

Gel Permeation Chromatography of Ethylene-Propylene Copolymerization Products

TOSHIO OGAWA and TADAMI INABA, *Hirakata Plastics Laboratory, Ube Industries Ltd., Hirakata, Osaka 573, Japan*

Synopsis

A simple method to calculate average molecular weights and D ($\equiv \overline{M}_w/\overline{M}_n$) value from the GPC chromatogram of copolymerization products, especially for ethylene-propylene copolymerization products, was investigated by simulation technique. The method is based on the use of the calibration curve determined by the average ethylene content of the products. In addition to this method, the calibration curve prepared for polypropylene was also applied to determine the D value. Average molecular weights and D values were determined, with small errors, for narrow distribution samples with respect to molecular weight and chemical composition.

INTRODUCTION

Gel permeation chromatography (GPC) is very useful for characterizing high molecular weight materials, especially for the determination of molecular weight distribution of homopolymers. The chromatogram approximately corresponds to the molecular weight distribution curve in shape. In the case of copolymers, however, the GPC chromatogram does not always reflect the molecular weight distribution. We must study profoundly the meaning of GPC chromatogram of copolymers.

Polymer species are separated according to the hydrodynamic volumes of molecules. As put forward by Benoit et al.,¹ when the hydrodynamic volumes of the sample and the standard polymer are the same, the elution volumes are also equal; the molecular weight distribution of the sample can be calculated from its chromatogram by a calibration curve of molecular weight versus elution volume, which is made by the well-characterized polymer standards. However, the hydrodynamic volume of copolymers in solution depends not only on the molecular weight, but also on the comonomer content. Thus, the mixture of the polymer species having a variety of molecular weight and comonomer content is eluted at a given elution count. In this case, the number of the calibration curve cannot, in principle, be fixed by a single one for a given sample, because it must be drawn in accordance with each polymer species. When one intends to obtain statistical values, such as number- and weight-average molecular weights, some assumptions cannot help being involved in the calculation of those values from the chromatogram.

The method proposed by Benoit et al.² may be good for this purpose. That is, the molecular weight of polymer eluted at each count is determined by mea-

asuring the viscosity of the eluate and applying the universal rule.¹ The error in the molecular weights thus calculated is decreased to some extent. However, the viscosity is averaged over all polymer species eluted at the elution count. Further, a specially designed viscometer accurate to at least 0.01 sec is required, since the eluted polymer solution is considerably diluted. Thus, we studied another simple method for treating the GPC chromatogram. In studies on the determination of the molecular weight distribution, the comonomer content of the products is previously known in the majority of cases. This paper is concerned with the method of treating GPC chromatograms for polymers of known comonomer content.

Our study is limited to ethylene-propylene copolymerization products, which are composed of ethylene-propylene copolymer (EP), polypropylene (PP), and polyethylene (PE) as described in the previous paper.³ A bivariate normal distribution function and a log-normal one were assumed for the compositional and molecular weight distributions of the copolymer and the molecular weight distribution of the homopolymers, respectively. In the first place, the hypothetical GPC chromatogram of the products was made by using the universal rule proposed by Benoit et al.¹ The statistical values were calculated from the GPC chromatogram by a single calibration curve, which was determined from the ethylene content of the product. The error in these values was discussed in detail.

EXPERIMENTAL

Fractionated copolymers were subjected to the determination of compositional dependence of the relation between molecular weight and intrinsic viscosity. The fractionation experiment by column elution was carried out in the xylene-butyl cellosolve system at 130°C. The fractionation procedure was described in a previous paper.⁴ The ethylene content of the fractions was determined by Corish's method,⁵ which is based on the ratio of the intensity at 1380 cm^{-1} to that at 1460 cm^{-1} arising from the methyl group and the methyl and methylene groups, respectively, in the infrared spectrum. The intrinsic viscosity of the fractions was determined at 135°C in decalin.

