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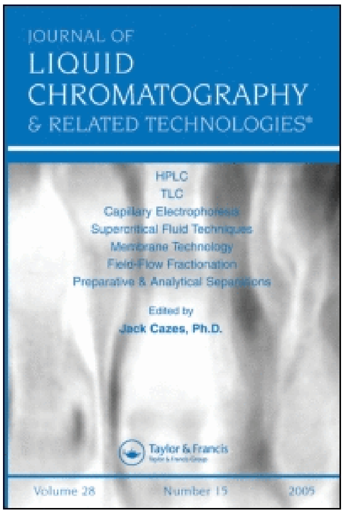

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DETERMINATION OF THE MONODISPERSE MARK-HOUWINK EQUATION OF HIGH-VINYL POLYBUTADIENE BY GEL CHROMATOGRAPHY AND LIGHT SCATTERING*

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ABSTRACT

Gel chromatographic, light scattering, viscosimetric and osmotic pressure measurements have been made for high vinyl polybutadiene fractions and whole polymer. Three alternative methods for deducing a monodisperse Mark-Houwink equation from gel chromatographic, light scattering and viscosimetric data of samples with unequal distribution widths are suggested. The monodisperse Mark-Houwink equations obtained by these methods for high vinyl poly(butadiene) are all alike.

INTRODUCTION

The chain structure of polydiene has several possibilities due to difference of addition scheme for the monomer. For example, when butadiene is polymerized, two kinds of products might be obtained, by 1,2 or 1,4 addition, and for the latter the product might be classified again into cis and trans forms.

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Changing the catalytic system, polybutadienes with different compositional chain units might be obtained, and their solution properties might also be different in some respects. In recent years, high-vinyl polybutadiene has been prepared by some organometallic catalysts. The molecular conformation and the solution properties of vinyl polybutadiene may be influenced seriously by the large amount of pendant side groups existing. In the study of polymer solution properties, the monodisperse Mark-Houwink equation plays an important role. First, for measuring molecular weight of polymer, only the monodisperse Mark-Houwink equation can give the correct viscosity-average molecular weight. Secondly, in the study of the effect of the structure and polydispersity on various physical properties of polymer, a monodisperse relationship is frequently required. However, the Mark-Houwink equations given in the literature are almost always determined from the weight-or number-average molecular weights of fractions with uncertain molecular weight distributions. The relationships thus obtained are

$$[\eta] = K_w \cdot \langle M \rangle_w^{\alpha} , \qquad (1)$$

or

$$[\eta] = K_n \cdot \langle M \rangle_n^{\alpha} , \qquad (2)$$

both of them are not the monodisperse equation. Several methods have been suggested in the literatures (1-5) for deducing the parameters of the monodisperse Mark-Houwink equation. In all of these methods, a requirement must be satisfied, i.e. the relative width of the molecular weight distribution of the sample used must be the same, and known exactly. Under this condition the alpha value obtained is independent of the width of the MWD of the sample; therefore, it is only necessary to correct the K value for polydispersity. Since the width of the distribution may vary from sample to sample, the applicability of the suggested methods would be limited. For high-vinyl polybutadiene, the only data found in literature was that reported by Anderson et al., (6) in which the number-average

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molecular weights were measured by osmotic pressure and the Mark-Houwink equation cited was treated as in Eq. 2.

In the present work, the molecular weight distribution of vinyl polybutadiene sample were measured by gel chromatography, and in connection with the light scattering and viscosity measurements, three alternative methods for deducing the monodisperse Mark-Houwink parameters from samples with unequal distribution widths were employed. The results obtained by these methods are all very much alike.

EXPERIMENTAL

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Sample: The vinyl polybutadiene was prepared in toluene at 50°C with molybdenum naphthenate-triisobutylaluminium as catalyst. The product was deactivated and coagulated by addition of ethyl alcohol, and then dried in vacuum.

