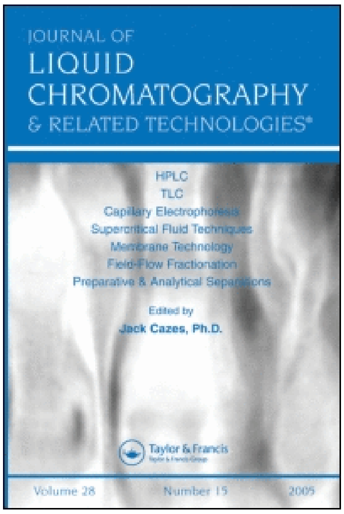

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Ke-Qiang Wang[a]; Shi-Yu Zhang[a]; Jia Xu[a]; Yang Li[a]
[a] Research Institute of Chemical Industry He Ping Li, Beijing, People's Republic of China

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GPC ANALYSIS OF ETHYLENE-PROPYLENE COPOLYMERS*

Ke-Qiang Wang, Shi-Yu Zhang,
Jia Xu, Yang Li
Research Institute of Chemical Industry
He Ping Li, Beijing,
People's Republic of China

ABSTRACT

Determination of the values of K and alpha of the Mark-Houwink equation by applying the universal calibration curve and using a trial and error method was performed with samples of ethylene - propylene copolymers with broad MW distributions and different intrinsic viscosities. The following equation was obtained, correlating K with composition of ethylene-propylene copolymer and alpha:

$$\log K = \log(5.755-4.65C3) - 5.75 \text{ alpha}$$

where C3 is the mole percent of propylene in the copolymer, alpha is a value within the range of 0.73 and 0.755 (i.e., K and alpha are dependent upon each other). Values of intrinsic viscosity or molecular weight determined by means of the universal calibration curve agree well with those determined by solution viscosity, light scattering, and osmometry.

INTRODUCTION

GPC experiments have shown that the universal calibration method proposed by Benoit (1) is valid for

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widely different species. One, therefore, can calculate the weight- and number-average molecular weights and molecular weight distribution (MWD) from the universal calibration curve if the Mark-Houwink relationship for the particular polymer-solvent pair is known. However, in the case of ethylene-propylene copolymer, the monomer contents have an effect on the values of K and alpha, especially the former (2,3) . Thus, it is difficult to determine, by GPC, the molecular weight and MWD of the copolymer. So far, a satisfactory method for solving this problem is yet to be found.

In our experiments, a number of ethylene - propylene copolymers, having broad MWD's and different intrinsic viscosities, were used as calibration samples. The intrinsic viscosity and GPC chromatogram for each sample were measured in o-dichlorobenzene (ODCB) at 135 deg.C. and the values of K and alpha were determined by the universal calibration and trial and error method. However, the column peak spreading effect was ignored.

The experimental data were treated by applying regression analysis and the following relatiuonship was set up:

$$\log K = \log(5.755 - 4.65\ C3) - 5.75\alpha$$

where C3 is the mole percent of propylene in the copolymer; alpha can take any value between 0.73 and 0.755.

EXPERIMENTAL

Materials:

Ethylene and propylene copolymerization products, prepared by vanadium catalysis, were used as samples; they were purified by extraction with methanol.

The propylene contents of the samples (C3-mole%) were 50.8 +/- 1% (six samples), 45.3 +/- 1.5% (six samples), 40.1 +/- 1% four samples), and 36 +/- 1% (six samples), respectively.

The solvent employed for all experiments described in this paper was distilled ODCB.

Intrinsic Viscosity:

Intrinsic viscosities were measured in ODCB at 135 deg.C. using Ubbelohde viscometers with flow times greater than 100 sec. For some of the data, the required extrapolation to zero concentration was made from measurements at five concentrations; for others, however, only a single measurement was made and Cheng's equation was employed (4) for calculating the intrinsic viscosity. The results have shown that, for the same sample, there was not much difference between the two methods.

Gel Permeation Chromatography:

The instrument employed for measuring the GPC data was a Waters Model 200 GPC, with Styragel-packed columns. Most of the measurements were made with a five-column assembly (10E7, 10E6, 10E5, 10E4, and 10E3 Angstroms, respectively). However, some measurements were done with a four-column assembly (10E7, 10E6, 10E4, and 10E3). ODCB was used as solvent; the flow rate was 1 ml/min.