The fractionation experiment for a commercially available high-impact polypropylene was carried out by column elution in the decalin-butyl carbitol system at 165°C.³ The GPC chromatogram of the polypropylene was measured by using a Shimadzu model-1A, which was mounted with a combination of four columns: 10^6 , 10^5 , 10^4 , and 10^3 Å permeability crosslinked polystyrene columns. The solvent was *o*-dichlorobenzene, the operational temperature was 135°C, and the elution rate was 1.0 ml/min. The calibration curve for the sample was prepared based on the method proposed in this paper, after the calibration curve of PP and PE was made from that of polystyrene by applying the universal rule. The details for other experimental conditions were described elsewhere.⁵

CALCULATIONS

Distribution Curve

The calibration curve varying with copolymer composition must be prepared in advance to make or treat the hypothetical GPC chromatogram of copolymers.

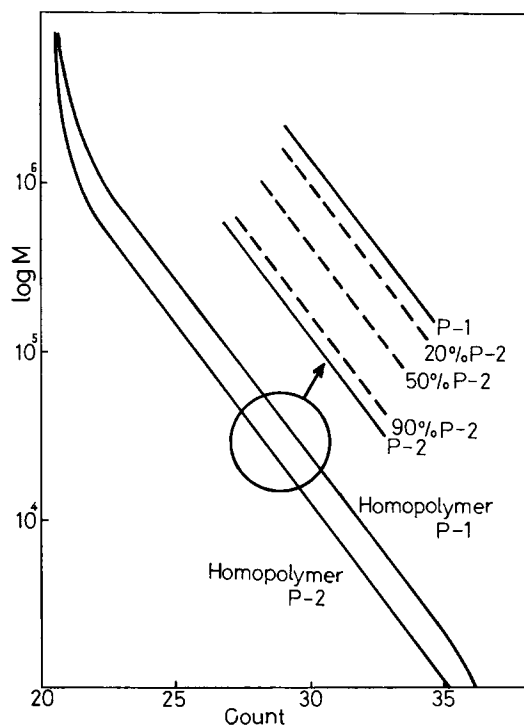


Fig. 1. Schematic calibration curves of homopolymers P-1 and P-2 and copolymers with various comonomer content.

The curve is schematically illustrated in Figure 1. Usually, the calibration curve is located between those of homopolymers composed of each monomer component. The location of the curve can be properly determined by applying the universal rule, which is in the form

$$\log [\eta]M = AV_e + B \quad (1)$$

where $[\eta]$ is the intrinsic viscosity of the copolymer eluted at the elution count V_e ; M is the molecular weight; and A and B are constants for a given set of experimental conditions and are independent of copolymer composition. The intrinsic viscosity is a function of molecular weight in the case of homopolymers. This is expressed by the Mark-Houwink equation, $[\eta] = KM^a$ (K and a are constants). Thus, the following calibration curve is derived from eq. (1):

$$\log M = \frac{AV_e}{1+a} + \frac{B - \log K}{1+a} \quad (2)$$

In the case of copolymers, however, K and a vary with copolymer composition. No general equations to express them as a function of copolymer composition are present as yet. In practical use, for EP copolymers, an empirical formula must be derived using fractionated copolymers. For choice of formula, it may be pertinent that the intrinsic viscosity of the copolymer $[\eta]_{EP}$ is correlated with those of PP ($\equiv [\eta]_{PP}$) and PE ($\equiv [\eta]_{PE}$), which have the same molecular weight as the corresponding EP copolymer. The following equations were used for this purpose: eq. (3) for PE reported by De La Cuesta⁴ and eq. (4) for PP reported by Kinsinger.⁵ These were determined in decalin at 135°C (superscript D indicates decalin).

