

# Determination of Compositional Heterogeneity in Butadiene-Styrene Copolymers by Density Gradient Ultracentrifugation

C. J. STACY, *Phillips Petroleum Company, Bartlesville, Oklahoma 74004*

## Synopsis

Sedimentation equilibrium in a density gradient gives a sensitive intermolecular composition analysis of styrene-butadiene copolymers. This information is sometimes unobtainable by other analytical techniques. The density gradient is formed by action of the centrifugal field upon a carbon tetrachloride-cyclohexane mixture, and the equilibrium position of each polymeric solute in the gradient depends upon its effective buoyant density. The large difference in styrene and butadiene densities makes possible accurate composition calibrations which are independent of molecular weight and branching.

## INTRODUCTION

Intermolecular compositional heterogeneity in butadiene-styrene copolymers, i.e., the presence of species of differing styrene content, may arise from several sources. These include deliberate blending as well as polymerization conditions. Heterogeneity may or may not be desirable, depending on the final application of the polymer. Methods for detection of compositional heterogeneity, therefore, provide useful information about the reactions occurring during synthesis and/or the nature of commercial products.

Methods for characterization of compositional heterogeneity include gel permeation chromatography (GPC) with simultaneous differential refractive index and ultraviolet<sup>1</sup> or infrared<sup>2</sup> detection, thin-layer chromatography (TLC),<sup>3</sup> and equilibrium density gradient ultracentrifugation (DGU).<sup>4</sup> GPC is useful only when species differing in composition also have different hydrodynamic volumes, so that at least partial separation is accomplished. Apparently TLC gives useful separations based on composition, with careful attention to elimination of molecular weight effects.<sup>3</sup> The most attractive feature of DGU is that it effects separation only by buoyant density (and hence composition). The experiment was first described<sup>5</sup> in 1957. Macromolecules of natural origin have been widely studied, and a number of applications to synthetic polymers have been reported.<sup>6,7</sup> The purpose of the present paper is to describe the application of the DGU technique to compositional distribution of butadiene-styrene copolymers.

## GENERAL DESCRIPTION

In this experiment, a polymer is dissolved in a solution of two solvents of different density and centrifuged to equilibrium. The polymer reaches equilibrium in a band about a point where its effective buoyant density matches that of the solvent; this point is independent of molecular weight and size. Calibration is, therefore, simple and direct—a given composition will always be found at a given point in a given gradient. Because of the substantial difference in density between polybutadiene and polystyrene, the effective density of a resolved styrene-butadiene copolymer component of a mixture provides a sensitive measurement of the amount of styrene in that component. Carbon tetrachloride-cyclohexane solutions are used; the concentration of carbon tetrachloride is adjusted to bring the desired polymer bands into the gradient range.

The breadth of a band is governed by diffusion; consequently, it is inversely proportional to molecular weight. Below  $M = 10^5$ , bands are broad; they are quite sharp at  $M \geq 500,000$ . Resolution, therefore, increases with molecular weight. Species of extremely high molecular weight such as "microgel" form quite sharp bands or vertical shadows giving a very sensitive method for detection of this type of material.

Band asymmetry can arise only if unresolved components of different density are present; consequently, it is a qualitative test for compositional heterogeneity.

Carbon black or other heavy fillers do not interfere since they migrate to the bottom of the cell. Low molecular weight additives such as extender oils do not interfere, as they are not banded.

## EXPERIMENTAL PROCEDURE

Sedimentation equilibrium experiments were made in a Beckman Model E analytical ultracentrifuge.

A premixed solution, of carbon tetrachloride in cyclohexane, was selected depending upon the composition range of interest. For example, with 0.522 g/ml carbon tetrachloride, 59,780 rpm, and cells nearly full, polystyrene was banded near the cell bottom and polybutadiene near the meniscus. Polymer concentration was normally near 0.2 g/100 ml.

General procedures for operation of the ultracentrifuge are adequately described elsewhere,<sup>8,9</sup> so that only a few details unique to the present experiments need be given. The sustained maximum centrifugal field dictated use of a titanium analytical rotor (An-H) and cells with aluminum centerpieces. Double-sector centerpieces and 2° negative wedge windows to displace the pattern from one cell allowed two samples, each with a solvent baseline, to be run simultaneously. It was found necessary to move the light source back to avoid loss of light from large positive deflections (as in Figs. 4c and 4e). To avoid cell leakage, new polyethylene centerpiece gaskets were used for each run, and the assembled cells were brought to temperature equilibrium at or above run temperature (35°C) before final tightening. Parts of cells used for density gradient experiments must not be interchanged unless replacement is necessary and should be checked occasionally for distortion (tolerance  $\pm 0.005$  cm.).

