

Compositional Variation as a Function of Elution Volume in Gel Permeation Chromatography of Copolymers and Physical Blends

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Synopsis

This paper is concerned with the theoretical aspects of the gel permeation chromatography of copolymers and physical blends, such as polypropylene homopolymer and copolymers. Such considerations have become important with the advent of modern UV and IR chromatographic detectors. The behavior of the compositional variation observed as a function of elution volume is investigated by a simulation technique. As an example, ethylene-propylene copolymers having a bivariate normal distribution for molecular weight and composition are taken for calculations. We deal with the effects of the molecular weight distribution, the compositional distribution, and the correlation coefficient between molecular weight and composition on the detected compositional variation. It is concluded that these three factors are equally important in evaluating the curves for the variation. Therefore, the difference between compositional distributions of copolymers is detectable only under limited conditions where the other factors are kept constant.

INTRODUCTION

Polymer species are separated by molecular size in gel permeation chromatography (GPC). The chromatogram is usually obtained by recording the difference in the refractive indices between solvent and solution as a function of elution volume, the refractive index (RI) detector being the commonly employed means of estimating weight of polymer in the eluant. On the other hand, many studies on suitable copolymers have been done using ultraviolet and/or infrared detectors connected to conventional GPC instruments, i.e., dual-detector GPC.

As reported by Adams,¹ Runyon,² and Mirabella,³ the composition of eluted copolymer species may vary with elution volume. The compositional distribution seems to be determined by the above GPC system. However, it is also possible that the variation of the detected composition may be largely due to molecular weight factors, since copolymer species as stated above are separated by molecular size. Further, other factors, such as correlation coefficient between molecular weight and composition, may cause that variation. In this report, the compositional variation observed in dual-detector GPC has been interpreted in detail by use of a simulation technique.

CALCULATIONS

Distributions with respect to molecular weight and chemical composition must be assumed for the construction of a hypothetical chromatogram. The following distribution function is adopted for copolymers according to previous papers,^{4,5} in which the distribution of ethylene-propylene copolymers (EP) were discussed:

$$W(\ln M, \alpha) = \frac{1}{2\pi\beta_M\beta_\alpha(1-\rho^2)^{1/2}} \times \exp \left[-\frac{1}{2(1-\rho^2)} \left(\frac{(\ln M - \ln M_0)^2}{\beta_M^2} - \frac{2\rho(\ln M - \ln M_0)(\alpha - \alpha_0) + (\alpha - \alpha_0)^2}{\beta_\alpha^2} \right) \right] \quad (1)$$

where $W(\ln M, \alpha)$ is the distribution function for the copolymer; $\ln M$ is the logarithm of molecular weight; α is the ethylene content on a weight basis, i.e., composition; $\ln M_0$ is the peak position for the molecular weight distribution; α_0 is the peak position for the compositional distribution; and β_M and β_α are the standard deviations for $\ln M$ and α , respectively. This distribution curve can be expressed as Figure 1. The hypothetical chromatogram is prepared by the following process. First the distribution surface of the copolymer, which is given by eq. (1), is divided into many increments. The weight fraction $h(V_i)$ at the elution count (5.0 ml of elution volume is commonly expressed as one count) V_i is given by

$$h(V_i) = \sum_k W(\ln M_k, \alpha_k)_i \quad (2)$$

where $W(\ln M_k, \alpha_k)_i$ shows the k th increment of the i th weight fraction, i.e., the polymer species eluted at count V_i . This fraction is expressed as Figure 2. The weight fraction $h(V_i)$ is obtained by summing up $W(\ln M_k, \alpha_k)_i$, which is calculated based on the universal rule proposed by Grubisic and Benoit et al.,⁶ see eq. (3). In this case, the calibration curve is assumed to be linear:

$$\log [\eta]M = AV + B \quad (3)$$

where A and B are constant for a given set of experimental conditions and independent of the kind of polymer; the values -0.353 cm^{-1} and 14.427 are adopted for A and B , respectively, $[\eta]$ is the intrinsic viscosity. If the Mark-Houwink

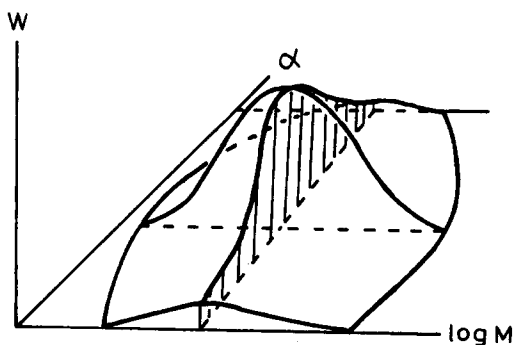


Fig. 1. Schematic representation of a hypothetical distribution function for copolymers. Surface filled with solid parallel lines shows compositional distribution. Surface parallel to the abscissa, formed by a dotted line and solid-line curve, shows molecular weight distribution.