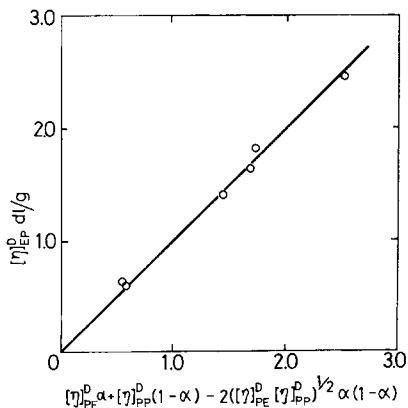


Fig. 2. Empirical relation between intrinsic viscosities of copolymers and homopolymers with same molecular weight as copolymers.

$$[\eta]_{PE}^D = 3.9 \times 10^{-4} M^{0.74} \quad (3)$$

$$[\eta]_{PP}^D = 1.10 \times 10^{-4} M^{0.80} \quad (4)$$

After a number of trials, we found that $[\eta]_{EP}$ can be expressed by the following equation as a function of comonomer content of the copolymer, $[\eta]_{PE}^D$, and $[\eta]_{PP}^D$. The result is shown in Figure 2:

$$[\eta]_{EP}^D = [\eta]_{PE}^D \alpha + [\eta]_{PP}^D (1 - \alpha) - 2([\eta]_{PE}^D [\eta]_{PP}^D)^{1/2} \alpha (1 - \alpha) \quad (5)$$

where α is the weight fraction of ethylene of the copolymer. Such an equation may be applicable in *o*-dichlorobenzene (ODCB) at the same temperature as well, since ODCB is very similar to decalin in solvent properties. $[\eta]_{EP}$ was determined under the conditions corresponding to those of GPC experiment, namely, in ODCB at 135°C. The following Mark-Houwink equations⁹ were used for PE and PP:

$$[\eta]_{PE} = 4.9 \times 10^{-4} M^{0.74} \quad (6)$$

$$[\eta]_{PP} = 1.0 \times 10^{-4} M^{0.78} \quad (7)$$

Since the value of a for PE ($\equiv a_{PE}$) was very similar to that for PP ($\equiv a_{PP}$), a for EP ($\equiv a_{EP}$) was assumed that $a_{EP} = (a_{PE} a_{PP})^{1/2}$. K for EP ($\equiv K_{EP}$) was derived from eq. (5) in the form

$$K_{EP} = K_{PE} \alpha + K_{PP} (1 - \alpha) - 2(K_{PE} K_{PP})^{1/2} \alpha (1 - \alpha) \quad (8)$$

Thus, the calibration curve can be drawn to make the hypothetical GPC chromatogram of the copolymer. Further, when the average ethylene content $\bar{\alpha}$ of the copolymer is known, the statistical values can be calculated from the GPC chromatogram by substitution of $\bar{\alpha}$ for α in eq. (8); this is the method presented in this paper.

As described previously, copolymer species having a variety of compositions are included in the fraction obtained at any elution count. The effect of composition on the chromatogram height should be taken into consideration. Generally, the chromatogram height obtained from the refractometer is not only proportional to the instantaneous concentration, but also depends on the copolymer composition. Fortunately, the refractive index increments (dn/dc) for

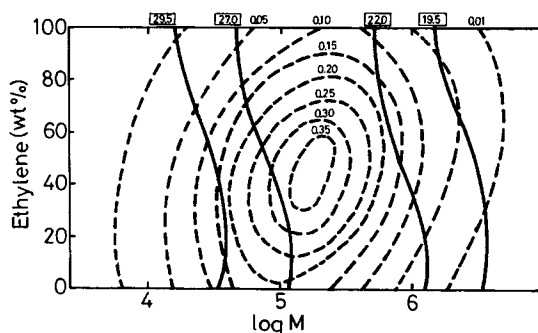


Fig. 3. Relation between molecular characteristics of copolymers and elution counts: numbers in rectangles indicate elution count; (—) copolymers and homopolymers with common elution count; (- - -) contour lines of molecular weight and compositional distributions. Numbers indicate relative weight.

PE and PP are very similar.^{10,11} The chromatogram height of the copolymer was taken as independent of copolymer composition. Further, the chromatogram height was assumed not to be influenced by the molecular weight.

