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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### The Newtonian Viscosity of Polymer Solutions

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**To cite this Article** Baloch, Musa Kaleem(1988) 'The Newtonian Viscosity of Polymer Solutions', Journal of Macromolecular Science, Part A, 25: 4, 363 – 372

**To link to this Article:** DOI: 10.1080/00222338808053374

**URL:** <http://dx.doi.org/10.1080/00222338808053374>

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## THE NEWTONIAN VISCOSITY OF POLYMER SOLUTIONS

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### ABSTRACT

Viscosity measurements of cellulose acetate and polyisobutylene over a wide range of concentrations and molecular weights have been made. The data so obtained and the data taken from the literature for schizophyllan show that the viscosity varies smoothly with concentration of the polymer for the whole range of concentrations and molecular weights investigated. The characteristic concentrations,  $c_{ch}$ , of the polymers are calculated by the following equations:  $c_{ch} = 0.77/[\eta]$  or  $c_{ch} = 1.08/[\eta]$ . The relationship between molecular weight and intrinsic viscosity is obtained by fitting the data by the method of least squares. By plotting the reduced viscosity versus the reduced concentration, superposition curves are obtained for both cellulose acetate and polyisobutylene. It is not possible to obtain superposition curves for schizophyllan, which is a more rigid polymer.

### INTRODUCTION

Zero-shear viscosity  $\eta^0$ , a measure of energy dissipation, is one of the parameters describing the rheological properties of polymer solutions or melts in the linear region of deformation [1, 2]. For dilute solutions in good solvents, the

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molecular coils are expanded by the excluded volume effect [3]. The coils contract with increasing concentration as excluded volume repulsions between segments in the same chain become screened by segments of the neighboring chains. At very high concentration the molecular dimensions remain unaffected by the nature of the solvent and approach their unperturbed values [4, 6]. The effect of concentration is reflected in viscoelastic behavior. The intrinsic viscosity in dilute solutions depends directly on the chain dimensions [3]. At moderate concentrations the viscosity is controlled primarily by the extent of coils overlapping and is characterized by the product of the concentration  $c$  and the intrinsic viscosity  $[\eta]$  [1, 2, 7, 8] or by the characteristic concentration  $c_{ch}$  [2, 5, 9, 10] of the solution. The latter is defined as [11]:

$$c_{ch} = (3M/4\pi \langle S^2 \rangle^{3/2} N_A), \quad (1)$$

where  $M$  is the molecular weight of the polymer,  $\langle S^2 \rangle$  is the mean square radius of gyration, and  $N_A$  is Avogadro's number. Generally,  $c_{ch}$  varies as  $[\eta]^{-1}$ , the numerical proportionality constant being dependent on the model chosen and on the interactions.

Simha et al. [9] suggested the following relation for hexagonal close packing:

$$c_{ch} = 1.08/[\eta], \quad (2)$$

while Graessley [10], considering a closely packed random array of spherical impenetrable coils, proposed the relation

$$c_{ch} = 0.77[\eta]. \quad (3)$$

Some of the investigators [12-15] concluded that the dependence of the logarithm of the relative viscosity  $\eta_r$  vs  $\log c$  can be represented by two intersecting straight lines, and that their point of intersection corresponds to  $c_{ch}$  of the polymer in the solvent in question, while others [16, 17] observed smooth curves.

On the other hand, the formulation of *scaled* functional relationships, i.e., the expression of relationships in terms of reduced quantities, has pragmatic and fundamental significance. Under isothermal or nearly isothermal conditions, reduced variables  $\tilde{\eta} = \eta_{sp}/c[\eta]$  and  $\tilde{c} = c/\gamma$  could be defined which result in a single curve for a given polymer series-solvent combination [18]. Here  $\gamma$  can be  $c_{ch}$  or  $[\eta]^{-1}$  and is a function of molecular weight.

