Rheological Properties of Concentrated Polymer Solution: Polybutadiene in Good and θ Solvents*

PHANIBHUSAN ROY-CHOWDHURY and VIVEK D. DEUSKAR

National Chemical Laboratory, Poona 411008, India

Synopsis

The zero shear viscosity, η^0 of three polybutadiene samples having different molecular weights over a wide range of concentration (1.0–35.0% polymer) in good and θ solvents has been studied. Superposition of viscosity data has been made to give a single composite curve for each solvent by shifting them vertically by a factor $(M^0/M)^{3.4}$, where M^0 represents the molecular weight of the reference sample. The shift factor is found to be proportional to $M^{3.4}$ in the region of higher concentration, which indicates that the 3.4-power law is valid for the data of polybutadiene. The double-logarithmic plots of relative viscosity η^0_r as a function of $c^5 M^{3.4}$ yielded a single composite curve approximating a straight line with slope of unity at the higher values of the variables. The results indicate that over a considerable range of the variables (molecular weight and concentration) at a constant temperature, the relative viscosity is a single function of $c^5 M^{3.4}$. The results for double-logarithmic plots of zero shear specific viscosity η^0_{csp} as a function of concentration confirmed those observed in polychloroprene samples studied earlier that the $\eta 0_{sp}$ values in θ solvents at higher concentration region are found to be higher than those found in good solvents, whereas in the moderately concentrated region the values are just opposite in θ and good solvents. The viscosity crossover in θ solvents is not as sharp as is found in case of polychloroprene samples and that crossover, too, has taken place in the range of concentration of 11.7–31.6% polymer, which is comparatively higher than that of polychloroprene samples (6.06–21.0% polymer). The results indicate some relation between viscosity crossover and polymer polarity, supporting the idea of enhanced intermolecular association in poor solvents. To correlatethe viscosity data obtained in good and poor solvents, two methods, one given by Graessley and the other given by Dreval and coworkers involving the correlating variable $c[\eta]$, were considered. The plots of relative viscosity η^0_r versus the correlating variable $c[\eta]$ in benzene (good solvent) yielded one curve, but in the case of θ solvents (dioxane and isobutyl acetate), the same plots yielded three separate curves instead of a single curve, which is rather unusual. The appropriate correction on the correlating variable for chain contraction in the concentrated region in a good solvent moved the data to a common curve, especially in lower concentration region, but at the higher concentration region a slight overestimation of data seems to have been effected. On the other hand, the plots of log $\bar{\eta}$ as a function of correlating variable $c[\eta]$ yielded a single curve for three samples in the good solvent benzene, but in poor solvents (diozane and isobutyl acetate) the same plots yielded three separate curves for three samples instead of a single curve, the reason for which is not known at present. However, the normalization of the correlating variable $c[\eta]$ with Martin constant K_M reduced all experimental data of the polymer samples to a common curve. The correlation of the viscosity data by either of the two methods seems to be possible in the case of the nonpolar flexible polymer, polybutadiene.

INTRODUCTION

In an earlier communication[1] the results of zero shear viscosity η^0 measurements of polychloroprene samples of different molecular weights over a wide range of concentration in good and poor solvents have been reported.

To correlate the viscosity data of polychloroprene samples obtained in good and θ solvents, the methods given by Graessley[2] as well as by Dreval and coworkers[3] were examined. It was observed that the approximate correction for the variation of chain dimension on correlating variable $c[\eta]$ by the former method, though, moved the correlations of θ and good solvents closer to a common curve, but the complete superposition of data had not been effected by this correction. On the other hand, by the second method, the normalization of the correlating variable $c[\eta]$ by Martin constant K_M, which is related to the flexibility of macromolecular chain and polymer solvent interaction, reduced all data of the polymer samples in both good and θ solvents to a common curve. This method had given better correlation of data than the former one. The present paper is an extension of a similar study in different solvents with polybutadiene samples to produce additional data involving the effects of solvent, concentration, and molecular weight on the rheologic properties of polymer solutions and to substantiate our considerations. We have chosen this polymer because polybutadiene is a cis compount (100% cis) and the chain of this polymer is more flexible than that of polychloroprene (probably a trans compound), which was studied earlier. Besides, this polychloroprene is a polar compound but polybutadiene is nonpolar. Graessley,[4] after examining the viscosity crossover results for a few polar and nonpolar polymers, has indicated that there exists a relation between the viscosity crossover in θ solvents and polymer polarity, which supports the idea of enhanced intermolecular association in poor solvents. Our study of both polar and nonpolar polymers may give further insight into this direction, also. It has been observed that, in case of polychloroprene samples, the onset of entanglements has been started at the crossover point concentration c_{cross}; that is, from this concentration the polymer molecules diffuse by reptation from the vertual tube enclosing each chain and the static shear viscosity depends on the 3.4-power of molecular weight. However, in case of polybutadiene samples, the data for c_{cross} are found deep inside the composite curve made by superposition of data for different samples in the higher concentration region, not at the starting points from where the data deviate from composite curve, as is found in case of polychloroprene.[1] This implies that entanglement started at a higher concentration in polybutadiene samples than in polychloroprene samples. If the polymer concentration and molecular weight dependence of η^0 for polybutadiene samples is determined by the mechanism similar to that in polychloroprene samples, then the polybutadiene solutions that show much greater viscosity than that of the polychloroprene solutions at the corresponding concentration are in the Rouse region, not in the entanglement region.

EXPERIMENTAL

The zero shear viscosity η^0 of the polymer solutions was measured by means of a Brookfield LVT viscometer. The experimental details have been described elsewhere.[1] The rate of shear is directly proportional to the speed of the spindle at which the measurements are made in this instrument, so

the η values taken at different speeds (RPM) were extrapolated to zero for the determination of the zero shear viscosity in this work.

The zero shear viscosity of the solvents was measured by a Maron-type capillary viscometer with continuously varying pressure head.[5] For Newtonian fluids, the viscosity was calculated by the equation

$$\frac{1}{\eta^0} = -\frac{1}{B}\left[\frac{d\,(\log\,h\,)}{dt}\right] = -\frac{m}{B}$$

where h is the height of the mercury manometer from is its equilibruim position and B is the apparatus constant. In this measurement, d (log h)/dt for solvents was found to be constant, and this comfirmed that the solvent flow was Newtonian. The data for zero shear viscosity measurements for the solvents are given in Table I. However, the zero shear viscosity for dilute polymer solutions (5% and below) having non-Newtonian flow was also measured with this capillary viscometer, and the apparent viscosity η_a was calculated employing the equation

$$\frac{1}{\eta_a} = -\left(\frac{m}{B}\right)\left(1 + \frac{1}{9.212m^2}\frac{dm}{dt}\right)$$

The zero shear viscosity η^0 was determined by extrapolating the rate of shear to zero.

