

Effect of Solvent, Concentration, and Molecular Weight on the Rheological Properties of Polymer Solutions*

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Synopsis

The zero-shear viscosity η^0 of polychloroprene samples of different molecular weights over a wide range of concentration in good and poor solvents has been studied. Butanone and cyclohexane were used as θ solvents and benzene at two different temperatures (25 and 45.5°C) was used as two good solvents. The zero shear specific viscosity η_{sp}^0 in θ solvents at the high concentration region is found to be higher compared to the values obtained in good solvents, whereas in a moderately concentrated region the values are just opposite in θ and good solvents. The high values of specific viscosity in poor solvent at the concentrated region have been explained as due to the fact that the efficiency of entanglements is much bigger in θ solvent than in good solvent. There are indications from our data that, at the crossover point concentration, the onset of entanglements begins, and from this concentration the entanglement begins to play a role in the viscosity. The superposition of viscosity data for each solvent was carried out by shifting vertically the curve along $\log \eta^0$ axis at constant concentration by a factor $(M/M^0)^{3.4}$, where M^0 is the molecular weight of the reference sample. The shift factor was found to be exactly proportional to $M^{3.4}$ in the range of higher concentration (beyond the crossover point concentration) and approximately to M in the lower concentration range (below the crossover point concentration). This showed that the relation $\eta^0 \propto M^{3.4}$ was obeyed by the present data. To correlate the viscosity data obtained at good and θ solvents, the method as given by Graessley has been employed, which has taken into account the contraction of dimensions of chains with concentration in good solvents. It has been observed that, though this approximate correction for variation of chain dimensions on correlating variable, $C[\eta]$, has moved the correlations for θ and good solvents closer to a common curve, complete superposition of data has not been effected by this correction. On the other hand, the correlation of the data by the method given by Dreval and co-workers showed the plot of $\log\{\eta_{sp}^0/(C[\eta])\}$ vs. $C[\eta]$ produced a single curve for solutions of polychloroprene samples in two different θ solvents (butanone and cyclohexane) over the entire concentration range. But in the case of good solvents (benzene at 25°C and benzene at 45.5°C) the similar plots yielded, instead of one, two curves. However, the normalization of the correlating variable, $C[\eta]$, by the Martin constant K_M , which is related to the flexibility of macromolecular chain and polymer-solvent interaction, reduced all data of the polymer samples to a common curve. This zero-shear viscosity master curve is valid for the entire range of concentration independent of molecular weight and the nature of solvents.

INTRODUCTION

The zero-shear viscosity η^0 of polymer solutions is an important rheological parameter used to characterize the flow properties of polymer solution or melt in the linear region of deformation. Several factors such as the concentration of the solution, its temperature, the molecular weight and molecular structure of the polymer, and the nature of the solvent are responsible for the viscosity of polymer solutions. Many endeavors have been made for many years to correlate

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the data for zero-shear viscosity of polymer solutions obtained at different concentrations (high and low), molecular weights, and solvents.¹⁻¹⁰ Most recently molecular dynamic models based on reptation in a "tube" formed from entanglement constrains have been successfully compared^{3,5-10} with experimental data in a few cases. In order to explain the discrepancies exhibited by the reptation theory that the terminal relaxation time T_1 and static shear viscosity η^0 are found to depend on the third power of the molecular weight while experiments yields $T_1 \sim \eta^0 \sim M^{3.4}$. Doi¹⁰ has recently proposed a correction applicable for samples of molecular weight of practical importance, which improves the above disagreements.

Dilute solutions usually have polymer concentrations less than 1% by volume, and contributions to properties by one polymer chain are unaffected by other chains. Semidilute solutions are generally 1-10% by volume, and contributions to properties from one chain are affected by the others, though chains are not entangled with one another as they are assumed in concentrated solution. The Newtonian viscosity η^0 for many polymers in bulk and at fixed diluent concentration is observed to increase sharply to a constant 3.4 power dependence on M as the molecular weight of the polymer is exceeded to a critical value M_c . The onset of entanglement or aggregation phenomena can be identified by a rather abrupt change in slope in plots of relative viscosity $\eta_r^0(C)$ vs. concentration C , $\eta_r^0(M)$ vs. molecular weight M , or $\eta_r^0(C, M)$ vs. CM^b . The attainment of C^5 or $M^{3.4}$ behavior is often used to mark "critical" entanglement conditions. When viscosities of solutions in different solvents are compared at the same values of concentration and molecular weight, the most important parameter is the solvent viscosity η_s , to which η^0 of the solution is proportional at moderate concentration.¹¹ This cannot hold as the concentration approaches the undiluted polymer, because all systems must then approach η^0 of the polymer regardless of η_s . In the region of low concentration, the specific viscosity η_{sp}^0 of polymer solutions in poor solvents is found to be lower, but it changes more rapidly with concentration. Therefore, as the concentration increases, the specific viscosity of polymer solutions in a poor solvent may be found higher than in a good solvent.^{12,13} Some observations of ours seem to indicate that, at the crossover point concentration, the onset of entanglements begins, as a result of which from this concentration the entanglement begins to play a role in the viscosity.

In the present paper we report the study of the zero-shear viscosity of polychloroprene samples of different molecular weights over a wide range of concentrations in both good and θ solvents and the probability of constructing a zero-shear viscosity master curve valid for the entire concentration range independent of molecular weight and nature of solvent has been considered. Attempts have been made to correlate the viscosity data of the present work employing the correlating variable $C[\eta]$. The solvent-solute interaction constant K_M , which is related to the flexibility of the macromolecular chain and the polymer-solvent interaction, obtained from the Martin equation, has been used to normalize the correlating variable $C[\eta]$ so as to reduce all experimental data of the polymer samples to a common curve. Further, the method as given by Graessley,¹⁴ which has taken into account the contraction of dimensions of chains with concentration in good solvent, has been employed to correlate the data obtained at good and θ solvents. This approximate correction on correlating variable $C[\eta]$, though, improves the correlations much, but it cannot eliminate

TABLE I
Values of Intrinsic Viscosity and Molecular Weight for the Polychloroprene Samples

Samples	Solvent	Temp (°C)	$[\eta]$ (dL/g)	$\bar{M}_v \times 10^{-5}$
F1B	Benzene	25	2.12	4.85
	Benzene	45.5	2.42	
	Cyclohexane	45.5	0.56	
F2A	Benzene	25	1.47	2.69
	Benzene	45.5	1.66	
	Cyclohexane	45.5	0.41	
F2B	Benzene	25	1.10	1.68
	Butanone	25	0.38	
F2C	Benzene	25	1.00	1.44
	Butanone	25	0.35	
F3A	Benzene	25	0.85	1.11
	Benzene	45.5	0.94	
	Cyclohexane	45.5	0.27	
F3B	Benzene	25	0.79	0.99
	Butanone	25	0.29	

completely the difference between the data obtained at good and θ solvents in the present work.

EXPERIMENTAL

Polychloroprene (Denkachloroprene type M-40) obtained as a gift from Swastic Rubber Products, Ltd., Poona was fractionated from benzene solution at 25°C with the addition of acetone as nonsolvent. Molecular weights of the fractions were calculated from the intrinsic viscosities measured in benzene solution at 25°C. The relation between intrinsic viscosity $\{[\eta](\text{dL/g})\}$ and molecular weight as $[\eta] = 63.28 \times 10^{-5} \bar{M}_w^{0.62}$ was determined in this laboratory using light scattering values of \bar{M}_w in benzene solution for five polychloroprene fractions (range: $0.88\text{--}10.0 \times 10^5$). The viscosity of the solutions were measured with a Ubbelohde capillary viscometer and the intrinsic viscosity $[\eta]$ was determined by extrapolation to infinite dilution according to the relation $\eta_{sp}/C = [\eta] + K'[\eta]^2C$, where K' is the Huggins constant. The data for intrinsic viscosity and molecular weight of the samples used in this work are given in Table I.

