

# Gel Permeation Chromatography in the Study of the Molecular Weight Distribution of the Copolymer Vinyl Chloride-Vinyl Acetate

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## Synopsis

A sample of the commercial copolymer vinyl chloride-vinyl acetate was fractionated by the GPC method in the preparative scale. The fractions thus obtained were characterized by light scattering, viscometry, GPC in the analytical scale, chemical analysis, and IR spectroscopy. They were compared with those obtained by precipitation fractionation. The  $\bar{M}_w$  and  $[\eta]$  values from the light scattering and viscometry of fractions of the commercial copolymer were employed for the calculation of the Mark-Houwink equation valid in THF at 25°C for a copolymer with vinyl acetate content of 10-13%. Universal calibration of the  $[\eta]\cdot M$  type was confirmed experimentally for the above polymer. Effects which could change the correct interpretation of the GPC data were discussed in detail. Correct interpretation of the GPC data showed an agreement between the GPC, light scattering, and viscometric data within 6-7%.

## INTRODUCTION

The only paper devoted to a systematic study of the molecular weight distribution (MWD) of the copolymer vinyl chloride-vinyl acetate (VC-VAc) by gel permeation chromatography (GPC) was published by Chen and Blanchard.<sup>1</sup> These authors found some anomalies which, however, were not given a sufficient explanation.

In the first place, disagreement was observed between the universal calibration curves<sup>2,3</sup> constructed by using the parameter  $[\eta]\cdot M$  for polystyrene (PS) standards and fractions of the copolymer VC-VAc. No agreement was reached between the distribution curve of the unfractionated copolymer VC-VAc constructed by means of the GPC chromatogram of the unfractionated sample, on the one hand, and the distribution curve of the above copolymer calculated from the GPC data for the individual fractions, on the other hand.

In a recent paper by Kálal et al.,<sup>4</sup> the  $\bar{M}_w$  values for the fractionated copolymer VC-VAc were determined by the light scattering method, and the intrinsic viscosity values  $[\eta]$  were also determined. At the same time, the authors determined the varying chemical composition of the individual fractions. The molecular weights calculated from the GPC data assuming the validity of universal calibration<sup>2,3</sup> measured for the above work at the Institute of Macromolecular Chemistry, Prague, did not show such pronounced systematic departure from the values measured independently as the paper of Chen and Blanchard<sup>1</sup> showed.

In the paper of Chen and Blanchard,<sup>1</sup> we considered the following as possible critical moments:

1. The use of  $\bar{M}_n$  for the correlation with the  $[\eta]$  values and for the calculation of the constants of the Mark-Houwink equation without correction for the possible polydispersity of fractions of the copolymer VC-VAc.

2. The possibility of distortion of the results of membrane osmometry in the determination of the  $\bar{M}_n$  values, especially for fractions containing a major amount of low molecular weight fractions.<sup>5</sup>

3. The assumption that the polydispersity of fractions of the copolymer VC-VAc is the same as that of the PS standards.

4. Evaluation of the applicability of the universal calibration parameter  $[\eta] \cdot M$  on the basis of the speculative combination of  $\bar{M}_n$  and  $[\eta]$  values criticized in our earlier paper.<sup>6</sup>

5. Ignorance of the chemical composition of the individual fractions of the copolymer VC-VAc and the subsequent possibility of a different solution behavior of these fractions.

In this paper, we have made an attempt to explain the above anomalies.

## EXPERIMENTAL

### Samples of the Copolymer VC-VAc

Two samples of various commercial copolymers (CHZWP, Nováky, denoted as A and B)<sup>7</sup> and fractions of samples A and B obtained by preparative GPC fractionation and precipitation fractionation were used in the investigation.

### Preparative GPC Fractionation of Copolymers VC-VAc

The GPC preparative fractionation of sample A was carried out on an apparatus built at the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences. The separation system consisted of two columns 25 mm in diameter, total length 2400 mm, packed with silica gel Sphérosil (Produits Chimiques, France). In this case, a mixture of types B, C, D, E, and F of different porosities was used. The optimum separation activity of this system lay within  $10^3$ – $10^6$  of molecular weights. Tetrahydrofuran (THF) was used as solvent. The samples of copolymer A were injected from a loop, 25 ml in volume, placed in the bypass. Concentration of the injected samples was 0.5% (w/v). Since the whole injected quantity of the copolymer was 0.125 g at the utmost, the injection was repeated several times until the total fractionated amount attained 2.25 g. After fractionation, the identical fractions from the individual injections were combined and the polymer was precipitated with an excess of distilled water. The precipitated fractions were dried *in vacuo* at 40°C to constant weight.