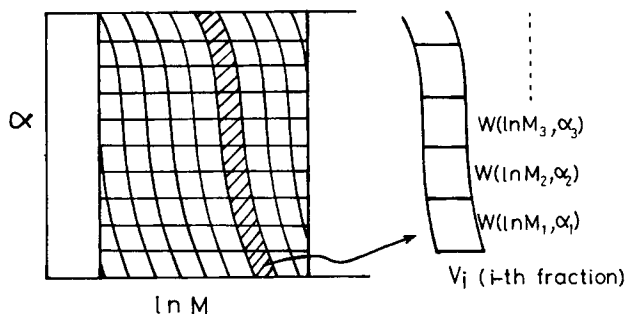


Fig. 2. Increments of copolymer distribution surface eluted at count V_i .

equation, namely, $[\eta] = KM^a$, holds, the M - V relationship is expressed as follows:

$$\log M = \frac{AV}{1+a} + \frac{B - \log K}{1+a} \quad (4)$$

But in the case of copolymers, these values can be expressed as a function of the copolymer composition and are given as the empirical equations which were reported in the previous paper.⁵ At any rate, when elution count V_i is fixed, the molecular weight M_k of the k th increment can be calculated from eq. (4) for a given composition α_k , i.e., ethylene content. This process is carried out for all the increments having different compositions. Thus, all the M - α pairs for V_i are obtained, and $W(\ln M, \alpha)$ for all the M - α pairs are calculated using eq. (1); $h(V_i)$ is obtained using eq. (2). When $h(V)$ for all the fractions are calculated over a wide range of elution count, the chromatogram is completed.

The average composition, i.e., ethylene content $\bar{\alpha}(V_i)$ of the copolymer species eluted at V_i , is given by eq. (5):

$$\bar{\alpha}(V_i) = \frac{\sum_k \alpha_k W(\ln M_k, \alpha_k)_i}{\sum_k W(\ln M_k, \alpha_k)_i} \quad (5)$$

Thus, the curve of the compositional variation is obtained as a function of elution count by calculating $\bar{\alpha}(V_i)$ over the elution range.

In this report the behavior of the compositional variation is discussed in relation to the properties of the original copolymers, such as compositional distribution and correlation coefficient. The D values ($\equiv \bar{M}_w/\bar{M}_n$) of the original copolymers are calculated as an index of the molecular weight distribution as follows:

$$D = \sum_i h(V_i) \sum_i \sum_k \frac{W(\ln M_k, \alpha_k)_i}{M_k} \quad (6)$$

The Cantow-Fuchs method^{7,8} is used as an index of the compositional distribution, namely, the index U_1 , as given by eq. (7):

$$U_1 = \frac{\sum_i \sum_k |\alpha_k^+ - E_t| W(\ln M_k, \alpha_k)_i^+}{\sum_i h(V_i)^+} + \frac{\sum_i \sum_k |\alpha_k^- - E_t| W(\ln M_k, \alpha_k)_i^-}{\sum_i h(V_i)^-} \quad (7)$$

where

$$E_t = \frac{\sum_i \sum_k \alpha_k W(\ln M_k, \alpha_k)_i}{\sum_i h(V_i)} \quad (8)$$

The superscript + and - denote the quantities of increments containing less and more of the ethylene than E_t ; U_1 increases as the breadth of the compositional distribution increases.

RESULTS AND DISCUSSION

Effect of Distribution Factors

Table I shows the values of the distribution factors. The statistical values of the original copolymers are given in Table II. To evaluate quantitatively the extent of the compositional variation, we will express it conventionally as $E_{22} - E_{27}$ (the difference in the ethylene content of copolymers eluted at 22 and 27 counts). The values $E_{22} - E_{27}$ for typical simulations are also shown in Table II.

A GPC chromatogram and a representative curve of the compositional variation are shown in Figure 3, where the ordinate shows $\bar{\alpha}(V_i)$. The chromatogram is almost the same in shape as the log-normal distribution function as illustrated in the previous paper.⁵ The ethylene content of the copolymer eluate decreases with increasing elution count. The curve given in Figure 3 is almost linear. However, in the general case, various patterns are possible.