The sample poly(cis -1,4-butadiene; PB) was obtained from Polysciences, Inc. (Warrington, PA). The polymer was fractionated from benzene solution at 25° C with the addition of acetone as nonsolvent. The samples were dried in vacuo to constant weight and stored in a cold and dark place under a vacuum desiccator. The molecular weight of the polybutadiene samples used in this work was determined from the intrinsic viscosities ([η] in dl/g) measured in benzene solution at 25° C. The [η] $= M_w$ relation in benzene solution at 25° C was determined in this laboratory as [η] $= 16.88 \times 10^{-5}$ $\overline{M}_w^{0.748}$ using the light-scattering values of $\overline{M}_w$ for six polybutadiene fractions in the range 1.22–6.3 $\times$ 10[5] . It may be pointed out that the same [η] $-$ $\overline{M}_w$ relationship for polybutadiene (100% cis) with [η] measured at 32° C in benzene was obtained by us as [η] $= 14.9 \times 10^{-5}\,\overline{M}_w^{0.76}$, which is in excellent agreement with that obtained by Cooper and coworkers.[6]

The viscosity of dilute polymer solutions was measured with a Ubbelohde capillary viscometer, and the intrinsic viscosity [η] was determined by

TABLE I
Zero Shear Viscosity, η^0 and Θ Temperature of the Solvents

Solvent	Temperature (°C)	η^0 (cps)	Θ temperature (°C)
Benzene	20.5	0.655	Good solvent
Isobutyl acetate	20.5	0.698	20.5[1]
Dioxane	20.2	1.240	20.2[a]

[a] Data taken from Ref. 7.

extrapolation to infinite dilution according to the relation $\eta_{sp}/c = [\eta] + K'[\eta]^2 c$, where k' is the Huggins constant. The data for $[\eta]$ and $\overline{M}_v$ of the samples used in this work are given in Table II.

The apparent specific volumes V_p and V_s of the polymer and the solvent, respectively, were determined at a number of temperatures above 20° C (20, 30, 40, 50, and 60° C), as described earlier,[1] which were represented by the following equations:

$$V_p \text{ (polybutadiene)} = 1.1055 + 9.00 \times 10^{-4} \quad (t = -20° \text{ C})$$

$$V_s \text{ (benzene)} = 1.1386 + 14.28 \times 10^{-4} \quad (t = -20° \text{ C})$$

$$V_s \text{ (isobutyl acetate)} = 1.1519 + 14.06 \times 10^{-4} \quad (t = -20° \text{ C})$$

$$V_s \text{ (dioxane)} = 0.9677 + 10.67 \times 10^{-4} \quad (t = -20° \text{ C})$$

where t is the temperature.

As described in the preceding paper,[1] the solutions of higher concentration were prepared by mixing the weighed amounts of the polymer and the solvent and the relation for V_p and V_s used to calculate the concentration of the solution (g/dl). Dilution was carried out by adding solvents by weight, and polymer concentration was converted to grams per deciliters assuming the additivity of specific volumes of polymer and solvent. Strictly speaking this assumption is not correct when the concentration of polymer in the solution exceeds 30%.

RESULTS AND DISCUSSION

The summary of results of zero shear viscosity measurements for polybutadiene samples in both good and θ solvents is given in Table III. Three polybutadiene samples, PB2F1, PB2F2, and PB2F3, have been used in this work. Benzene was used as a good solvent, and isobutyl acetate (IBA) and

TABLE II
Values of Intrinsic Viscosity and Molecular Weight for Polybutadiene Samples

Samples	Solvent	Temperature (°C)	$[\eta]$ (dl/g)	$\overline{M}_v \times 10^{-5}$
PB2F1	Benzene	32	3.80	6.17
		25	3.62	
		20.5	3.40	
	IBA	20.5	1.03	
	Dioxane	20.2	1.03	
PB2F2	Benzene	32	2.00	2.61
		25	1.90	
		20.5	1.82	
	IBA	20.5	0.68	
	Dioxane	20.2	0.68	
PB2F3	Benzene	32	1.32	1.54
		25	1.28	
		20.5	1.24	
	IBA	20.5	0.52	
	Dioxane	20.2	0.52	

TABLE III
Zero Shear Viscosity η^0 for Polybutadiene Samples in Benzene, Isobutyl Acetate
and Dioxane Solutions

Sample	Solvent	Temperature (°C)	Concentrations at 20.5 or 20.2°C (g/dl)	η^0 (Poise)
PP2F1	Benzene	20.5	0.99	7.20×10^{-2} [a]
			2.52	5.20×10^{-1}
			5.07	5.41×10^0
			7.50	3.31×10^1
			9.78	1.65×10^2
			13.1	1.14×10^3
	IBA	20.5	1.01	2.20×10^{-2} [a]
			2.51	2.70×10^{-1}
			5.00	3.85×10^0
			7.50	2.74×10^1
			10.0	1.80×10^2
			13.0	$1.24_2 \times 10^3$
	Dioxane	20.2	1.04	5.20×10^{-2} [a]
			2.42	3.82×10^{-1}
			4.99	5.80×10^0
			7.51	5.05×10^1
			9.53	2.09×10^2
			11.6	8.90×10^2
PB2F2	Benzene	20.5	2.51	9.40×10^{-2} [a]
			5.00	8.10×10^{-1}
			7.50	3.64×10^0
			10.1	1.14×10^1
			15.1	8.56×10^1
			18.9	3.49×10^2
			20.1	4.50×10^2
			24.8	$1.56_2 \times 10^3$
			25.2	$1.63_8 \times 10^3$
	IBA	20.5	2.51	4.60×10^{-2} [a]
			5.03	5.10×10^{-1}
			7.57	2.65×10^0
			9.99	8.40×10^0
			12.4	2.44×10^1
			15.0	6.35×10^1
			20.0	3.90×10^2
			23.5	$1.20_6 \times 10^3$
	Dioxane	20.2	2.51	9.25×10^{-2} [a]
			5.01	8.20×10^{-1}
			7.50	4.25×10^0
			9.97	1.46×10^1
			12.5	4.55×10^1
			15.0	1.26×10^2
			19.0	5.54×10^2
			20.7	8.71×10^2
			22.7	1.57×10^3
PB2F3	Benzene	20.5	2.50	4.60×10^{-2} [a]
			5.01	2.09×10^{-1} [a]
			7.55	8.20×10^{-1}
			10.1	2.58×10^0
			15.0	1.12×10^1
			20.1	4.50×10^1
			25.2	1.44×10^2