### Precipitation Fractionation of Copolymer VC-VAc

Fractionation of a sample of the commercial copolymer B was carried out by using the system THF–water from a 0.6% solution of copolymer. The required amount of copolymer was precipitated by adding water to the solution at 40°C.

The sediment was dissolved by heating to 49°C; the copolymer fraction was reprecipitated by a slow cooling with stirring down to 35°C during 10 hr. At such a slow decrease in temperature, the precipitation of the fraction occurs at thermodynamical equilibrium. After that, the stirring was stopped and the system maintained at 35°C for 12 hr in order to achieve perfect phase separation. After separation, the fraction was reprecipitated and dried at 30°C and at reduced pressure to constant weight.<sup>7</sup>

### Analytical Procedures

IR spectroscopy was used for the determination of the VAc content in the VC-VAc copolymers and their fractions. The measurement was carried out with a double-beam UR-20 spectroscope (Zeiss, GDR) by using the compensation method in a THF solution. The calibration curve was constructed with poly(vinyl acetate) (PVAc) solutions. The VAc content was evaluated from the absorption of the C=O groups in the wave frequency region of 1745 cm<sup>-1</sup>.<sup>8</sup>

Chlorine in the samples of the VC-VAc copolymer was determined by the classical Schöniger method. The results obtained allowed the determination of the content of the vinyl chloride units in the copolymers.

The molecular weights,  $\bar{M}_w$ , were determined from the light-scattering data with a Photogoniometer (Sofica, France) in THF at 25°C. The refractive index increments were calculated by linear interpolation for the individual copolymer samples having a known chemical composition from the increment values for pure PVC and PVAc.

Standard Ubbelohde viscometers were used, and the measurements were carried out in THF at 25° ± 0.005°C. The flow times of pure solvent lay within 75–110 sec in different viscometers.

Gel permeation chromatography in the analytical scale was carried out with an apparatus built at the Institute of Macromolecular Chemistry. The separation system consisted of six columns (diameter 8 mm, length 1200 mm) packed with Sphérosil E, D, and B (two columns for each type of silica gel). THF was used as solvent, at a flow rate of 0.345 ml/min.<sup>6</sup> Each time, 1.636 ml of the solution of copolymer samples of the VC-VAc and PS standards (Waters Associates, U.S.A.), concentration 0.2% (w/v) was injected. Within the concentration range of 0.05–0.25% (w/v), no effect of concentration on the calculated molecular weights could be observed.

The universal calibration curve was constructed with the PS standards so that the product  $[\eta] \cdot M$  was plotted against the elution volume of the maximum of the GPC chromatogram;  $M_{\text{peak}}$  given by the manufacturer was used for  $M$ ;  $[\eta]$  was calculated for  $M_{\text{peak}}$  from the equation:<sup>6</sup>

$$[\eta] = 1.17 \times 10^{-4} M^{0.717}$$

No correction for axial dispersion was used in the molecular weight calculations because, for the given region of the calibration curve, the difference between the polydispersity indices  $\bar{M}_w/\bar{M}_n$  given by the manufacturer for the PS standards and the values calculated from the GPC chromatograms lay within the limits of experimental error under given experimental conditions, i.e., ±5% at the utmost.

## RESULTS AND DISCUSSION

## Preparative GPC Fractionation

Sample A was divided into 17 fractions, the losses were 4.76%. The weight yields of the individual fractions varied depending on the distribution curve of copolymer A or on the course of the GPC preparative chromatogram. The results of the GPC preparative fractionation are summarized in Table I.

## Heterogeneity in Composition of Commercial VC-VAc Copolymers

The composition of commercial samples of the VC-VAc copolymers and their fractions was determined by chemical analysis and IR spectroscopy. The results are summarized in Table I.