The apparent specific volume V_p of the polymer was determined at a number of temperatures above 20°C (20°C, 30°C, 40°C, 50°C, and 60°C) by specific gravity bottle using ethylene glycol as confining liquid, and the apparent specific volume V_s of the solvents, namely, benzene, cyclohexane, and butanone, was determined pycnometrically over the same range of temperature (20–60°C) which were represented by the following equations:

$$V_p (\text{polychloroprene}) = 0.8230 + 6.36 \times 10^{-4} (\theta - 20^\circ\text{C})$$

$$V_s (\text{butanone}) = 1.2421 + 17.40 \times 10^{-4} (\theta - 20^\circ\text{C})$$

$$V_s (\text{cyclohexane}) = 1.2849 + 16.30 \times 10^{-4} (\theta - 20^\circ\text{C})$$

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

where θ is the temperature.

The solutions of higher concentration were prepared by mixing the weighed

TABLE II
Values of Zero-Shear Viscosity η^0 and θ -Temperature for the Solvents

Solvent	Temp (°C)	η^0 (cps)	θ -temp (°C)
Benzene	25	0.598	Good solvent
Benzene	45.5	0.473	Good solvent
Cyclohexane	45.5	0.648	45.5
Butanone	25	0.381	25

amounts of the polymer and the solvent and the relations for V_p and V_s were used to calculate the concentration of the solution (g/dL), assuming that there was no volume change on mixing. However, in higher concentrations (>30%), this assumption is not correct. Dilution was carried out by adding solvents by weight, and polymer concentration was converted to g/dL. Benzene at two different temperatures (25°C and 45.5°C) was used as good solvent, and cyclohexane and butanone were used as θ solvents. The θ temperature of the solvents used in this work is listed in Table II.

The zero shear viscosity η^0 of the polymer solutions was measured by means of a Brookfield LVT Viscometer (manufactured by Brookfield Engineering Laboratories, Inc., Stoughton, Mass.). In this instrument the shear rate and the shear stress are not readily calculated, but the simple approximation that the shear rate is approximately 0.2 times the rpm of the cylinder is useful.^{15,16} The viscosity of the non-Newtonian fluids is dependent on the rate of shear at which they are measured, and the shearing rate depends on the speed at which the spindle rotates. Since the rate of shear is directly proportional to rpm of the spindle at which the measurements are made, the η values taken at different speeds (rpm) were extrapolated to zero for the determination of the zero-shear viscosity in this work.

The Brookfield viscometer was recalibrated with smaller container (cell) made with stainless steel (35 mm diameter) and with this container the measurements were carried out with 63 cc of solution. The cell was kept immersed into a thermostatic water both at $25 \pm 0.02^\circ\text{C}$ and $45.5 \pm 0.02^\circ\text{C}$ temperatures. Only three spindles, nos. 2, 3, and 4, were used. The viscosity of each solution was measured at least with four different speeds and the plot of η vs. speed (rpm) was extrapolated to zero for the determination of zero-shear viscosity. The typical plots of viscosity as a function of speed at which the spindle rotates (i. e., shear rate) corresponding to the highest viscosities and then an order of magnitude of the shear rate for all other concentrations for the sample F2A in benzene and cyclohexane are given in Figures 1 and 2, respectively. Since the flow curves are curvilinear at low shear rate, direct extension of such plots to zero values of the experimental variable is somewhat subjective. However, the same plots of semilog paper converted the data to a somewhat linear form, and subsequent extrapolation to η^0 produced the same results.

The zero-shear viscosity of the solvents was measured by a capillary viscometer with a continuously varying pressure head designed by Maron and co-workers.¹⁷ The water from the thermostatic water baths maintained at $25 \pm 0.02^\circ\text{C}$ and $45.5 \pm 0.02^\circ\text{C}$ temperatures was circulated through the instrument for maintaining the constant temperatures. For Newtonian fluids, the viscosity was calculated

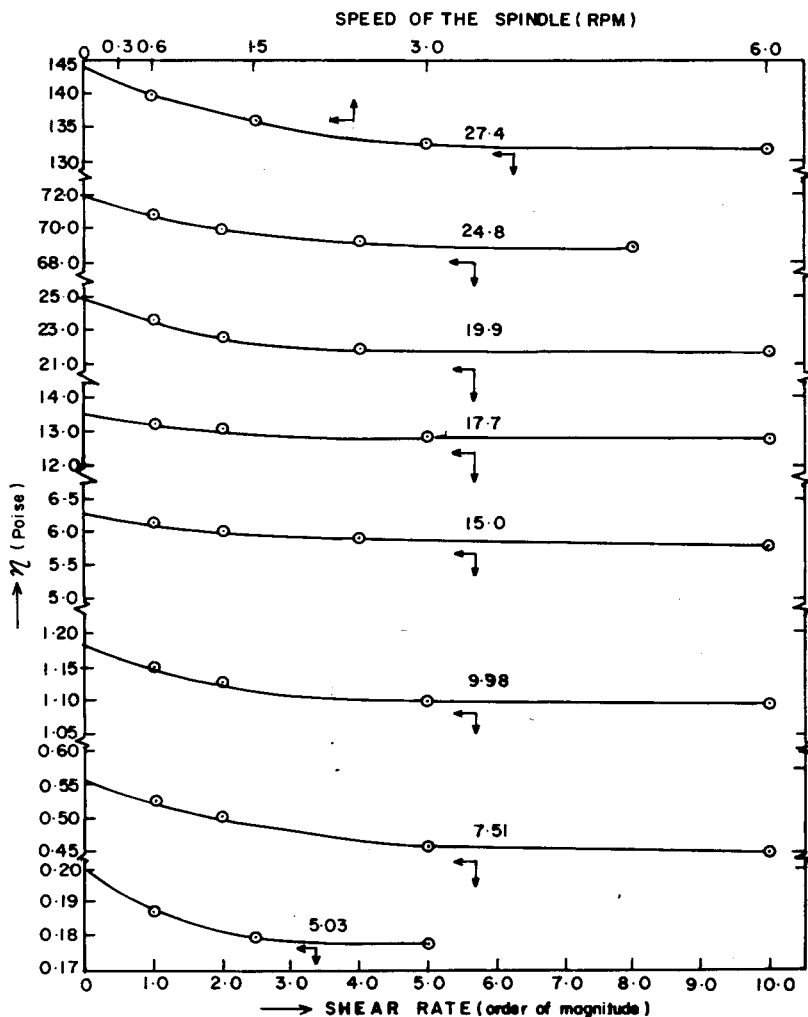


Fig. 1. Plots of viscosity as a function of shear rate (order of magnitude) for polychloroprene sample F2A in benzene for different concentrations at 45.5°C.

by the equation as given below:

$$1/\eta^0 = -(1/B)[d(\log h)/dt] = -m/B$$

where h is the height of the mercury manometer from its equilibrium position and B is the apparatus constant. The solvents used in this work showed Newtonian flow as $d(\log h)/dt$ was constant. However, the zero-shear viscosity for some dilute polymer solutions (below 5%) having non-Newtonian flow was measured with this instrument. The apparent viscosity η_a was calculated by the following equation:

$$1/\eta_a = -(m/B)\{1 + [1/(9.212m^2)](dm/dt)\}$$

The zero shear viscosity was determined by extrapolating the rate of shear to zero. The zero shear viscosity of the solvents are given in Table II.

