

# Gel Permeation Chromatography in the Study of the Molecular Weight Distribution Vinyl Chloride–Vinyl Acetate Copolymer. III. Influence of the Incompatibility of Polymers and Some Problems of Interpretation of Experimental Data

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## Synopsis

The influence of incompatibility in the ternary systems gel–polymer–solvent and polymer–polymer–solvent on the results of gel permeation chromatography of the copolymer vinyl chloride–vinyl acetate was investigated. The measurements were performed on styrene–divinylbenzene gels and on porous silica gels. Detection in GPC was made using a differential refractometer together with a UV detector, which permitted evaluation of the extent of interactions of the polymer components in the mixture. Some aspects of the GPC data are discussed for the application of universal calibration, the validity of which for the copolymer vinyl chloride–vinyl acetate has been proved.

## INTRODUCTION

In our earlier papers<sup>1,2</sup> we studied the possibility of application of a universal calibration method<sup>3</sup> in the determination of the molecular weight parameters of vinyl chloride–vinyl acetate (VC–VAc) copolymers by gel permeation chromatography (GPC). We used the GPC method on a preparative scale to fractionate a sample of a commercial VC–VAc copolymer; fractions thus obtained were characterized from the viewpoint of molecular parameters and chemical composition. At the same time, samples fractionated by precipitation were also studied. Data obtained for fractions containing 10%–13% by weight of vinyl acetate were used to calculate the constants of the Mark–Houwink equation valid for tetrahydrofuran (THF) at 25°C. We determined experimentally the increase in the vinyl acetate content with decreasing molecular weight of the individual fractions of VC–VAc copolymers. This dependence can be explained by conditions of the industrial preparation of the VC–VAc copolymer. The validity of universal calibration for samples of the VC–VAc copolymer under investigation has been confirmed, and a very good agreement has been reached between the molecular parameters of unfractionated samples of the VC–VAc copolymer, i.e., those measured directly and those calculated from data for the individual fractions. GPC measurements were performed on columns packed with the porous silica gel Spherosil.<sup>1</sup> In a further work<sup>2</sup> we studied the possible influence of the chemical composition of the VC–VAc copolymer on the GPC results.

We prepared samples of the statistical VC–VAc copolymer with vinyl acetate contents ranging between ca. 5% and 30% by weight and possessing high chemical

homogeneity. The samples were fractionated by preparative GPC, and the fractions thus obtained as well as unfractionated copolymers were studied by the GPC method on an analytical scale using the universal calibration. We found that within the range of chemical composition and molecular weights studied, the chemical composition of the copolymer had no essential influence on the results obtained by GPC.<sup>2</sup>

It should be mentioned, however, that results of an investigation<sup>4</sup> of VC-VAc copolymers by GPC (separation columns packed with the styrene-divinylbenzene gel Styragel) showed considerable disagreement between the universal calibration curves of polystyrene standards and fractions of the VC-VAc copolymer as well as disagreement between the distribution curves of molecular weights measured directly with GPC and those calculated from data for the individual fractions.

For this reason, we reproduce here part of our earlier GPC measurements of the VC-VAc copolymers, using Styragel as packing of the chromatographic columns. We also injected mixtures of polystyrene (PS) samples with VC-VAc copolymers (within a concentration range usual for GPC) on the original GPC separation system (columns packed with porous silica gel) in order to evaluate the effect of polymer-polymer-solvent interactions in GPC in those cases where both polymers are in solution. This problem has been intensely studied particularly in recent years.<sup>5-7</sup> The same experiment was performed with a mixture of PS and poly(methyl methacrylate) (PMMA), that is, with a mixture which is incompatible according to the literature.<sup>7</sup> In the two latter cases we used a double detection in GPC, i.e., a differential refractometer and an ultraviolet (UV) detector, in order to decide, if needed, the degree of interactions of the particular components of the mixture. The results are supplemented by the viscometric measurement of PS and its mixtures with the VC-VAc copolymers. All results obtained are discussed.

