

The Determination of Copolymer Composition as a Function of Molecular Weight by Preparative Gel Permeation Chromatography and Comparison to the Rapid Stop-and-Go GPC/IR Method

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Synopsis

The determination of the copolymer composition as a function of molecular weight by preparative gel permeation chromatography (GPC) for a poly(styrene-co-vinyl stearate) sample is described. These results were compared to data obtained on the same copolymer by the previously described rapid stop-and-go GPC/IR method of analysis of copolymer composition as a function of molecular weight and found to be in good agreement.

INTRODUCTION

In two previous papers,^{1,2} the relationship of copolymer composition to molecular weight was investigated by a rapid technique combining gel permeation chromatography and infrared detection. In order to check this technique by another method, the copolymer composition as a function of molecular weight of one of the samples previously investigated was determined by collecting large fractions from a preparatory gel permeation chromatograph (GPC). The copolymer composition and average molecular weight of each fraction were determined, giving the copolymer composition as a function of molecular weight. These data were then compared to those generated previously for this copolymer by the rapid stop-and-go GPC/IR technique.

EXPERIMENTAL

A GPC was constructed with a high-capacity Milton-Roy (St. Petersburg, Fla.) pump (No. D-19-60029-002-GG) with a six-port injection valve, 50.0-cc

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TABLE I
Copolymer Composition Versus Molecular Weight Data for Sample 422-103-5 of
Poly(styrene-co-Vinyl Stearate)

Fraction no.	Average "working" molecular weight (M_C)	Log average "working" MW ($\log M_C$)	Weight per cent styrene in copolymer ^a
1	1.43 (10^6)	6.16	89.20
2	5.61 (10^5)	5.75	91.30
3	3.01 (10^5)	5.48	92.60
4	1.88 (10^5)	5.27	95.90
5	1.30 (10^5)	5.11	90.90
6	1.01 (10^5)	5.00	91.80
7	7.64 (10^4)	4.88	92.10
8	5.91 (10^4)	4.77	90.90
9	4.11 (10^4)	4.61	93.30
10	3.28 (10^4)	4.52	90.20
11	2.49 (10^4)	4.40	87.30
12	2.01 (10^4)	4.30	87.80
13	9.72 (10^3)	3.99	88.70
14	6.61 (10^3)	3.82	75.80
15	3.65 (10^3)	3.56	62.40
16	2.00 (10^3)	3.30	45.00
17	7.47 (10^2)	2.87	31.10
18	2.79 (10^2)	2.44	27.00
19	1.08 (10^2)	2.03	25.50
20	4.79 (10^1)	1.68	17.70

^aWeight per cent vinyl stearate in copolymer is the difference totalling 100% w/w.

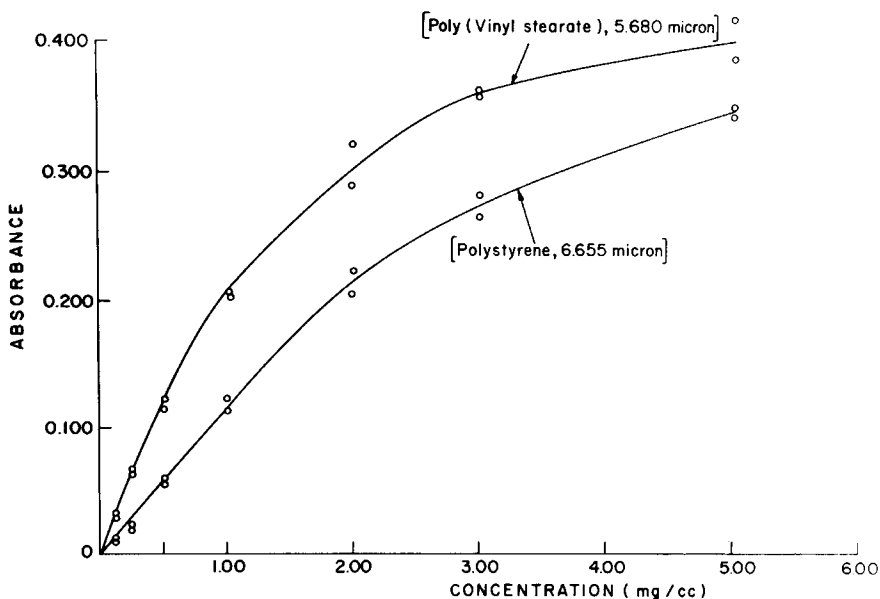


Fig. 1. Calibration curves for the determination of vinyl stearate and styrene in poly(styrene-co-vinyl stearate) copolymer. Upper curve was used to obtain poly(vinyl stearate) concentrations while lower curve was used to obtain polystyrene concentrations.

