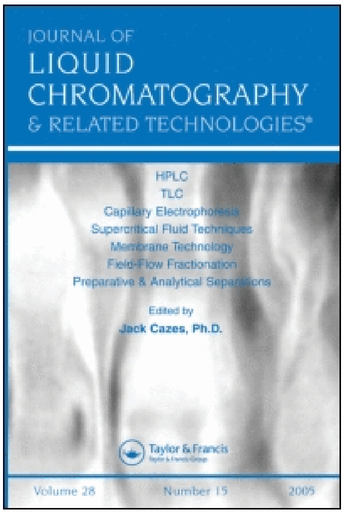

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A METHOD FOR DETERMINING MOLECULAR WEIGHT OF COPOLYMERS BY GPC

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ABSTRACT

In this paper, a method is described that makes easier application of Chang's method for the determination of molecular weight of copolymers by GPC. Determinations of molecular weight of EP-copolymers have been performed with this method. The values of the resultant weight- and number-average molecular weight are rather close to the experimental data, and the values of intrinsic viscosity $[\eta]_c$ are close to the values measured with Ubbelodhe viscometers $[\eta]_d$.

INTRODUCTION

Gel permeation chromatography (GPC) experiments have shown that the universal calibration method proposed by Benoit[1] is valid for widely different polymer species. One, therefore, can calculate weight- and number-average molecular weight (MW) and molecular weight distribution (MWD) from the universal calibration curve if the Mark-Houwink relation, $[\eta] = k\ M^{\alpha}$, for the particular polymer-solvent pair is known. However, in the case of copolymer, the monomer contents have effects on the values of k and α, especially on the former.[2] Thus, it presents difficulty to GPC determination of MW and MWD of the copolymer. So far, a satisfactory method of solving such a problem is yet to be found for copolymers, except for ethylene-propylene copolymer (EP-copolymer).[2, 3]

Chang[4] has indicated, theoretically, that experimental elution volume can be converted to MW of linear block copolymer by use of the calibration curve for homopolymers, i.e., when the calibration curve of the homopolymer A is parallel to that of the homopolymer B, the molecular weight of the copolymer composed of A and B can be expressed by: $M_C = M_A' /[1+ (r-1)W_2]$, where r is a constant.

In practice, however, GPC calibration curves of different homopolymers are generally not parallel to each other and r is a variable, thus affecting its application. We have solved this problem, as presented in this paper, and have used it in the determination of MW and MWD of EP-copolymers.

The values of the resultant weight- and number-average MW are rather close to the experimental data, and those of intrinsic viscosity $[\eta]_c$ are close to those measured with the Ubbelodhe viscometers $[\eta]_d$.

EXPERIMENTAL

Materials

EP-copolymer: Ethylene and propylene copolymerization products were prepared with vanadium catalyst and purified by extraction with methanol. Reagent: o-Dichlorobenzene (ODCB).

Infrared Spectrometer

The instrument employed for analyzing the propylene content of the EP-copolymer was an infrared spectrometer, Model SP-200.

GPC

The instrument employed for measuring the GPC data was a Waters GPC Model 200 with styragel-packed columns.

The column arrangement was of four-column assembly (10E3, 10E4, 10E6, and 10E7 Angstroms).

To minimize the effect of solution concentration, the columns were connected in series of small to large permeation limit. The determination of GPC data was made at 135ºC. ODCB was used as solvent; the flow rate was 1mL/min.

Chang's Method[4]

Based on the universal calibration curve and the Mark-Houwink equation, the following relationships can be derived:

$$\log M_A = [f(v) - \log k_A] / (1+\alpha_A) \qquad (1)$$

$$\log M_B = [f(v) - \log k_B] / (1+\alpha_B) \qquad (2)$$

Subtracting equation (2) from equation (1), we have

$$\log (M_A / M_B) = [1/(1+\alpha_A)]\,[f(v) - \log k_A] - [1/(1+\alpha_B)]\,[f(v) - \log k_B]$$

When $\alpha_A = \alpha_B = \alpha$, we have

$$\log (M_A / M_B) = \log (k_B / k_A)^{[1/(1+\alpha)]}$$

$$M_A / M_B = (k_B / k_A)^{[1/(1+\alpha)]} = r \qquad (3)$$

$$M_A = r\,M_B \qquad (4)$$

Where k and α are the parameters in Mark-Houwink equation; M_A and M_B are the molecular weight of A and B homopolymers, respectively, at elution volume v; f(v) is a universal calibration function, i.e., $\log [\eta]M = a + bv + cv^2 = f(v)$, which can be obtained from calibrating the columns with standards.