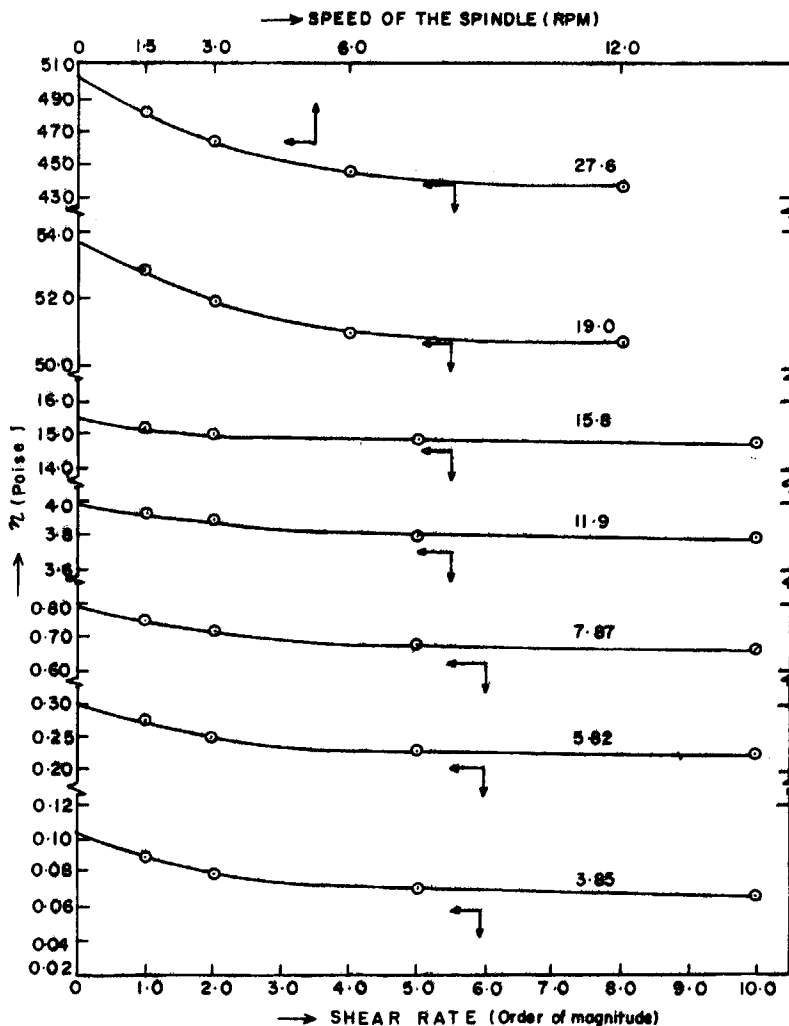


Fig. 2. Plots of viscosity as a function of shear rate (order of magnitude) for polychloroprene sample F2A in cyclohexane for different concentrations at 45.5°C.

RESULTS AND DISCUSSION

The experimental data for viscosity measurements are summarized in Tables III and IV. Table III gives the data for three polychloroprene samples (F1B, F2A, and F3A) in benzene and cyclohexane at 45.5°C, while Table IV gives the data for another three samples (F2B, F2C, and F3B) in butanone and benzene at 25°C. Butanone and cyclohexane were used as poor solvents, while benzene at two temperatures (25°C and 45.5°C) was used as two good solvents. The viscosity data given in Tables III and IV have been plotted as $\log \eta^0$ vs. $\log C$ in Figures 3 and 4. The viscosity is strongly dependent on concentration. The slope $d \log \eta^0 / d \log C$ becomes steeper with increasing concentration as entanglement of polymer chains and crosslinkings are increased with increasing concentration. It is observed that the curves 2 (F2A) and 4 (F2B) in Figure 3 have

TABLE III
 Summary of Results of Zero-Shear Viscosity η^0 for Polychloroprene Samples in Benzene and Cyclohexane at 45.5°C

Sample	Solvent	Concn at 45.5°C (g/dL)	η^0 (P)
F1B	Cyclohexane	2.02	2.91×10^{-2} ^a
		4.05	2.12×10^{-1}
		5.42	6.35×10^{-1}
		8.12	3.63×10^0
		10.4	1.14×10^1
	Benzene	1.26	2.56×10^{-2} ^a
		2.53	8.40×10^{-2} ^a
		5.08	4.25×10^{-1}
		7.57	1.46×10^0
		10.0	3.79×10^0
F2A	Cyclohexane	1.89	2.60×10^{-2} ^a
		3.85	1.03×10^{-1}
		5.82	3.00×10^{-1}
		7.87	7.80×10^{-1}
		11.9	4.00×10^0
		15.8	1.55×10^1
		19.0	5.37×10^1
		21.9	1.07×10^2
	Benzene	27.6	5.03×10^2
		2.55	5.20×10^{-2} ^a
		5.03	1.99×10^{-1}
		7.51	5.55×10^{-1}
		9.98	1.18×10^0
		15.0	6.22×10^0
		17.7	1.35×10^1
F3A	Cyclohexane	19.9	2.47×10^1
		24.8	7.17×10^1
		27.4	1.44×10^2
		2.50	2.61×10^{-2} ^a
		4.87	7.55×10^{-2} ^a
		10.5	4.55×10^{-1}
		15.0	2.00×10^0
		20.0	5.92×10^0
	Benzene	25.1	1.82×10^1
		30.1	4.80×10^1
	Benzene	32.5	6.65×10^1
		2.45	2.41×10^{-2} ^a
		5.19	7.60×10^{-2} ^a
		10.1	4.13×10^{-1}
		15.0	1.54×10^0
		20.1	4.50×10^0
		25.1	1.25×10^1
		30.0	2.80×10^1
		35.1	6.22×10^1

^a Viscosity was measured by capillary viscometer with varying pressure head.

crossed each other at the lower concentration range. However, there is no apparent reason for the same. The double logarithmic plots of zero-shear specific viscosity η_{sp}^0 as a function of concentration for each sample both in good and poor solvents are shown in Figures 5 and 6. In the high concentration region, the η_{sp}^0

TABLE IV
Summary of Results of Zero-Shear Viscosity η^0 for Polychloroprene Samples in Benzene and Butanone at 25°C

Samples	Solvent	Concn at 25°C (g/dL)	η^0 (P)
F2B	Butanone	2.51	1.47×10^{-2} ^a
		4.47	6.40×10^{-2} ^a
		7.50	3.34×10^{-1}
		10.1	9.90×10^{-1}
		15.0	4.79×10^0
		20.0	2.46×10^1
		24.2	7.60×10^1
	Benzene	2.54	4.94×10^{-2} ^a
		5.53	2.46×10^{-1}
		7.54	5.25×10^{-1}
		10.0	1.44×10^0
		15.0	6.70×10^0
		20.0	2.95×10^1
		22.9	5.86×10^1
F2C	Butanone	2.62	1.39×10^{-2} ^a
		5.23	5.20×10^{-2} ^a
		7.51	1.95×10^{-1}
		10.0	4.90×10^{-1}
		15.0	3.01×10^0
		20.1	1.45×10^1
		25.3	4.72×10^1
	Benzene	2.49	3.96×10^{-2} ^a
		5.01	1.29×10^{-1}
		7.51	3.00×10^{-1}
		10.0	7.41×10^{-1}
		15.2	3.64×10^0
		20.1	1.35×10^1
		25.4	5.04×10^1
F3B	Butanone	2.52	1.07×10^{-2} ^a
		4.76	3.10×10^{-2} ^a
		7.08	9.55×10^{-2} ^a
		10.0	2.90×10^{-1}
		15.1	1.26×10^0
		20.0	4.18×10^0
		25.1	1.26×10^1
	29.5	2.92×10^1	
	Benzene	2.50	2.38×10^{-2} ^a
		5.07	7.90×10^{-2} ^a
		6.75	1.90×10^{-1}
		11.2	7.20×10^{-1}
		15.0	1.49×10^0
		20.1	4.15×10^0
23.8		8.90×10^0	

^a Viscosity was measured by capillary viscometer with varying pressure head.

values in θ solvents are higher than those obtained in good solvents, whereas in the moderately concentrated region (the so-called Rouse region) the values are just the opposite in θ and good solvents. These results are in accord with those reported by other authors^{12,13} that the poor solvent η_{sp}^0 increases faster than the good solvent η_{sp}^0 and eventually exceeds it. The reversal of η_{sp}^0 is generally found