TABLE I  
Fractionation and Composition of Copolymers VC-VAc and Their Fractions

| Designation of sample             | Yield, % | Chemical analysis VC content, % | IR spectroscopy VAc content, % |
|-----------------------------------|----------|---------------------------------|--------------------------------|
| Preparative GPC                   |          |                                 |                                |
| A-1                               | 0.1      | —                               | —                              |
| A-2                               | 0.112    | —                               | —                              |
| A-3                               | 0.141    | —                               | —                              |
| A-4                               | 1.500    | 81.3                            | —                              |
| A-5                               | 3.375    | 86.2                            | —                              |
| A-6                               | 5.859    | 82.9                            | —                              |
| A-7                               | 8.953    | 86.7                            | 9.7                            |
| A-8                               | 12.750   | 85.2                            | 11.0                           |
| A-9                               | 16.218   | 84.2                            | 18.3                           |
| A-10                              | 14.390   | 86.4                            | 13.1                           |
| A-11                              | 14.671   | 84.8                            | 17.7                           |
| A-12                              | 11.484   | 82.4                            | 11.2                           |
| A-13                              | 6.375    | 78.4                            | —                              |
| A-14                              | 2.351    | 80.5                            | 24.5                           |
| A-15                              | 1.125    | 78.9                            | —                              |
| A-16                              | 0.636    | 52.5                            | —                              |
| A-17                              | 0.1      | —                               | —                              |
| Precipitation Fractionation       |          |                                 |                                |
| B-1                               | 8.59     | —                               | 10.7                           |
| B-2                               | 10.36    | —                               | —                              |
| B-3                               | 9.83     | —                               | 9.4                            |
| B-4                               | 8.81     | —                               | 9.4                            |
| B-5                               | 8.05     | —                               | —                              |
| B-6                               | 7.05     | —                               | —                              |
| B-7                               | 7.57     | —                               | 12.0                           |
| B-8                               | 5.92     | —                               | —                              |
| B-9                               | 4.78     | —                               | —                              |
| B-10                              | 4.57     | —                               | 27.1                           |
| B-11                              | 4.58     | —                               | 24.3                           |
| B-12                              | 19.89    | —                               | 31.3                           |
| Commercial Unfractionated Samples |          |                                 |                                |
| A                                 | —        | 89.1                            | 10.2                           |
| B                                 | —        | 86.0                            | 13.2                           |

For copolymers A and B, one can observe a tendency of increasing content of VAc from the first fractions to the last, as shown by Table I. The following measurement confirmed that the molecular weight decreases in the same order of fractions obtained by the preparative GPC and precipitation fractionation. During the copolymerization of the comonomeric pair VC-VAc, there is a faster loss of VC from the reaction monomeric mixture. Therefore, the content of VAc in the forming VC-VAc copolymer increases with progressing conversion. At the same time the molecular weight of the forming copolymer decreases with progressing conversion, which is due to the increasing concentration of the terminating components.<sup>7</sup>

For instance, the momentary composition of the forming copolymer at various conversions has been calculated for the commercial copolymer B, using a current copolymerization equation. The conditions of industrial copolymerization were as follows: VAc content in the batch, 17%; the polymerization proceeded up to

TABLE II  
Survey of GPC, Viscometric, and Light-Scattering Data for Fractions and Unfractionated Copolymers VC-VAc