In order to minimize error, the copolymer solution, after determination of intrinsic viscosity, was divided into four parts, which were then separately injected into the GPC instrument. Thus, four GPC chromatograms were obtained from each sample. These were then individually normalized, and the average value

$$1/4 \sum_{j=1}^{4} (H_i / \sum_{i=1}^{n} H_i)_j = W_i$$

of the normalized height of the i-th count was taken.

$$(H_i / \Sigma H_i)$$

Methods:

Weiss (5) has proposed that the K and alpha of the Mark-Houwink relationship may be determined by using two polymers having relatively broad MWD with different intrinsic viscosities. The procedure is as follows:

$$J_i = [\eta]_i M_i \qquad (1)$$

$$[\eta]_i = KM_i^{\alpha} = K^{1/1+\alpha} J_i^{\alpha/1+\alpha} \qquad (2)$$

$$[\eta] = K^{1/1+\alpha} \Sigma W_i \, J_i^{\alpha/1+\alpha} \qquad (3)$$

$$\frac{[\eta]_1}{[\eta]_2} = \frac{\sum_i W_{1i} \, J_i^{\alpha/1+\alpha}}{\sum_i W_{2i} \, J_i^{\alpha/1+\alpha}} \qquad (4)$$

where wi and $[\eta]_i$ are, respectively, the weight-fraction and the intrinsic viscosity of the i-th species; $[\eta]$ is the intrinsic viscosity of the polymer. Therefore, using wi's from GPC, Ji's from the universal calibration curve, and $[\eta]$ determined by viscometry, one can solve for alpha and K from equations (4) and (3), respectively, and ultimately calculate weight- and number-average molecular weights according to the definition for molecular weight of polymer.

In applying Weiss's method to ethylene - propylene copolymers, besides errors inherent in the determination of intrinsic viscosity and the GPC chromatogram, compositional distribution might also introduce errors. Our experiments have shown that the calculated alpha and K from data based on samples 1 and 2 might not be appropriate for other samples. Therefore, we employ samples having the same compositions but different intrinsic viscosities for determinig alpha and K by means of a trial and error method. There are two steps in this procedure. In the first step, let

$$\left| \left(\frac{[\eta]_1}{[\eta]_2} - \frac{\sum_i W_{1i} \, J_i^{\alpha/1+\alpha}}{\sum_i W_{2i} \, J_i^{\alpha/1+\alpha}} \right) \cdot \frac{[\eta]_2}{[\eta]_1} \times 100 \right| \leq u (0 < u \leq 7) \qquad (5)$$

After determination of the intrinsic viscosity, the GPC chromatogram and the universal calibration curve, using polystyrene standards (the intrinsic viscosity - molecular weight relationship of polystyrene in ODCB at 135 deg.C. is $[\eta] = 1.38 \times 10^{-4} M^{0.70}$), the α values (denoted as α_0) may be calculated from equation (5) with given values of u by an iteration method with a computer. Since molecular chains of ethylene - propylene copolymer are flexible, and ODCB is a good solvent, the range of iteration for alpha values may be set as 0.59 - 0.9. By substituting α_0 and the intrinsic viscosity as well as the GPC data of sample 1 into equation (3), K_1 can be calculated. Similarly, K_2 for sample 2 may be obtained. Since α_0

is obtained from the inequality (5), K_1 and K_2 are not equal. Take K_3 as the average of K_1 and K_2. Apply α_0 and the experimental data of sample 3 to determine K_4 from equation (3). Take the average of K_1, K_2, and K_4 as K_5. Calculate, by means of the iteration method, the value of alpha (denoted as α_1) from equation (6):

$$\left| ([\eta]_3 - K_5^{1/1+\alpha} \Sigma W_{3i} J_i^{\alpha/1+\alpha} \Big/ [\eta]_3 \times 100 \right| \leqslant z \qquad (6)$$

$$(0 < z \leqslant 7)$$

Substitute α_1 and experimental data of samples 1, 2, and 3, respectively, into equation (3) to calculate K_6, K_7, and K_8. Take K_9 as the average of these three values. Take the average of α_0 and α_1 to obtain α_2 and, subsequently, K_{10}, K_{11}, K_{12} and their average value K_{13}. Thus, 13 groups of K and alpha

(α_0, K_1, K_2, K_3, K_4, and K_5; α_1, K_6, K_7, K_8, and K_9;
α_2, K_{10}, K_{11}, K_{12}, and K_{13})

were obtained. Finally, using the corresponding values for K and alpha of each group, and applying equation (3), the intrinsic viscosity $[\eta]$ of each sample having the same composition may be calculated. Then, the relative error between $[\eta]$ and the measured value of the intrinsic viscosity $[\eta]$ is calculated and is used as a criterion for the preliminary selection of K and alpha.