Photographs were taken at infrequent intervals during a run to check for cell

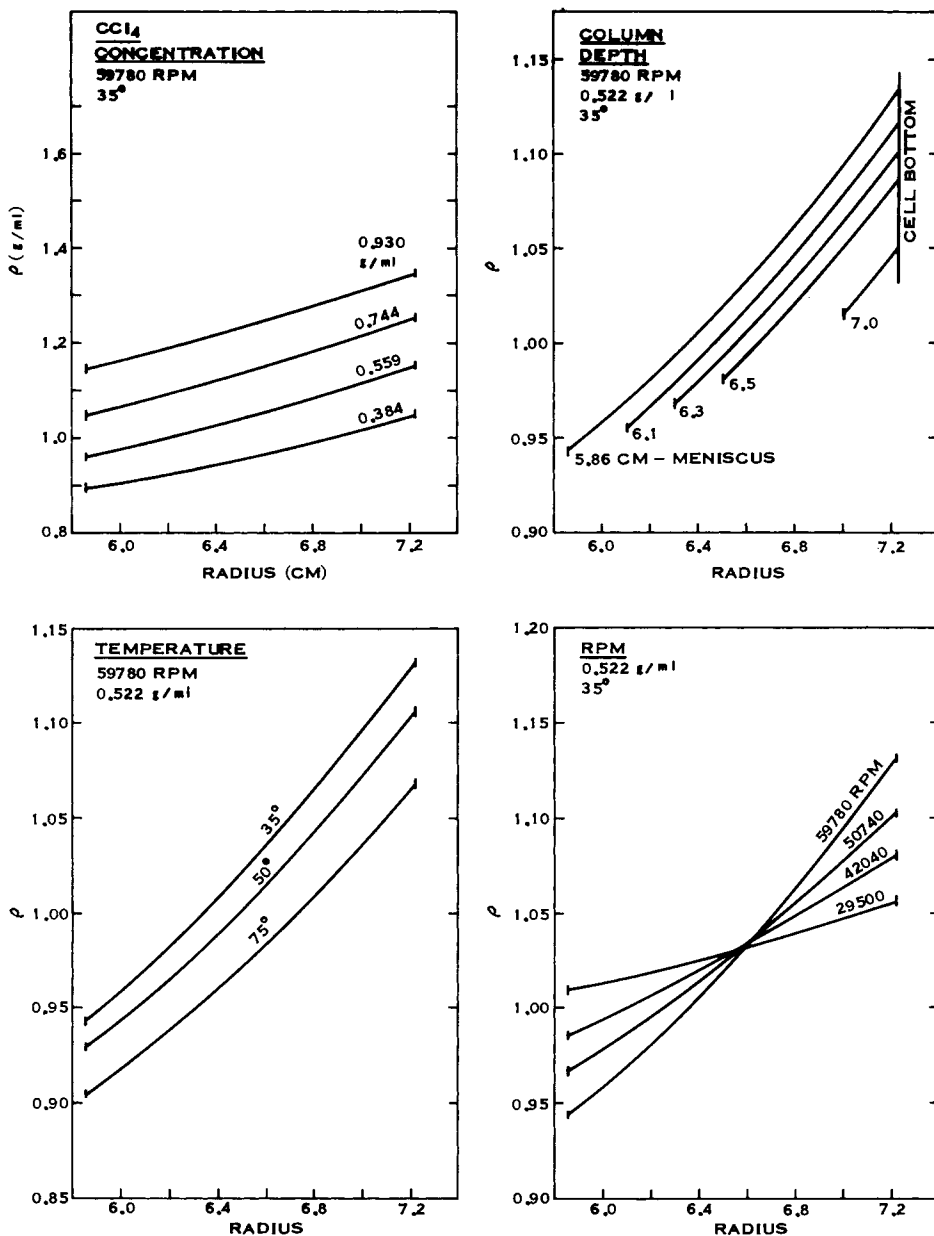


Fig. 1. Calculated density gradients.