Chromatogram of Products

Distributions with respect to the molecular weight and chemical composition must be assumed to make hypothetical chromatogram for the products. The following distribution function was adopted for the homopolymers according to previous papers:^{3,12}

$$W(\ln M) = \frac{1}{\beta_h \sqrt{2\pi}} \exp \left[-\frac{1}{2\beta_h^2} (\ln M - \ln M_0)^2 \right] \quad (9)$$

where $W(\ln M)$ is the weight distribution function; β_h is the standard deviation for $\ln M$ (usually β_P for PP and β_E for PE instead of β_h); and $\ln M_0$ is the logarithmic peak molecular weight in the log-normal distribution curve (usually $\ln M_P$ for PP and $\ln M_E$ for PE instead of $\ln M_0$). A bivariate normal distribution function was adopted for the distribution of the copolymer:

$$W(\ln M, \alpha) = \frac{1}{2\pi\beta_M\beta_\alpha(1-\rho^2)^{1/2}} \exp \left\{ -\frac{1}{2(1-\rho^2)} \right. \\ \left. \times \left[\frac{(\ln M - \ln M_{EP})^2}{\beta_M^2} - \frac{2\rho(\ln M - \ln M_{EP})(\alpha - \alpha_0)}{\beta_M\beta_\alpha} + \frac{(\alpha - \alpha_0)^2}{\beta_\alpha^2} \right] \right\} \quad (10)$$

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; $\ln M_{EP}$ is the peak position for the molecular weight distribution; α_0 is the peak position for the compositional distribution; β_M and β_α are the standard deviations for $\ln M$ and α , respectively; and ρ is the correlation coefficient between $\ln M$ and α .

The distribution curve of the homopolymers was divided into 55 increments in simulation. The distribution surface of the copolymer was divided into 5500 increments. Since it is practically impossible to treat these functions in the range from zero to infinity, the distribution range was limited to polymer species eluted from 13.5 to 40.5 count in the GPC chromatogram. Now we defined WPP, WEP, and WPE by

$$WPP = \sum_j f_{PP}(\ln M_j) \quad (11)$$

$$WEP = \sum_j \sum_k f_{EP}(\ln M_j, \alpha_k) \quad (12)$$

$$WPE = \sum_j f_{PE}(\ln M_j) \quad (13)$$

where $f_{PP}(\ln M_j)$, $f_{EP}(\ln M_j, \alpha_k)$, and $f_{PE}(\ln M_j)$ express the weights of j th, (j,k) th and j th increments of PP, EP, and PE components, respectively. The above functions were normalized as follows:

$$WPP + WEP + WPE = 1.0 \quad (14)$$

Obviously, the ratio of PP, EP, and PE is

$$PP:EP:PE = WPP:WEP:WPE \quad (15)$$

In practice, the weight fraction of all copolymer species eluted at a given count V_i is obtained using eq. (10) for given α and $\ln M$, and it can be expressed as $f_{EP}(\ln M_j, \alpha_k)$. Here, the other parameters in eq. (10) were adequately assumed by taking into account the experimental results. In the same manner as with f_{EP} , $f_{PE}(\ln M_j)$ is calculated from eq. (9) after calculation of $\ln M$ at $\alpha = 1.0$ by eq. (8), and $f_{PP}(\ln M_j)$ at $\alpha = 0.0$. Thus, the sum of weight fraction of the polymer species eluted at V_i is given by

$$W(V_i) = \sum_j f_{PP}(\ln M_j)_i + \sum_j \sum_k f_{EP}(\ln M_j, \alpha_k)_i + \sum_j f_{PE}(\ln M_j)_i \quad (16)$$

The hypothetical GPC chromatogram was obtained by calculating $W(V_i)$ for each 2.5-ml increment in elution volume.

The average ethylene content of the original product is given by

$$\bar{\alpha} = \sum_j \sum_k \alpha_{j,k} f_{EP}(\ln M_j, \alpha_k) + WPE \quad (17)$$

TABLE I
Assumed Characteristic Parameters for EP Copolymers

Sample	$\ln M_{EP}$	β_M	α_0	β_α	ρ
EP-1	12.0	1.25	0.435	0.365	0.25
EP-2	12.0	1.25	0.435	0.100	0.25
EP-3	12.0	1.25	0.435	0.600	0.25
EP-4	12.0	1.70	0.435	0.365	0.25
EP-5	12.0	0.80	0.435	0.365	0.25