Fractionation: The sample was dissolved in hydrogenated gasoline, filtered through a G5 sintered glass funnel and precipitated with 1:1 methyl alcohol-acetone mixture for purification. The purified polymer was then fractionated by reverse fractional precipitation at 30°C in toluene by addition of methyl alcohol as precipitant.

Structure Analysis: The vinyl contents of the fractions were determined by infrared absorption spectra (PEKIN ELMER 599 B) and 13C nuclear magnetic resonance spectra (JEOL FX 100) respectively.

Gel Chromatography: The molecular weight distributions of the samples were determined with a ARL 950 Gel Permeation Chromatograph. The column was packed with deactivated porous-silica beads prepared in this laboratory. THF was used as the elution solvent with flow rate 1 ml/min at 42°C. The concentration of the eluted polymer solution was detected with a differential refractometer. The elution volume was measured with a siphon tube with a volume of 1.98 ml.

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Light Scattering: The weight-average molecular weights of the samples were determined simultaneously with a Chromatix KMX-6 Low Angle Laser Light Scattering Photometer and a Shimadzu PG-21 Light Scattering Photometer, using cyclohexane as solvent at ambient temperature. The dn/dc of the vinyl polybutadiene is 0.0816 at 30°C determined by a Chromatix KMX-16 Differential Refractometer at 632.8 nm. The incident light of 436 nm and a dn/dc value of 0.094 were chosen for the conventional light scattering measurements.

Viscosity: Viscosities were measured for toluene and THF solutions using an Ubbelohde viscometer at 30°C. A kinetic energy correction was applied. The intrinsic viscosity of the sample was obtained by extrapolation to infinite dilution.

Osmotic Pressure: A Knauer Membrane Osmometer was used to determine the number-average molecular weight of arbitrarily selected samples for checking the gel chromatographic data; toluene was used as solvent.

RESULTS AND DISCUSSIONS

Experimental Results: The vinyl contents of the fractions and the whole polymer determined by 13C NMR and IR are listed in Table 1.

TABLE 1

Vinyl Contents of Polybutadiene Samples

Fraction	Vinyl Wt. %	
	IR	NMR
S1 - A	89.2	-
S1	93.8	93.5
S2	94.0	93.2
S3	93.1	94.7
S4	94.3	-
whole polymer	93.1	92.0

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TABLE 2

Weight Average Molecular Weights and Intrinsic Viscosities of Vinyl Polybutadiene Samples

Fraction	$\langle M\rangle_w \times 10^{-5}$			$[\eta]$ ml/g, 30°C	
	LALLS	LS	Average value	THF	Toluene
S1 - A	2.33	2.33	2.33	162	148
S1	6.85	6.06	6.46	388	330
S2	10.8	10.5	10.7	540	484
S3	11.8	14.9	13.4	670	571
S4	21.6	20.8	21.2	941	832
whole polymer	19.2	22.9	21.1	760	646