leakage and to confirm equilibrium. Higher molecular weight polymers reached equilibrium within 20 hr; lower molecular weights required as much as 60 hr. The final pattern was enlarged a known amount, and the absolute position of the meniscus, cell bottom, and crossover point for each peak were read using the known total magnification factor and reference image position. Density gradient and compositions were calculated by computer, based on methods described below. When a more complete analysis of the curve was desired, vertical de-

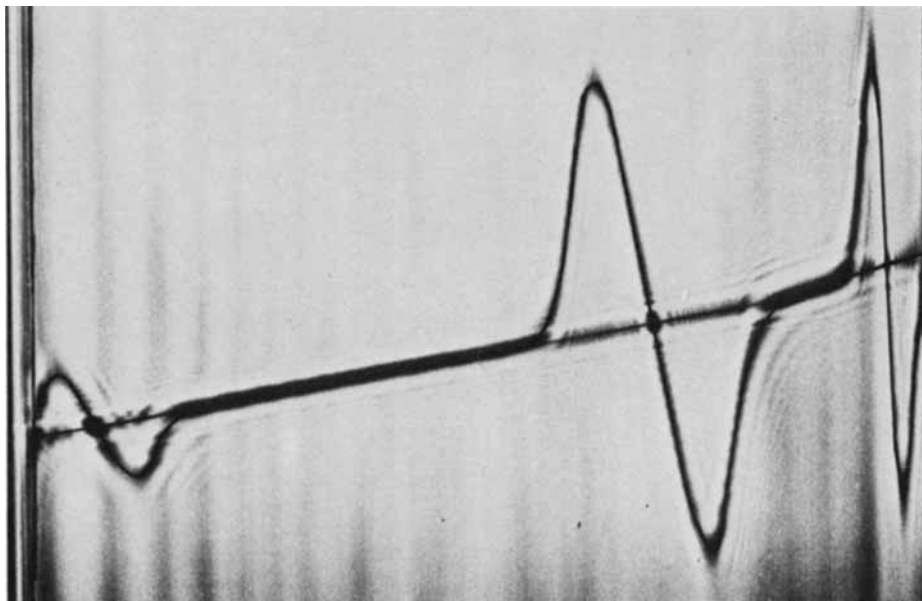


Fig. 2. Schlieren pattern for mixture of polybutadiene, polystyrene, and B/S random copolymer (66% styrene) in 0.522 g/ml  $\text{CCl}_4$  solution.

flections at equal radius values from the meniscus to the cell bottom were read and used as additional input.

Specific refractive increments were measured using a Brice-Phoenix differential refractometer. Bulk density of copolymers was obtained by suspending polymer pellets in preformed, calibrated density gradient columns.

## CALIBRATIONS

### Composition Calibration

Calibration for composition as a function of equilibrium position consisted of the following steps: (1) calculation of solvent densities as function of position in the cell, (2) determination of effective density of homopolymer and copolymer standards by their position, and (3) correlation of density values with copolymer composition.

Density and density gradient may be calculated starting with the relation for sedimentation equilibrium in two-component systems:<sup>10</sup>

$$d\rho/dr = (d\rho/d \ln a)(1 - \bar{v}\rho)M\omega^2r/RT \quad (1)$$

where  $M$ ,  $a$ , and  $\bar{v}$  are the molecular weight, activity, and partial specific volume of the heavy solvent species (carbon tetrachloride), respectively;  $\rho$  is the solution density at radius  $r$ ; and  $\omega$  is the angular velocity (in radians/sec). This system closely follows the linear relation

$$\rho = \rho_0 + (1 - \bar{v}\rho_0)c \quad (2)$$

where  $c$  is the concentration of carbon tetrachloride in g/ml and  $\rho_0$  is the density of the light solvent species (cyclohexane). This expression assumes additivity

of volume on mixing. In fact, any deviation from ideality is small,<sup>11</sup> so that assuming  $c = a$  and combining eqs. (2) and (1) gives, after integration,

$$\ln \frac{(\rho - \rho_0)(1 - \bar{v}\rho_e)}{(\rho_e - \rho_0)(1 - \bar{v}\rho)} = \frac{\omega^2 M(1 - \bar{v}\rho_0)(r^2 - r_e^2)}{2RT} \quad (3)$$

where  $r_e$  is the position in the equilibrium gradient where the density of the solvent mixture is equivalent to the density  $\rho_e$  of the original solution. With a first approximation to  $r_e$  preliminary values of  $\rho(r)$  are calculated from eq. (3) and tested using the conservation condition:<sup>10</sup>

$$\rho_e = 2 \left( \int_{r_a}^{r_b} \rho r dr \right) / (r_b^2 - r_a^2) \quad (4)$$

The value of  $r_e$  is then adjusted and the gradient recalculated by eq. (3) until  $\rho_e$  from eq. (4) matches the known density of the solution. Gradients for different experimental conditions are shown in Figure 1.