Assume new values for u and z, repeat the foregoing procedure until the accumulation of sufficient data.

Exchange the experimental data of sample 3 in equation (6) with that of sample 1 or sample 2 in equation (5), or, alternatively, substitute the experimental data of another sample of the same composition for the corresponding ones in (5) or (6). Calculate as before using a computer. The flow diagram for the iteration calculation is presented in Figure 1.

The result of the above treatment has shown that, within the range of allowance error of intrinsic viscosity, most of the ethylene - propylene copolymers of different composition have the same value of alpha. It has been reported in the literature that alpha is independent of composition (2,3). Therefore, we treated the experimental data with respect to alpha and thereby simplified the situation. Thus, with alpha within the range of 0.73 - 0.78, we obtained 11 groups of alpha's and the corresponding K's, K being dependent upon composition. The group of experimental data with alpha value of 0.745 are tabulated in Table I.

After having obtained 11 groups of values of K and alpha, we proceeded to apply a trial and error approach to determine the optimal value of K corresponding to each value of alpha. Again, take alpha = 0.745 as an

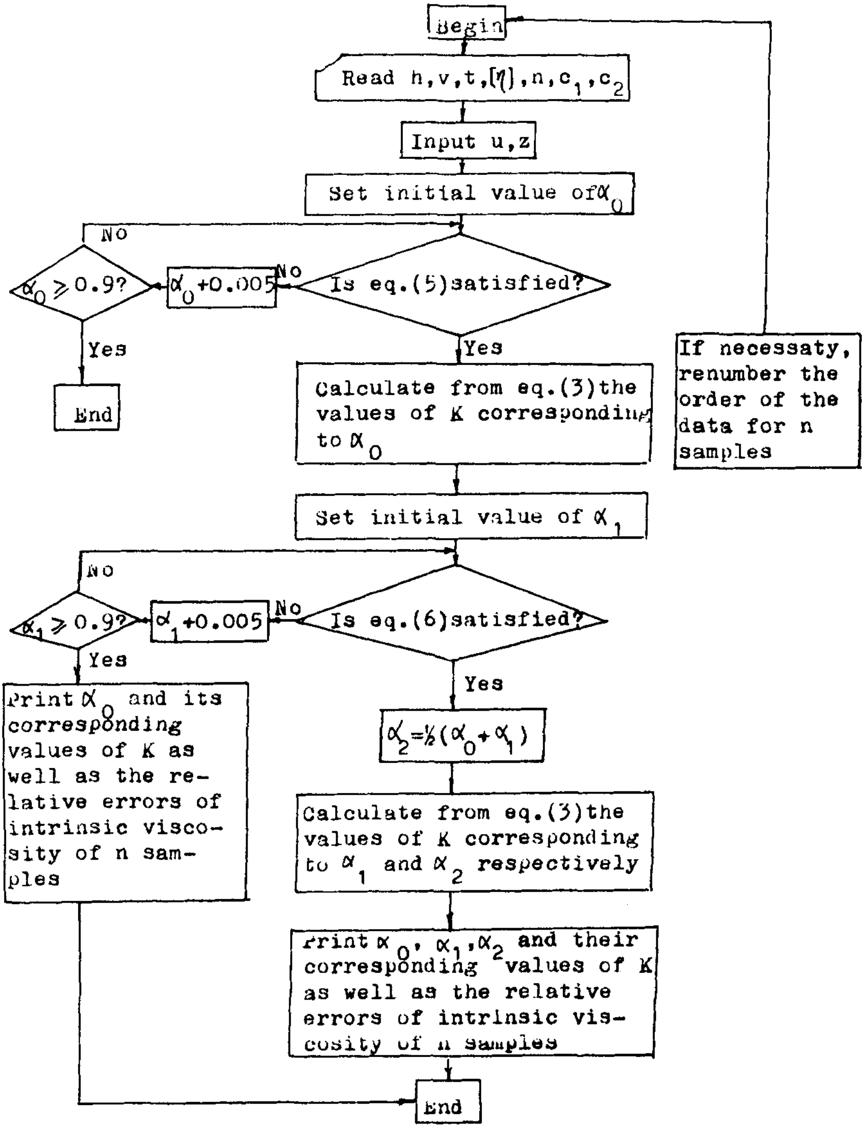

FIGURE 1

Flow Diagram of Iterative Calculation. h = height of interval from Baseline; v = elution volume (count number; t = total count intervals; $[\eta]$ = intrinsic viscosity of sample; n = number of samples; c_1 and c_2 are the intercept and slope of the universal calibration curve.

TABLE I

Composition of Ethylene-Propylene Coploymers and Values of K Corresponding to α= 0.745

Composition of C_3, mol%	K x 10^4
50.8	1.72 - 1.90
45.3	1.76 - 1.97
40.1	1.97 - 2.07
36.0	2.03 - 2.15

example. When the C3 content of the copolymer is 50.8%, the corresponding value of K falls between 1.72 - 1.90. If alpha remains constant, the value of K increases by constant steps. Calculate the relative error of the intrinsic viscosity of each sample and the standard deviation

$$\sigma = \sqrt{\sum_i ([\eta]_c - [\eta]_d)_i^2 \ / \ n}$$