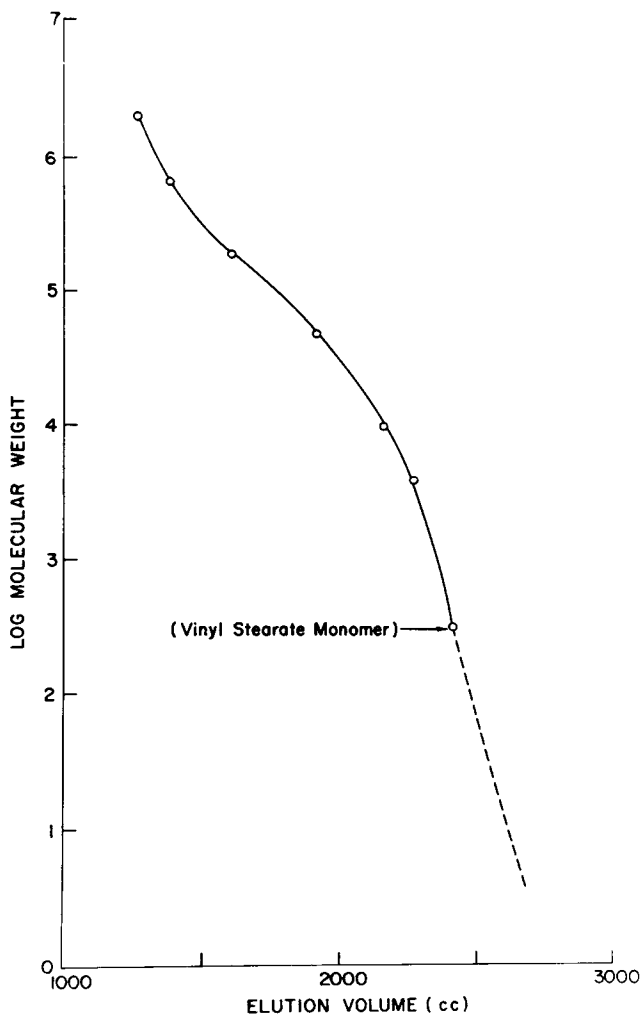


Fig. 2. Calibration curve for GPC system using polystyrene narrow NWD standards (Pressure Chemical Co.) and vinyl stearate monomer. See text for explanation of extrapolation.

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 (Bio-Rad Labs., Richmond, Cal.) deactivated porous glass beads. A 15.0 mg/cc solution of poly(styrene-co-vinyl stearate), sample 422-103-5, which was previously described² (supplied by Edmund F. Jordan, Jr., U.S. Agriculture Dept., Philadelphia, Pa.) was prepared in tetrachloroethylene (Fisher Scientific, Co., technical grade) by heating at 110°C for 10 min. A 50.0-cc portion of this solution was injected at room temperature on the aforementioned GPC system with tetrachloroethylene as the eluent solvent. The pump rate was 295 cc/hr.

A Perkin-Elmer (Norwalk, Conn.) 21 infrared spectrometer was used for detection of the eluent stream. A 3-mm-pathlength flow-through cell with a 3-mm-pathlength tetrachloroethylene reference was used, with the spectrometer set at 3.413 microns (2930 cm^{-1}) in order to detect the copolymer as it

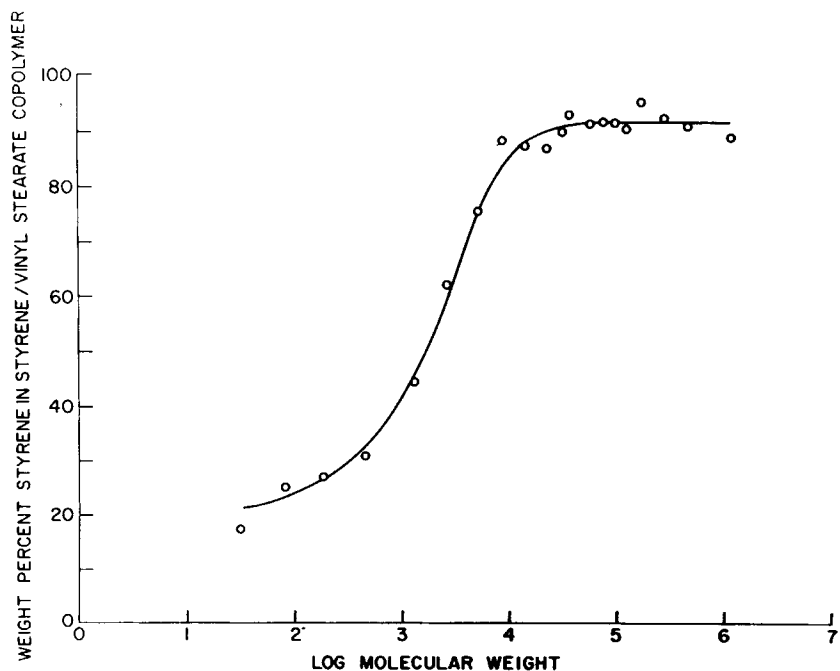


Fig. 3. Weight per cent styrene in sample 422-103-5 of poly(styrene-co-vinyl stearate) vs. log average "working" molecular weight of the fractions M_C .