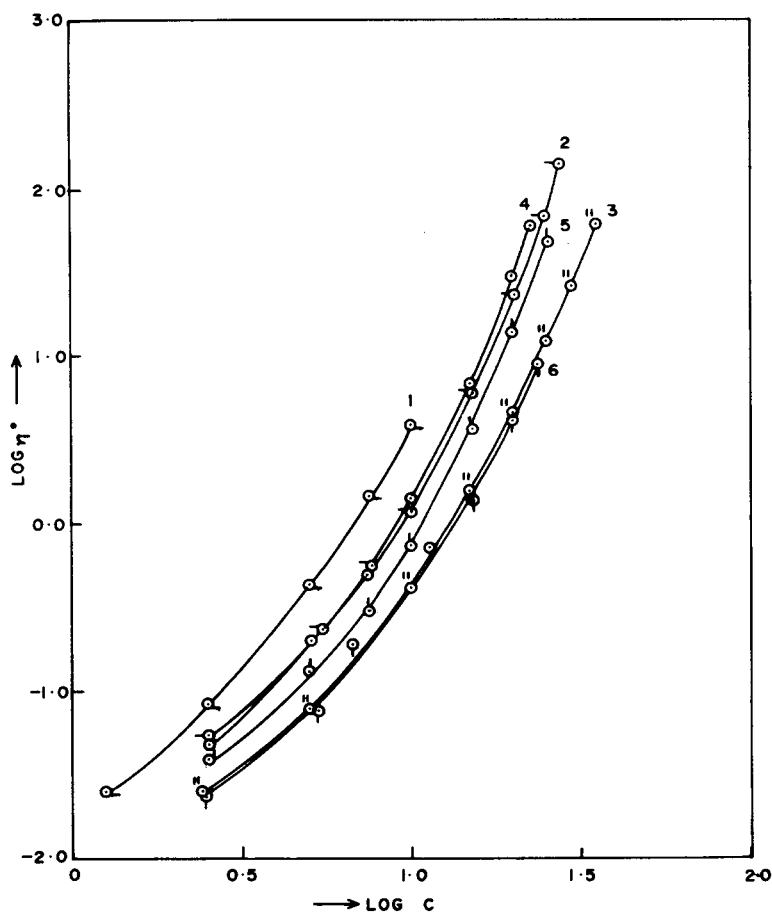


Fig. 3. Plots of $\log \eta^0$ vs. $\log C$ for polychloroprene samples in benzene at 45.5°C: (1) F1B; (2) F2A; (3) F3A and in benzene at 25°C: (4) F2B; (5) F2C; (6) F3B.

in the higher concentration range where the values of radius of gyration in good and poor solvents become almost identical.¹⁸⁻²¹ Hence the difference of the radius of gyration is not the cause for the reversal of η_{sp}^0 in concentrated solutions. Williams and co-workers¹² has explained this solvent effect in terms of polymer aggregation in poor solvents. It may be pointed out that Isono and Nagasawa¹³ have explained this phenomena that the strength of entanglement coupling in poor solvent is higher than in good solvent. However, the efficiency of entanglements is much bigger in θ solvent than in good solvent as the polymer-polymer contacts are more favored in θ solvent, and this seems to be the reason for the higher specific viscosity in poor than in good solvent.

From Figure 5 the concentrations for crossover points for F1B, F2A, and F3A have been obtained as 6.03, 10.5, and 21.1 g/dL, respectively. The same value for F2B, F2C, and F3B samples have been obtained as (from Fig. 6) as 8.71, 10.0, and 13.2 g/dL, respectively. It is presumed that the onset of entanglement has started at the crossover point concentration (to be discussed later) at which the entanglement begins to play a role in the viscosity. The variations of crossover point concentration, C_{cross} with molecular weight is shown in Figure 7. Two

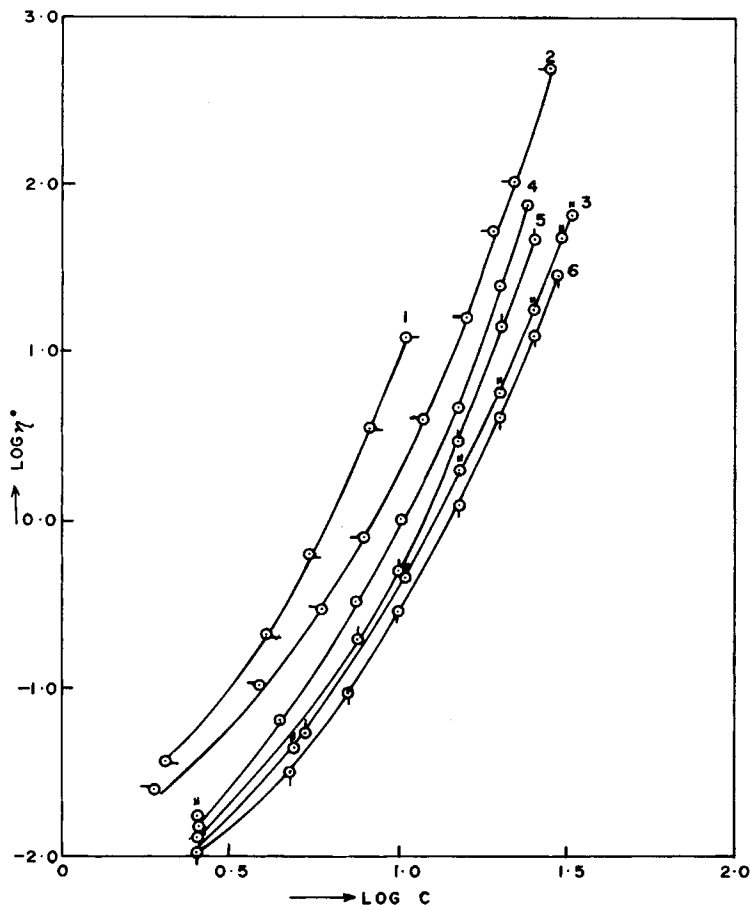


Fig. 4. Plots of $\log \eta^0$ vs. $\log C$ for polychloroprene samples in cyclohexane at 45.5°C : (1) F1B; (2) F2A; (3) F3A and in butanone at 25°C : (4) F2B; (5) F2C; (6) F3B.

separate straight lines (instead of one) almost parallel to each other were obtained with our data. From the figure it is clearly seen that the molecular weight M is proportional to -1.20 power of C_{cross} . It may be pointed out that similar to our results, Bueche and co-workers²² observed that the entanglement molecular weight M_e was proportional to the -1.20 power of the concentration in case of poly(methyl methacrylate)-diethyl phthalate system. However, the data obtained from different solvents were fitted on a single curve. It is not understood at present why our data obtained from two systems, benzene-cyclohexane and benzene-butane, are not fitted in one curve.

Superposition of the data in Figures 3 and 4 have been made so as to obtain a single composite curve for each solvent by shifting them vertically by a factor $(M/M^0)^{3.4}$. Here M^0 represents the molecular weight of sample F1B (or F2B) as a reference material. The composite curves thus obtained for benzene and cyclohexane solutions at 45.5°C and for benzene and butanone solutions at 25°C are shown in Figures 8 and 9, respectively, where K is chosen as $3.4 \log(M/M^0)$. It is interesting to note that the shift factor is found to be exactly proportional to $M^{3.4}$ in the higher concentration range, starting from the crossover point

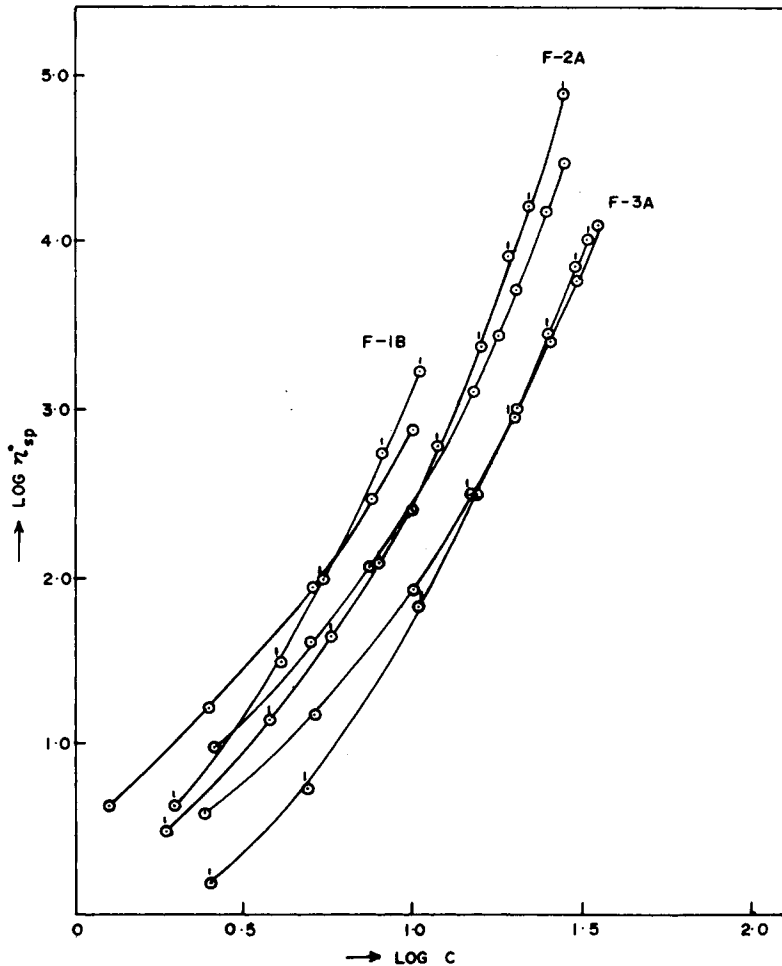


Fig. 5. Plots of $\log \eta_{sp}^0$ vs. $\log C$ for polychloroprene samples in benzene (\odot) and in cyclohexane (\odot) at 45.5°C .

concentration. This confirmed that the relation $\eta^0 \propto M^{3.4}$ was obeyed by the present data. However, for benzene solutions the data for C_{cross} are slightly away from the composite curves. On the other hand, the shift factor is found to be approximately proportional to M in the lower concentration (below the crossover point) range. (Superposition curves for lower concentration range are not shown.)