(continued)

Table III
(continued from previous page)

Sample	Solvent	Temperature (°C)	Concentrations at 20.5 or 20.2°C (g/dl)	η^0 (Poise)
			30.3	4.30×10^2
			32.9	6.68×10^2
			35.5	9.25×10^2
	IBA	20.5	2.50	3.20×10^{-2a}
			5.03	1.07×10^{-1a}
			7.51	6.00×10^{-1}
			10.0	2.07×10^0
			15.0	1.05×10^1
			19.8	4.03×10^1
			24.7	1.43×10^2
			30.0	4.55×10^2
			34.0	9.06×10^2
	Dioxane	20.2	2.50	6.40×10^{-2a}
			5.00	3.45×10^{-1a}
			7.56	1.10×10^0
			10.2	3.66×10^0
			15.1	1.84×10^1
			20.3	7.68×10^1
			25.0	2.93×10^2
			30.0	7.75×10^2
			33.3	1.34×10^3

[a] Data obtained from capillary viscometer with varying pressure head.

dioxane were used as θ solvents.[7] The values of η^0 for the samples of different molecular weights are plotted logarithmically against polymer concentration c (g/dl) in Figure 1. Superposition of data in Figure 1 has been made to give a single composite curve for each solvent by shifting them vertically by a factor $(M^0/M)^{3.4}$, here M^0 represents the molecular weight of the reference sample, PB2F1. The composite curves thus obtained for a good solvent (benzene at 20.5° C) and two θ solvents, dioxane and IBA, are shown in Figures 2 and 3, respectively, where K is chosen as 3.4 log (M^0/M). The superposition is not successful, however, over the entire range of concentration. The shift factor is found to be proportional to $M^{3.4}$ in the range of higher concentration. The data that deviated from the composite curve (at the lower concentration region) are shown by dashed lines. The results indicate that the 3.4-power law is valid for the present data of polybutadiene. In this connection, it may be mentioned that Kraus and Gruver[8] observed similar results that the zero shear viscosity η^0 for linear polybutadiene melts increased in a 3.4th-power proportion to molecular weight M above a certain critical molecular weight M_c.

The onset of entanglement can be identified by rather abrupt change of slope in the plots of relative viscosity $\eta^0_r(C)$ versus concentration c, $\eta^0_r(M)$ versus molecular weight M, or $\eta^0_r(c, M)$ versus cM^b. At high cM^b, it is frequently reported[9] that the relative viscosity η^0_r is a single function of $c^5M^{3.4}$. The plots of log η^0_r versus 5 log c + 3.4 log M have been shown in Figure 4. A single composite curve has been obtained with good coincidence
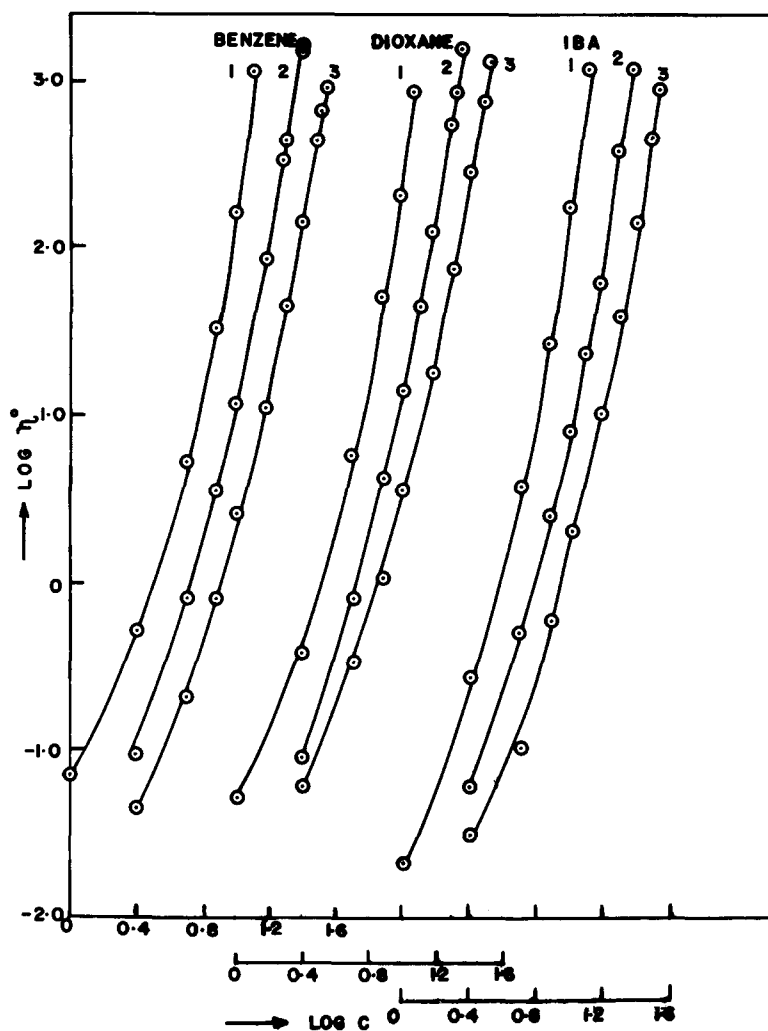
Fig. 1. Double-logarithmic plots of zero shear viscosity η^0 versus concentration for polybutadiene samples in good and θ solvents: (1) PB2F1 (2) PB2F2 (3) PB2F3.

for the three samples of different molecular weights both good and poor solvents. At the higher values of variables, the logarithmic plot yielded a straight line with slope of unity, but at lower values the scattering of data are more and the slope changed gradually. Since the change of the slope of the curve is not sharp, the concentration or molecular weight (critical) at which the entanglement started cannot be ascertained. The results indicate that, over a considerable range of the variables (molecular weight and concentration) at a constant temperature, the relative viscosity is a single function of $c^5 M^{3.4}$.