eluted from the chromatograph, as previously described.² Twenty fractions were collected over the elution range of the copolymer.

The copolymer composition of each fraction was determined, as previously described,² using the standard calibration curve shown in Figure 1. The upper curve is the absorbance versus concentration of vinyl stearate, determined from the carbonyl absorbance at 5.680 microns (1760 cm^{-1}), and the lower curve is the absorbance versus concentration of styrene, determined from an aromatic ring vibration absorbance at 6.655 microns (1503 cm^{-1}). The weight per cent of styrene in the copolymer was determined by direct calibration using the peak at 6.655 microns (1503 cm^{-1}) and the lower calibration curve in Figure 1. Similarly, the weight per cent of vinyl stearate was determined using the peak at 5.680 microns (1760 cm^{-1}) and the upper calibration curve in Figure 1.

The average molecular weight of each fraction was determined from the average elution volume of the fraction. The elution volumes were converted to "working" molecular weights, as in the previous paper,¹ by using a polystyrene and vinyl stearate calibration curve (Fig. 2) and converting the molecular weights obtained therefrom to "working" molecular weights using the formula

$$M_C = \frac{M_A}{M_U} M_S$$

where M_C = "working" molecular weight of poly(styrene-co-vinyl stearate); M_A = molecular weight of an average unit of the above copolymer as deter-

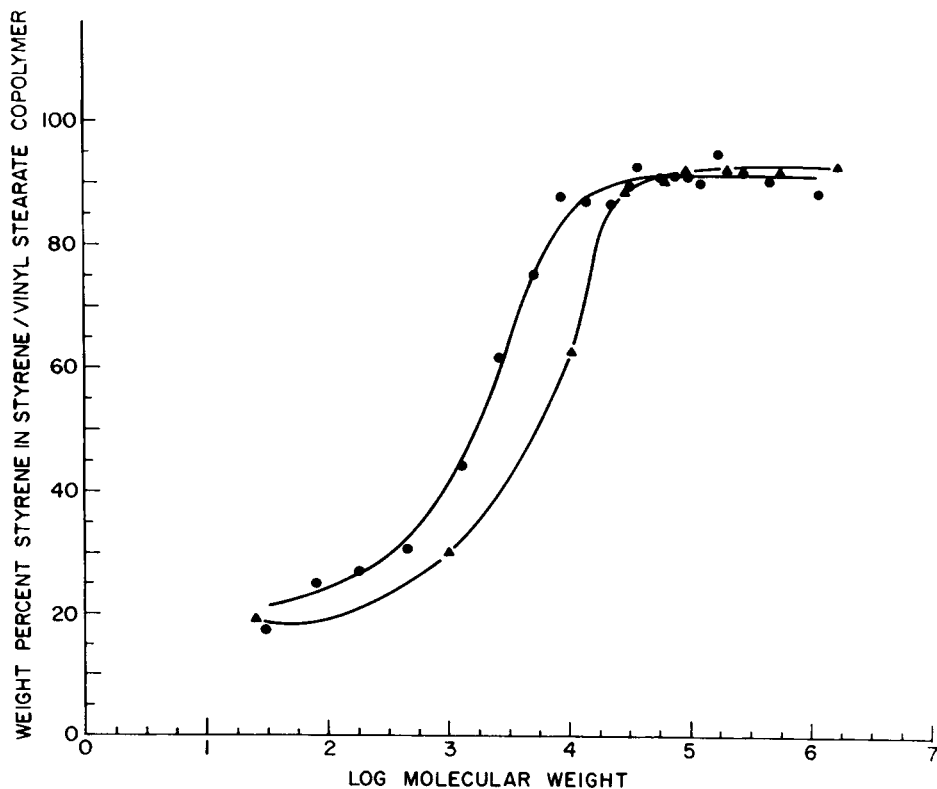


Fig. 4. (●) Weight per cent styrene in sample 422-103-5 of poly(styrene-co-vinyl stearate) versus log "working" molecular weight. Data from Fig. 3. (▲) Weight per cent styrene in sample 422-103-5 of poly(styrene-co-vinyl stearate) vs. log "working" molecular weight. Data from ref. 2.

mined by copolymer composition data for the elution volume in question; M_U = molecular weight of a styrene unit (104.15); and M_S = molecular weight from polystyrene and vinyl stearate calibration curve (Fig. 2).

