86(10^5)	5.46	82.20	17.80	53.05	39.15
Fraction 12	1441.5	2.32(10^5)	5.37	86.77	13.23	49.91	36.86
Fraction 13	1472.5	1.89(10^5)	5.28	86.80	13.20	51.80	35.00
Fraction 14	1503.5	1.61(10^5)	5.21	84.14	15.86	45.38	38.76
Fraction 15	1534.5	1.40(10^5)	5.15	84.97	15.03	43.09	41.88
Fraction 16	1565.5	1.22(10^5)	5.08	84.66	15.34	48.93	35.73
Fraction 17	1596.5	1.08(10^5)	5.03	84.13	15.87	46.09	38.04
Fraction 18	1627.5	9.69(10^4)	4.99	85.19	14.81	39.58	45.61
Fraction 19	1658.5	8.61(10^4)	4.93	82.79	17.21	35.56	47.23
Fraction 20	1689.5	7.67(10^4)	4.88	83.46	16.54	42.22	38.24
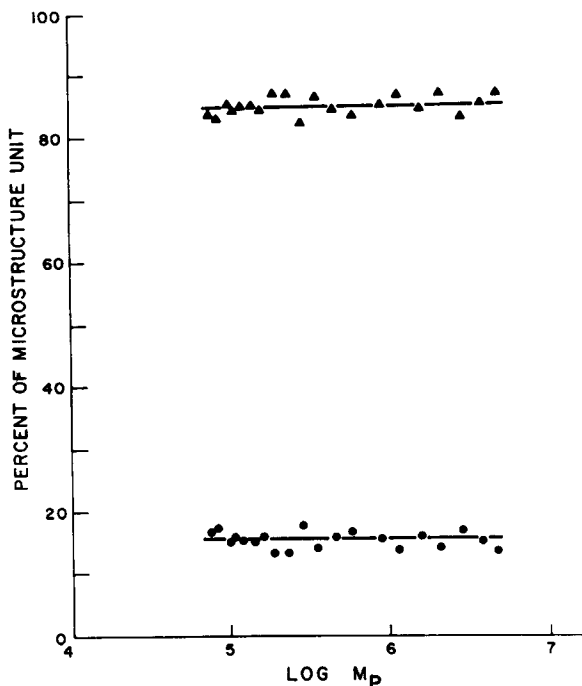
Fig. 4. Per cent microstructure units in polybutadiene vs. log "working" molecular weight (M_p): (●) 1,2 units; (▲) 1,4 units. The least-squares fit to each data set is shown.

Equations (5), (6), and (7) were summed up, and each response was expressed as a normalized percentage of the total.

This procedure was calibrated with 95% 1,4-*cis*, 83% 1,4-*trans*, and 64% 1,2 polybutadiene standards. This method was developed by Puchalski and Newell.[4] They reported an accuracy of 3% absolute.

RESULTS AND DISCUSSION

The polybutadiene microstructure as a function of average "working" molecular weight of the fractions is tabulated in Table I.

The "working" molecular weight scale based on polystyrene standards was employed since polybutadiene standards were not available. The "working" molecular weight scale was used to calculate $\bar{M}_w$ (GPC) to compare this value to the $\bar{M}_w$ obtained by light scattering. The values obtained were $\bar{M}_w$ (GPC) = 898,000 and $\bar{M}_w$ (light scattering) = 444,000. This indicates that the "working" molecular weight scale yields values which are of the correct magnitude. However, the implicit assumption made in this scale that the hydrodynamic volumes of a polystyrene and polybutadiene chain of the same number of mer units are equal in tetrachloroethylene solution was assumed only for convenience and is admittedly a crude assumption as indicated by the comparison of the two $\bar{M}_w$ values. The "working" molecular weight scale could have been corrected using this comparison, however, it appeared to contribute nothing to the conclusions of this work.

Figure 4 is a plot of addition variation versus log molecular weight. Figure 5 is a plot of geometrical isomerism of the 1,4 units versus log molecular
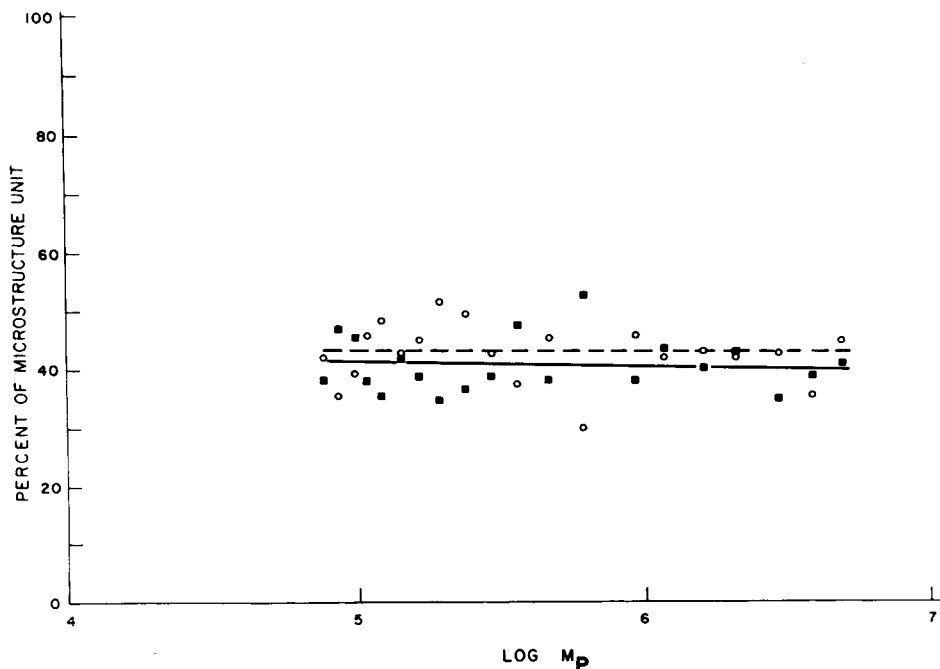
Fig. 5. Per cent microstructure units in polybutadiene vs. log "working" molecular weight (M_p): (——■——) 1,4-cis units; (---O---) 1,4-trans units. The least-squares fit to each data set is shown.

weight. Figure 4 clearly shows that addition variation is constant, within fairly narrow limits, across the molecular weight distribution (MWD). Figure 5 shows that geometrical isomerism is also constant, within somewhat larger limits, across the MWD. The larger scatter observed in Figure 5 was suspected to be due to the difficulties in measuring the "integrated" absorbance of the broad *cis* peak at 13.7 microns (730 cm^{-1}). This resulted in larger scatter of the 1,4-*trans* and 1,4-*cis* values while the total 1,4 content remained fairly constant.

These results confirmed the expectation that BuLi catalysts yield polybutadienes of consistent microstructure across the MWD.[5]

References

1. P. J. Flory, *Ind. Eng. Chem.*, **38,** 417 (1946).

2. J. N. Anderson, *J. Appl. Polym. Sci.*, **18,** 2819 (1974).

3. F. M. Mirabella, Jr., E. M. Barrall II, and J. F. Johnson, *J. Appl. Polym. Sci.*, **19,** 2131 (1975).

4. C. Puchalski and J. Newell, private communication.

5. W. M. Saltman, in *Encyclopedia of Polymer Science and Technology*, Vol. 2, H. F. Mark, N. D. Gaylord, and N. M. Bikales, Eds., Interscience, New York, 1967, pp. 678–754.