Generally the characteristic entanglement compositions are developed from the abrupt changes in the slope in plots of $\log \eta^0$ vs. $\log C$, as well as $\log M$. If the onset point for the bulk polymer of density ρ is M^* , the estimate for the onset of entanglement in solution has been recommended by Porter and Johnson²³ as $C_{\text{ent}}M = CM_{\text{ent}} = \rho M^*$. However, this scheme totally ignores the effect of the solvents. For a number of polar and nonpolar polymers it was found that the characteristic entanglement composition, $(MC)_{\text{ent}}$ was essentially constant over a range of concentrations and molecular weights.²⁴ In the present case the (MC_{cross}) values are fairly constant over a range of concentrations and molecular

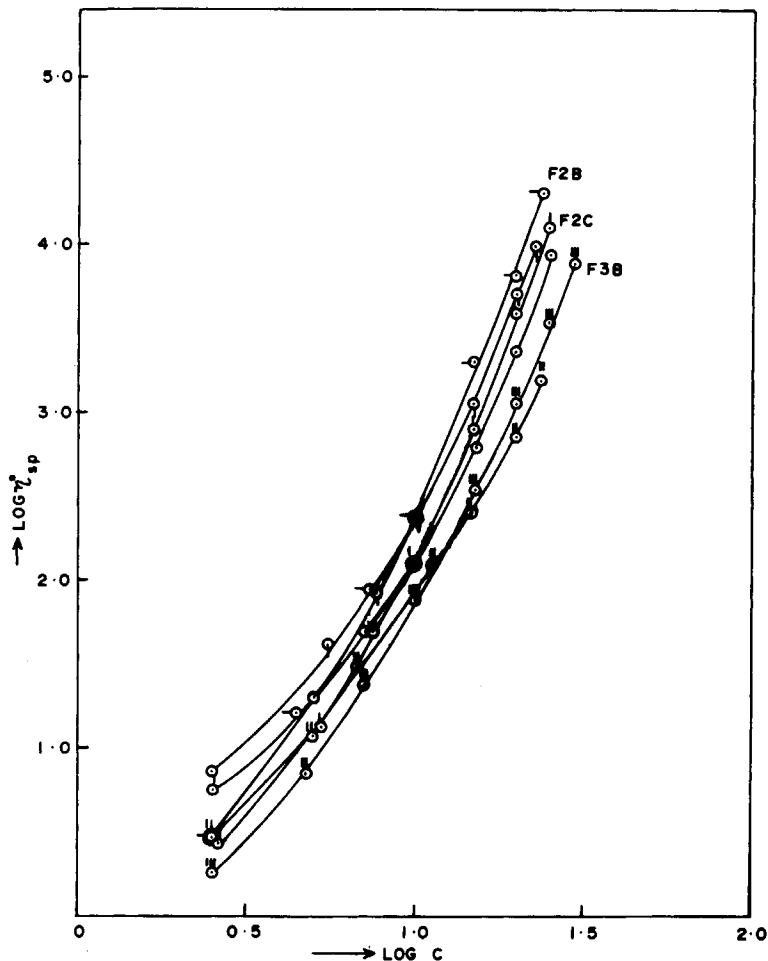


Fig. 6. Plots of $\log \eta_{sp}^0$ vs. $\log C$ for polychloroprene samples in benzene and butanone at 25°C: F2B in benzene (\circ) and in butanone (\bullet); F2C in benzene (\odot) and in butanone (\odot); F3B in benzene (\ominus) and in butanone (\ominus).

weights in each system [e. g., $(MC_{\text{cross}}) \sim 28.0 \times 10^5$ for the polychloroprene-benzene-cyclohexane system and $(MC_{\text{cross}}) \sim 14.0 \times 10^5$ for the polychloroprene-benzene-butanone system], indicating that the onset of entanglement has begun at the crossover point concentration. However, the entanglement composition is not independent of the solvent system used in the present case.

Correlation of Data

Several relations have been used by various authors to correlate the viscometric data for moderately concentrated solutions. The effect of solvent and concentration on chain dimensions are reflected in viscoelastic behavior. Graessley¹⁴ recently has proposed a method for correlating viscometric properties in the semidilute region which takes into account the contraction of coil dimensions

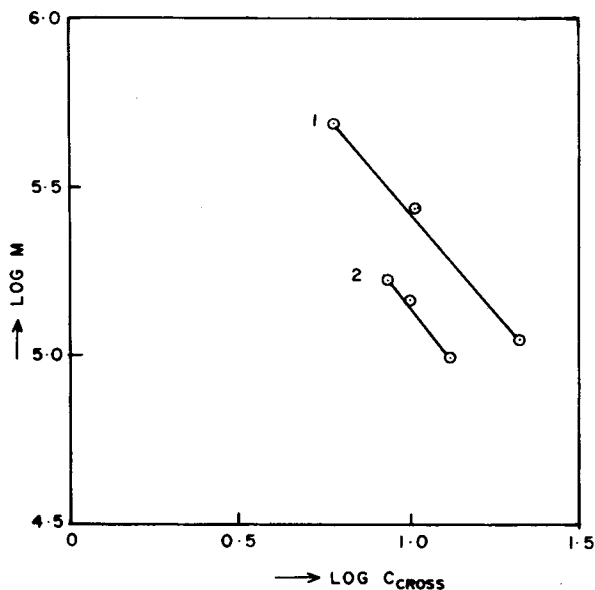


Fig. 7. Double logarithmic plots of molecular weight as a function of crossover point concentration: (1) benzene-cyclohexane; (2) benzene-butanone.

with concentration at good solvent. Since in semidilute solutions relative viscosity is a function of coil overlap (measured in a θ solvent by the product $C[\eta]_{\theta}$ at all concentrations since coil dimension do not change), the correlating variable in good solvents $C[\eta]$ should be corrected for coil contraction at each concentration. The appropriate correlating variable has been derived by Graessley¹⁴ as $0.77 (C[\eta]/0.77)^{1/2a}$, where a is the exponent of the Mark-Houwink relation. The correlating variable, however, reduces to $C[\eta]$ in the θ solvent where the exponent $a = 0.5$. The plots of relative viscosity η_r of polychloroprene samples as a function of the appropriate correlating variable are shown in Figures 10 and 11 for benzene (45.5°C) and cyclohexane solutions and benzene (25°C) and butanone solutions, respectively. The values of exponent a for polychloroprene in benzene solution at 45.5°C and 25°C have been taken as 0.64 and 0.62, respectively. For comparison, the plots of relative viscosity vs. the correlating variable $C[\eta]$ in good solvent (without correction for change of coil dimension with concentration) has been shown on the same graph. In good solvents, especially in benzene at 45.5°C, the relative viscosity increases less rapidly with $C[\eta]$ compared to that in θ solvents, and small but systematic differences appear for samples of different molecular weights. It may be pointed out that Graessley observed small but systematic differences¹⁴ similar to our results in the data⁴ of polystyrene samples of different molecular weights in toluene. The most important point that emerges from this observation is that the appropriate correction for variations in chain dimensions with concentration has positively moved the correlations for θ and good solvents closer to a common curve, but it has not been able to eliminate the difference between the data completely.

