

A Rapid Technique For Measuring Copolymer Composition as a Function of Molecular Weight Using Gel Permeation Chromatography and Infrared Detection

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Synopsis

A gel permeation chromatograph using an infrared spectrometer detector is described. Operation in a stop-and-go fashion permits rapid determination of copolymer composition as a function of molecular weight. A broad distribution copolymer, poly(vinyl chloride-co-vinyl stearate), showed marked compositional changes with molecular weight. The changes observed are not in agreement with those predicted from reactivity ratios.

INTRODUCTION

The variation of copolymer composition as a function of molecular weight has received relatively little attention. Studies investigating the relationship between these variables are included in a current review.¹ Various techniques have been employed to study this relationship including fraction collection followed by copolymer composition analysis (e.g., by NMR, IR, or elemental analysis),²⁻⁹ sedimentation,¹⁰ thin-layer chromatography,¹¹ and light scattering.¹²⁻¹⁴ Studies which involve fraction collection followed by analysis of copolymer composition are tedious; and since each fraction is not monodisperse, the copolymer composition data are an average over the MWD and composition distribution of each fraction. Only the tedious task of collecting a large number of narrow-MWD fractions can improve this situation. The light-scattering technique seemed to offer a promising alternative since no fractions need to be taken. However, a recent review¹⁴ of the technique concluded that it was disappointingly insensitive and of limited applicability.

This paper describes a rapid technique to measure copolymer composition as a function of molecular weight. The method employs gel permeation chromatography (GPC) to fractionate the copolymer according to molecular size, followed by IR analysis of the effluent to determine copolymer composition.

EXPERIMENTAL

A simple gel permeation chromatograph was constructed with a 4.00-cc injection loop connected to five 1-m columns packed with Bioglas glass beads.

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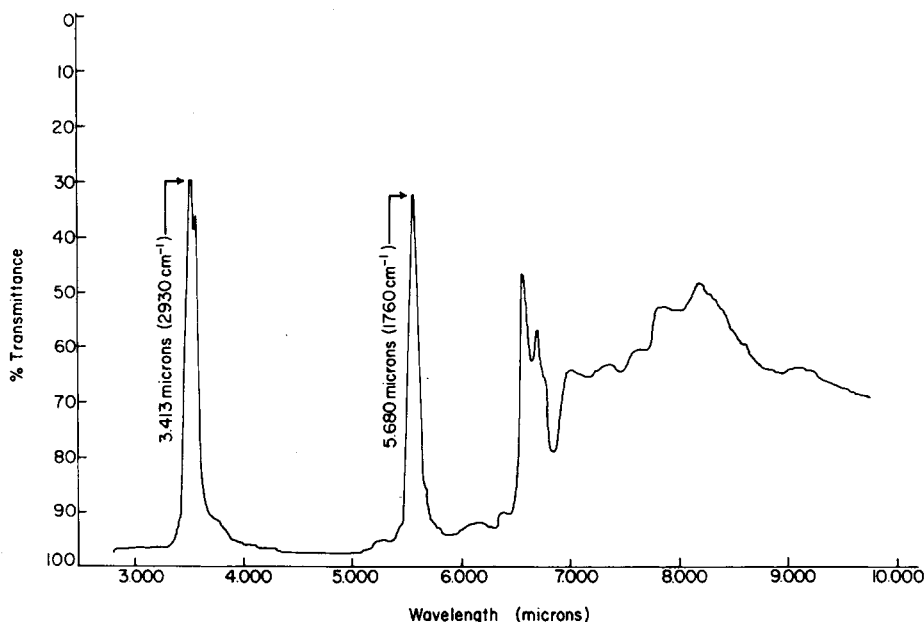


Fig. 1. IR spectrum of a solution of 4 mg/cc poly(vinyl chloride-co-vinyl stearate), 3-mm pathlength vs. 3-mm pathlength tetrachloroethylene reference. The spectrum was recorded on a Varian A-25 recorder at 100 mV scale expansion. Wave numbers of pertinent peaks have been noted.

The column packing used was as follows: column 1, 1250 Å nominal exclusion limit, 200–400 mesh; column 2, 370 Å nominal exclusion limit, 200–400 mesh; column 3, 2000 Å nominal exclusion limit, 200–400 mesh; column 4, 200 Å nominal exclusion limit, 50–100 mesh; column 5, 1000 Å nominal exclusion limit, 50–100 mesh. The syphon volume was 3.1 cc.