## EXPERIMENTAL

### Gel Permeation Chromatography, Viscometry

Procedures and experimental conditions of the methods reported in this paper have been described in detail in our earlier paper.<sup>1</sup> The method of evaluation of GPC data using universal calibration based on polystyrene standards has also been described in our preceding communications.<sup>1,8</sup> The GPC chromatograph was supplemented with a UV detector with variable wavelength (Development Works of the Czechoslovak Academy of Sciences, Prague), set to a wavelength of 254 nm in all measurements and connected behind the refractometer. Concentrations of the injected PS and PMMA solutions were 0.2% and 0.4% w/v; those of mixtures of PS with VC-VAc or PMMA were 0.2% + 0.2% w/v of each component.

Experiments with the separation system containing styrene-divinylbenzene gel as column packing were performed on two columns of standard dimensions (8 × 1200 mm) packed with Styragel (Waters Associates, Milford, USA). Experimental conditions were the same as in the preceding case,<sup>1</sup> with the exception of flow, which was 0.6 ml/min.

### Polymer Samples

Polydisperse PS used in the investigation was a commercial sample (BDH Chemicals Ltd., Poole, England), denoted PS-1. The VC-VAc copolymer samples were low-conversion, chemically homogenous statistical copolymers prepared in our earlier work,<sup>2</sup> denoted C-1, C-4, and C-6. The vinyl acetate contents in the samples were 6% by weight (C-1), 15.2% by weight (C-4), and 28.1% by weight (C-6). A sample of polydisperse PMMA was prepared and studied in one of our earlier works<sup>9</sup> and is denoted PMMA-3 in accordance with this work. The PS and PMMA samples were chosen so as to be eluted in approximately the same range of elution volumes on the given GPC separation system as samples of the VC-VAc copolymers. Detailed data on all samples under study are given in the papers referred to in this paper.

### RESULTS AND DISCUSSION

Table I presents results of the determination of molecular weights of the VC-VAc copolymers using the GPC method with Styragel column packings, calculated from universal calibration based on PS standards.<sup>1</sup> Values obtained earlier with Spherosil are also given for comparison. All GPC values in Table I were calculated employing the Mark-Houwink equation given below. It can be seen that GPC results obtained with Styragel agree very well within the limits of experimental error with those obtained with Spherosil. The values were not corrected for spreading of the separation systems, which means that if a correction were used, the differences would be yet more reduced.

Note that experimental errors are usually in the range of  $\pm 5\%$ – $\pm 8\%$  for a given experimental condition. A small diverging trend with increasing molecular weight passing from 2% for the C-6 sample to 12% for the C-1 sample cannot rigorously be interpreted as relevant when comparing the results obtained using two separation systems.

Such results of the VC-VAc copolymer GPC on columns packed with Styragel do not indicate that under given experimental conditions the effect of incompatibility of the polymer toward the gel would come into play.

Results of the GPC measurements of the PS sample with the VC-VAc copolymers and PMMA-3 with the simultaneous use of double detection are given in Table II. Results of the GPC analyses of unmixed samples of the VC-VAc copolymers, PMMA-3, and PS together with results obtained with their mixtures may be evaluated either by means of the distribution curve of hydrodynamic volumes or, more simply, by comparing chromatograms (i.e., directly in the coordinates detector response vs. elution volume). We used the latter procedure. Table II shows the average elution volumes  $V_e = (\sum V_i h_i) / (\sum h_i)$  for the individual samples and their mixtures. The first column contains results calculated from

TABLE I  
Weight-Average Molecular Weights of VC-VAc Copolymer Samples Obtained by GPC

Copolymer	$\bar{M}_w \times 10^{-3}$	
	Styragel	Spherosil
C-1	115	103
C-4	80	74
C-6	53	52

TABLE II  
Elution Volumes of Samples of VC-VAc Copolymers, PS, and PMMA and Their Mixtures<sup>a</sup>

Sample	Elution volume, counts	
	Differential refractometer	UV detector
C-1	86.5	—
C-4	89.5	—
C-6	93.6	—
PS-I (0.2%)	82.1	82.6
PS-I (0.4%)	82.9	83.4
PMMA-3 (0.2%)	86.0	—
C-1 + PS-I measured	85.4	83.4
C-1 + PS-I calculated	84.3	—
C-4 + PS-I measured	86.0	82.4
C-4 + PS-I calculated	85.5	—
C-6 + PS-I measured	85.2	82.4
C-6 + PS-I calculated	87.1	—
PMMA-3 + PS-I measured	85.5	82.5
PMMA-3 + PS-I calculated	84.0	—