The second step is to determine the positions  $r_p$  of standards of known composition in known gradients. With guidance from calculated gradients it was found possible to band polystyrene and polybutadiene standards in a single experiment, with any copolymer at an intermediate level. An enlarged pattern from such a run is shown in Figure 2. From  $r_p$ , the effective buoyant density  $\rho_{\text{eff}}$  for a number of polymers of known composition and structure was obtained. Results are summarized in Table I. A preliminary examination of bulk density data revealed that the specific volume  $\rho^{-1}$  is linear with composition for copolymers, as shown in Figure 3. This confirms volume additivity. A plot of effective specific volume  $\rho_{\text{eff}}^{-1}$  from density gradient experiments was likewise found linear for block copolymers but very slightly curved for random copoly-

TABLE I  
Standardization Runs for Density Gradient Ultracentrifugation

| Sample                                   | % Styrene | CCl <sub>4</sub> ,<br>g/ml | $\rho_{\text{eff}}$ ,<br>g/ml |
|--|-----------|----------------------------|-------------------------------|
| Polybutadiene                            |           |                            |                               |
| B1, 93% cis                              | 0         | 0.392                      | 0.949                         |
| B2, BuLi type                            | 0         | 0.392                      | 0.936                         |
| B3, BuLi type                            | 0         | 0.522                      | 0.930                         |
| Butadiene-Styrene Copolymers             |           |                            |                               |
| C1, Block                                | 25        | 0.392                      | 0.979                         |
| C2, Block                                | 24.4      | 0.522                      | 0.981                         |
| C3, Block                                | 30        | 0.470                      | 0.985                         |
| C4, Random                               | 66        | 0.522                      | 1.082                         |
| C5, Random                               | 25.3      | 0.522                      | 0.971                         |
| Polystyrene Standard 300-12 <sup>a</sup> |           |                            |                               |
|  | 100       | 0.522                      | 1.192                         |
|  |           | 0.554                      | 1.183                         |
|  |           | 0.622                      | 1.170                         |
|  |           | 0.694                      | 1.144                         |
|  |           | 0.694                      | 1.149                         |
|  |           | 0.771                      | 1.126                         |
|  |           | 0.852                      | 1.107                         |
|  |           | 0.941                      | 1.082                         |
| Styrene-Isoprene Block Copolymer         | 15.4      | 0.392                      | 0.969                         |

<sup>a</sup> ARRO Laboratories, Joliet, Illinois.

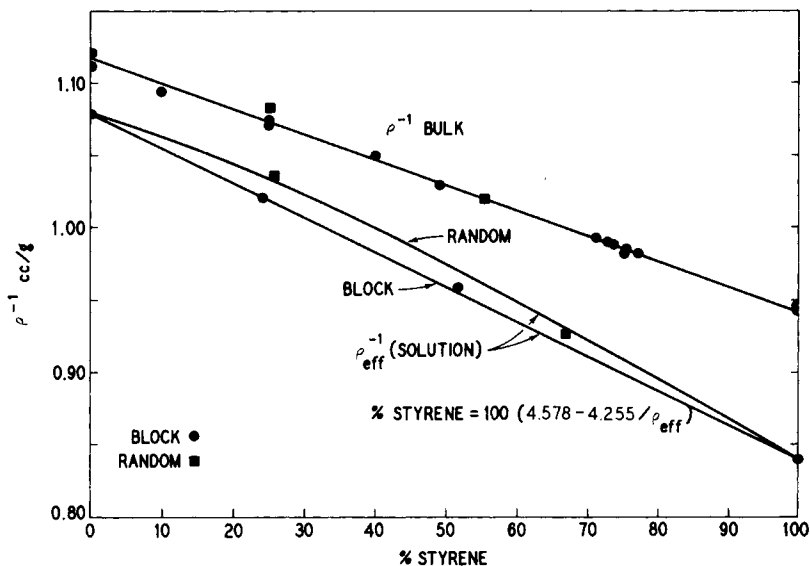


Fig. 3. Composition calibration for 0.522 g/ml  $\text{CCl}_4$  solution.