If the different curves depend upon the U_1 of copolymers, it may be possible

TABLE I
Values of Distribution Factors Used for Calculations

Sim. No.	$\ln M_0$	β_M	α	β_α	ρ
Sim. 1	12.0	1.25	0.435	0.365	0.00
Sim. 2	12.0	1.25	0.435	0.365	0.25
Sim. 3	12.0	1.25	0.435	0.100	0.25
Sim. 4	12.0	1.25	0.435	0.365	0.75
Sim. 5	12.0	1.25	0.435	1.00	0.00
Sim. 6	13.7	1.25	0.85	0.100	0.25
	$\ln M_p = 12.0, \beta_p = 1.25$ (polypropylene)				
	PP:EP = 8:2 (wt)				

TABLE II
Statistical Values Calculated From Hypothetical Copolymers

Sim. No.	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	D value	E_t , wt. %	$E_{22} - E_{27}$	U_1
Sim. 1	7.47	35.6	4.76	46.8	9.0	0.429
Sim. 2	7.87	35.7	4.53	46.8	17.5	0.429
Sim. 3	7.47	35.5	4.76	43.5	8.5	0.160
Sim. 4	10.3	30.9	3.00	46.8	39.5	0.429
Sim. 5	7.46	35.6	4.76	49.4	12.0	0.494
Sim. 6	9.07	91.2	10.0	16.7	—	—

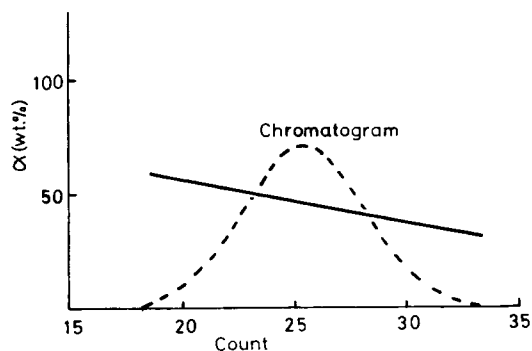


Fig. 3. Representative chromatogram and curve of compositional variation (Sim. 1).

for GPC to be used as one method for detecting compositional variation. Figure 4 shows the compositional variation for copolymers having different U_1 , 0.429 (Sim. 2) and 0.160 (Sim. 3), where the other factors other than β_α are the same. The curve of Sim. 2 varies considerably with elution count, and is different from that of Sim. 3. Therefore, GPC is apparently capable of detecting the difference between compositional distributions, see Figure 5.

As described previously, various distribution factors other than compositional distribution, affecting $E_{22} - E_{27}$, are considered. These are average comonomer content, molecular weight distribution, average molecular weight, and the cor-

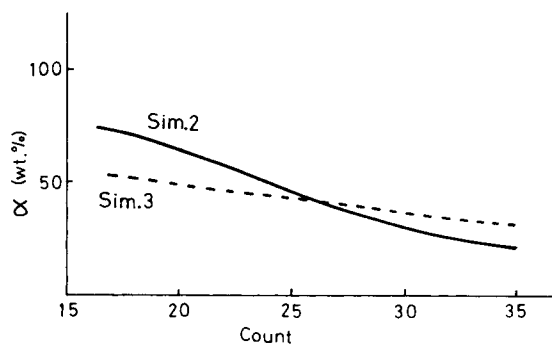


Fig. 4. Detection of compositional distribution differences with a GPC-monitor system.

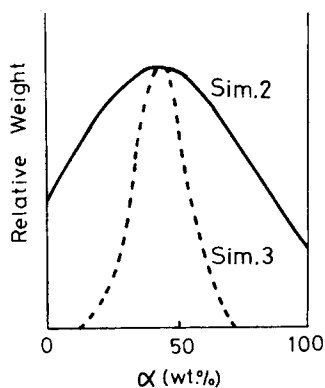


Fig. 5. Compositional distributions from Sim. 2 and Sim. 3.

relation coefficient. Various calculations have revealed that the average comonomer content and the average molecular weight have little effect on $E_{22} - E_{27}$. However, the correlation coefficient and the molecular weight distribution are very significant in evaluating $E_{22} - E_{27}$. As shown in Table II, U_1 in Sim. 5 is larger than that in Sim. 4, while $E_{22} - E_{27}$ values are the opposite: Table II shows that $E_{22} - E_{27}$ in Sim. 4 is 39.5 and in Sim. 5, 12.0. The distribution factor raising $E_{22} - E_{27}$ in Sim. 4 must be ρ because the other factors are the same as in Sim. 5.