where n is the number of samples. The K value is then determined on the basis of the minimum value of σ ; in the case of successive appearance of two equal values of minimum σ , the K-value should be determined by reference to all the corresponding relative errors of the intrinsic viscosities of the various samples of that particular composition. The same procedure was employed in the treatment of experimental data with the C3 contents of the polymer samples equal to 45.3%, 40.1%, and 36%, respectively.

The remaining 10 groups of K and alpha values were treated with the same procedure; the results are tabulated in Table II.

RESULTS AND DISCUSSION

It can be seen from Table II that, when alpha is greater than 0.75, the standard deviation of the intrinsic viscosities of the ethylene - propylene copolymers having different compositions tend to increase with alpha. For samples having compositions of 50.8% and 36%, minimum values of σ , corresponding to alpha values between 0.73 - 0.755, have lower values than the rest. The relative errors of intrinsic viscosities calculated from different groups of values of K and alpha show little deviation. It may be inferred from Table III that most of the intrinsic viscosity deviations for the group of data with alpha = 0.745 as an example are below 7% and that the determined values of K and alpha are applicable to all ethylene - propylene copolymers having molecular weights of 10E5 to 10E6, MWD'S (Mw/Mn) of 3.2 to 12.9, and GPC chromatograms of either single peak or double peaks.

TABLE II
Optimal Value of K and Stad. Deviation Corresponding to Composition of Ethylene-Propylene Coploymer and Alpha.

Comp.		Alpha										
C_3-mol%	K,σ	0.73	0.735	0.74	0.745	0.75	0.755	0.76	0.765	0.77	0.775	0.78
50.8	$Kx10^4$	2.20	2.02	1.94	1.78-1.80	1.66-1.68	1.56	1.46	1.34-1.36	1.28	1.18	1.08-1.10
	σ	0.196	0.194	0.197	0.197	0.198	0.199	0.199	0.200	0.201	0.202	0.204
45.3	$Kx10^4$	2.26-2.28	2.12	1.98	1.86	1.74	1.62	1.52	1.42	1.32	1.24	1.14
	σ	0.090	0.092	0.095	0.099	0.103	0.110	0.110	0.114	0.116	0.121	0.123
40.1	$Kx10^4$	2.48-2.50	2.32-2.34	2.16	2.04	1.90	1.78	1.66	1.56	1.46	1.36	1.26-1.28
	σ	0.058	0.058	0.059	0.058	0.059	0.059	0.059	0.060	0.060	0.060	0.062
36.0	$Kx10^4$	2.56-2.58	2.38-2.40	2.22	2.10	1.96-1.98	1.84	1.72	1.60	1.50	1.40	1.32
	σ	0.122	0.122	0.120	0.122	0.122	0.123	0.123	0.123	0.124	0.124	0.125