A Perkin-Elmer 21 infrared spectrometer (Norwalk, Conn.) was used as a detector with a Perkin-Elmer refracting beam condenser (Cat. No. 127-1271) to reduce the slit image to 1 mm × 4 mm in the plane of the sample cell. The sample cell used was a Wilks (Norwalk, Conn.) NaCl, 3-mm pathlength microflow-through cell with a volume of 50 microliters (Cat. No. 7607). A Wilks variable pathlength cell (Cat. No. 4060), adjustable from 0 to 5 mm, filled with pure solvent was used as reference. Recording was done on a Varian A-25 dual-pen recorder. The recording system on the PE-21 was disconnected. The speed of the Varian A-25 recorder was set at 100 in./hr in order to give roughly the same spectrum display as obtained on the PE-21 recorder. The pen-drive shaft on the PE-21 spectrometer was connected directly to the shaft of a 10-turn, 10-Kohm potentiometer by means of a universal lateral coupling to eliminate backlash and friction due to nonalignment of the shafts. The potentiometer was connected to an amplifier and attached to the Varian A-25 recorder. The maximum amplification of the IR signal attainable was 80 times on a 1-mV scale expansion. Amplification of 1.6 to 8 times was routinely employed.

The copolymer used was poly(vinyl chloride-co-vinyl stearate) (supplied by Edmund F. Jordan, Jr., U.S. Department of Agriculture, Philadelphia, Penn.). This copolymer has been described.¹⁶ Its overall composition was

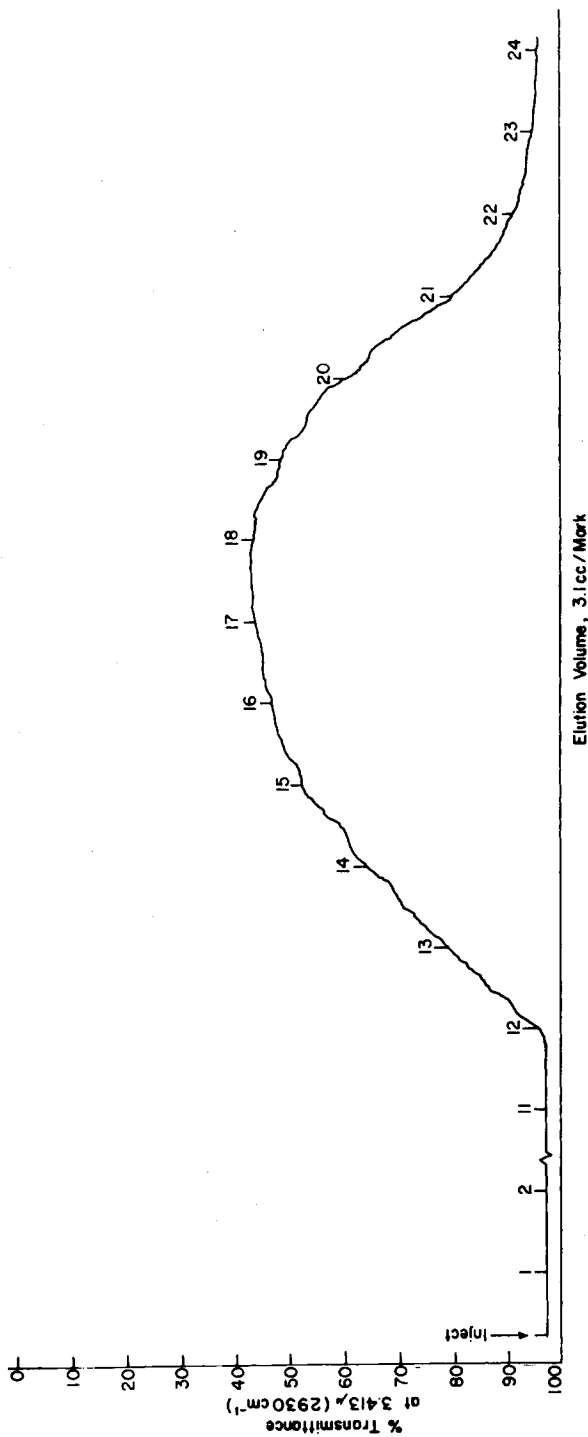


Fig. 2. GPC of poly(vinyl chloride-co-vinyl stearate), 15.00 mg/cc in tetrachloroethylene, 4.00-cc injection on the GPC system described. Recorded at 100 mV expansion.