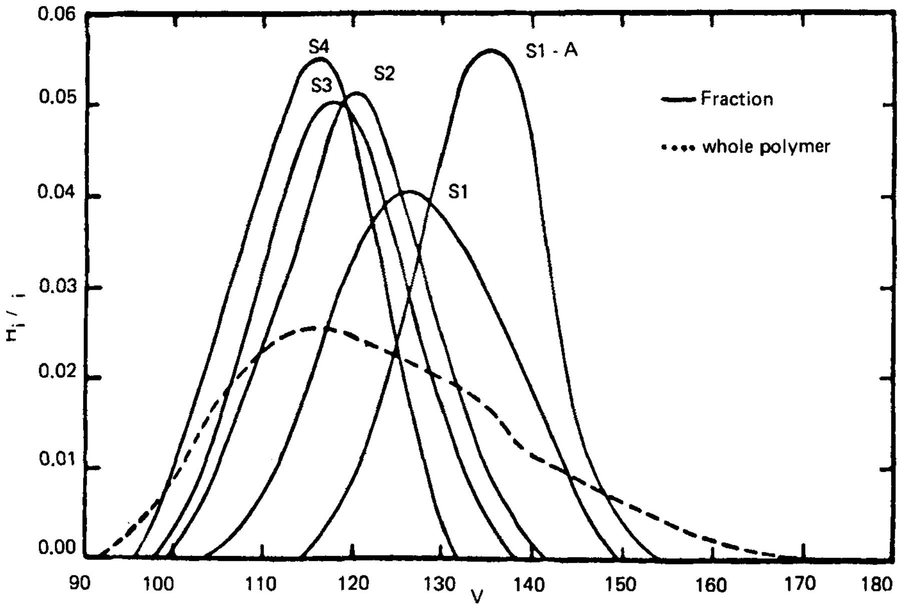

FIGURE 1. Normalized Gel Chromatograms of Vinyl Polybutadiene Samples.

TABLE 3

GPC Data in Elution Volume Count of Vinyl Polybutadiene Samples

Fraction	σ_T^2	$\bar{V}$	$V'_R \langle M\rangle_w$	$V'_R \cdot \langle[\eta]\rangle$
S1 - A	46.36	133.87	131.27	131.82
S1	79.17	127.28	123.11	123.93
S2	60.96	120.40	117.15	117.80
S3	55.45	117.91	114.96	115.55
S4	47.33	114.75	112.13	112.67
whole polymer	232.7	123.48	-	-

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The vinyl contents are alike, independent of the molecular weight of the sample, except S1-A, which is a fraction of another sample with lower molecular weight. The light scattering and viscosity data are shown in Table 2. The weight-average molecular weights measured by conventional light scattering were very close to those measured by LALLS; therefore the average values were used to calibrate the gel chromatographic column. The normalized gel chromatogram for each fraction is shown in Figure 1; the mean elution volumes and variances calculated from experimental chromatograms are shown in Table 3.

Calibration of Gel Chromatographic Column: The calibration relationship of the gel chromatographic column represents the relationship between certain molecular size parameters of monodisperse polymer and its retention column under ideal working conditions. For a linear chromatographic column, the monodisperse calibration relationship may be written as

$$M(V_R) : \quad \ln M = A_M - B_M V_R, \tag{3}$$

$$[\eta](V_R) : \quad \ln[\eta] = A_\eta - B_\eta V_R, \tag{4}$$

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The coefficients of the above relationships may be determined from the known experimental average values $\langle M\rangle$ or $\langle[\eta]\rangle$ of polydispersed polymer standards, and the corresponding retention volumes calculated by

$$V_{R},\langle M\rangle_{w} = (-1/B_{M})\ \ln\ \Sigma\, W(V_{R})\ e^{-B_{M}\ V_{R}}\ , \qquad (5)$$

$$V_{R},\langle M\rangle_{n} = (\ 1/B_{M})\ \ln\ \Sigma\, W(V_{R})\ e^{\ B_{M}\ V_{R}}\ , \qquad (6)$$

$$V_{R},\langle[\eta]\rangle = (-1/B\ )\ \ln\ \Sigma\, W(V_{R})\ e^{-B_{\eta}\ V_{R}}, \qquad (7)$$

where $W(V_R)$ is the true chromatogram of the polydispersed sample (7). If the experimental chromatogram $F(V)$ of the polydispersed polymer is used instead of $W(V_R)$, the calculated results are translated to corresponding retention volumes as

$$V'_{R,\langle M\rangle w} = (-1/B_{M})\ln\ \Sigma F(V_{R})\ e^{-B_{M}V_{R}} \qquad (8)$$

$$V'_{R,\langle M\rangle n} = (\ 1/B_{M})\ln\ \Sigma F(V_{R})\ e^{\ B_{M}V_{R}} \qquad (9)$$

$$V'_{R,}\langle[\eta]\rangle = (-1/B_{\eta})\ln\ \Sigma F(V_{R})\ e^{-B_{\eta}V_{R}}\ , \qquad (10)$$

due to the existence of the instrumental spreading effect. From Tung's integral equation