TABLE II
Calculated Values for EP Copolymers

Sample	Ethylene wt-%	Original			α Calibration			PP Calibration
		$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	D	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	D	D
EP-1	0.468	7.85	35.6	4.54	7.39	40.1	5.43	5.23
EP-2	0.435	7.45	35.5	4.77	7.18	37.2	5.18	4.99
EP-3	0.486	7.95	35.1	4.41	7.55	39.1	5.18	5.00
EP-4	0.468	4.21	64.6	15.4	3.89	73.6	18.9	17.7
EP-5	0.468	12.2	22.6	1.86	11.6	24.9	2.14	2.10

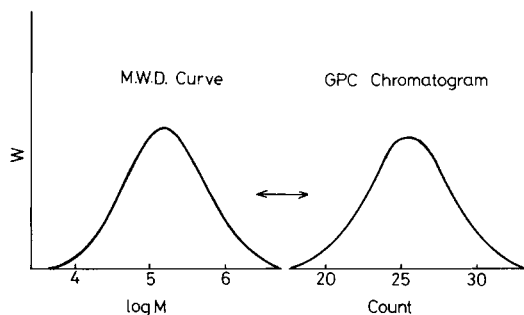


Fig. 4. Molecular weight distribution curve and GPC chromatogram for a EP copolymer.

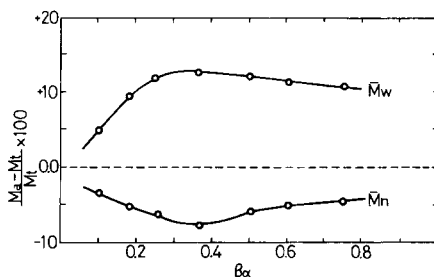


Fig. 5. Error in apparent \bar{M}_n , \bar{M}_w as a function of β_α for EP copolymers: M_t , true molecular weight; M_a , apparent molecular weight.

Thus, the apparent average molecular weights of the original products are calculated from the chromatogram obtained above and the calibration curve, which is determined from $\bar{\alpha}$ by using eqs. (8) and (12). When we use the calibration curve exclusive for polypropylene, the calculation is accomplished by setting $\alpha = 0$ in eq. (8). The so-called true average molecular weights of the original products are calculated from the above f_{PP} , f_{EP} , and f_{PE} by the conventional method.

RESULTS AND DISCUSSION

Polymer Species Eluted at a Given Count

As expressed by eq. (16), various kinds of polymer species are included in a given eluate. In the case of EP copolymers, the polymer species are different in both molecular weight and ethylene content, and their molecular weight and ethylene content were calculated using eqs. (8), (2), and (17). The results is shown in Figure 3; the polymer species having low molecular weight and ethylene content are eluted together with those having high molecular weight and low ethylene content. For example, polypropylene having $M = 10^6$ is eluted together with polyethylene having $M = 3.8 \times 10^5$. However, the shape of the curve on which the polymer species have a common elution count is almost independent of molecular weight and compositional regions, as illustrated by the solid line. In this respect, the elution behavior is different from that of solutional fractionation.⁹ Therefore, the statistical values of copolymers obtained from the GPC chromatogram are expected to be less erroneous than those obtained by solutional fractionation.

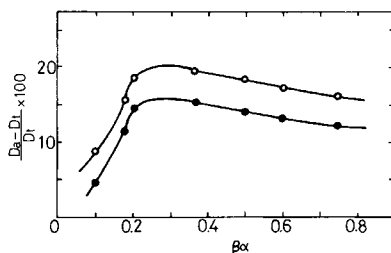


Fig. 6. Error in apparent D value as a function of β_α for EP copolymers: D_t , true D value; D_a , apparent D value.

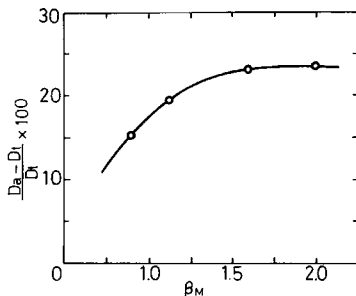


Fig. 7. Error in apparent D value as a function of β_M for EP copolymers.