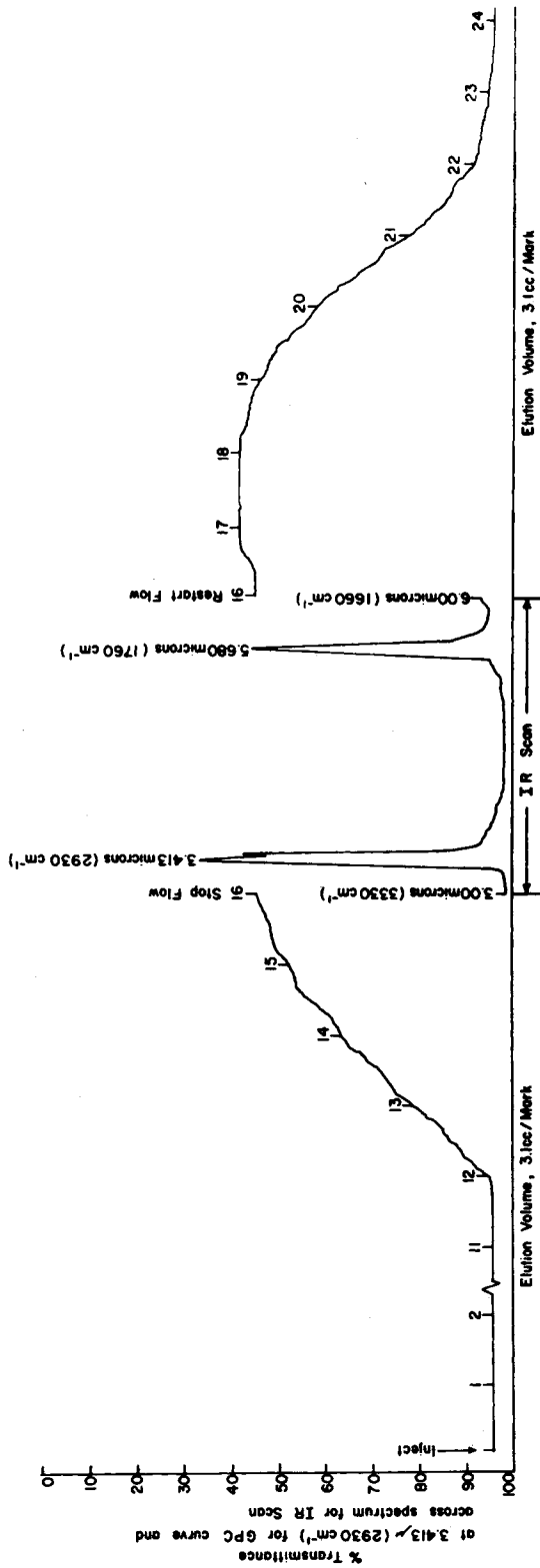


Fig. 3. Stop-flow GPC of poly(vinyl chloride-co-vinyl stearate) as in Fig. 2, but with the IR scan of the 49.6-cc elution volume fraction showing the carbon-hydrogen stretching band at 3.413μ (2930 cm^{-1}) and the carbonyl stretching band at 5.680μ (1760 cm^{-1}). Both GPC and IR scans recorded at 100 mV expansion.