$$F(V) = \int_{V_R} W(V_{R})\ G(V\ ,\ V_{R})\ dV_{R} \qquad (11)$$

and if the spreading function $G(V,V_R)$ is Gaussian

$$G(V,V_{R}) = (1/\sigma\sqrt{2\pi}) \quad \exp\left\{(1/2\,\sigma_{0}^{2})\quad (V-V_{R})^{2}\right\}, \qquad (12)$$

then (7)

$$V'_{R,\langle M\rangle w} = V_{R,\langle M\rangle w} - B_{M}\,\sigma_{o}^{2}\ /\ 2\ , \qquad (13)$$

$$V'_{R,\langle M\rangle n} = V_{R,\langle M\rangle n} + B_M \sigma_o^2 / 2 \,, \tag{14}$$

$$V'_{R,\langle[\eta]\rangle} = V_{R,\langle[\eta]\rangle} - B_\eta \sigma_o^2 / 2 \,, \tag{15}$$

Hence, the resultant calibration relationships are translated calibration relationships $M'(V_R)$ and $[\eta]'(V_R)$. Since the volume displacement directly depends upon the spreading factor σ_o^2 and the slope of the calibration curve, and also upon the initial calibration parameter chosen, the correction factors for the average molecular weight and intrinsic viscosity calculated from the experimental chromatogram F(V) using translated calibration relations are likewise related to the initial calibration parameter. If the calculated average and the initial calibration parameter are of the same type spreading correction is unnecessary. For example, for the translated calibration relation $M'_w(V_R)$ using weight-average molecular weight as the initial calibration parameter, the spreading correction factors for the average molecular weights calculated from experimental chromatogram F(V) are

$$\langle M\rangle_w,\ \text{corr.} = \langle M\rangle_{w,\text{cal.}} \,, \tag{16}$$

$$\langle M\rangle_n,\ \text{corr.} = e^{B_M^2 \sigma_o^2} \langle M\rangle_{n,\ \text{cal.}} \,, \tag{17}$$

$$(\langle M\rangle_w / M_n)_{\text{corr.}} = e^{-B_M^2 \sigma_o^2} (\langle M\rangle_w / \langle M\rangle_n)_{\text{cal.}} \,, \tag{18}$$

$$\langle M\rangle\ ,\ \text{corr.} = e^{(1/2)(1-\alpha)B_M^2 \sigma_o^2} \langle M\rangle_\eta\ ,\ \text{cal.} \,, \tag{19}$$

respectively.

The translated calibration relationships obtained from the corresponding retention volumes calculated from the experimental chromatograms with $\langle M\rangle_w$ and $\langle[\eta]\rangle$ as initial calibration parameters for vinyl polybutadiene are shown in Figure 2. The least square fit of the data gives

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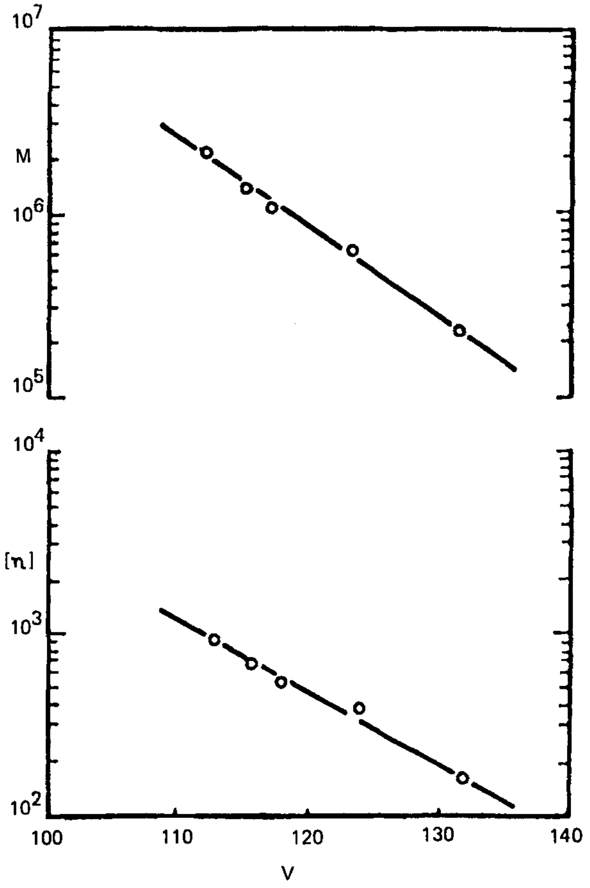