The values of zero shear specific viscosity η^0_{sp} for each polymer sample in both good and θ solvents are double-logarithmically plotted against poly-
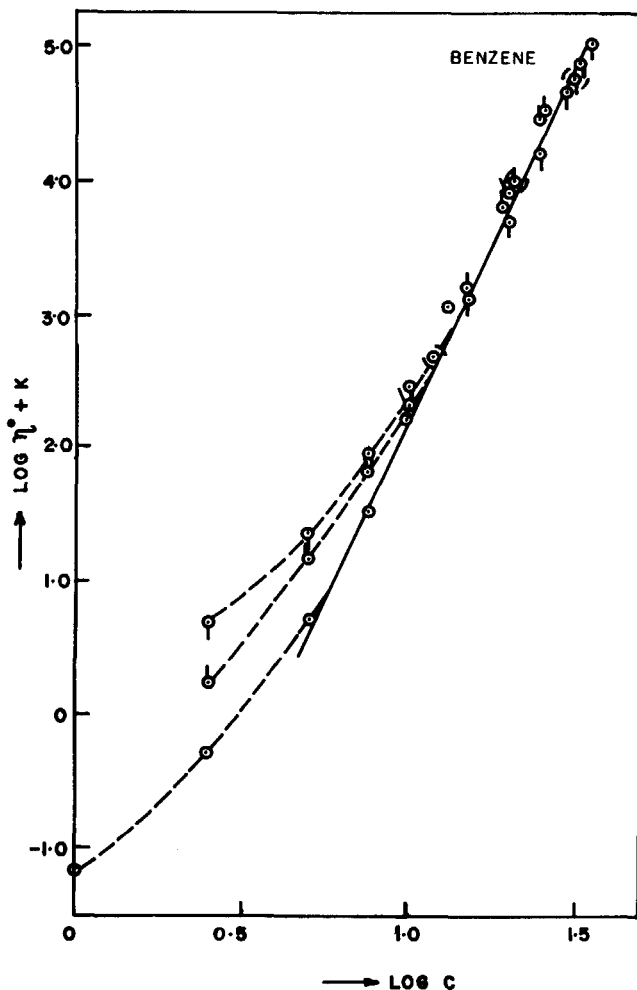
Fig. 2. Composite curve for polybutadiene samples in benzene: ⊙ PB2F1; ⊖PB2F2; ⊙ PB2F3.

mer concentration c (g/dl) in Figures 5 and 6. The data obtained at 20.5° C for benzene solutions have been used for comparison with those of dioxane and isobutyl acetate solutions measured at 20.2 and 20.5° C, respectively. The difference between the viscosity data obtained at 20.2 and 20.5° C in benzene solution was very small and hence neglected. The results confirmed in many respects those observed earlier[1] that the η^0_{sp} values in θ solvents at higher concentration region are found to be higher than those observed in good solvents, whereas in the moderately concentrated region the values are just opposite in θ and good solvents. It may be pointed out that, contrary to our results in polychloroprene,[1] the viscosity crossover in poor solvents for polybutadiene samples is not very sharp and that crossover, too, has taken place in the range of concentration 11.7–31.6% polymer which is comparitively higher than that of polychloroprene samples (6.05–21.0%
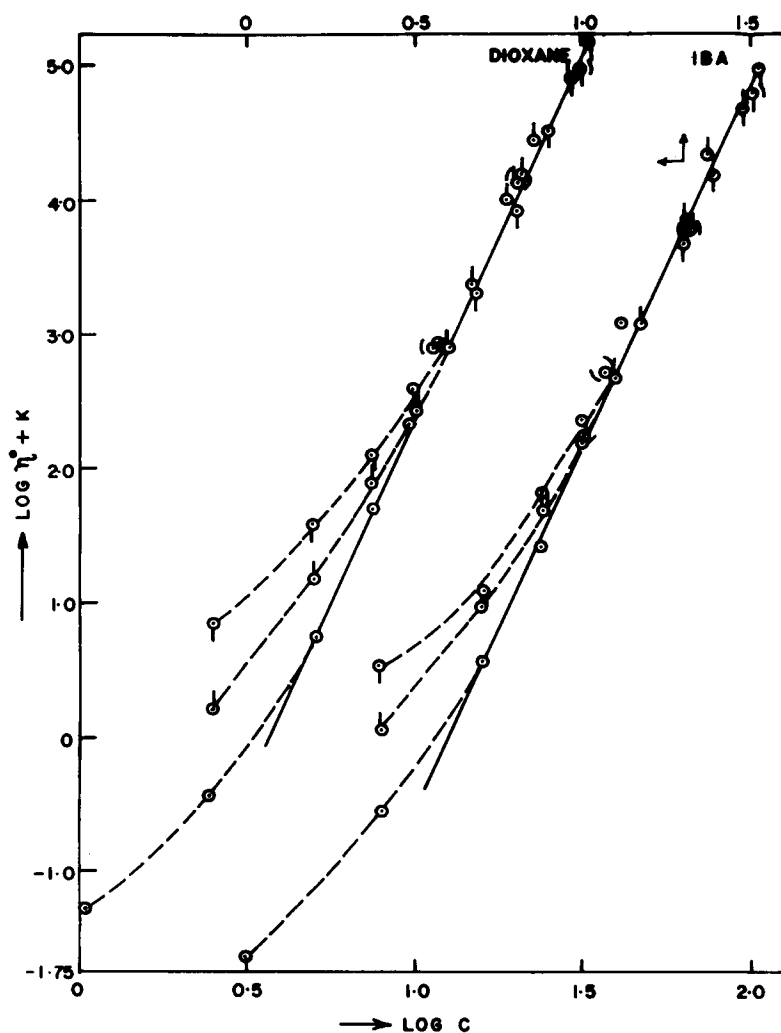
Fig. 3. Composite curve for polybutadiene samples in θ solvents: ⊙ PB2F1; ⊙ PB2F2; ⊙ PB2F3.