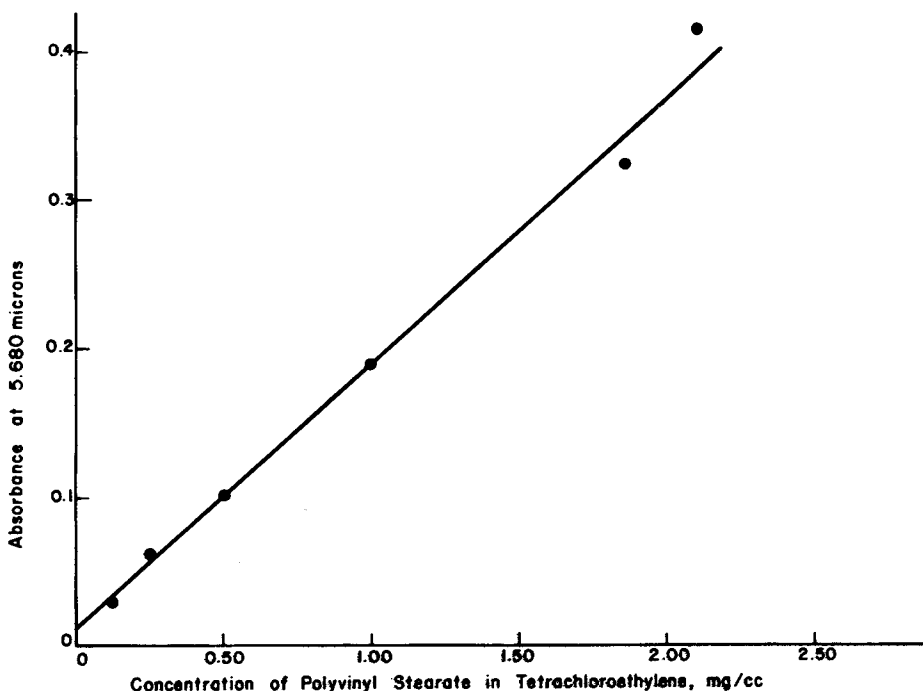


Fig. 4. Infrared absorbance at 5.680 microns (1760 cm^{-1}) vs. concentration of poly(vinyl stearate) measured in tetrachloroethylene solution in a 3-mm-pathlength cell with a 3-mm-pathlength tetrachloroethylene reference. Absorbance units were calculated at 100 mV scale expansion. Line represents a least-squares fit to the experimental points.

73.48 mole-% (35.80% w/w) vinyl chloride and 26.52 mole-% (64.20% w/w) vinyl stearate, based on chloride analysis. The IR spectrum of a 3-mm-pathlength solution of 4 mg/cc poly(vinyl chloride-co-vinyl stearate) in tetrachloroethylene versus 3-mm-pathlength pure tetrachloroethylene reference is shown in Figure 1. This spectrum was run on the modified PE-21 spectrometer and recorded on the Varian A-25 recorder. Wave numbers are noted on pertinent peaks. Solutions in tetrachloroethylene (Fisher Scientific Co., technical grade) were prepared by heating for 5 to 30 min just below the boiling point. Tetrachloroethylene was also used as the GPC solvent. A 15.00 mg/cc solution of the copolymer was prepared in tetrachloroethylene. A 4.00-cc volume of this solution was chromatographed giving a total solute load of 60.00 mg using the apparatus previously described at a flow rate of 0.8 cc/min at room temperature. The gel permeation chromatogram was recorded by monitoring the carbon-hydrogen absorption at 3.413 microns (2930 cm^{-1}). At each syphon dump event, the flow was stopped by closing a valve and the copolymer composition determined by scanning the IR spectrum on the 50-microliter volume of solution in the flow-through cell. This small volume represents an essentially monodisperse fraction of the copolymer. Cooper et al.¹⁵ have shown that stopping the flow for extended periods produced no loss in resolution of the molecular size separation. Thus, the stoppage of flow many times over the elution range was expected to have no effect on resolution. Five replicate runs were made in which composition of the copolymer was determined.