mers, also shown in Figure 3. However, the effective buoyant density in solution ranges 3–11% higher than the bulk density over the composition range. Further,  $\rho_{\text{eff}}$  is also sensitive to carbon tetrachloride concentration, as shown by the extensive data on polystyrene in Table I. This behavior is usually attributed to solvation of the polymer by the heavier component. Were this the case,  $\rho_{\text{eff}}^{-1}$  would be expected to extrapolate to the partial specific volume of polystyrene at 100% carbon tetrachloride ( $c = \rho = 1.5665$  g/ml), since at this point the density difference between the solvent in the interior of the molecular domain and the bulk of the solvent disappears. However, it does not; instead, a plot of  $\rho_{\text{eff}}^{-1}$  versus depth of the band in the cell forms a good linear extrapolation to the partial specific volume of polystyrene at the meniscus position. This suggests that the difference is a pressure effect, at least for polystyrene.

Pressure is not accounted for in the above calculation. Taking it into account might provide a basis for eliminating the effect of solvent composition, yielding a calibration essentially in terms of real specific volume of polymer. However, to set this up would require more determinations of  $\rho_{\text{eff}}$  of polybutadiene and copolymers at different carbon tetrachloride concentrations. This is not necessary for determination of composition of unknowns in a given gradient, such as shown in Figure 3.

### Concentration Calculation

Composition analysis with the above calibration uses only the band peak position (crossover point in the schlieren pattern). Much more information is available in the complete curve. Band asymmetry, or skewness, indicates unresolved components differing in density. This may be obvious by inspection, but if small, conversion to a concentration distribution is helpful. Further, conversion to concentration distribution and integration of resolved, symmetrical peaks directly yield the amount of each component in a mixture.