Pure EP Copolymers

There are many types of copolymerization products. The pure EP copolymer type is the most representative. Characteristic parameters in eqs. (9) and (10) assumed for calculations are shown in Table I. True and apparent molecular weights and their D values were calculated using two kinds of calibration curves: one was obtained from the average ethylene content, eq. (17), of a copolymer sample, i.e., $\bar{\alpha}$ calibration, and the other was that for polypropylene, i.e., PP calibration. The calibration curve prepared for polyethylene was not used for these calculations, because the behavior was expected to be similar to that for PP calibration. The results are shown in Table II and Figures 4–7.

As shown in Figure 4, the GPC chromatogram is very similar in shape to the molecular weight distribution curve. However, the statistical values calculated numerically are sometimes very different from the corresponding true ones. Figure 5 shows that the apparent weight- and number-average molecular weights are larger than the true ones and depend on β_α of the copolymers to some extent. The error, i.e., the deviation from the true values, reaches a maximum at approximately $\beta_\alpha = 0.35$. As shown in Figure 6, a similar behavior is present for D values. Further, it is noticeable that the values obtained by PP calibration are less erroneous rather than those obtained by $\bar{\alpha}$ calibration. So long as we discuss the behavior of D values, the use of the calibration curve exclusive for polypropylene is also preferable to EP copolymers. The effect of molecular weight distribution on the apparent D values (Fig. 7) becomes considerable with increase in β_M , and is almost independent of the apparent D value in the large β_M region. Since ordinarily copolymerized EP copolymers in heptane give 0.35–0.45 for β_α and 1.0–1.5 for β_M ,⁹ the error in the statistical values is +15–20%, while in fractionated samples it may be within 10%. Thus, the GPC method is

definitely useful for characterizing the copolymer fractions having narrow molecular weight and compositional distributions.

PP-PE Blend

This blend belongs to an extreme case among copolymerization products. Its behavior in GPC is important for considering complicated copolymerization products. The molecular weight distribution curve and GPC chromatogram for the blend composed of homopolymers showing broad molecular weight distribution seemingly have a similar shape. However, the result of numerical calculation reveals that this blend has peculiar characteristics in the behavior of apparent \bar{M}_n , \bar{M}_w , and D values. The results are shown in Tables III and IV and Figures 8-10. Figure 8 demonstrates that the apparent \bar{M}_n and \bar{M}_w largely depend on the difference between two peak molecular weights of component homopolymers. Namely, when the peak position of the PE component is smaller than that of the PP component, the apparent \bar{M}_n is larger than the true one. The apparent \bar{M}_n approaches the true one with an increase of \bar{M}_n ; and in $M_P > M_E$, this tendency is reversed. On the other hand, the behavior of the apparent \bar{M}_w is completely contrary to that of the apparent \bar{M}_n . As shown in Figure 9, the apparent D value coincides with the true one when $M_P \simeq M_E$. The apparent D value is different from the true one when the difference between M_P and M_E is large. Namely, the relation between the true and apparent D values can be classified into two categories; Figure 10 shows this situation schematically.

TABLE III
Characteristic Parameters for Components in PP-PE Blend

Sample	PP		PE		Weight ratios	
	$\ln M_P$	β_P	$\ln M_E$	β_E	PP	PE
PPPE-1	12.0	1.25	9.0	1.25	0.50	0.50
PPPE-2	12.0	1.25	11.0	1.25	0.50	0.50
PPPE-3	12.0	1.25	12.0	1.25	0.50	0.50
PPPE-4	12.0	1.25	13.0	1.25	0.50	0.50
PPPE-5	12.0	1.25	15.0	1.25	0.50	0.50
PPPE-6	12.0	1.25	11.0	1.25	0.70	0.30
PPPE-7	12.0	1.25	11.0	1.25	0.30	0.70