Another correlation of η^0 which is connected to $C[\eta]$ may be considered here also. It is well known that in very dilute solution the viscosity tends to the limiting behavior

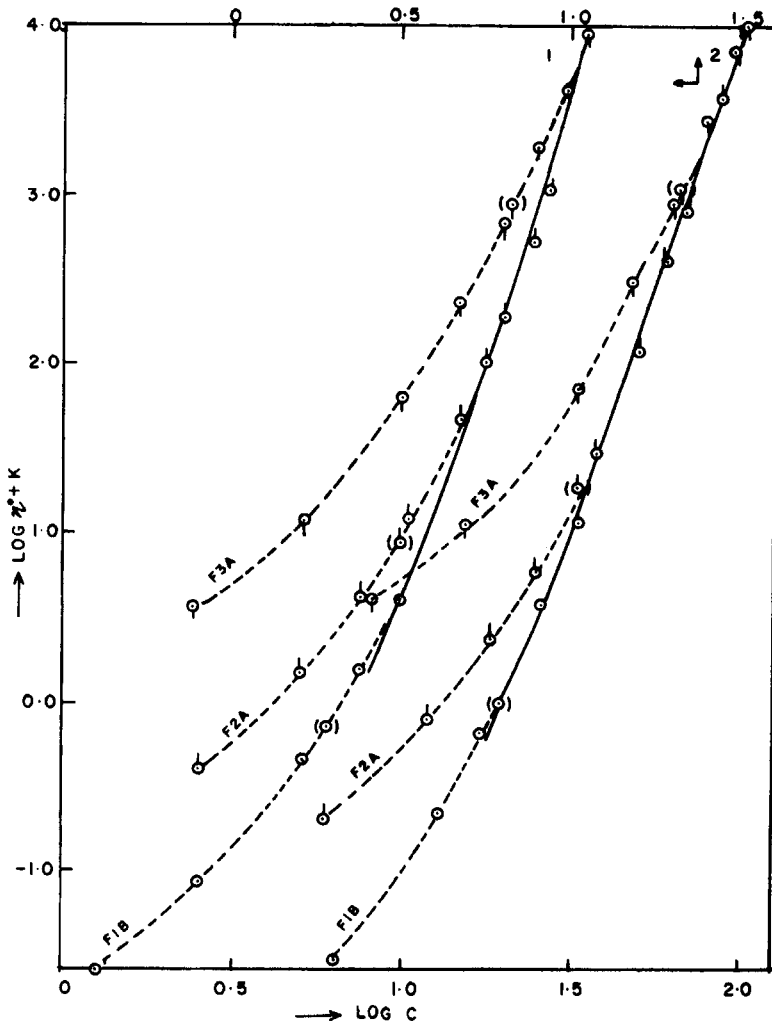


Fig. 8. Composite curves for polychloroprene samples in benzene and cyclohexane at 45.5°C: (1) benzene; (2) cyclohexane. Parentheses denote the value estimated from the crossover points. Dashed lines have been drawn with data which are away from the composite curve.

$$\eta_r^0 = \exp(C[\eta]) \quad (1)$$

and the intrinsic viscosity $[\eta]$ with the Flory-Fox equation is given as $[\eta] = \Phi \langle S^2 \rangle^{3/2} / M$, where $\Phi \approx 2.5 \times 10^{23}$ (cgs. units) and $\langle S^2 \rangle^{1/2}$ is the root mean square radius of gyration. In terms of $[\eta]$, the overlap concentration C^* at moderately concentrated solution is given as

$$C^* = \frac{6^{3/2} \Phi}{8N_a} \frac{1}{[\eta]} = \frac{0.77}{[\eta]} \quad (2)$$

in which N_a is the Avogadro's number.

To correlate the viscometric data for moderately concentrated solutions Simha and co-worker²⁵ have used a relation of the form (for $\eta_r^0 \gg 1$)

$$\eta_r^0 = C[\eta]P(CM^\epsilon) \quad (3)$$

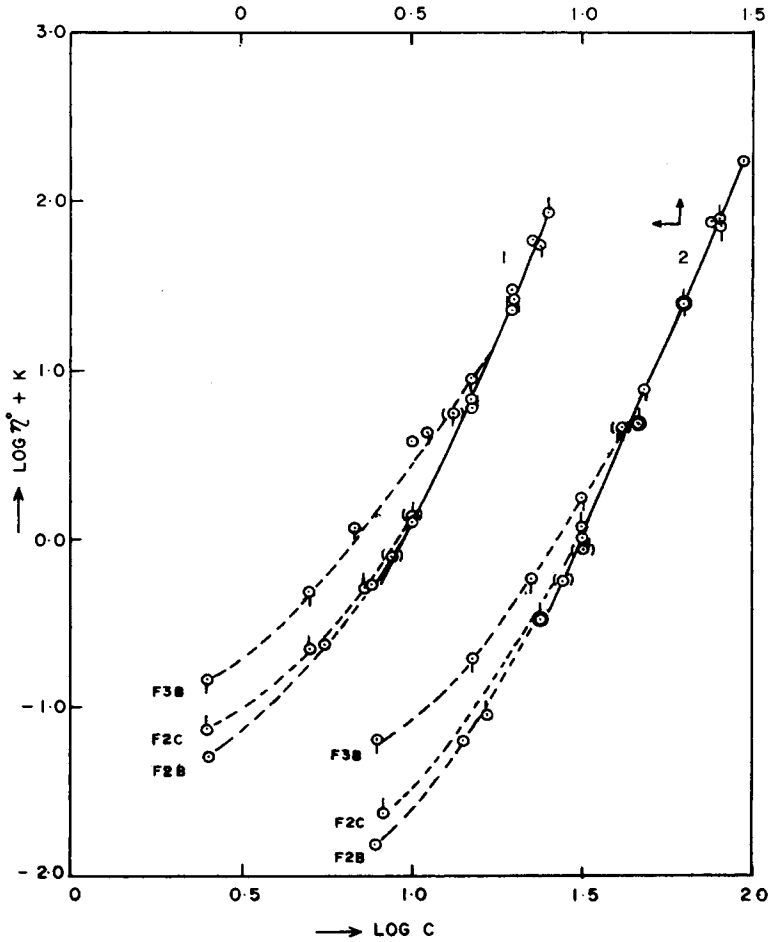


Fig. 9. Composite curves for polychloroprene samples in benzene and butanone at 25°C: (1) benzene; (2) butanone. Parentheses denote the value estimated from the crossover points. Dashed lines have been drawn with data which are away from the composite curve.

where ϵ is often equal to $d \ln[\eta]/d \ln M$. If it is obtained precisely, then eq. (2) reduces to

$$\eta_r^0 = HC[\eta] \tag{4}$$

which emphasizes the role of chain dimensions in dilute solutions (with screening length \approx root mean square radius of gyration) in the correlation of η^0 with C and M .²⁶ Here eq. (4) may be considered as a generalization of eq. (1). One variation of eq. (4) is the Martin's relation

$$\eta_r^0 = 1 + C[\eta] \exp(K'_M C[\eta])$$

or

$$\frac{\eta_{sp}^0}{C[\eta]} = \bar{\eta} = \exp K'_M C[\eta] \tag{5}$$

Dreval and co-workers²⁷ have used this Martin relation to correlate the viscosity