| Copolymer<br>or fraction | GPC data                   |                            |                       | [ $\eta$ ],<br>dl/g | Viscom-<br>etry<br>[ $\eta$ ],<br>dl/g | Light-<br>scattering<br>$\bar{M}_w \times 10^{-3}$ |
|--------------------------|----------------------------|----------------------------|-----------------------|---------------------|--|--|
|                          | $\bar{M}_w \times 10^{-3}$ | $\bar{M}_n \times 10^{-3}$ | $\bar{M}_w/\bar{M}_n$ |                     |  |  |
| A-1                      | —                          | —                          | —                     | —                   |  |  |
| A-2                      | 721                        | 390                        | 1.85                  | 2.264               |  |  |
| A-3                      | 601                        | 337                        | 1.78                  | 2.049               |  |  |
| A-4                      | 408                        | 267                        | 1.53                  | 1.702               |  |  |
| A-5                      | 316                        | 217                        | 1.46                  | 1.466               |  |  |
| A-6                      | 241                        | 173                        | 1.39                  | 1.238               | 1.248                                  | 250.0  |
| A-7                      | 166                        | 130                        | 1.28                  | 1.011               |  |  |
| A-8                      | 137.8                      | 100.1                      | 1.38                  | 0.893               |  |  |
| A-9                      | 99.3                       | 72.8                       | 1.36                  | 0.735               | 0.819                                  | 115.0  |
| A-10                     | 80.3                       | 62.0                       | 1.30                  | 0.649               |  |  |
| A-11                     | 67.3                       | 50.4                       | 1.34                  | 0.580               | 0.593                                  | 66.5   |
| A-12                     | 48.1                       | 35.4                       | 1.36                  | 0.472               |  |  |
| A-13                     | 36.8                       | 24.2                       | 1.52                  | 0.397               | 0.340                                  | 28.6   |
| A-14                     | 26.8                       | 17.2                       | 1.56                  | 0.320               |  |  |
| A-15                     | 16.8                       | 10.2                       | 1.64                  | 0.243               |  |  |
| A-16                     | 9.9                        | 4.8                        | 2.07                  | 0.172               |  |  |
| A-17                     | —                          | —                          | —                     | —                   |  |  |
| A                        | 109.6                      | 48.8                       | 2.25                  | 0.739               | 0.809                                  | 110.0  |
| A calculation            | 111.3                      | 50.7                       | 2.20                  | 0.746               | —                                      | —  |
| B-1                      | 120.8                      | 86.1                       | 1.40                  | 0.826               | 0.917                                  | 123.0  |
| B-2                      | 86.3                       | 66.7                       | 1.29                  | 0.679               |  |  |
| B-3                      | 76.0                       | 59.7                       | 1.27                  | 0.629               | 0.674                                  | 71.0   |
| B-4                      | 65.3                       | 51.2                       | 1.27                  | 0.574               |  |  |
| B-5                      | 61.7                       | 48.6                       | 1.27                  | 0.554               | 0.550                                  | 60.0   |
| B-6                      | 51.1                       | 38.9                       | 1.31                  | 0.493               |  |  |
| B-7                      | 47.9                       | 38.2                       | 1.25                  | 0.475               | 0.442                                  | 43.0   |
| B-8                      | 41.1                       | 31.8                       | 1.29                  | 0.432               |  |  |
| B-9                      | 36.8                       | 27.7                       | 1.33                  | 0.402               |  |  |
| B-10                     | 32.5                       | 23.7                       | 1.37                  | 0.372               | 0.326                                  | 31.5   |
| B-11                     | 30.3                       | 23.5                       | 1.29                  | 0.358               | —                                      | 26.5–31.0  |
| B-12                     | 18.0                       | 10.3                       | 1.75                  | 0.253               |  |  |
| B                        | 53.3                       | 26.0                       | 2.05                  | 0.486               | 0.490                                  | 48.0   |
| B calculation            | 53.9                       | 25.3                       | 2.13                  | 0.490               | —                                      | —  |

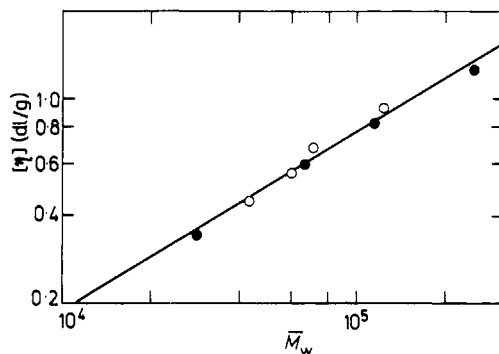


Fig. 1 Determination of constants of Mark-Houwink equation for VC-VAc copolymer in THF at 25°C: (●) fractions of copolymer A; (○) fractions of copolymer B.

a conversion of 90%. The calculation was carried out by using the copolymerization parameters  $r_1 = 1.68$ ,  $r_2 = 0.23$ .<sup>9</sup> The mean calculated VAc content in the copolymer thus formed is 14.84%; the VAc content can vary from ca. 10% to 26%. Experimental results given in Table I agree with this calculation; the composition of fractions of both copolymers A and B varies within the limits indicated above.