TABLE IV
Calculated Values for PP-PE Blend

Sample	Original			$\bar{\alpha}$ Calibration			PP Calibration
	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	D	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	D	D
PPPE-1	0.72	18.8	26.2	1.08	15.9	14.7	13.9
PPPE-2	4.03	24.4	6.06	4.95	24.4	4.93	4.75
PPPE-3	7.45	35.5	4.77	7.79	41.0	5.26	5.07
PPPE-4	10.8	65.0	6.00	9.90	84.6	8.55	8.16
PPPE-5	13.8	276	20.0	11.4	395	34.7	32.4
PPPE-6	4.94	28.9	5.84	6.65	33.1	4.97	4.79
PPPE-7	3.40	19.9	5.87	3.66	17.7	4.84	4.67

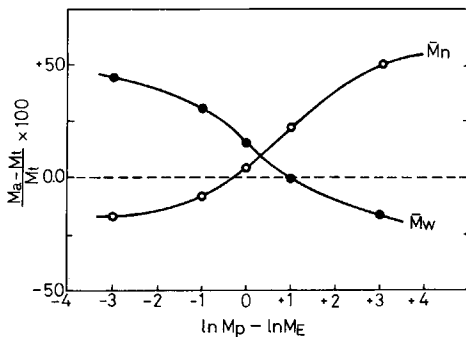


Fig. 8. Error in apparent \bar{M}_n and \bar{M}_w as a function of $(\ln M_P - \ln M_E)$ of PP-PE blend. PP:PE = 50:50 (wt): M_P , peak molecular weight of PP component; M_E , peak molecular weight of PE component.

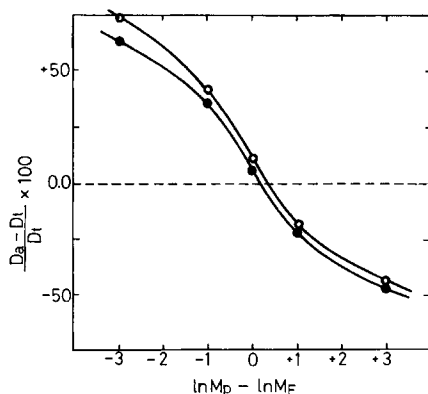


Fig. 9. Error in apparent D value as a function of $(\ln M_P - \ln M_E)$ of PP-PE blend. PP:PE = 50:50 (wt): (—○—) $\bar{\alpha}$ calibration; (—●—) PP calibration.

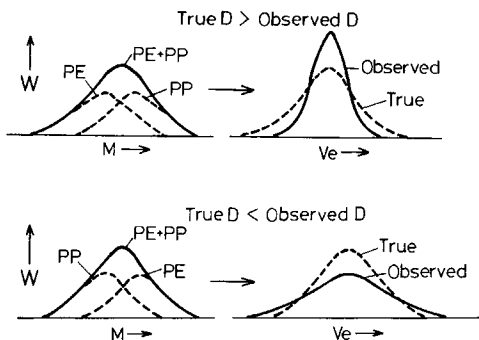


Fig. 10. Schematic representation for relations between peak molecular weights of component homopolymers and apparent D values.

Other Blend Types

PP-EP-PE, PP-EP, and EP-PE blends are classified into the other blend types. We understand the GPC behavior as overlapping that of EP copolymers and PP-PE blend; and, therefore, the behavior is fundamentally the same as shown in Figure 10. Characteristic parameters assumed for calculation are

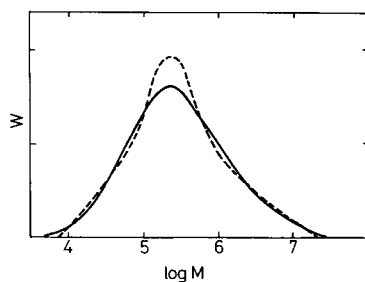


Fig. 11. Calculated and apparent molecular weight distribution curve D for a commercial polymer: (---) molecular weight distribution curve obtained from GPC chromatogram, $\bar{M}_n = 1.17 \times 10^5$, $\bar{M}_w = 9.52 \times 10^5$; (—) molecular weight distribution curve calculated based on the column fractionation data. PP:EP = 80:20 (wt), $\bar{M}_n = 9.97 \times 10^4$, $\bar{M}_w = 9.38 \times 10^5$. PP: $\ln M_P = 12.0$, $\beta_P = 1.25$; EP: $\ln M_{EP} = 13.5$, $\beta_M = 1.25$, $\beta_\alpha = 0.10$, $\alpha_0 = 0.85$, $\rho = 0.25$.