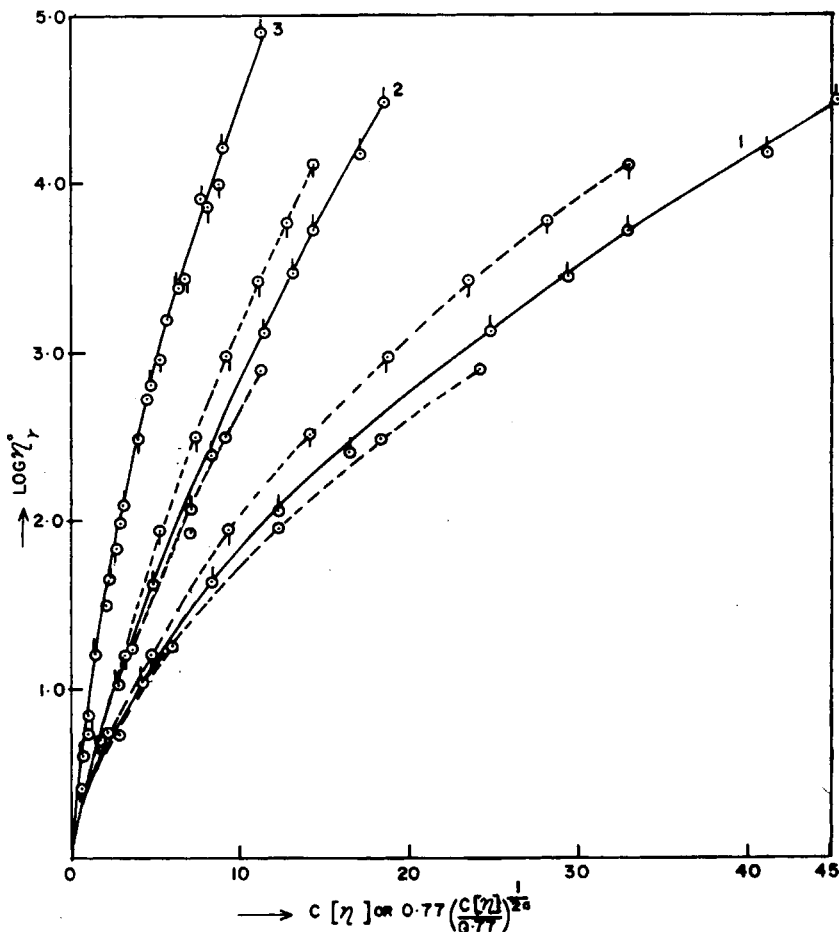


Fig. 10. Plots of $\log \eta_r^0$ vs. correlating variable $C[\eta]$ or $0.77 (C[\eta]/0.77)^{1/2a}$ for polychloroprene samples in good and θ solvents at 45.5°C : (1) in benzene, not corrected for coil contraction [F1B (\odot); F2A (\diamond); F3A (\square)]; (2) in benzene, corrected for coil contraction (same symbols for F1B, F2A, and F3A); (3) in cyclohexane (same symbols for F1B, F2A, and F3A). Small but systematic differences of data for samples of different molecular weight were observed. Dashed lines show the deviations.

data in moderately concentrated solution in which a plot of $\log [\eta_{sp}^0/C[\eta]]$ vs. $C[\eta]$ produced a single curve for samples of various molecular weights in a single good solvent over the entire concentration range. However, a similar plot of $\log [\eta_{sp}^0/C[\eta]]$ as a function of concentration, C was proposed by Gandhi and Williams,¹² but this produced separate curves in an ordered way as a function of solvent power. The empirical representation of our data according to Dreval and co-workers²⁷ by plotting $\log [\eta_{sp}^0/(C[\eta])] vs. C[\eta]$ are given in Figures 12 and 13 for good and poor solvents, respectively. As expected, the data taken in good solvents (benzene at two different temperatures are considered here as two different solvents) are fitted in two separate curves according to their solvent power (the coil dimensions vary according to their solvent power), whereas the data taken in θ solvents (butanone and cyclohexane) are fitted in a single curve as the different θ solvents are considered to have the similar solvent power, where the

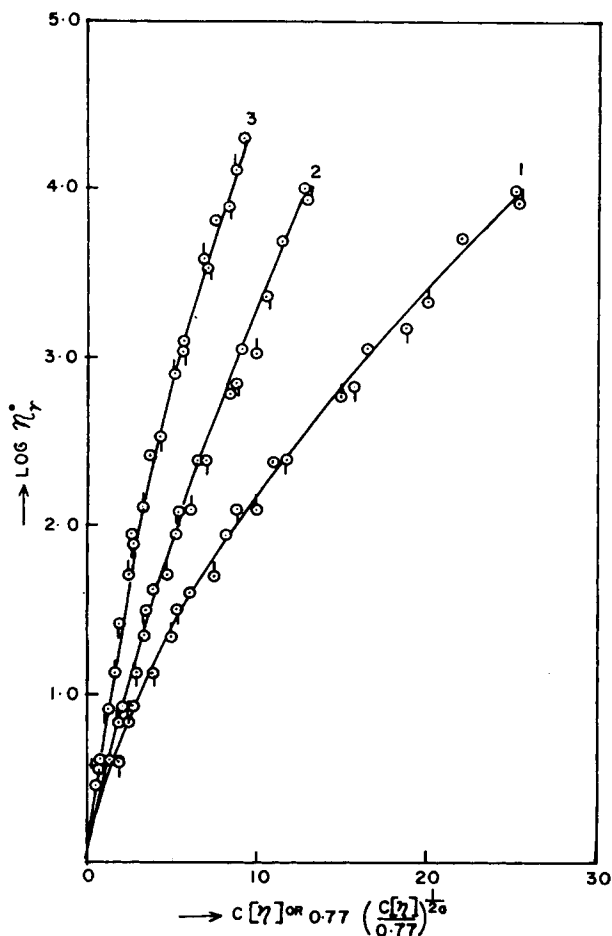


Fig. 11. Plots of $\log \eta_r^0$ vs. correlating variable $C[\eta]$ or $0.77 (C[\eta]/0.77)^{1/2a}$ for polychloroprene samples in good and θ solvents at 25°C : (1) in benzene, not corrected for coil contraction [F2B (\odot); F2C (\circ); F3B (\square)]; (2) in benzene, corrected for coil contraction (same symbols for F2B, F2C, and F3B); (3) in butanone (same symbols for F2B, F2C, and F3B). Differences of data for samples of different molecular weights were very little (as the molecular weight of the samples were close to one another) and hence all data are shown in a single curve.

chain dimensions remain the same. The intrinsic viscosity $[\eta]_\theta$ of the polymer in two θ solvents, cyclohexane and butanone, was proportional to $M^{0.50}$.

The solvent solute interaction constant K_M obtained from the Martin equation [eq. (5)] has been used to normalize the dimensionless concentration $C[\eta]$ so as to move the correlations for θ and good solvents to a common curve. It may be pointed out that the Huggins constant K_H is theoretically equal to the Martin constant K'_M and K_M is taken as $K'_M/2.303$. The K_M was determined from the initial slope of $\log \bar{\eta}$ vs. $C[\eta]$ curves. There was a small but systemic difference of the data for three samples of different molecular weights in benzene at 45.5°C , so three different K_M values (instead of one) were determined from the curves. This scatter of data may be due to a larger difference of molecular weights among the samples. However, for samples in benzene at 25°C , only one

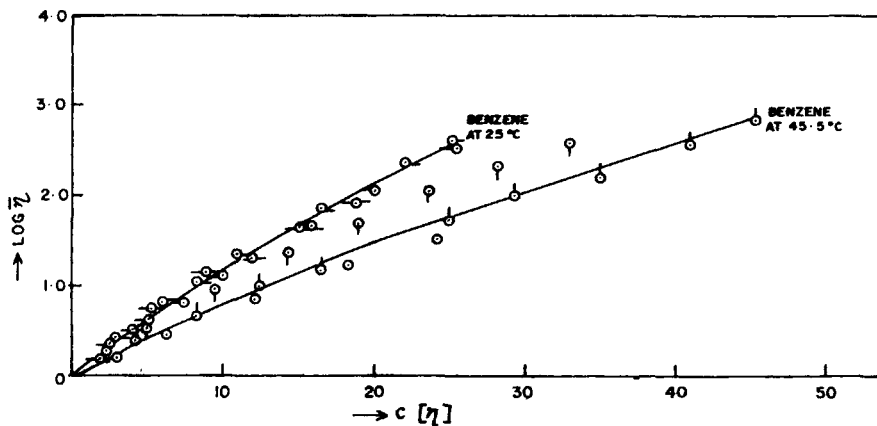


Fig. 12. Plots of $\log \bar{\eta}$ vs. $C[\eta]$ for polychloroprene samples in benzene at 45.5°C [F1B (○); F2A (◐); F3A (◑)] and in benzene at 25°C [F2B (○—); F2C (—○); F3B (—○—)]. Small but systematic differences of data for samples of different molecular weight especially in benzene at 45.5°C were observed.