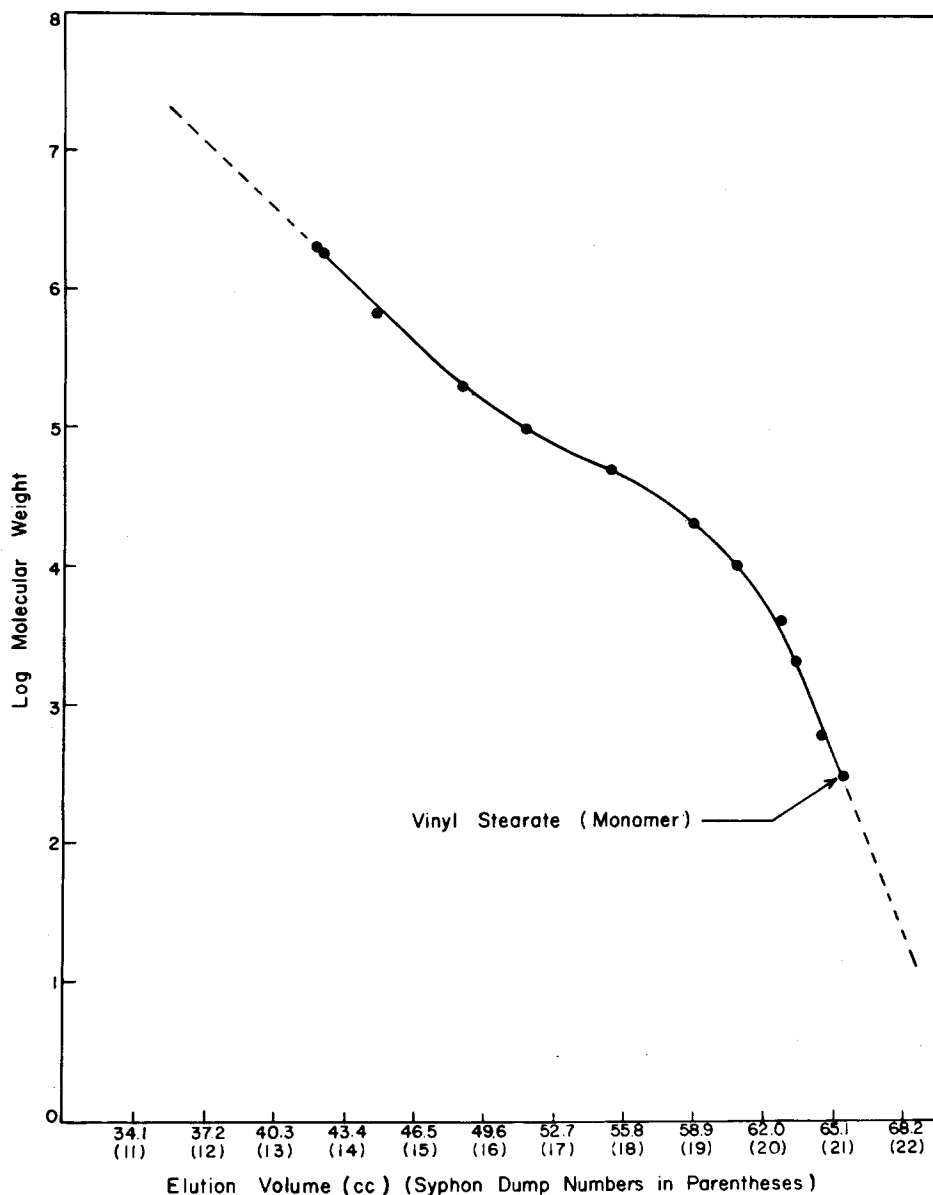


Fig. 5. Calibration curve for GPC system using polystyrene narrow-MWD standards (Pressure Chemical Co.) and vinyl stearate monomer. See text for explanation of extrapolations.

A typical gel permeation chromatogram of the copolymer is shown in Figure 2. A typical stop-flow chromatogram with an IR scan of the $3.0\text{-}\mu$ (3330 cm^{-1}) to $6.0\text{-}\mu$ (1660 cm^{-1}) region of the 49.6-cc elution volume fraction is shown in Figure 3. One run takes about 2.5 hr, of which time 1.5 hr is consumed by the elution of the copolymer. Thus, about 1 hr is consumed in scanning IR spectra. Total copolymer concentration was determined by measuring the total area under the chromatogram and then measuring the area under narrow bands centered at each syphon dump event. The fraction

of the total area under these narrow bands times 60 mg (total solute weight) was taken as the weight of sample over the elution range covered by the band. This weight of sample divided by the volume of solvent eluted over this elution range was taken as the concentration of the solution in the IR cell at that syphon dump event.

It should be noted that the deconvoluting of the chromatogram previously described for the determination of total copolymer composition is in error by the difference in the absorptivity of the vinyl chloride units relative to the vinyl stearate units at 3.413 microns (2930 cm^{-1}). Any differences in absorption at this wavelength as a function of compositional changes would yield erroneous concentration data. However, the ideal case where a separate IR band could be monitored for each comonomer concentration was not possible with poly(vinyl chloride-co-vinyl stearate) in tetrachloroethylene. Thus, the deconvoluting method was used. The results indicate that this method was not seriously in error.

The vinyl stearate concentration was determined by measuring the carbonyl absorbance at 5.680 microns (1760 cm^{-1}) and then obtaining the concentration graphically from an experimentally established plot (see Fig. 4) of carbonyl absorption versus concentration for vinyl stearate homopolymer. The difference between the total copolymer concentration and vinyl stearate concentration was taken as the vinyl chloride concentration. The elution volumes were converted to "working" molecular weights of the copolymer by calibration with polystyrene narrow-MWD standards (Pressure Chemical Co.) and vinyl stearate. The lowest molecular weight standard was vinyl stearate which was chosen since its hydrodynamic volume was assumed to be representative of the lowest molecular weight species observed in the poly(vinyl chloride-co-vinyl stearate).