FIGURE 2. The Translated Calibration Curves of Vinyl Polybutadiene.

$$M'(V_R) : \ln M = 26.8697 - 0.1103\ V_R\ (r^2=0.992), \qquad (20)$$

$$[\eta]'(V_R) : \ln[\eta] = 16.6242 - 0.0871\ V_R\ (r^2=0.984), \qquad (21)$$

respectively. The weight average molecular weights and intrinsic viscosities of the samples studied, calculated from the experimental chromatogram using the above two relationships are listed in Table 4; both of them are very close to the experimentally determined values.

TABLE 4

The Experimental and GPC Calculated Average Molecular Weights and Instrinsic Viscosity of Vinyl Polybutadiene Samples

Fraction	$\langle M\rangle_w\ 10^{-5}$		$\langle M\rangle_n\ 10^{-5}$			$\langle[\eta]\rangle$THF, ml/g		$\langle M\rangle_w/\langle M\rangle_n$
	LS	GPC	Osmotic	GPC		Exp.	GPC	Corr.
				Cal.	Corr.			
S1 - A	2.33	2.41	-	1.39	1.67	162	171	1.44
S1	6.46	5.92	3.00	2.36	2.83	388	340	2.09
S2	10.7	11.4	-	5.53	6.64	540	580	1.72
S3	13.4	14.5	8.69	7.51	9.01	670	706	1.61
S4	21.2	19.9	-	11.4	13.6	941	907	1.45
whole polymer	21.1	16.4	-	1.21	1.45	760	716	11.3

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The number-average molecular weights, calculated from the experimental chromatograms using $M'_w(V_R)$ and the corrected values according to Equation (17) are also in Table 4. Two fractions were arbitrarily selected to take osmotic pressure measurement for checking the gel chromatographic data. The corrected number-average molecular weight from gel chromatography conforms to the experimentally determined value.

Monodisperse Mark-Houwink Equation:

The width of the molecular weight distribution of the polybutadiene sample studied varies considerably as seen in Table 4. It is difficult to determine the monodisperse Mark-Houwink parameters accurately for such cases using the literature-proposed methods. The parameters for the monodisperse Mark-Houwink equation

$$[\eta] = K\ M^{\alpha} \qquad (22)$$

should be identical to those of the relationship between intrinsic viscosity and viscosity-average molecular weight for the polydispersed samples

$$\langle[\eta]\rangle = K\,\langle M\rangle_\eta^\alpha \tag{23}$$

where the viscosity average molecular weight is defined as

$$\langle M\rangle_\eta = \left\{\Sigma W(M)\ M^\alpha\right\}^{1/\alpha} \tag{24}$$

For deducing the monodisperse Mark-Houwink parameters, three alternative methods were employed in the present work. In method I and II the viscosity-average molecular weights are first calculated following different routes, while in method III they are deduced from the theoretical relationship between the monodisperse calibration curve $[\eta](V_R)$ and $M(V_R)$.