The results of chemical analysis are in better agreement with the theoretical calculation than those obtained by IR spectroscopy. Theoretically, the sum of the VAc content determined by IR spectroscopy and that determined by chemical analysis (see Table I) should be 100%. Impurities, particularly retained solvents,<sup>4</sup> and experimental errors of the two methods are obviously the cause of the deviations. Retained THF is probably the cause of the fact that unfractionated copolymer sample A has a higher VC content than any of its fractions. The IR-spectroscopic method is particularly subjected to higher experimental errors in this case. The reproducibility of the results of chemical analysis is better than  $\pm 1\%$  rel., while that of the IR-spectroscopic measurements is poorer,  $\pm 15\%$  rel., on the average (rel. = relative). These values were obtained by repeated measurements of some samples of the VC-VAc copolymers using both methods.

#### Determination of the Mark-Houwink Equation for VC-VAc Copolymer of Constant Composition

For the determination of the constants of the Mark-Houwink equation, we selected fractions of copolymers A and B having virtually the same VAc content (between 10% and 13%). The  $[\eta]$  and  $\bar{M}_w$  values measured viscometrically in THF at 25°C and by the light-scattering method for selected fractions are given in Table II and Figure 1. Table II contains also  $[\eta]$  and  $\bar{M}_w$  for unfractionated copolymers A and B.

The  $[\eta]$  and  $\bar{M}_w$  values of copolymers A and B were used to calculate the Mark-Houwink equation for a copolymer with 10–13% VAc by the linear regression method:

$$[\eta] = 6.72 \times 10^{-4} \bar{M}_w^{0.611}$$

The equation holds for THF at 25°C. The straight line in Figure 1 corresponds

to the above equation, which was calculated without correction for polydispersity of copolymer fractions. The  $[\eta]$  versus  $M$  functions are less sensitive to differences in polydispersity when using  $\bar{M}_w$  values than in the case of  $\bar{M}_n$  values.<sup>10</sup> This is true for log-normal distribution<sup>10</sup> and for Schulz-Zimm distribution as well.<sup>11</sup> The correction factors for our copolymer fractions are in the range of experimental error.

### Evaluation of Applicability of Universal Calibration for VC-VAc Copolymer

The applicability of the universal calibration parameter  $[\eta]$  versus  $M$  was evaluated by the calculation procedure described in our earlier paper.<sup>6</sup> This procedure was independent of the speculative combination of various molecular weight average values used for calculating the product  $[\eta]$  versus  $M$  correlated with the elution volume of the maximum of the chromatogram. Molecular parameters of copolymer fractions were calculated from GPC chromatograms using the universal calibration curve constructed as described in the experimental part. Agreement between GPC calculated values and independently measured values is a criterion of the applicability of the universal calibration. Using this procedure, the whole chromatograms of copolymer fractions are needed. The values of  $\bar{M}_w$  and  $V_e$  of the maximum of a chromatogram are not sufficient for the calculation and are not included in Table II;  $\bar{M}_w$ ,  $\bar{M}_n$ ,  $\bar{M}_w/\bar{M}_n$ , and  $[\eta]$  calculated from the GPC chromatograms of fractions and unfractionated copolymers A and B are given in Table II. The described Mark-Houwink equation was used in the calculations.

Comparison of the GPC-calculated  $\bar{M}_w$  and  $[\eta]$  values for fractions and unfractionated VC-VAc copolymers with those obtained by light scattering and viscometry gave the mean difference of  $\pm 6-7\%$ . The mean agreement between the GPC  $\bar{M}_w$ ,  $\bar{M}_n$ , and  $[\eta]$  values for unfractionated copolymers measured directly and calculated from the GPC data for the individual fractions is better than  $\pm 2\%$ .

In order to verify whether there is any important aggregation of macromolecules of the VC-VAc copolymer in THF solution which would essentially affect the GPC results, the sample of copolymer A was dissolved in cyclohexanone and heated up to the boiling point. The copolymer solution was injected into the GPC separation system. The calculated molecular weights did not differ to any essential degree from the mean values given in Table II.

The results described in this paper indicate that universal calibration using the parameter  $[\eta] \cdot M$  is suitable also for the VC-VAc copolymer. However, one must correctly interpret the results obtained and eliminate errors which may arise.

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