The standards were made up at a concentration of 15 mg/cc in tetrachloroethylene and chromatographed exactly as described for the copolymer samples. The calibration curve obtained is shown in Figure 5. Molecular weights at each elution volume were interpolated from the curve except at 37.2 cc, 40.3 cc, 65.1 cc, and 68.2 cc, which were obtained by extrapolation. The values obtained from the polystyrene and vinyl stearate calibration were converted to "working" molecular weights for the copolymer by using the formula

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

where M_C = "working" MW of poly(vinyl chloride-co-vinyl stearate), M_A = MW of an average diad of the copolymer as determined from composition data, M_U = MW of a styrene unit. (104.15), and M_S = MW from polystyrene and vinyl stearate calibration curve (Figure 5).

These "working" molecular weights would be accurate provided that the hydrodynamic volume of polystyrene was the same as that of a chain of an equal number of units of poly(vinyl chloride-co-vinyl stearate). However, this was not tested, and the rather low molecular weight obtained for the material eluting at 68.2 cc indicates that it probably is not true. Nevertheless, the "working" molecular weights provide a useful rough guide.

RESULTS AND DISCUSSION

The composition data obtained for the poly(vinyl chloride-co-vinyl stearate) are tabulated in terms of syphon dump numbers in Table I. These data are plotted in Figure 6 as weight per cent vinyl stearate versus elution volume

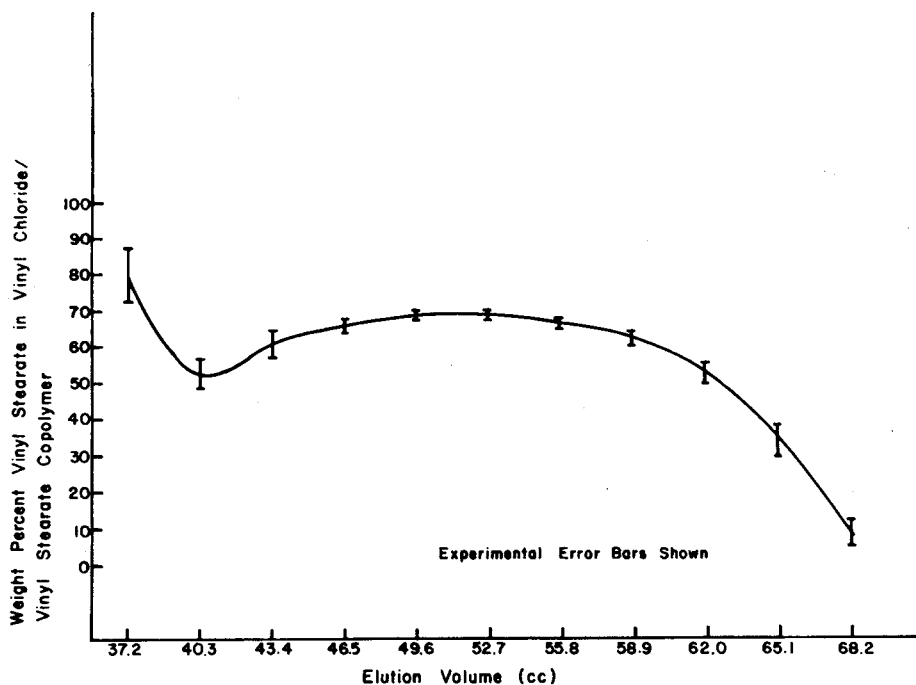


Fig. 6. Weight per cent vinyl stearate in poly(vinyl chloride-co-vinyl stearate) vs. elution volume.

TABLE I

Syphon dump no.	Elution volume, cc	"Working" molecular weight	Mean weight percent of vinyl stearate in poly(vinyl chloride-co-vinyl stearate), %	Standard Deviation for 5 replicate measurements, % w/w
12	37.2	3.16×10^7	79.77	± 7.77
13	40.3	7.36×10^6	52.43	± 4.04
14	43.4	2.66×10^6	61.64	± 3.79
15	46.5	9.16×10^5	64.23	± 2.05
16	49.6	3.34×10^5	68.58	± 1.49
17	52.7	1.62×10^5	68.35	± 1.47
18	55.8	1.01×10^5	65.91	± 1.55
19	58.9	4.36×10^4	60.50	± 2.03
20	62.0	1.04×10^4	52.11	± 2.98
21	65.1	5.72×10^3	34.02	± 4.37
22	68.2	17.32	8.81	± 3.73