Method I, Assuming the molecular weight distribution fits the logarithmic normal distribution

$$W(M) = 1/\beta\sqrt{\pi}\ \cdot\ 1/M\cdot\ \exp\left\{-(1/\beta^2)\ln^2(M/M_0)\right\} \tag{25}$$

then

$$\langle M\rangle_w = M_o e^{(1/4)\beta^2}\ , \tag{26}$$

$$\langle M\rangle_n = M_o e^{(-1/4)\beta^2}\ , \tag{27}$$

$$\langle M\rangle_\eta = M_o e^{(1/4)\alpha\beta^2}\ , \tag{28}$$

the polydispersity index

$$\langle M\rangle_w / \langle M\rangle_n = e^{(1/2)\beta^2} \tag{29}$$

Combine above equations, we see that

$$\langle M\rangle_\eta = (\langle M\rangle_w / \langle M\rangle_n)^{(1/2)(\alpha-1)}\langle M\rangle_w\ , \tag{30}$$

Thus, the viscosity average molecular weight can be calculated from the experimental weight-average molecular weight, polydispersity index and the parameter α to be determined. For this purpose, weight-

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average molecular weight from light scattering measurement and polydispersity index from gel chromatographic data, after applying instrumental spreading correction, were used. The parameter α was determined by an iterative procedure. The initial value of α was taken from the least square fit of the experimentally determined $\langle[\eta]\rangle$ and $\langle M\rangle_w$, with which the viscosity average molecular weight was calculated according Eq.30. A new pair of parameters, K and α, was then deduced from $\langle[\eta]\rangle$ and $\langle M\rangle$ by the least square fit. This iterative procedure was repeated until the value no longer changed. A similar procedure for deducing the monodisperse Mark-Houwink equation for polyisbutene was employed by Mrkvickova and Lapour (8), in which the MWD of the sample was assumed to be a Schulz-Zimm distribution.

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Method II, The same initial value of α as method I was used to calculate the viscosity-average molecular weight directly from F(V) and $M'_w(V_R)$ according to Equation 24. The calculated $\langle M\rangle_\eta$ was then corrected for instrumental spreading by Eq. 19. The new K and α values were deduced again from the experimentally determined intrinsic viscosity and the corrected viscosity-average molecular weight by a least square fit. The procedure is repeated until the value of α becomes constant.

Method III, If the coefficients of the monodisperse calibration relationships $M(V_R)$ and $[\eta]$ (V_R) as Eq. 3 and 4 are known, simple correlations between the Mark-Houwink parameters and the coefficients of the calibration relationships

$$\alpha = B_\eta / B_M , \tag{31}$$

$$K = e^{A_\eta - \alpha A_M} , \tag{32}$$

must be satisfied. Since the calibration relationship obtained from the initial calibration parameter, and corresponding retention volume calculated by F(V), is a translated calibration relationship, i.e.

$$M'(V_R) \quad : \quad \ln M = A'_M - B_M V_R \quad , \tag{33}$$

$$[\eta](V_R) \quad : \quad \ln[\eta] = A'_\eta - B_\eta V_R \quad , \tag{34}$$

it is necessary to apply a displacement correction on coefficients A'_M and $A'\eta$ for deducing the monodisperse relationship. From Eqs. 13 and 15, if the spreading factor σ_o^2 is considered as a constant equal to the middle value of the variable $\sigma_o^2(V_R)$ over the entire range of elution volume (9), then

$$A_M = A'_M + (1/2)B_M^2 \sigma_o^2 \quad , \tag{35}$$

$$A\eta = A'\eta + (1/2)B_\eta^2 \sigma_o^2 \quad , \tag{36}$$

Thus, the resultant monodisperse calibration relationships are

$$M(V_R) \quad : \quad \ln M = 26.9609 - 0.1103\ V_R \quad , \tag{37}$$

$$[\eta](V_R) \quad : \quad \ln[\eta] = 16.6811 - 0.0871\ V_R \quad , \tag{38}$$

respectively, and the monodisperse Mark-Houwink parameters can be deduced.

The α value became constant simply after two iterations for methods I and II; the calculated viscosity-average molecular weights are listed in Table 5. The parameters for the monodisperse Mark-Houwink equation thus obtained for vinyl polybutadiene in THF are listed in Table 6, in which the linear correlation coefficient r^2, for the least square fit, and the results of method III are also listed.