<sup>a</sup> Measured on porous silica gel Spherosil with double detection using a differential refractometer and a UV detector.

a record obtained with a differential refractometer. One can see that values of the average elution volumes of mixtures calculated from chromatograms obtained after injection of the individual components (PS and VC-VAc copolymer at concentrations 0.2%) agree fairly well with the  $V_e$  values of mixtures measured directly. Even though it seems at first sight that the difference between measured and calculated values is somewhat dependent on the content of vinyl acetate in the samples under investigation, one should remember that with the separation system used, the highest difference of 2 counts corresponds to a difference between molecular weights of ca. 10%. In this range, in addition to the respective influence of incompatibility, some other possible effects, such as the concentration effect and secondary exclusion, also cannot be ruled out. The same conclusions can be drawn from the data on PMMA-3 and PS.

Records made with the UV detector permitted evaluation of the possible effect of incompatibility on one of the components of the mixture, that is, on PS. The average elution volumes of the PS sample (in the second column of Table II) injected under different conditions (alone at various concentrations and in mixtures with other samples) are the same within the limits of experimental error. In both cases demonstrated by the average elution volumes in Table II, these conclusions hold also for the whole course of the chromatogram.

Results of the viscometric analysis of the PS sample, a fraction of the VC-VAc copolymer (fraction C-6d, see ref. 2), and of their mixture in a weight ratio of 1:1 are given in Figure 1. As shown in Figure 1, it cannot be inferred from the viscometric data that these polymers are incompatible. Similar results have been obtained for samples C-1, C-6, and their mixtures with PS.

Differences exist between values of the constants of the Mark-Houwink equations published for the VC-VAc copolymers (THF, 25°C):

$$[\eta] = 1.81 \times 10^{-4} M^{0.746} \quad (\text{ref. 4}) \quad (1)$$

$$[\eta] = 1.64 \times 10^{-4} M^{0.742} \quad (\text{ref. 10}) \quad (2)$$

$$[\eta] = 6.72 \times 10^{-4} M^{0.611} \quad (\text{ref. 1}) \quad (3)$$

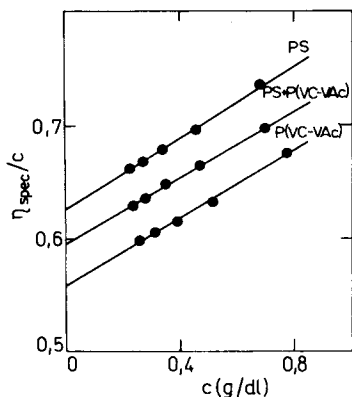


Fig. 1. Viscometric data for polystyrene, a fraction of the VC-VAc copolymer (C-6d), and their mixture 1:1 (weight ratio).

The range of molecular weights for which the above equations have been derived is approximately the same in all cases. No correction for the polydispersity of the fractions under investigation was used in either case, but the  $\bar{M}_n$  values were used in the first case for correlation. The very good correlation of the  $[\eta]$ -versus- $\bar{M}_n$  values obtained by plotting the experimental data of all three papers ( $\bar{M}_n$  values from refs. 1 and 10 are from GPC) as seen in Figure 2 seems to be noteworthy. An exception is made by the values of some of the fractions mentioned in reference 10 in the molecular weight range of 34,000–47,000 and by the highest of our experimental values.<sup>1</sup> Differences in the structure of this highest fraction cannot be ruled out, especially in branching. Of course, none of the investigated fractions of various commercial VC-VAc copolymers can be defined from this standpoint. The straight line plotted by the method of linear regression through the experimental points of all three papers in Figure 2 (with the exclusion of the above exceptions) is described by

$$[\eta] = 2.361 \times 10^{-4} \bar{M}_n^{0.72} \quad (4)$$

The regression coefficient for the set of treated experimental data was  $r = 0.993$ . The correlation  $[\eta]$  versus  $\bar{M}_n$  should be corrected according to