Equation (4) shows that M_A and rM_B are equivalent at the same elution volume. Let us assume that this equivalence can be applied to the component segments A and B in a copolymer. That is to say, a homopolymer with molecular weight M_A' will have the same elution volume as a copolymer $M_1 + M_2$ when $M_A' = M_1 + rM_2$, where M_1 and M_2 are the molecular weights of the segments or blocks of monomers A and B, respectively.

Since the MW of the copolymer $M_C = M_1 + M_2$, $M_1 = W_1 M_C$ and $M_2 = W_2 M_C$, it follows that

$$M_C = M_A' / [1 + (r-1)W_2] \qquad (5)$$

where W_2 is the weight fraction of monomer B in the copolymer M_C.

Thus, the molecular weight M_C of the copolymer can be calculated from equation (5) after evaluating the value of r from equation (3), calculating the value of M_A' from equation (1) for homopolymer, and determining the value of W_2 by IR or UV spectroscopy.

Procedures for Obtaining $\alpha_A = \alpha_B = \alpha$

It can be known from our previous work[2, 5] that the relationships between log k and α show good linearity (ODCB, 135ºC for polypropylene (PP), polyethylene(PE), polystyrene(PS), and EP-copolymer(EP), etc. Generally, however, any pair of α and k values obtained from these relationships can meet the requirements of experiment only when they fall within the particular ranges of the individual α values as noted below. Examples are shown below:

$$\text{PP:}\quad \log k_{PP} = 0.403 - 5.682\alpha_{PP} \tag{6}$$
$$0.695 \leq \alpha_{PP} \leq 0.755 \quad \text{(ODCB, 135ºC)}$$

$$\text{PE:}\quad \log k_{PE} = -0.610 - 3.876\alpha_{PE} \tag{7}$$
$$0.705 \leq \alpha_{PE} \leq 0.74 \quad \text{(ODCB, 135ºC)}$$

$$\text{PS:}\quad \log k_{PS} = 0.3757 - 6.03\alpha_{PS} \tag{8}$$
$$0.70 \leq \alpha_{PS} \leq 0.76 \quad \text{(ODCB, 135ºC)}$$

$$\text{EP:}\quad \log k_{EP} = \log (5.755 - 4.65C_3) - 5.75\alpha_{EP} \tag{9}$$
$$0.73 \leq \alpha_{EP} \leq 0.755 \quad \text{(ODCB, 135ºC)}$$

In equation (9), C_3 is the mole fraction of propylene.[2] The relative error of $[\eta]$ calculated from the above relationships are below 6%, 4%, 3%, and 7%, respectively, as compared with that of $[\eta]_d$ determined with Ubbelodhe viscometers. The viscosity-average molecular weights (M_ϖ) of polystyrene standards agree well with those of samples supplied by Pressure Chemical Co., and the weight- and number-average molecular weights of EP-copolymer also agree well with those measured with low angle laser light scattering KMX-6 and Knauer membrane osmometer, respectively. Moreover, these relationships are applicable to a wide range of molecular weights and molecular weight distributions of polymers.

For example, equation (9) can be applied to EP-copolymers having a weight-average molecular weight of 10^4 to 10^6, a polydispersity index M_Ω/M_ν of 1.7 -12.9, a propylene content of 30 -55 mole %, and a GPC curve with either single peak or double peaks.[2, 5]

As can be seen from the above equations, as the ranges of the individual α values meeting the requirement of the experiment are overlapping, one can take values of α from among the overlapping portions to calculate the corresponding k values. If the relationship between log k and α is unknown for a particular polymer-solvent pair, it can be determined with the method previously proposed by the authors.[5]

RESULTS AND DISCUSSION

Molecular weights for EP-copolymers (ODCB, 135ºC) have been determined with the above-mentioned method. The procedure is as follows. Take 0.73 as the α value for PP- and PE- ODCB pairs (see the range of α values noted under equations (6) and (7) above), and substitute $\alpha = 0.73$ into equations (6) and (7), respectively, and calculate the values for k_{PP} and k_{PE}.