The data in Table 6 indicate that the results obtained by the three alternative methods are very close to each other and nearly indistinguishable in the investigated molecular weight range as illustrated by Figure 3. That is to say, the monodisperse Mark-Houwink equation could be deduced by any one of the above three

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TABLE 5

Viscosity-Average Molecular Weight for Vinyl Polybutadiene Samples

Fraction	$\langle M\rangle_\eta\ 10^{-5}$		
	THF		Toluene
	Method I	Method II	Method I
S1 - A	2.24	2.31	2.24
S1	5.98	5.52	5.95
S2	10.1	10.8	10.1
S3	12.8	13.9	12.7
S4	20.4	19.1	20.3
whole polymer	16.3	14.1	-

methods if the polydispersity of the polymer spreading effect in gel chromatography are considered. The small difference in the values of the parameters shown in Table 6 originated from the slight difference of the calculated viscosity-average molecular weights by methods I and II. If the average value of $\langle M\rangle_\eta$ was considered, the

TABLE 6

The Monodisperse Mark-Houwink Parameters for Vinyl Polybutadiene in THF at 30°C

Methods	$K\ 10^3$	α	r^2
I	9.65	0.79	0.997
II	9.84	0.79	0.986
III	9.87	0.79	-

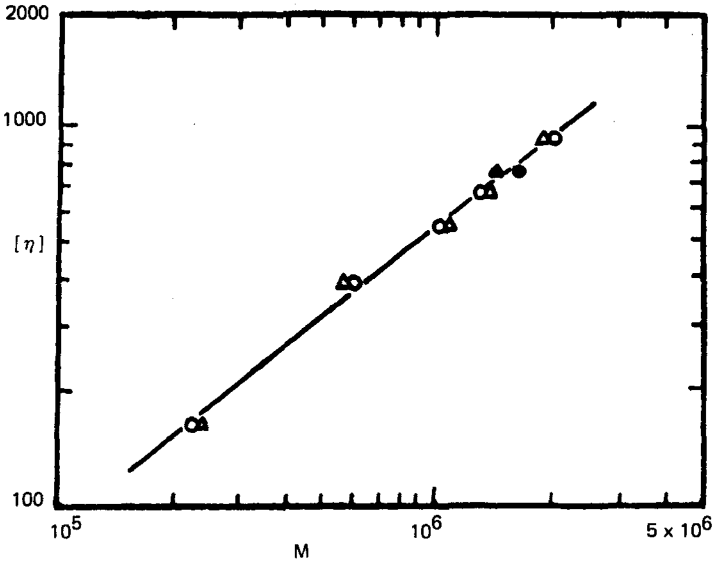

FIGURE 3. The Intrinsic Viscosity-Viscosity Average Molecular Weight Log-Log Plots of Vinyl Polybutadiene in THF at 30°C.

○ Fractions ● Whole Polymer/Method I
△ Fractions ▲ Whole Polymer/Method II
— For Method III

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monodisperse Mark-Houwink equation of vinyl polybutadiene in THF 30°C could be expressed as

$$[\eta] = 9.97 \times 10^{-3} \cdot M^{0.79} \quad \text{THF, 30°C} \quad , \qquad (39)$$

The experimental data for the toluene solution were treated with method I; the resultant monodisperse Mark-Houwink equation is

$$[\eta] = 1.04 \times 10^{-2} . M^{0.78} \quad \text{toluene, 30°C, } r^2=0.999 \qquad (40)$$

Anderson et al. (6) have reported some data including number-average molecular weight, polydispersity index, and intrinsic viscosity of high 1,2-polybutadiene samples in toluene, but the deduced Mark-Houwink equation was not the monodisperse equation. Suppose the molecular weight distribution of their sample fits the logarithmic normal distribution; the relationship between the viscosity-average and number-average molecular weight should be

$$\langle M\rangle_\eta = (\langle M\rangle_w / \langle M\rangle_n)^{(1+\alpha)/2} \langle M\rangle_n \quad , \qquad (41)$$