Vinyl stearate was chosen as the lowest molecular weight standard since it was expected that its elution volume would be representative of the lowest molecular weight species in the copolymer. The extrapolation of the curve in Figure 2 was used to obtain molecular weights for elution volumes outside the range of the standards used.

RESULTS AND DISCUSSION

The fractions with their respective copolymer compositions and average "working" molecular weights are tabulated in Table I. These data are plotted in Figure 3 as weight per cent styrene in the copolymer versus log average "working" molecular weight. Figure 4 shows these data plotted on the same graph with the corresponding data for this copolymer sample as determined by the rapid stop-and-go GPC/IR technique in the previous paper.²

The essential features of the two curves are in agreement, but they are shifted apart along the log molecular weight axis. This was due to the differ-

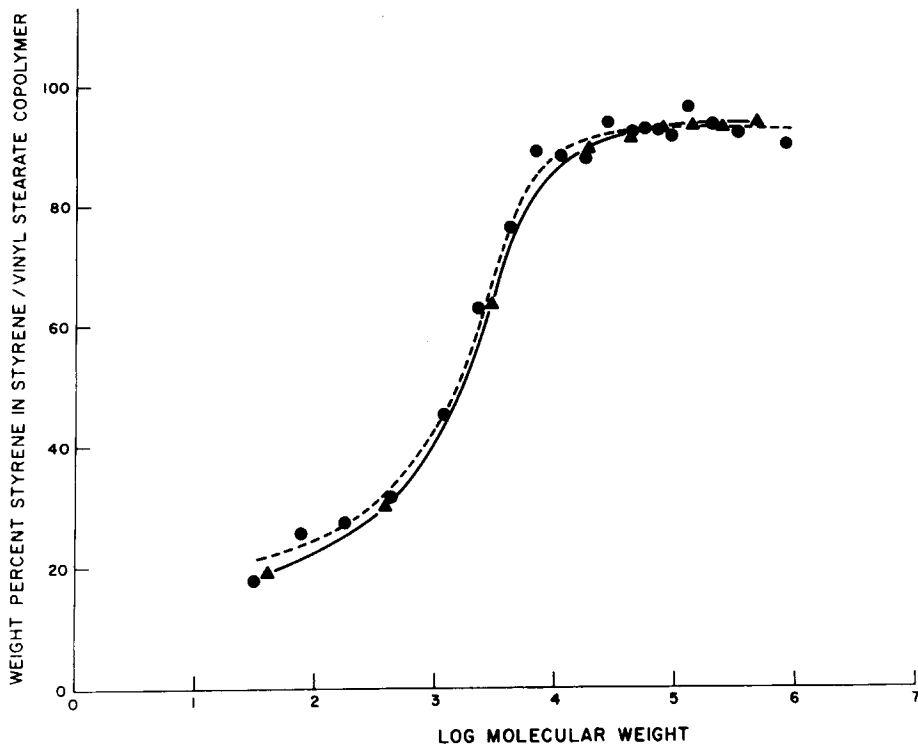


Fig. 5. (---●---) Weight per cent styrene in sample 422-103-5 of poly(styrene-co-vinyl stearate) vs. log "working" molecular weight. Data from Fig. 3. (—▲—) Weight per cent styrene in sample 422-103-5 of poly(styrene-co-vinyl stearate) vs. log "working" molecular weight. Data recalculated from ref. 2 using a new molecular weight calibration curve for the rapid stop-and-go GPC/IR system.

ent loading conditions at which the two GPC systems were calibrated. Thus the GPC system used in the rapid stop-and-go GPC/IR technique was recalibrated at the same loading conditions as used in the present paper. This resulted in a shifting of the calibration curve used for the stop-and-go GPC system toward lower elution volume. The points in Figure 4 were then recalculated for the rapid stop-and-go method using this new calibration curve. This resulted in a shifting of this curve toward higher molecular weight. The two curves, which were now determined at the same loading conditions, are shown in Figure 5.

The two curves are now in good agreement, indicating that the rapid stop-and-go GPC/IR method of analysis is acceptedly accurate when compared to the preparative fractionation method.

The preparative fractionation method required 20 hr, while the rapid stop-and-go GPC/IR method required 2½ hr per copolymer sample. It is hoped that this rapid technique will be useful in generating the data needed to more fully elucidate the relationship between copolymer composition and molecular weight.

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