value for K_M was obtained as the deviation of the data was very small and only a single curve was drawn with the data (Fig. 13). The values for K_M obtained at different solvents are listed in Table V. In all cases the normalization of the correlating variable $C[\eta]$ with the Martin constant K_M reduced all experimental

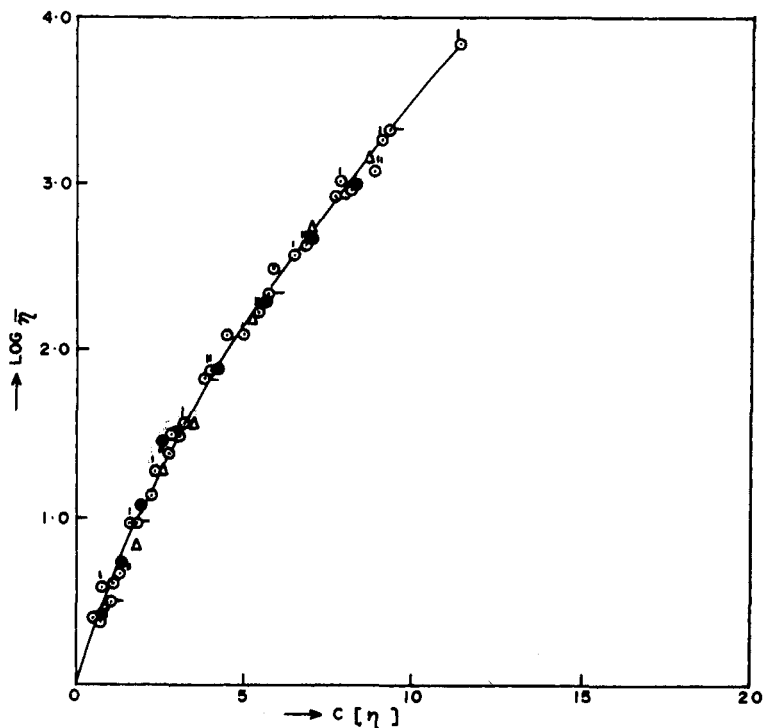


Fig. 13. Plots of $\log \bar{\eta}$ vs. $C[\eta]$ for polychloroprene samples in cyclohexane [F1B (○); F2A (◐); F3A (◑)] and in butanone [F2B (○—); F2C (Δ); F3B (●)]. A single curve was obtained for all the samples in two θ solvents. The scatter of the data was very little.

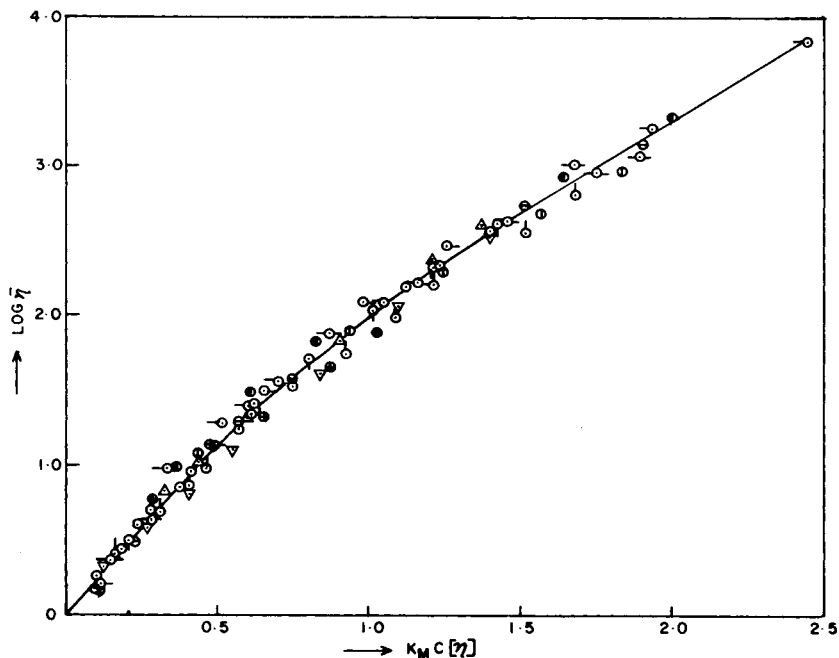


Fig. 14. Plots of $\log \bar{\eta}$ vs. $K_M C [\eta]$ for polychloroprene samples in different solvents: benzene at 45.5°C [F1B (○); F2A (—○); F3A (—○—)], cyclohexane [F1B (○—); F2A (—○); F3A (—○—)], benzene at 25°C [F2B (Δ); F2C (▽); F3B (⊕)], butanone [F2B (●); F2C (⊖); F3B (⊙)]. A single curve was obtained for all the samples in different solvents.

data for each polymer sample to the master-curve, as shown in Figure 14. The zero-shear viscosity master curve as obtained with our experimental data by plotting $\log \bar{\eta}$ vs. $K_M C [\eta]$ is valid for the entire concentration range, independent of molecular weight and nature of solvent. The introduction of the Martin constant K_M allows one to take into account effectively the flexibility of the macromolecular chain and the polymer solvent interaction. From Table V it is observed that, as the quality of the solvent deteriorates (becomes poor), the quantity K_M and consequently the viscosity of the solution becomes greater. The Martin constant K_M can be correlated with different thermodynamic properties of dilute polymer solutions, particularly with the expansion factor, α^3 of a polymer coil. The values for α^3 have been determined as the ratio of intrinsic viscosity $[\eta]$ at a given solvent to that in a θ solvent. The plots of K_M as a function of expansion factor is shown in Figure 15. The increase in expansion factor is accompanied with the decrease of K_M . The normalization of the cor-

TABLE V
Values of Martin Constant K_M and Expansion Factor α^3 for Polychloroprene-Solvent Systems

Samples	Solvent, temp (°C)	K_M	$\alpha^3 = [\eta]/[\eta]_\theta$
F1B	Benzene, 45.5	0.031	4.32
F2A		0.037	4.05
F3A		0.043	3.48
F2B, F2C, F3B	Benzene, 25	0.055	2.89, 2.86, 2.72
F1B, F2A, F3A	Cyclohexane, 45.5	0.216	1.0
F2B, F2C, F3B	Butanone, 25	0.216	1.0

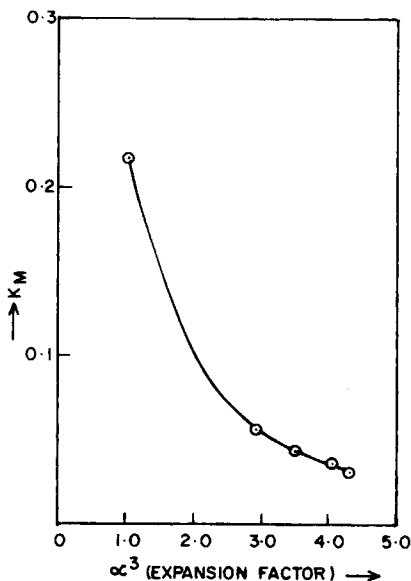


Fig. 15. Plots of K_M vs. α^3 (expansion factor).

relating variable $C[\eta]$ with K_M hence, in effect, may be to make a correction of chain dimension related to expansion factor.

In conclusion, it may be stated that the appropriate correction of the correlating variable $C[\eta]$ by the method given by Graessley for the contraction of coil dimension with concentration in good solvents no doubt improves the correlation, but it does not eliminate completely the difference between the data in the present work obtained at θ and good solvents. Further this method does not account for the increased deviations with increase of molecular weight which appeared in good solvent correlation.¹⁴ However, a few more solvent-solute systems need to be studied in detail before coming to a definite conclusion.

On the other hand, the correlation of the data by the method given by Dreval and co-workers (plot of $\log \bar{\eta}$ vs. $C[\eta]$) produced a single curve for solutions of polychloroprene samples in two different θ solvents, whereas in good solvents a separate curve for each solvent was produced. However, the normalization of the reduced concentration $C[\eta]$ by the Martin constant K_M eliminated completely all the differences between the data obtained at θ and good solvents. K_M can be correlated with the expansion factor α of a polymer coil. The normalization of this correlating variable $C[\eta]$ with K_M hence, in effect, is to make a suitable correction for chain dimension characterized by the expansion factor. This method has no doubt yielded better correlation of the data than the previous one.

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