Though the models discussed above give reasonably good results for flexible polymers or at theta conditions, they are not verified for rigid polymers.

On the other hand, rigid and semirigid types of polymers are gaining more and more importance due to their industrial applications. Therefore, the aim of this communication is to investigate the viscosity of polymers having different degrees of flexibility with respect to their molecular weight and concentration, and to test these models by constructing superpositions curves.

## EXPERIMENTAL

The polymers investigated in this report are polyisobutylene (PIB), cellulose acetate (CA), and schizophyllan. The PIB was kindly supplied by BASF, West Germany, and the CA by Ravi Rayon Ltd., Pakistan. The PIB and CA were fractionated with respect to molecular weight by the fractional precipitation method and were then characterized by light scattering and viscometry. The details of the method are given elsewhere [19]. For viscosity measurements the PIB was dissolved in cyclohexane and the CA in acetone. Both solvents were E. Merck brand and were doubly distilled before use. The viscosity was measured by an Ostwald-type viscometer and a concentric rotational-type (Haake) viscometer. The temperature was kept constant at  $25 \pm 0.02^\circ\text{C}$  and the concentration was varied from 0.001 to  $0.40 \text{ g/cm}^3$  for PIB and CA. The viscosity data for schizophyllan dissolved in water at  $25^\circ\text{C}$  were obtained from the literature [20].

The intrinsic viscosities of all the fractions of PIB and CA were determined by using the Huggins equation

$$\eta_{sp}/c = [\eta] + k_1 [\eta]^2 c + \dots, \quad (4)$$

where  $\eta_{sp}$  and  $k_1$  are the specific viscosity and the Huggins constant, respectively, and extrapolating to zero concentration. The values so obtained are listed in Table 1. The intrinsic viscosity of schizophyllan was taken from the literature [20]. The values of  $c_{ch}$  were calculated by using Eqs. (2) and (3). The viscosity data for PIB and CA are given in Tables 2 and 3.

## RESULTS AND DISCUSSION

Plots of  $\log \eta_r$  vs  $\log c$  (Fig. 1) show that the viscosity increases smoothly with concentration for every fraction of all the polymers, so that it is difficult to consider these curves as two intersecting straight lines, as suggested by Refs. 12-15, and to find the  $c_{ch}$  values in this way. This figure also shows

TABLE 1. Characteristics of Polymers Investigated

Cellulose acetate in acetone			Polyisobutylene in cyclohexane		
Sample no.	$M \times 10^{-4}$	$[\eta]$ , $\text{cm}^3/\text{g}$	Sample no.	$M \times 10^{-5}$	$[\eta]$ , $\text{cm}^3/\text{g}$
CA-1	2.2	54.7	PIB-1	1.41	122.0
CA-2	2.5	60.3	PIB-2	2.82	207.6
CA-3	2.9	69.2	PIB-3	12.69	437.6
CA-4	4.6	99.0	PIB-4	26.30	639.7
CA-5	5.7	121.3	PIB-5	31.62	771.0
CA-6	6.9	140.6			
CA-7	11.2	205.1			
CA-8	12.2	224.9			
CA-9	15.5	288.4			

that the viscosity does not vary linearly with concentration except in very dilute regions. This may be because the interactions between the polymer molecules increase with concentration and will become more important above certain concentrations, resulting in an additional increase in viscosity. A further increase in concentration will bring the polymer molecules even closer, and hence will result in overlapping of molecules, and ultimately the crowding limit will be reached and the viscosity will approach infinity [3, 4, 6, 9, 10].