TABLE III

Examples of Viscosity Deviation and Molecular Weight Calculated from the Determined Values of K and alpha (alpha = 0.745)

Comp. C_3-mol%	Sample No.	Type Peak	$[\eta]_d$	$K \times 10^4$	$(M_w)_c \times 10^{-4}$	$(M_w/M_n)_c$	$\frac{[\eta]_c - [\eta]_d}{[\eta]_d}$ %
50.8	1	doub	4.22	1.80	99.7	12.9	2.67
	2	doub	3.62	1.80	85.3	6.98	8.92
	3	sing	1.35	1.80	22.1	4.81	4.41
	4	doub	4.52	1.80	93.2	9.30	-5.68
	5	sing	2.48	1.80	42.1	7.39	-5.89
	6	doub	0.90	1.80	10.3	5.84	-6.65
45.3	7	doub	2.17	1.86	33.8	4.96	-6.60
	8	doub	1.69	1.86	23.9	3.82	-4.79
	9	sing	1.29	1.86	17.8	2.58	4.76
	10	doub	4.33	1.86	97.1	9.72	3.32
	11	sing	1.83	1.86	25.8	5.28	-4.79
	12	sing	1.68	1.86	24.9	3.19	0.62
40.1	13	doub	3.07	2.04	50.1	4.55	-0.30
	14	doub	2.24	2.04	32.1	5.78	-1.64
	15	doub	2.95	2.04	48.4	5.69	-0.86
	16	doub	2.11	2.04	37.1	9.47	6.29
36.0	17	sing	3.87	2.10	64.4	4.51	0.17
	18	sing	2.83	2.10	43.9	5.72	4.23
	19	doub	1.77	2.10	28.6	6.81	7.84
	20	doub	3.07	2.10	45.8	5.03	-1.22
	21	sing	2.65	2.10	34.2	4.79	-8.72
	22	doub	1.43	2.10	16.6	4.25	1.84

Using data in Table II, if the values of K are plotted against copolymer composition (C3-mole%), a linear relationship is obtained.

With a view to testing the validity of the linear relationship between K and copolymer composition, we determined the intrinsic viscosity and GPC chromatogram of an additional five samples and, by interpolation and extrapolation of the straight line of Figure 2, the corresponding values of K and alpha were obtained. Intrinsic viscosity errors of the various samples were then calculated and the results are tabulated in Table IV. Moreover, we determined the number-average molecular weight, by osmometry, of samples 24 and 25 using a Knauer membrane osmometer and the weight-average molecular weight of sample 24 using a low-angle laser light-scattering photometer (Type KMX-6, Chromatix, Inc., USA). These are compared with data obtained by GPC (after corrections for peak spreading effects) as shown in Table V.

From Tables IV and V, it is apparent that deviations in intrinsic viscosities and molecular weights of the different samples all fall within the permissible range, and the data calculated from different groups of K and alpha show little variation. It is thus inferred that the linear relationship, as shown in Figure 2 is reliable and is applicable to