$$[\eta] = \bar{Q}_n \times K \times M^a \quad (5)$$

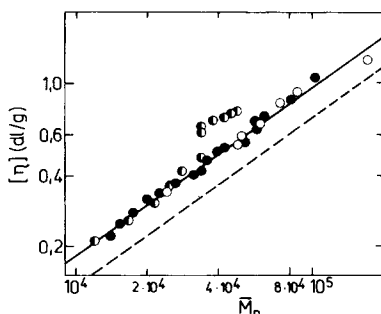


Fig. 2. Dependence of intrinsic viscosity  $[\eta]$  on molecular weight  $\bar{M}_n$  for fractions of the VC-VAc copolymer: (O) data of reference 1; (●) data of reference 4; (◐) data of reference 10; (—) linear regression of chosen data; (---) straight line corresponding to the Mark-Houwink equation corrected for the polydispersity of fractions used.

where the correction function  $\bar{Q}_n$  for the polydispersity  $\bar{M}_w/\bar{M}_n = 1.50$  and for the exponent  $a = 0.75$  becomes approximately  $\bar{Q}_n = 1.31$ , assuming the Schulz-Zimm distribution.<sup>11</sup>  $K \times \bar{Q}_n$  is equal to the constant  $K'$ , the value of which, determined from uncorrected experimental data, is  $2.361 \times 10^{-4}$  in eq. (4). If eq. (4) is corrected as indicated above, i.e., by dividing the constant  $K'$  by the factor  $\bar{Q}_n$ , the Mark-Houwink equation is obtained:

$$[\eta] = 1.8 \times 10^{-4} M^{0.72} \quad (6)$$

If the calibration is carried out by using a quantity proportional to the apparent hydrodynamic volume

$$([\eta] \times M) = K' \times \bar{M}_n^{a+1} \quad (7)$$

where

$$K' = \bar{Q}_n \times K \quad (8)$$

instead of the real hydrodynamic volume

$$([\eta] \times M) = K \times M^{a+1} \quad (9)$$

then

$$\frac{([\eta] \times M)'}{([\eta] \times M)} = \bar{Q}_n \quad (10)$$

is the measure of a deviation of the apparent hydrodynamic volume  $([\eta] \times M)'$  from the real volume  $([\eta] \times M)$ , i.e., approximately 30% in our case. If in the calibration of GPC this apparent parameter is assigned to the elution volume of the peak of the chromatogram, to which  $\bar{M}_w$  corresponds with good approximation under the given conditions, the deviation just mentioned is proportional to the polydispersity  $\bar{M}_w/\bar{M}_n$ , and the total error in our case is  $20 \pm 5\%$ . If the validity of universal calibration is evaluated using a method suggested by the authors of this work,<sup>8</sup> i.e., correlation of the  $\bar{M}_w$ ,  $\bar{M}_n$ , and  $[\eta]$  values of polymers under investigation measured by independent methods with those calculated from universal calibration based on really narrow standards (e.g., PS) and using real Mark-Houwink equations, all difficulties of the interpretation outlined above can be dismissed.

On recalculating results of earlier works<sup>1,2</sup> using eq. (6), an even better agreement between the GPC results and results obtained by independent methods (light scattering, osmometry, viscometry) was reached in most cases. Also the agreement between results obtained for unfractionated samples calculated from GPC data for individual fractions and measured directly was improved. Consequently, it can be said that recalculation has no influence on the conclusions drawn from these papers.

Within the limits examined in an earlier paper,<sup>2</sup> the chemical composition of the VC-VAc copolymer has no influence that would demonstrably exceed experimental error. An extension of the range of chemical composition does not seem to be of any major importance for this work either, because a recent paper<sup>12</sup> produced confirmation of the validity of universal calibration for the homopolymer poly(vinyl acetate). Molecular aggregation has not been proved either. Incompatibility or some other effect may become operative under given conditions to the extent demonstrated experimentally in this part of our work. It

cannot be ruled out, of course, that in some cases all the latter effects may become operative simultaneously in one sense so that together with the main cause (incorrect interpretation of GPC data), which contributes in a decisive manner, anomalous experimental results may be obtained, which markedly exceed the limits of experimental error.

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