More detailed relations among $E_{22} - E_{27}$, U_1 , and ρ were examined. The results are shown in Figure 6. As expected, ρ is very significant in evaluating $E_{22} - E_{27}$. At high values of ρ , $E_{22} - E_{27}$ becomes more sensitive to any small changes in ρ as well as U_1 . When factors other than ρ are held constant, $E_{22} - E_{27}$ varies markedly with increasing ρ , see Figure 7. It is noteworthy that E_{22}

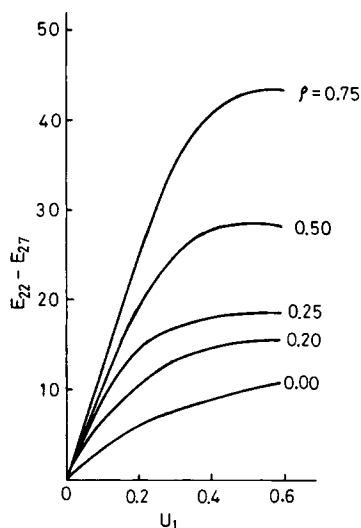


Fig. 6. $E_{22}-E_{27}$ expressed as function of ρ and U_1 , where $\ln M_0 = 12.0$, $\beta_M = 1.25$, $\alpha_0 = 0.435$.

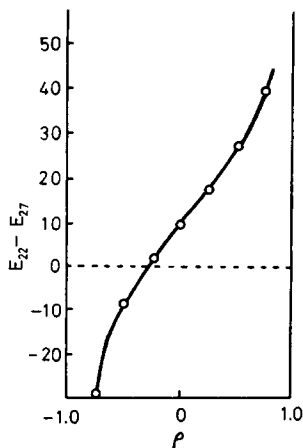


Fig. 7. Effect of correlation coefficient on observed variation, where $\ln M_0 = 12.0$, $\beta_M = 1.25$, $\beta_\alpha = 0.365$, and $\alpha_0 = 0.435$.

$-E_{27}$ has, in practice, values from plus to minus in spite of constant U_1 ($U_1 = 0.429$) throughout these calculations. Therefore, the evaluation of U_1 from a curve of the compositional variation is generally very complicated. In some cases the curve of the compositional variation will preferentially reflect changes of ρ . Generally, the polymerized copolymers in experiments have $0.20 \sim 0.25$ for ρ . Under such limited conditions, the compositional variation observed in GPC may be used for evaluating U_1 .

The effect of the molecular weight distribution on $E_{22} - E_{27}$ was examined, and the results are shown in Figure 8. As shown in this figure, $E_{22} - E_{27}$ largely depends on the D values of the copolymers as supplied. The effect of the D values is greater than that of U_1 in the case of narrow molecular weight distributions. Therefore, when one wants to evaluate the values $E_{22} - E_{27}$, one must pay close attention to the difference of D values among the copolymers.

Explanation with a Scheme of Fractionation

As described above, the curves of the compositional variation are very complicated. The following is carried out to explain the complicated behavior with the scheme of fractionation in GPC.

Various types of the copolymer distributions are illustrated in Figure 9, in

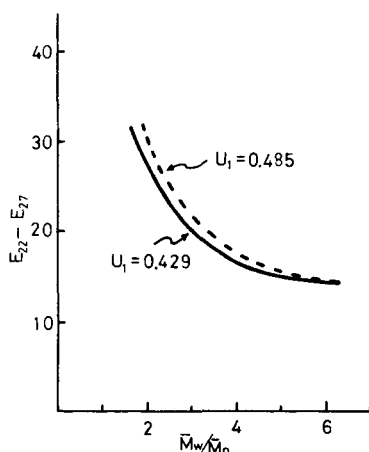


Fig. 8. Dependence of $E_{22} - E_{27}$ on D values, where $\ln M_0 = 12.0$, $\alpha_0 = 0.435$, $\rho = 0.20$, and $\beta_\alpha = 0.365$ ($U_1 = 0.429$), and $\beta_\alpha = 0.730$ ($U_1 = 0.485$).