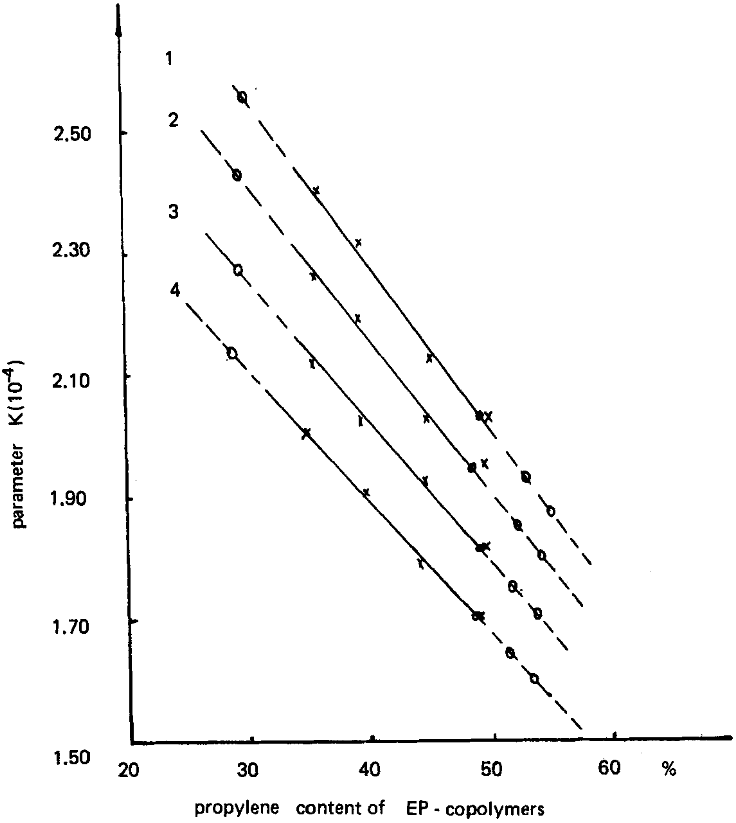

FIGURE 2

Relationship Between K and Propylene Content of EP-copolymers. -x-: Experimental values; -o-: Values of linear interpolation or extrapolation; 1 :α = 0.735; 2: α = 0.740; 3: α = 0.745; 4: α = 0.750.

samples with a narrow MWD, i.e., equal to 1.69 (see Table V).

In order to further investigate the relationship between k, alpha, and copolymer composition, we treated the data by means of regression analysis, i.e., to plot log K against alpha; this resulted in a very good

TABLE IV

Comparison of Measured Values of Intrinsic Viscosity With Those Calculated Form K & Alpha as Indicated in Figure 2.

No.	Comp. C_3-mol%	α=0.75 $Kx10^4$	α=0.75 $\frac{[\eta]_c-[\eta]_d}{[\eta]_d}\%$	α=0.745 $Kx10^4$	α=0.745 $\frac{[\eta]_c-[\eta]_d}{[\eta]_d}\%$	α=0.735 $Kx10^4$	α=0.735 $\frac{[\eta]_c-[\eta]_d}{[\eta]_d}\%$
23	30.0	2.12	-5.49	2.26	-5.45	2.56	-5.54
24	49.5	1.68	-5.43	1.80	-5.40	2.04	-6.56
25	53.9	1.58	1.68	1.68	1.58	1.90	1.39
26	55.4	1.54	6.30	1.64	6.30	1.86	6.63
27	55.4	1.54	-0.43	1.64	-0.43	1.86	-0.12

TABLE V

Comparison of Data From GPC and Absolute Methods.

No.	$Kx10^4$	Alpha	$(M_n)_{GPC}$ $x10^{-4}$	$(M_n)_{OSM}$ $x10^{-4}$	Rel. Error %	$(M_w)_{GPC}$ $x10^{-4}$	$(M_w)_{LS}$ $x10^{-4}$	Rel. Error%	$(M_w/M_n)_{GPC}$
24	2.04	0.735	29.9	29.8	0.33	63.3	62.3	1.60	2.12
	1.92	0.74	30.1	29.8	1.00	63.3	62.3	1.60	2.10
	1.80	0.745	30.0	29.8	0.67	62.8	62.3	0.82	2.09
	1.68	0.75	30.1	29.8	1.00	62.9	62.3	0.90	2.09
25	1.90	0.735	13.9	13.0	7.0	23.8	----	----	1.71
	1.80	0.74	14.0	13.0	7.9	23.7	----	----	1.69
	1.68	0.745	14.0	13.0	7.9	23.8	----	----	1.70
	1.58	0.75	14.0	13.0	7.7	23.7	----	----	1.69

linear fit. The lines were parallel to each other, as shown in Figures 3 and 4. The following general equation was established from the plots:

$$\log K = A - 5.75\alpha = \log B - 5.75\alpha \qquad (7)$$

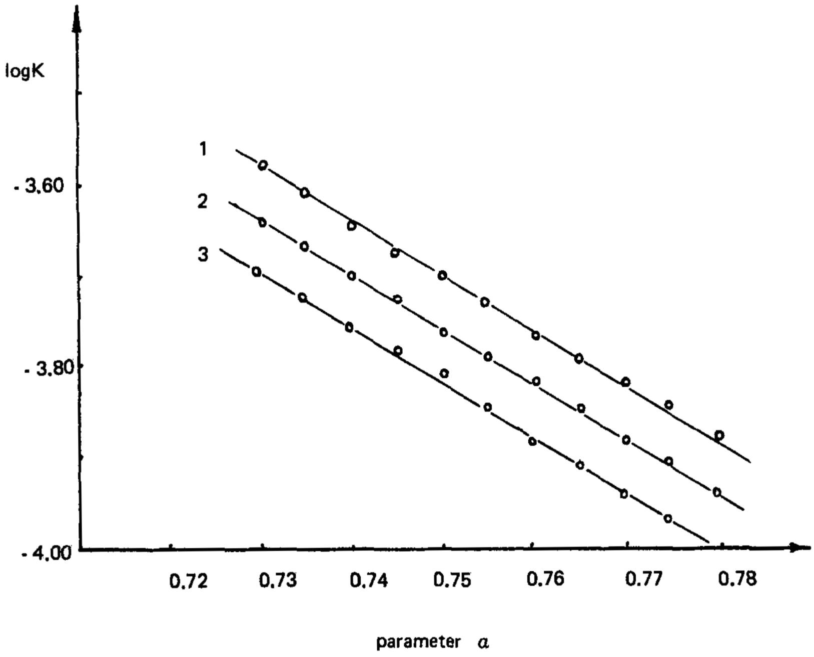

FIGURE 3

Relationship Between K and Alpha. 1: C_3=36%; 2: C_3=45.3% 3: C_3=55%.

The relationship between A, B, and composition is shown in Table VI. By plotting B against composition, straight lines as shown in Figure 5 were obtained and, by solving the straight lines graphically, we obtained

$$B = 5.755 - 4.65\ C_3 \tag{8}$$

Substituting (8) into (7), we obtain

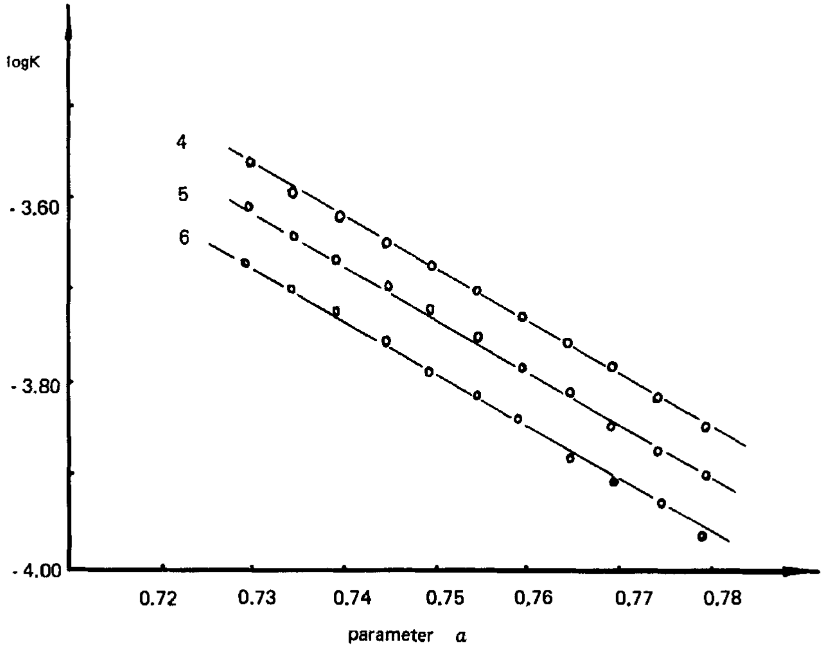

FIGURE 4

Relationship Between K and Alpha. 4: C_3=30%; 5: C_3=40.1% 6: C_3=50.8%.