shown in Table V, and the results are shown in Table VI. The error in the calculated values is expected to be within 10% since the average molecular weights of component polymers have similar values. GPC measurement for broad molecular weight distribution polymer leads to large error in D values due to the fluctuation of the baseline of chromatogram, even though we deal with homopolymers.¹³ Therefore, the error due to the assumption for the calibration curve is not worthy of mention in the case of these blend types.

Comparison of Simulated Curve with Experimental Curve

The result of solutional fractionation which was performed previously revealed that a commercially available high-impact polypropylene was composed of polypropylene homopolymer and ethylene-rich EP copolymer.³ The homopolymer content resembled commercial polypropylenes in molecular characteristics, such as molecular weight and its distribution. So, ordinary values for polypropylenes were assumed for β_P and M_P . Appropriate values were also

TABLE V
Characteristic Parameters for Components in PP-EP-PE, PP-EP, and EP-PE Blends

Sample	PP		EP				PE		Weight ratios			
	$\ln M_P$	β_P	$\ln M_{EP}$	β_M	α_0	β_α	ρ	$\ln M_E$	β_E	PP	EP	PE
PEM-1	12.0	1.25	12.0	1.25	0.435	0.365	0.25	11.0	1.25	0.4	0.2	0.4
PEM-2	12.0	1.25	12.0	1.25	0.435	0.365	0.25	11.0	1.25	0.2	0.6	0.2
PEM-3	12.0	1.25	12.0	1.25	0.435	0.365	0.25	—	—	0.6	0.4	0.0
PEM-4	—	—	12.0	1.25	0.435	0.365	0.25	11.0	1.25	0.0	0.4	0.6

TABLE VI
Calculated Values for PP-EP-PE, PP-EP, and EP-PE Blends

Sample	Ethylene wt-%	Original			$\bar{\alpha}$ Calibration			PP Calibration
		$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	D	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	D	D
PEM-1	0.498	4.39	26.3	5.99	5.32	27.4	5.16	4.98
PEM-2	0.483	5.51	30.6	5.56	6.20	33.7	5.43	5.22
PEM-3	0.187	7.59	35.6	4.69	8.72	45.4	5.20	5.01
PEM-4	0.794	3.57	21.1	5.91	3.62	19.4	5.35	5.15

estimated for β_M , M_{EP} , and so on, from viscosity measurement of the EP copolymer component. Thus, we prepared the molecular weight distribution curve from the hypothetical GPC chromatogram. On the other hand, the distribution curve was also obtained from the GPC chromatogram which was determined by experiment. The results are shown in Figure 11. These curves are very much in agreement with each other. Therefore, the results discussed above should be fully taken into consideration when we deal with GPC chromatograms obtained from these copolymerization products.

CONCLUSIONS

A method for treating GPC chromatograms obtained from ethylene-propylene copolymerization products was investigated by simulation technique. The most important problem was how to convert elution count to molecular weight. In this study, the calibration curve to use for this purpose was determined by the average ethylene content of samples. \bar{M}_n , \bar{M}_w , and D values were obtained for broad distribution copolymers in molecular weight and chemical composition, and these included an error of 15–20%. However, in the case of narrow distribution fractions such as those obtained by solutional fractionation, the error was within 10%. The GPC method is highly useful in this case. In the case of PP-PE blends, the deviation of the apparent values from the true ones became small with decrease in difference between two peak molecular weights. The apparent values are valuable under this special condition. The behaviors for PP-EP-PE, PE-EP, and PP-PE blends are more complicated than for PE-PP blends. The behavior can be fundamentally understood as an overlapping of that of EP copolymer and PP-PE blend. As far as the D values are concerned, the use of the calibration curve for polypropylene as well as the above one is also valuable to the copolymerization products.

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