polymer). The result supports the idea that there exists a relation between viscosity crossover in θ solvents and polymer polarity, supporting the idea of enhanced intermolecular association in poor solvents. It may be recalled that the relative viscosity of polyisobutylene[10] (a nonpolar polymer with a flexible chain) showed the same values at equiconcentrated solutions in good and θ solvents, whereas in polyvinyl acetate,[11] polystyrene,[12–14] and poly(methyl methacrylate)[12,15] (polystyrene is nonpolar, but the other two are polar polymers), the relative viscosities in a θ solvent cross over and become somewhat higher than good solvent values with crossover point concentrations respectively higher than the 35% polymer in the range of 15–30% polymer and in the range of 5–7% polymer.
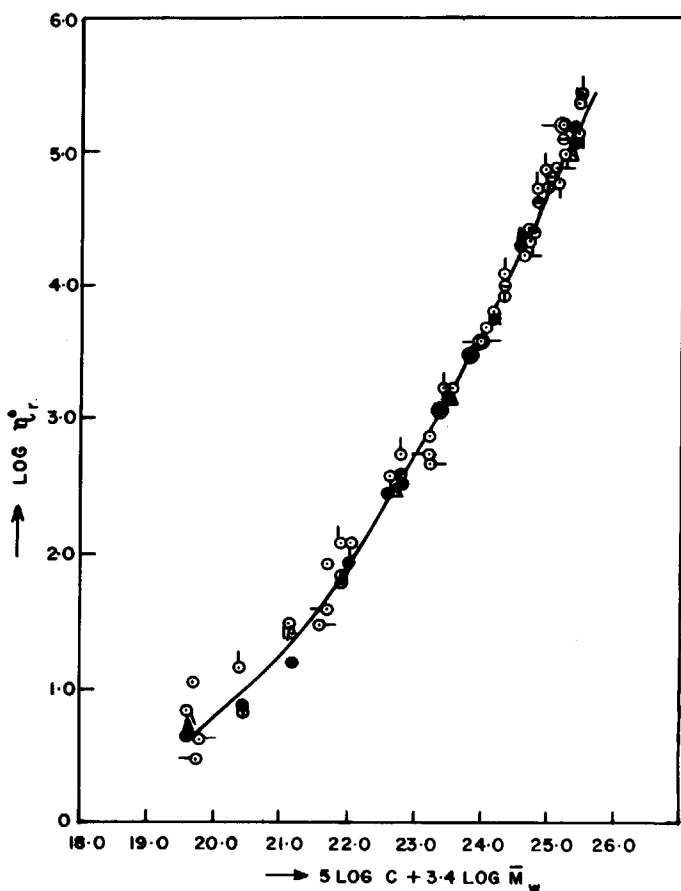
Fig. 4.   Double-logarithmic plots of zero shear relative viscosity η_r^0 versus $C^5M^{3.4}$ for poly-butadiene samples in good and θ solvents: Benzene (⊙ PB2F1; ☉ PB2F2; ⊙ PB2F3); IBA (— ⊙ PB2F1; ⊙ PB2F2; ●PB2F3); Dioxane (⊙ PB2F1; ⊙ PB2F2; △ PB2F3).

The crossover point concentrations for polybutadiene samples and their corresponding viscosities in both good and θ solvents are given in Table IV. The viscosities at crossover points for polybutadiene samples are much higher than those of polychloroprene samples. It was observed in our previous paper[1] that the onset of entanglement (the free diffusion of polymer chains by reptation) started at the crossover point concentration, where the entanglement begins to play a role in the viscosity. From the composite curves in Figures 2 and 3, in the present work it was observed that the date for c_{cross} (denoted by parentheses) are deep inside the composite curve in the higher concentration region, not at the starting points from where the data deviate from the composite curve represented by dashed lines. This implies that the quasi-network formation (entanglement) is higher in polybutadiene solutions than in polychloroprene solutions.
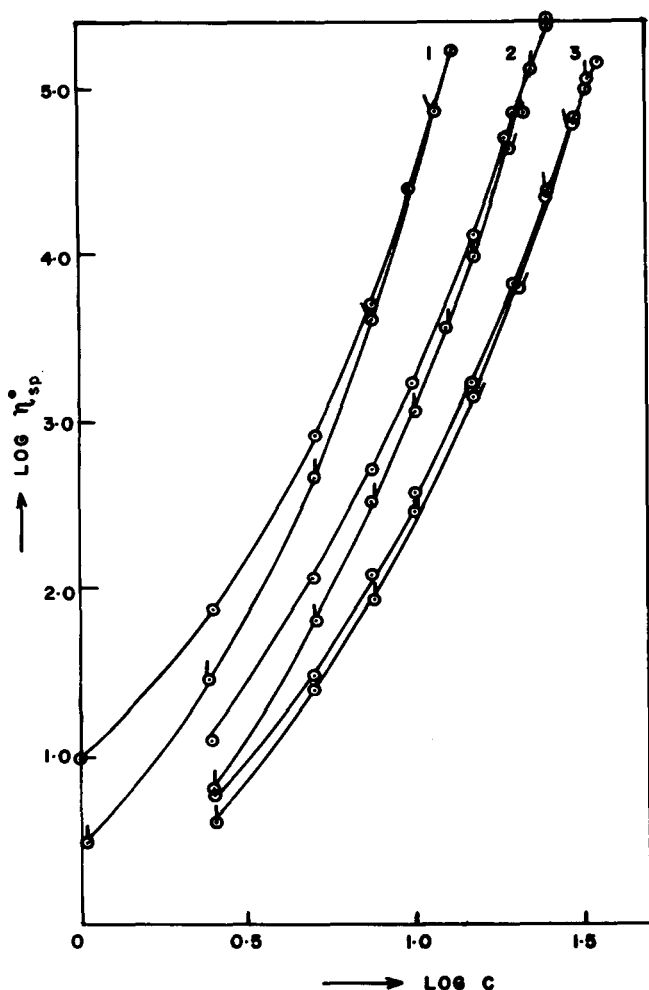
Fig. 5. Double-logarithmic plots of zero shear specific viscosity η_{sp}^0 versus concentration c in good and θ solvents: (1) PB2F1; (2)PB2F2; (3)PB2F3 (⊙ benzene and ⊙ dioxane).