Their data were retreated by method I, using Eq. 41, to calculate $\langle M\rangle_\eta$. The monodisperse Mark-Houwink equation obtained by the least square fit was

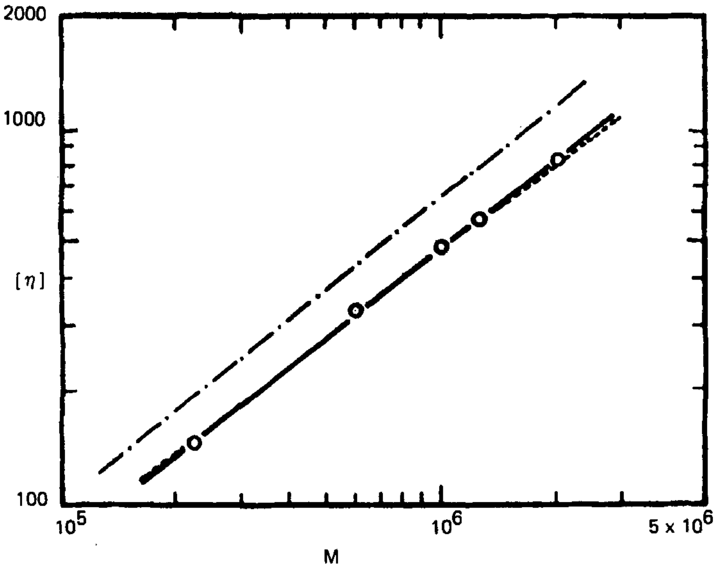

FIGURE 4. The Intrinsic Viscosity-Viscosity Average Molecular Weight Log-Log Plots of Vinyl Polybutadiene in Toluene at 30°C.

— The Present Work: $[\eta] = 1.04X10^{-2}M^{0.78}$

· — Anderson, et al.(6): $[\eta] = 9.01X10^{-3}M_n$

···· Anderson's Data, Corrected for Polydispersity: $[\eta] = 1.24X10^{-2}M^{0.76}$

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$$[\eta] = 1.24 \times 10^{-2} \cdot M^{0.76} \quad \text{toluene, } 30°\text{C, } r^2=0.996 \quad , \quad (42)$$

Comparing it with our results, there are no distinct differences, as shown in Figure 4. For the three alternative methods employed in the present work, there are no restrictions on the molecular weight distribution of the sample used. Thus, some conveniences are realized for planning experiments and selecting samples. For samples with broad molecular weight distribution, as for the whole polymer used in the present work (the polydispersity index is as high as 11.3) the data points of $\langle[\eta]\rangle$ against $\langle M\rangle_\eta$ calculated by method I or II also are located near the determined monodisperse line as shown in Figure 3. This fact indicates that the monodisperse Mark-Houwink equation obtained is valid.

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REFERENCES

1. Kodera, Akira, Science (Japan) 27, 38-9 (1957).
2. Koningsveld, R. and Tuiznman, C.A.F., Makromol. Chem. 38, 39 (1960).
3. Qian Renyuan and Ying Qizong, Scientia Sinica, 1962(1), 66.
4. Kurata, M., Tsunashima, Y., Iwama, M. and Kamada, K., Polymer Handbook, Second Edition, Brandrup J., Immergut E.H., eds. Wiley and Sons, New York, 1975, IV-1.

5. Bareiss, R.E., Polymer Handbook, Second Edition, Brandrup J., Immergut E.H., eds. Wiley and Sons, New York, 1975, IV-115.
6. Anderson, J.N., Barzan, M.L. and Adams, H.E., Rubber Chem. Technol., 45, 1270-82 (1972)
7. Cheng Rongshi, J.Liq.Chromatogr., in press
8. Mrkvicková, L. and Lòpour, P., Angew. Makromol. Chem. 69, 117 (1978)
9. He Zhiduan, Zhang Xuanqi and Cgeng Rongshi, J. Liq. Chromatogr., in press.

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