TABLE VI

Values of A and B in Equation (7)

	C_3-mol %					
	30.0	36.0	40.1	45.3	50.8	55.0
A:	0.635	0.610	0.590	0.555	0.533	0.500
B:	4.32	4.07	3.89	3.59	3.40	3.16

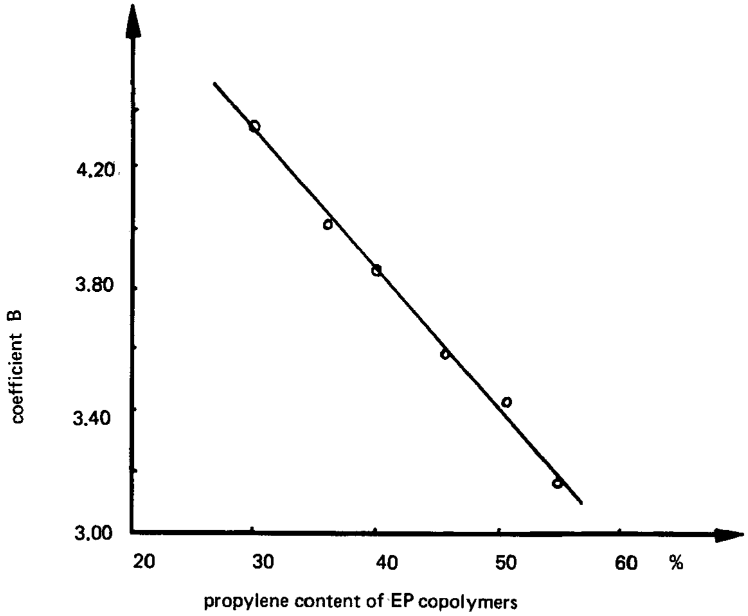

FIGURE 5

Relationship Between B of Equation (7) and Propylene Content of EP-Copolymers.

$$\log K = \log(5.755 - 4.65\ C_3) - 5.75\ \alpha \qquad (9)$$

(ODCB, 135°C)

Substituting (9) into the Mark - Houwink equation and rearranging,

$$[\eta] = (5.755 - 4.65C_3)\ (M/5.623\mathrm{x}10^5)^{\alpha} \qquad (10)$$

(ODCB, 135°C)

Table VII shows that the K_c value calculated from (9) agrees well with values of K previously determined. This proves that equation (9) is valid, as is equation

TABLE VII

Comparison of Calculated and Determined Values of K (10^{-4})

Compos'n, C_3-mol %	K_d, K_c	Alpha 0.73	0.735	0.745	0.75	0.755	0.76	0.775	0.78
30.0	K_d	2.72	2.57	2.27	2.13	2.01	1.88	1.55	1.44
	K_c	2.77	2.58	2.27	2.12	1.98	1.86	1.53	1.43
50.8	K_d	2.20	2.02	1.80	1.68	1.56	1.46	1.18	1.08-1.10
	K_c	2.16	2.02	1.77	1.66	1.55	1.45	1.19	1.11

(10). In fact, intrinsic viscosity calculated from equation (19) agrees well with measured values, with errors generally below 7%. Moreover, equation (9) shows that K and alpha are mutually dependent; the logarithm of K is a function of alpha.

Since equations (9) and (10) are obtained from experimental data through regression analysis, they are primarily applicable to ethylene - propylene copolymers prepared with a vanadium catalyst system, with propylene contents in the range of 30 - 55%, and alpha in the range of 0.73 - 0.755. The intrinsic viscosity or molecular weight calculated from different values of alpha approximate each other.

With the establishment of equation (9), it is possible to calculate the molecular weight and MWD from GPC chromatogram using the universal calibration curve.

Also, by using equation (10), the viscosity - average molecular weight may be calculated from intrinsic viscosity data of the samples.

CONCLUSION

Using ethylene - propylene copolymers of broad molecular weight distribution and different intrinsic viscosities as samples, and by employing the trial and error method reported in this paper, we have been able to determine the parameters K and alpha of the Mark - Houwink equation and, by further treating these by regression analysis, the following relationship is ultimately established:

$$\log K = \log(5.755 - 4.65\ C_3) - 5.75\ \alpha$$

$$[\eta] = (5.755 - 4.65\ C_3)\ (M/5.623\text{x}10^5)^{\alpha}$$

(ODCB, 135°C)

The above relationship shows that K and alpha are mutually dependent, the logarithm of K is a function of alpha, and alpha may be any value between 0.73 and 0.755. The above relationship is applicable to ethylene - propylene copolymers having a weight - average molecular weight of 10E5 to 10E6, a Mw/Mn of 1.7 - 12.9, a propylene content of 30 - 50 mole% and a GPC curve with either a single peak or two peaks. It is thus possible to apply universal calibration to calculate molecular weight and molecular weight distribution from the GPC chromatogram.

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