The results obtained are as follows:

$k_{PP} = 1.80x10^{-4}$, $\alpha_{PP} = \alpha = 0.73$

$k_{PE} = 3.635x10^{-4}$, $\alpha_{PE} = \alpha = 0.73$

Now, let PP and PE represent homopolymers A and B in equations (1) and (3), respectively, i.e., $k_{PP} = k_A$, $k_{PE} = k_B$, $\alpha_{PP} = \alpha_A$, $\alpha_{PE} = \alpha_B$, $M_{PP} = M_A$, and $M_{PE} = M_B$. Substituting the values of k_{PP} and k_{PE} and $\alpha = 0.73$ into equation (3), we have

$r = (k_B/ k_A)^{[1/(1+\alpha)]}$

$= (k_{PE}/ k_{PP})^{[1/(1+0.73)]}$

$= (3.635\times10^{-4}/1.80\times10^{-4})^{1/1.73}$ and, therefore

$r = 1.50$

Finally, substituting the value of r into equation (5) and rearranging, we have

$$M_C = M_A'/(1+ 0.5W_2) \qquad (10)$$

where M_A' is the molecular weight of polypropylene M_{PP}, and can be calculated by use of equation (1), in which $M_A= M_A'= M_{PP}$, $k_A = k_{PP} =1.80\times10^{-4}$, $\alpha_A = \alpha_{PP} = 0.73$; W_2 is the weight fraction of ethylene for EP-copolymer, which can be determined with the IR detector. Then, the molecular weight of EP-copolymer M_C can be calculated by use of equation (10).

The molecular weights calculated by use of equation (10) and empirical formula (9), previously proposed by the authors,[2] from the universal calibration curve are tabulated in Table 1.

Since on-line values of W_2 are unavailable and the samples have narrow MWDs, in equation (10) we use the average weight fraction of ethylene to substitute for W_2.

Table 1

Comparison of Results Obtained by Two Different Methods

No.	C_3 Mole Fract.	M_2 Wt. Fract.	Equation (9)[2] Mw x 10^{-4}	Mw/Mn	Equation (10) Mw x 10^{-4}	Mw/Mn	$[\eta]_\chi$	$[\eta]_\delta$	$\frac{[\eta]_d - [\eta]_c}{[\eta]_d}$ %
S-05	0.391	0.509	24.1	3.66	23.3	3.66	1.93	2.11	8.49
S-05-1	0.453	0.446	5.01	1.47	4.80	1.47	0.632	0.626	-0.96
S-05-2	0.415	0.484	11.0	1.50	10.5	1.50	1.15	1.06	-8.41
S-05-3	0.282	0.629	65.8	1.57	65.1	1.57	4.75	4.80	1.04
S-63	0.376	0.525	17.6	3.62	17.3	3.59	1.65	1.81	8.70
S-63-1	0.425	0.474	2.21	1.49	2.12	1.49	0.353	0.347	-1.83
S-63-2	0.420	0.479	7.14	1.44	6.85	1.44	0.842	0.906	7.04
S-63-3	0.380	0.521	11.2	1.54	10.6	1.54	1.18	1.19	0.86
S-63-4	0.331	0.574	39.9	1.73	39.2	1.73	3.18	3.12	-1.99
ZK-53	0.363	0.539	45.4	6.29	44.1	6.29	2.97	3.07	3.11

It can be seen, from Table 1 that the MW of EP-copolymers determined with GPC on the basis of the foregoing method are rather close to those obtained with the empirical formula,[2] and the values of intrinsic viscosity $[\eta]_c$ are close to the values measured by Ubbelodhe viscometers $[\eta]_d$. That is to say, the method described in this paper possesses higher precision.

On the other hand, analyses of EP-copolymers performed with DSC and X-ray show that sample S-63 and its fractions [S-63-(1-4)] contain some polyethylene type crystals, while other samples do not contain any crystals.[6] This implies that the former are partial ethylene block EP-copolymers, and the latter are random EP-copolymers. That is to say, the method reported in this paper also applies to block and random copolymers as well.

It should be noted, however, that in order to analyze the composition of copolymer on-line, the GPC instrument should be additionally equipped with a UV or an IR detector in addition to the differential refractometer.[7]

CONCLUSIONS

For polymers in a common solvent system, values of α can be taken to calculate the corresponding k values. For polymers A and B, when $\alpha_A = \alpha_B = \alpha$, then the ratio r of the molecular weights M_A and M_B is a constant (at the same elution volume), i.e., $r = (k_B/k_A)^{[1/(1+\alpha)]}$. Thus, the molecular weight of any copolymer can be more easily determined with GPC from the universal calibration curve, employing Chang's equation $M_C = M_A' /[1+ (r-1)W_2]$. Moreover, results show high precision on verifying Chang's method with GPC data for EP copolymers.

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