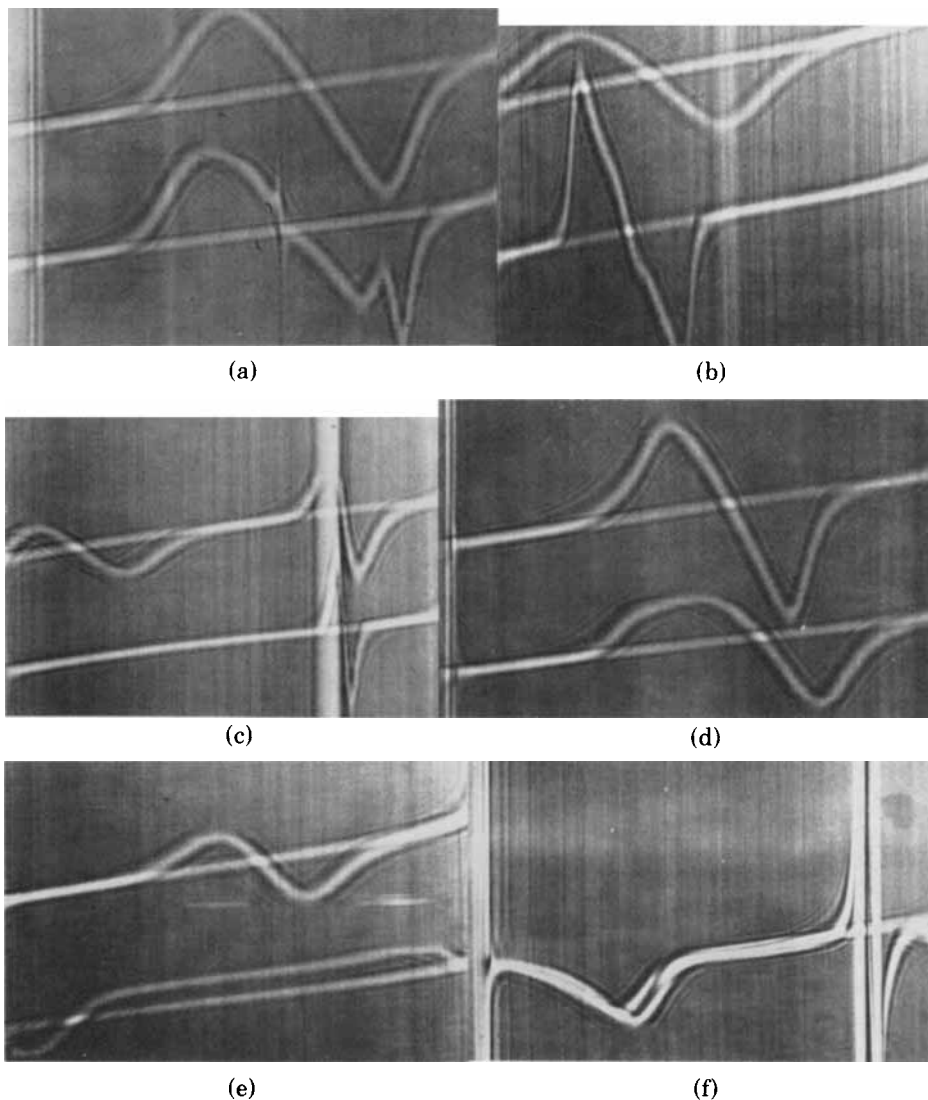


Fig. 4. Schlieren patterns for DGU runs: (A) B/S random copolymers, nominally 15% styrene. (B) Fractions from emulsion copolymer SBR 1805; upper, low molecular weight; lower, high molecular weight. (C) Upper, Kraton 3102; lower, polystyrene standard 300-12. (D) B/S random copolymers. (E) Upper, Kraton 3102; lower, graft copolymer. (F) Precursor and different graft copolymer in single sector cell. Carbon tetrachloride concentration 0.392 g/ml for runs (A) and (D); 0.522 g/ml for (B), (E), and (F); 0.622 g/ml for (C).

Conversion to concentration gradient requires knowledge of the specific refractive increment,  $dn/dc$ , as

$$\frac{dc}{dr} = \frac{dn/dr}{dn/dc} \quad (5)$$

The problem in this experiment is that the refractive increment, and hence the sensitivity, depend upon position in the cell. This arises from the variation in

composition (refractive index) of both solvent and polymer across the cell. Solvent composition changes continuously with depth, but polymer composition is constant across each homogeneous, resolved band at the level corresponding to the peak. The required information is thus  $dn/dc$  as function of carbon tetrachloride concentration and styrene content in the copolymer, both of which are directly available from the above gradient calculations.

Specific refractive increments of polystyrene and polybutadiene were measured in carbon tetrachloride-cyclohexane solutions and found to be linear functions of the weight fraction of carbon tetrachloride,  $w_2$ :

$$(dn/dc)_S = 0.1706 - 0.0215w_2 \quad (6)$$

$$(dn/dc)_B = 0.1140 - 0.0241w_2 \quad (7)$$

Similarly, refractive increments of copolymers are known to be additive by weight of components,

$$(dn/dc)_{SB} = w_S(dn/dc)_S + (1 - w_S)(dn/dc)_B \quad (8)$$

where  $w_S$  is the weight fraction of styrene, so that numerically

$$(dn/dc)_{SB} = 0.114 + 0.0566w_S + 0.0026w_Sw_2 - 0.0241w_2. \quad (9)$$

The effect across a typical broad band ( $w_2$  increasing,  $w_S$  constant) is a decrease in  $dn/dc$  of about 5%, but the difference between bands of a low-styrene copolymer and polystyrene ( $w_2$  increasing,  $w_S$  different) may be over 25%. The correction, thus, has little effect on the shape of a single band, but is of significant magnitude when the relative amounts of different components are desired.

## APPLICATIONS

DGU as described above is applicable to a wide variety of copolymer problems; some examples are given in Figure 4. Run (A) compares two butadiene-styrene random copolymers, nominally of 15% styrene content. From calibration in the gradient formed by 0.392 g/ml  $CCl_4$ , peak compositions were found to be 17.4% and 14.9% styrene. Additionally, the upper pattern indicates a relatively homogeneous sample, while the lower pattern by the sharp spike shows microgel near the composition of the peak. A small amount of higher molecular weight, higher styrene component is also present.

Run (B) compares low and high molecular weight fractions from a commercial sample of SBR 1805. This very large difference in bandwidth reflects the large difference in molecular weight from the broad distribution in the whole sample. The high fraction (lower pattern) is several percent lower in styrene than the low fraction (upper pattern) and contains a discrete higher molecular weight component of the same composition.