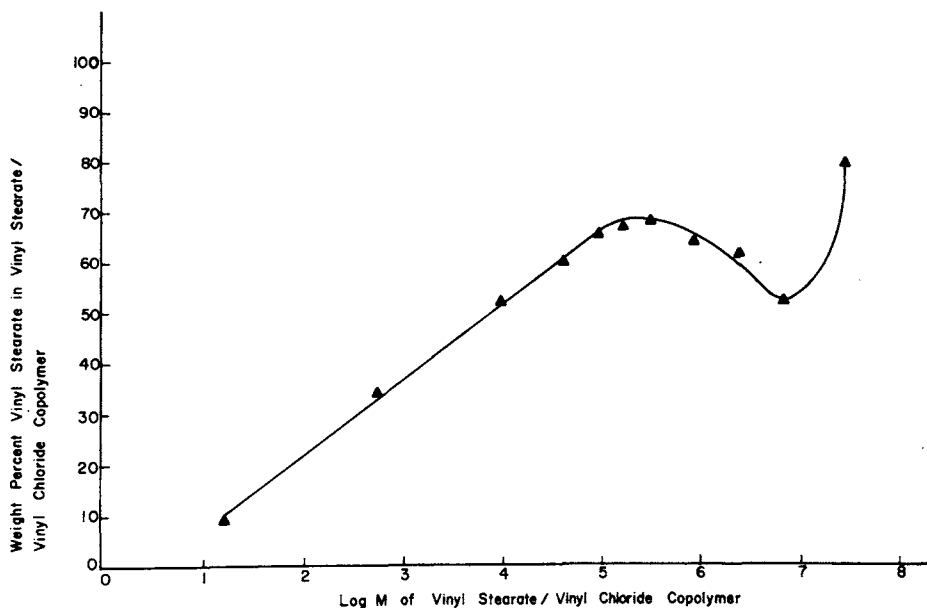


Fig. 7. Mean weight per cent vinyl stearate in poly(vinyl chloride-co-vinyl stearate) vs. log "working" molecular weight.

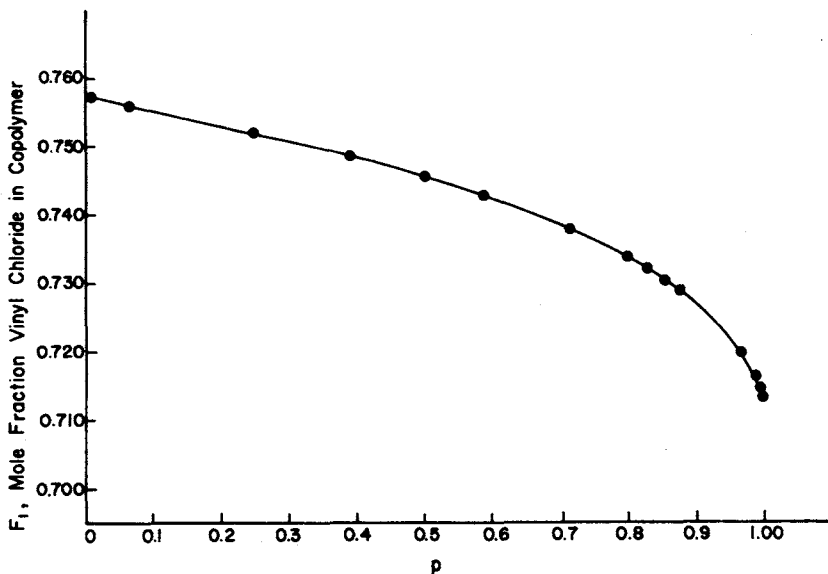


Fig. 8. Mole fraction of vinyl chloride F_1 in poly(vinyl chloride-co-vinyl stearate) vs. conversion p as calculated by the method of Kruse.¹⁹

and in Figure 7 as weight per cent vinyl stearate versus log "working" molecular weight. For this copolymer, an $\bar{M}_n = 57,800$ was reported.¹⁷ The lowest molecular weight obtained at an elution volume of 68.2 cc may be due to impurities separated from the copolymer by the chromatograph. The copolymer composition calculated at this elution volume is probably not significant