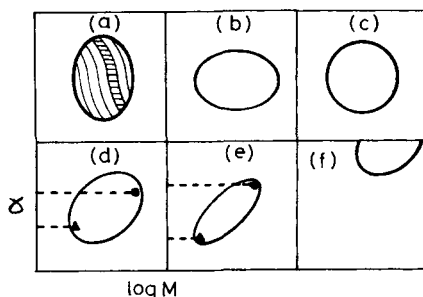


Fig. 9. Schemes of compositional and molecular weight distributions: (\blacktriangle) average ethylene content of the first fraction; (\bullet) average ethylene content of the last fraction.

which the curves indicate contour lines of the distributions. Individual ranges of composition and molecular weight of the copolymers fractionated by GPC are shown in Figure 9(a). The range eluted at a given count is illustrated with horizontal lines. The same range can be applied to that of the others: the part fractionated by GPC is independent of copolymer distribution. The correlation coefficient ρ is zero in the case of (a), (b) and (c). Figure 9(a), which has a broad compositional distribution, will give the largest compositional variation in GPC. $E_{22} - E_{27}$ of (c) is larger than that of (b) in spite of the same U_1 . This phenomenon is caused entirely by the difference in the molecular weight distribution and corresponds to the behavior shown in Figure 8. Figures 9(a) and 9(d) have the same U_1 but are different with respect to ρ . As is clear from the curves for fractionation, the compositional variation of (a) is less than that of (d). This behavior corresponds to that shown in Figure 6. When ρ becomes larger, the shape of the contour lines changes from (d) to (e). The compositional variation of (e) should be larger than that of (d). This is the same as the behavior shown in Figure 6. The difference is only due to the fact that the ethylene content $\bar{\alpha}(V_i)$ of each fraction is always obtained by averaging the ethylene content of copolymer species over a wide range of composition. Because of this averaging, the difference of (d) in the ethylene content between the first and the last fractions is small compared with that of (e). Figures (d) and (f) are different only with respect to the average ethylene content. The compositional variation of (f) is almost equal to that of (d). The other factors, such as average molecular weight and average composition, are not so important.

The compositional distribution, the correlation coefficient, and the molecular weight distribution are very important in evaluating the compositional variation observed in dual-detector GPC. Accordingly, the variation may be a good method of determining the correlation coefficient for which no method has been found, if the molecular weight distribution and the compositional distribution are previously known.

Detection of Blend

It is evident that GPC is not a good method to determine the compositional distribution. However, this method may be useful for detecting the components of blend, such as polypropylene homopolymer (PP) and EP in commercially available high-impact polypropylenes. It was assumed that PP and EP having different peak molecular weights were blended in the ratio of 8:2 by weight.⁵ The resulting curve for this blend is illustrated in Figure 10 (Sim. 6). When compared with that of Figure 1, the curve of the compositional variation approaches zero in the region of high elution counts, although the polymer species still go on eluting. Thus, we can detect the PP component.

On the other hand, as described in the other paper,⁹ the solution fractionation technique is capable of detecting EP component in the same blend, but not PP component. Therefore, the dual-detector GPC technique will be very useful for detecting the PP component.

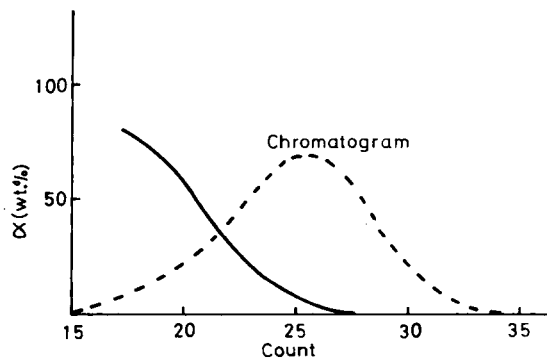


Fig. 10. Compositional variation and chromatogram of a PP-EP blend (Sim. 6).

CONCLUSIONS

The compositional variation of a copolymer as a function of elution count has been shown to follow a very complicated pattern. Molecular weight distribution affected the curve of the compositional variation. The larger the correlation coefficient, the more the compositional variation changed. The broader the compositional distribution, the more the variation changed. Further, the broader the molecular weight distribution, the less the curve changed. Accordingly, only when the molecular weight distribution and the correlation coefficient are regarded as constant does the curve reflect the compositional distribution. In other words, the compositional variation observed in dual-detector GPC may be valuable as a method for evaluating the correlation coefficient, for which no method of determining has been found. On the other hand, the GPC surely serves to detect the homopolymer component in a homopolymer-copolymer blend.

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