Correlation of Data

To correlate the viscosity data obtained at good and poor solvents, the method given by Graessley,[2] in which the contraction of dimensions of chains with concentration in good solvent has been accounted for as well as the method given Dreval and coworkers,[3] in which the normalization of the correlating variable c [η] by Martin constant K_M has been made, were examined. The plots of relative viscosity η_r^0 of polybutadiene samples in both good and θ solvents as a function of appropriate correlating variable derived by Graessley[2] as $0.77 \left(\dfrac{c}{0.77}\right)^{1/2a}$, where a is the exponent of the Mark-Hauwink relation, have been shown in Figure 7. This correlating
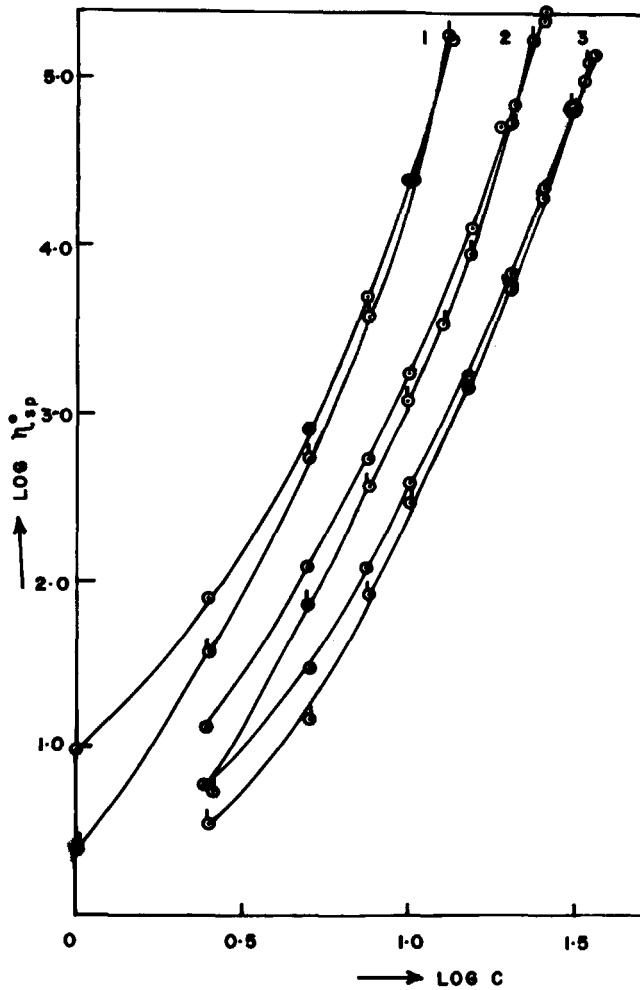
Fig. 6. Double-logarithmic plots of zero shear specific viscosity η^0_{sp} versus contration c in good and θ solvents: (1)PB2F1; (2) PB2F2; (3) PB2F3 ($\odot$ benzene; $\odot$ IBA).

TABLE IV

Crossover Point Concentration and Viscosity for Polybutadiene Samples in Benzene-Isobutyl Acetate, and Benzene-Dioxane Systems

			η^0 cross (poise)	
Sample	Solvent System	^{c}cross (g/dl)	Benzene	IBA/dioxane
PB2F1	Benzene-IBA	11.7	520	554
PB2F2		20.4	520	554
PB2F3		31.6	520	554
PB2F1	Benzene-dioxane	11.5		858
PB2F2		20.4		858
PB2F3		30.9		858
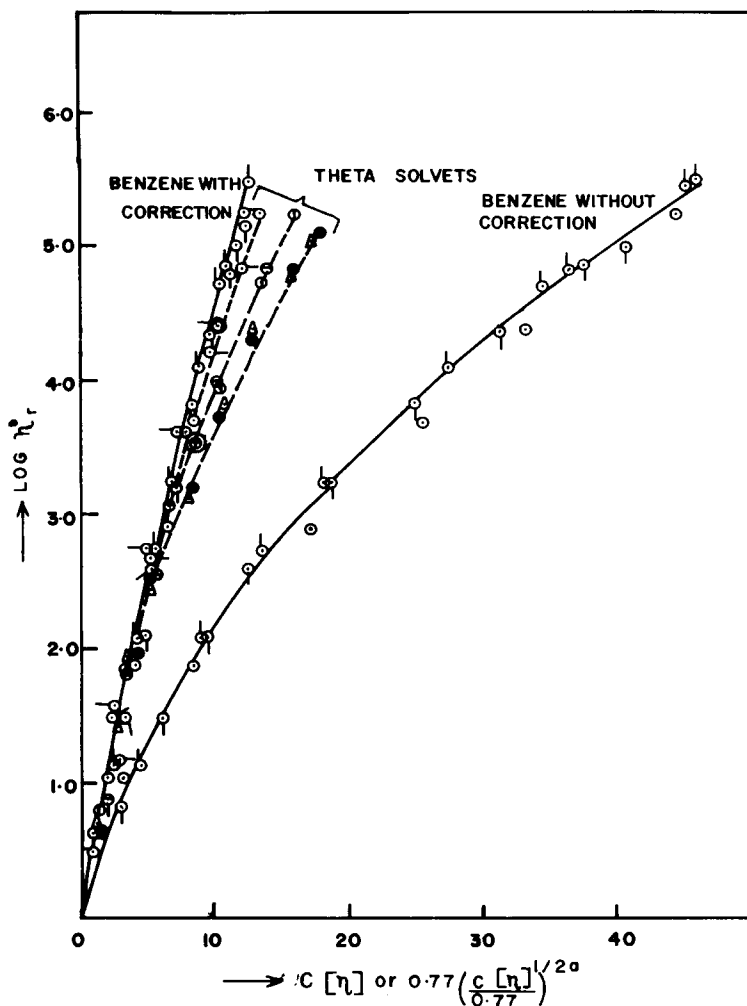
Fig. 7.   Plots of log η_r^0 versus correlating variable $c[\eta]$ or $0.77\,(c[\eta]/0.77^{1/2a}$ for polybutadiene samples in good and θ solvents: Benzene: ($\odot$ PB2F1; $\odot$ PB2F2; $\odot$ PB2F3); IBA: ($\odot$ PB2F1; $\odot$PB2F2; $\bullet$ PB2F3; dioxane $\odot$ PB2F1; $\odot$ PB2F2; $\triangle$ PB2F3). Differences of data for samples of different molecular weights were observed in θ solvents, especially at the higher concentration range, and hence three curves were drawn as shown by dashed lines.

variable reduces to $c[\eta]$ in θ solvent, where the exponent $a = 0.5$. The value of the exponent a for polybutadiene in benzene at 20.5° C has been taken as 0.73 and in isobutyl acetate (20.5° C) and dioxane (20.2° C) as 0.5. For comparison, the plots of relative viscosity versus the uncorrected correlating variable $c[\eta]$ in benzene (good solvent) has been shown in the same graph (Fig. 7). It is very surprising that in θ solvents, contrary to our earlier results in polychloroprene, the scatter of data at the higher concentration was such that they can be fitted in three different curves (shown by dashed lines) instead of a single curve. It is not understood at present why the

three samples yielded three separate curves instead of a single curve. However, the benzene (good solvent), the deviations of the data were very small, and only a single curve has been drawn with data for three samples. In good solvent, the relative viscosity increases less rapidly with $c[\eta]$ compared with that in θ solvents. It may be pointed out that since the three polybutadiene samples have produced three curves instead of one, especially at the higher concentration region, the superposition of data obtained in benzene (good solvent) and θ solvents (IBA and dioxane) has become somewhat irrelevant. However, the curve for benzene obtained after correction for chain contraction in the concentrated region was found to be exactly fitted with the curve obtained for the θ solvents in the lower concentration region; in the higher concentration region, it has moved away slightly from the curves (three) obtained in θ solvents, after crossing them. A slight overestimation of the data by this correction to have been effected.