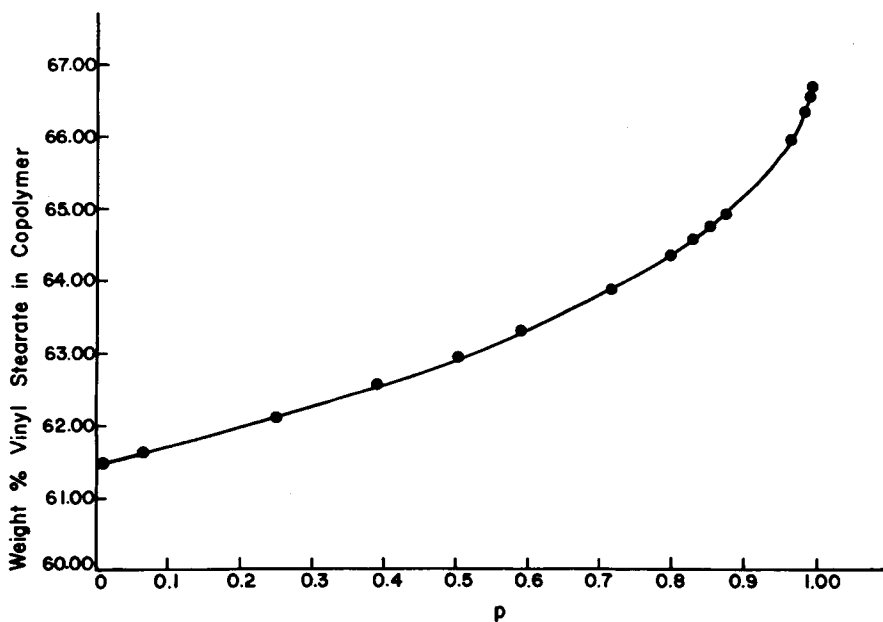


Fig. 9. Weight fraction of vinyl stearate in the copolymer vs. p as calculated by the method of Kruse.¹⁹

since it most likely represents a peak broadening artifact. The composition obtained at the highest molecular weight at an elution volume of 37.2 cc might also be fallacious due to band broadening effects. The data from syphon dump numbers 13 to 21 are undoubtedly more reliable.

The spread in mean composition of vinyl stearate in the copolymers found was 8.81–79.77% w/w. In order to compare this heterogeneity with the theoretically predicted heterogeneity, the method of Skeist¹⁸ as modified by Kruse¹⁹ was employed. The values of the reactivity ratios were calculated using the Alfrey-Price treatment as described in the monograph edited by Ham²⁰ and average Q and e values tabulated in reference 21. The values obtained for the reactivity ratios were $r_1 = 1.12$ and $r_2 = 0.53$, where vinyl chloride is monomer 1 and vinyl stearate is monomer 2. The calculated compositional drift as a function of conversion p is shown in Figure 8, where F_1 , the mole fraction of vinyl chloride in the copolymer, is plotted against conversion p .

In Figure 9, the weight fraction of vinyl stearate is plotted versus p obtained from this same calculation. The value of p obtained for the poly(vinyl chloride-co-vinyl stearate) investigated was 0.7801.¹⁷ The corresponding average weight per cent of vinyl stearate in the whole copolymer from Figure 9 is 64.20% w/w. This is the same value obtained by chloride analysis on the whole copolymer as previously mentioned. The weighted average composition of all eleven fractions (syphon dump numbers 12–22) is 61.09% w/w vinyl stearate. This differs by only 3.11% w/w vinyl stearate from the average value for the whole copolymer, indicating a reasonable accuracy for the IR method employed.

The compositional drift observed was 8.81–79.77% w/w, as compared to the calculated drift of 61.44–64.20% w/w vinyl stearate (from zero up to 78.01%

conversion) in the copolymer. If the two least reliable points on either end of the MWD are discarded, the spread of 34.02–68.58% w/w vinyl stearate is still much larger than theoretically predicted. This large discrepancy indicates that the existing theory apparently does not consider enough of the essential parameters in order to predict a reasonably accurate compositional heterogeneity. Further, the existing theory cannot yield the composition as a function of the molecular weight. Experimental work, as described in this paper, could be useful in providing a basis for improvement of the existing theory.

The experimental data indicate that the weight per cent of vinyl stearate in poly(vinyl chloride-co-vinyl stearate) increases from a low value at low molecular weight of the copolymer, goes through maxima and minima as molecular weight increases, and attains the highest value at the highest molecular weight. In considering the data presented in this paper, it must be remembered that the separation mechanism of GPC is based, primarily, on molecular size and not absolute molecular weight. It is possible that variations in copolymer composition could alter the hydrodynamic volume for equivalent molecular weights. Thus, the size distribution may not precisely correspond to the molecular weight distribution.

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