Run (C) compares a commercial block copolymer, Shell Kraton 3202 (upper pattern), with polystyrene (lower pattern) in 0.622 g/ml  $CCl_4$ . This product contains a significant fraction of material with effective density exactly matching that of polystyrene; it is clearly a blend of the copolymer with styrene homopolymer. Because of similar hydrodynamic volume distributions, polystyrene was not detected by GPC. The upper pattern in run (E) shows the same polymer in the density gradient formed by 0.522 g/ml  $CCl_4$ . The copolymer component



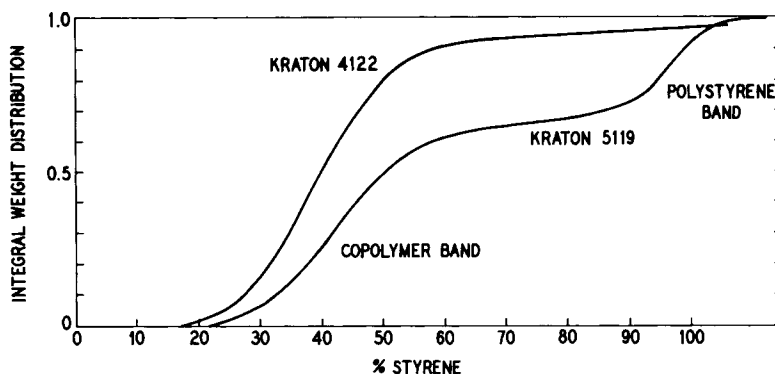


Fig. 5. Integral composition distributions for Kratons 4112 and 5119.

is banded much lower in the cell, and the polystyrene on the bottom of the cell is not observed, emphasizing that all components of interest must be in the range of the gradient.

Much more subtle heterogeneity is shown for the two random copolymers in run (D); the upper pattern is nearly symmetrical, but the lower pattern is somewhat skewed to the low end, indicating presence of copolymer with less styrene content than the bulk of the material. This difference has also been detected by TLC.<sup>12</sup>

Runs (E) and (F) illustrate an application to some experimental graft copolymers. Run (E) lower pattern shows the polybutadiene backbone polymer near the meniscus and styrene-containing species over the complete range of composition. Run (F), a direct comparison between polybutadiene backbone and another graft copolymer (in two single-sector cells), illustrates an entirely different grafting pattern: the product is 82% polystyrene and of extremely high molecular weight.

Figure 5 shows integral composition distributions calculated from DGU runs on two block copolymers, Kratons 4122 and 5119. The latter is found to be 35% styrene homopolymer; the copolymer components of these products are of similar composition. Such complete calculations are justified only when all bands are completely within the range of the gradient and reasonably well resolved.

The author is indebted to J. D. Wood and J. R. Donaldson for assistance with the experiments and to Gerard Kraus for helpful discussions.

## References

1. J. R. Runyon, D. E. Barnes, J. F. Rudd, and L. H. Tung, *J. Appl. Polym. Sci.*, **13**, 2359 (1969).
2. F. M. Mirabella, Jr., E. M. Barrall, II, and J. F. Johnson, *J. Appl. Polym. Sci.*, **19**, 2131 (1975).
3. T. Kotaka and James L. White, *Macromolecules*, **7**, 106 (1974).
4. J. J. Hermans and H. A. Ende, in *Newer Methods of Polymer Characterization*, B. Ke, Ed., Interscience, New York, 1964, p. 525.
5. M. Meselson, F. W. Stahl, and J. Vinograd, *Proc. Nat. Acad. Sci.* **43**, 581 (1957).
6. H. A. Ende and V. Stannett, *J. Polym. Sci. A*, **2**, 2047 (1964).
7. J. Prudhomme and S. Bywater, *ACS Polymer Prepr.*, **10** (2), 518 (1969).

8. A. J. Fryar and S. Kaufman, *J. Coll. Interfac. Sci.*, **36**, 369 (1971).
9. C. H. Chervenka, *A Manual of Methods for the Analytical Ultracentrifuge*, Spinco Division of Beckman Instruments, Inc., Stanford Industrial Park, Palo Alto, California.
10. J. B. Ifft, D. H. Voet, and J. Vinograd, *J. Phys. Chem.*, **65**, 1138 (1961).
11. G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Amer. Chem. Soc.*, **61**, 3206 (1939).
12. James L. White, private communication to Gerard Kraus.

Received May 14, 1976

Revised July 16, 1976