Further, the correlation of data obtained in good and θ solvents by another method given by Dreval and coworkers[3] has also been considered. In this method, Martin relation $\eta^0_{sp}/(c[\eta]) = \bar{\eta} = \exp K_M(c[\theta])$ has been used. The plots of log $[\eta^0_{sp}/(c[\eta])]$ versus $c[\eta]$ for good and poor solvents are shown in Figures 8 and 9, respectively. Similar to our earlier results for
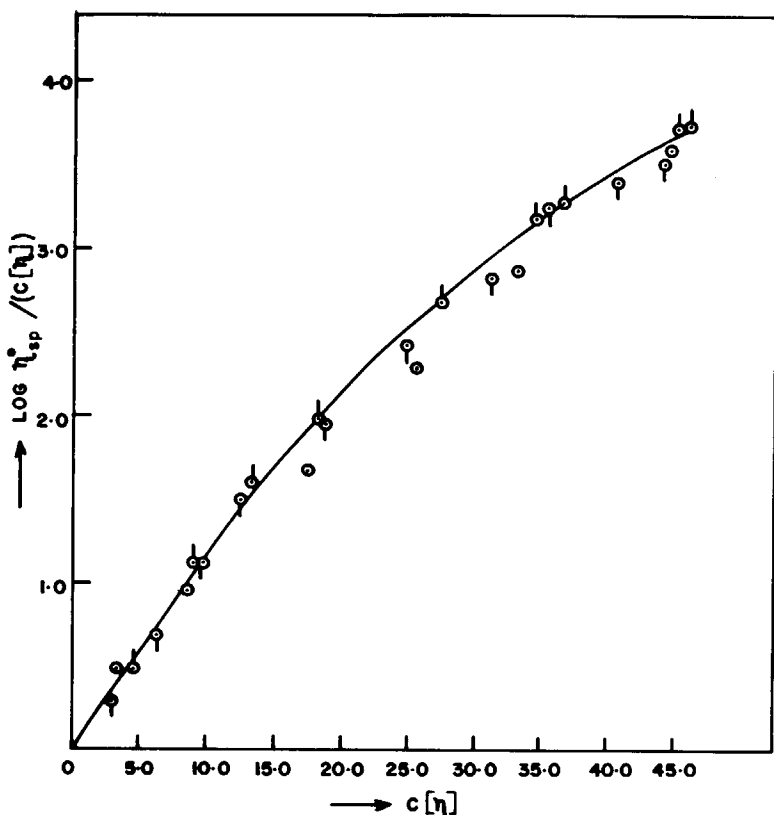

Fig. 8. Plots of log $[\eta^0_{sp}/(c[\eta])]$ versus correlating variable $c[\eta]$ for polybutadiene samples in benzene. Single curve was obtained as the scatter of the data was small (⊙ PB2F1; ⊙ PB2F2; ⊙Pb2F3).
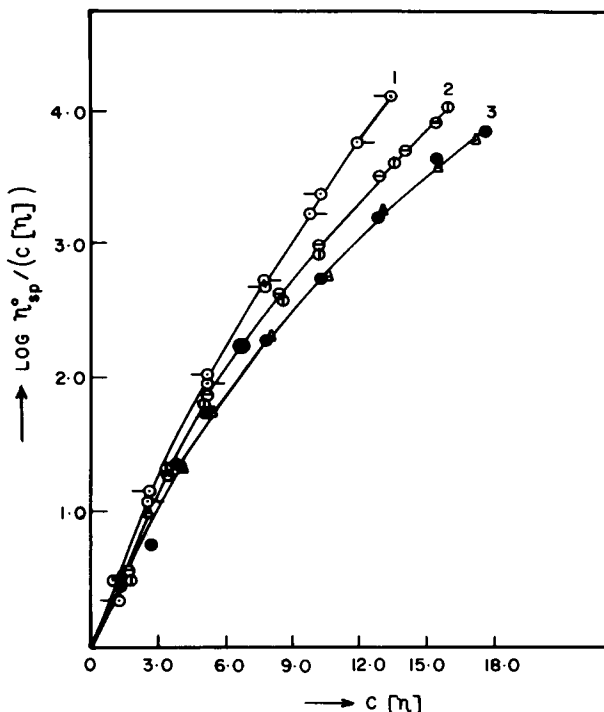
Fig. 9. Plots of log $[\eta^0_{sp}/(c[\eta])]$ versus correlating variable $c[\eta]$ for polybutadiene samples in θ solvents. Three curves were obtained for three samples of different molecular weights, and the data for two $\bigcirc$ solvents for each sample were fitted in one curve: dioxane ($\odot$ PB2F1; $\oslash$ PB2F2; $\triangle$ PB2F3); IBA ($\ominus$ PB2F1 $\bigcirc$ PB2F2; $\bullet$ PB2F3).

polychloroprene, the data taken in good solvent (benzene at 20.5° C) for three samples are fitted in a single curve, but the data taken in poor solvents (IBA and dioxane) for three polymer samples of different molecular weights are fitted in three separate curves, which is certainly of very different observation. Since the intrinsic viscosity $[\eta]_\theta$ of the polymer in two θ solvents, dioxane and isobutyl acetate, was proportional to $M^{0.5}$ and since the two θ solvents are considered to have a similar solvent power, it is not understood why the plots yielded three separate curves, instead of a single curve in the present case. However, the data for two θ solvents for each sample are fitted in one curve. The Martin constant K_M was determined from the initial slope of log $[\eta^0_{sp}/(c[\eta])]$ versus $c[\eta]$ plots, and K_M has been obtained as $K'_M/2.303$. The values of $K'_M (= 2.303 K_M)$ obtained for different samples in good and θ solvents are listed in Table V. Since three separate curves were obtained for three samples in θ solvents, three different values of K_M have been obtained from them, whereas in benzene solution only one K_M value has been obtained since the data are fitted in a single curve. It may be pointed out that the Huggins constant K' is theoretically equal to the Martin constant K'_M. The values of Huggins constant K' obtained in the course of establishing the intrinsic viscosities for the samples in good and θ solvents are listed along with K'_M in the same table for comparison. For all polymer-solvent systems investigated, it was confirmed that the

TABLE V

Values of Martin Constant K'_M and Huggins Constant K' for Polybutadiene Samples in Good and $\ominus$ Solvents

Sample	Solvent, temperature (°C)	K'_M	K'
PB2F1	Benzene, 20.5	0.27_6	0.38
PB2F2		0.27_6	0.29
PB2F3		0.27_6	0.18
PB2F1	IBA, 20.5, and dioxane, 20.2	0.97_6 ·	0.92_4
PB2F2		0.91_6	0.82
PB2F3		0.81	0.85

Huggins constant K' and Martin constant K'_M evaluated by the two procedures agree fairly well with each other. However, in the case of the good solvent, benzene, instead of a single K' value for three samples, three slightly different values were obtained, the average (0.28) of which was in excellent agreement with K'_M values have been used to normalize the correlating variable $c[\eta]$ to move the correlations for θ and good solvents to a common curve. The plots of log $[\eta^0_{sp}/(c[\eta])$ versus $K_M c[\eta]$ for all the samples in good and θ solvents are shown in Figure 10. It is observed from the figure that the normalization of the correlating variable $c[\eta]$ with Martin constant K_M
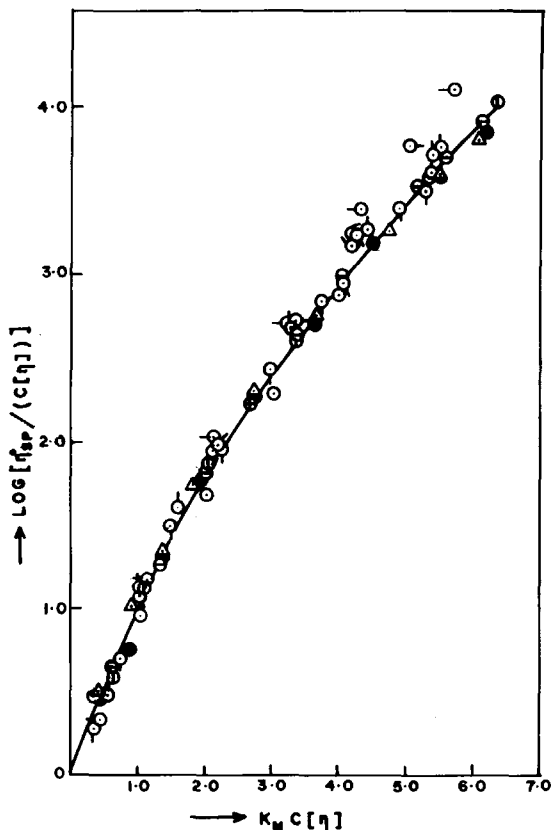

Fig. 10. Plots of log $[\eta^0_{sp}/(c[\eta])]$ versus $K_M c[\eta]$ for polybutadiene samples in good and θ solvents. Single curve was obtained for all samples in different solvenets: benzene ($\odot$ PB2F1; $\odot$ PB2F2; $\bigcirc$ PB2F3; dioxane $\odot$ PB2F1; $\bigcirc$ PB2F2; $\triangle$ PB2F3); IBA ($\odot$ PB2F1; $\odot$ PB2F2; $\bullet$ PB2F3).

has reduced all experimental data for three polymer samples of different molecular weights and in different solvents to the master curve.

In conclusion, it may be stated that the correlation of the date by the method given by Drevel and coworkers (plot of log $\bar{\eta}$ versus $c[\eta]$) produced a single curve with comparatively less scatter of data than that of polychloroprene samples in good solvent (benzene), whereas in θ solvents, though the data for two θ solvents, dioxane and IBA, were fitted into a single curve for each sample, three separate curves (instead of a single curve) were obtained for three polybutadiene samples. However, the normalization of the correlating variable, $c[\eta]$ by Martin constant, K_M eliminated completely all the differences between the data obtained for three samples in both good and θ solvents.

On the other hand, the appropriate correction of the correlating variable $c[\eta]$ by the method given by Graessley for contraction of coil dimension with concentration in good solvent has moved the correlations for θ and good solvents to a common curve, especially in the lower concentration region. Strictly speaking, Graessley's correction should apply only at low concentration when contraction is complete (θ dimension) and the good and θ solvents results should agree. The correlation of the data by either of the two methods seems to be possible in case of the nonpolar flexible polymer, polybutadiene.

References

1. P. Roy-Chowdhury and V. D. Deuskar, *J. Appl. Polym. Sci.*, **29**, 153 (1984).

2. W. W. Graessley, *Polymer*, **21**, 258 (1980).

3. V. E. Dreval, A. Y. Malkin, and G. C. Botvinnik, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 1055 (1973).

4. W. W. Graessley, *Advan. Polym. Sci.*, **16**, 1 (1974).

5. S. H. Maron, I. M. Krieger, and A. W. Sisko, *J. Appl. Phys.*, **25**, 971 (1954).

6. W. G. Cooper, D. E. Eaves, and G. Vaughan, *J. Polym. Sci.*, **59**, 241 (1962).

7. J. Brandrup and E. M. Immergut, *Polymer Handbook*, John Wiley, New York, 1975, pp.4–6, 159.

8. G. Kraus and J. T. Gruver, *J. Polym. Sci., Part A,***3**, 105 (1965).; *J. Polym. Sci., Part A-2*, **8**, 305 (1970).

9. R. F. Landel, J. W. Berge, and J. D. Ferry, *J. Colloid Sci.*, **12**, 400 (1957).

10. M. P. Johnson, W. W. Evans, I. Jordan, and J. D. Ferry, *J. Colloid Sci.*, **7**, 498 (1952).

11. J. D. Ferry, E. L. Foster, G. V. Browning, and W. M. Sawyer, *J. Colloid Sci.*, **6**, 377 (1951).

12. K. S. Gandhi and M. C. Williams, *J. Polym Sci., Part C,***35**, 211 (1971).

13. R. Simha and J. L. Zakin, *J. Colloid Sci.*, **17**, 270 (1962).

14. J. D. Ferry, L. D. Grandine, Jr., and D. C. Udy, *J. Colloid Sci,*, **8**, 529 (1953).

15. B. A. Toms and D. J. Strawbridge, *Trans. Faraday Soc.*, **49**, 1225 (1953).