To establish a relationship between molecular weight and intrinsic viscosity, the double logarithmic data were fitted to a least squares best fit (Fig. 2) and it is clear from the figure that the deviations from straight lines are not very large in either case. The relations so obtained for PIB, CA, and schizophyllan are presented by Eqs. (5)–(7), respectively:

$$[\eta] = 1.638 \times 10^{-1} M^{0.563} \text{ cm}^3/\text{g}, \quad (5)$$

$$[\eta] = 1.302 \times 10^{-2} M^{0.833} \text{ cm}^3/\text{g}, \quad (6)$$

$$[\eta] = 1.306 \times 10^{-5} M^{1.335} \text{ cm}^3/\text{g}. \quad (7)$$

TABLE 2. Relative Viscosities of Polyisobutylene in Cyclohexane at 25°C

$c \times 100,$ $\text{g/cm}^3$	$\log \eta_r$				
	Sample PIB-1	Sample PIB-2	Sample PIB-3	Sample PIB-4	Sample PIB-5
40	5.21	6.40	9.02	10.42	11.31
30	4.60	5.71	7.82	9.31	10.01
20	3.82	4.70	6.61	7.80	8.45
15	3.31	4.12	5.82	7.01	7.61
10	2.51	3.31	5.01	6.01	6.40
5	1.50	1.91	3.51	4.41	4.61
2	0.78	1.10	1.91	2.42	2.72
1	0.45	0.65	1.10	1.55	1.75
0.8	0.37	0.54	1.03	1.32	1.54
0.6	0.27	0.44	0.98	0.95	1.12
0.4	0.19	0.32	0.57	0.78	0.89
0.2	0.10	0.16	0.32	0.44	0.51
0.1	0.05	0.09	0.17	0.236	0.27

To obtain the superposition curves, the logarithms of the reduced viscosity ( $\eta_{sp}/c[\eta]$ ) are plotted versus the reduced concentration ( $c[\eta]$ ). The data for PIB in Fig. 3 show almost no deviations from the superposition curve. This remains true even when the plots are scaled according to the models of Simha et al. [9] and Graessley [10] (Eqs. 2 and 3). The deviations for CA are more noticeable (Fig. 4), especially in the low range of concentration, but these appear to be smallest when the data are scaled according to the model of Graessley. On the other hand, no single superposition curve could be obtained for schizophyllan by using any of the three models discussed above (Fig. 5) or by plotting  $\log \eta^0$  vs  $\log c[\eta]$  [20], except for dilute solutions.

From the above observations it can be concluded that the existing models do not exactly explain the variations in viscosity with concentration, especially for semiflexible or rigid polymers. Therefore, the reduced variable cor-

TABLE 3. Relative Viscosities of Cellulose Acetate in Acetone at 25°C

$c \times 100,$ g/cm <sup>3</sup>	log $\eta_r$								
	Sample CA-1	Sample CA-2	Sample CA-3	Sample CA-4	Sample CA-5	Sample CA-6	Sample CA-7	Sample CA-8	Sample CA-9
40	3.52	3.76	4.04	4.80	5.28	5.72	6.88	7.28	7.92
30	3.01	3.12	3.44	4.24	4.56	4.92	6.02	6.16	6.92
20	2.28	2.36	2.68	3.36	3.76	4.08	4.96	5.16	5.72
15	1.36	1.84	2.26	2.68	3.12	3.49	4.40	4.60	5.02
10	1.14	1.14	1.24	2.08	2.40	2.76	2.44	3.81	4.36
7.5	0.76	0.86	0.96	1.68	1.80	2.20	2.88	3.20	3.14
5.0	0.45	0.50	0.65	1.12	1.12	1.66	2.04	2.44	2.56
2.5	0.36	0.36	0.50	0.64	0.75	0.81	1.05	1.56	1.64
1.0	0.23	0.25	0.30	0.40	0.47	0.50	0.55	0.75	0.88
0.8	0.18	0.19	0.24	0.33	0.39	0.41	0.47	0.62	0.75
0.4	0.088	0.11	0.12	0.17	0.20	0.22	0.27	0.36	0.44
0.2	0.047	0.05	0.06	0.09	0.10	0.11	0.16	0.19	0.24
0.1	0.023	0.026	0.03	0.04	0.05	0.06	0.08	0.09	0.12

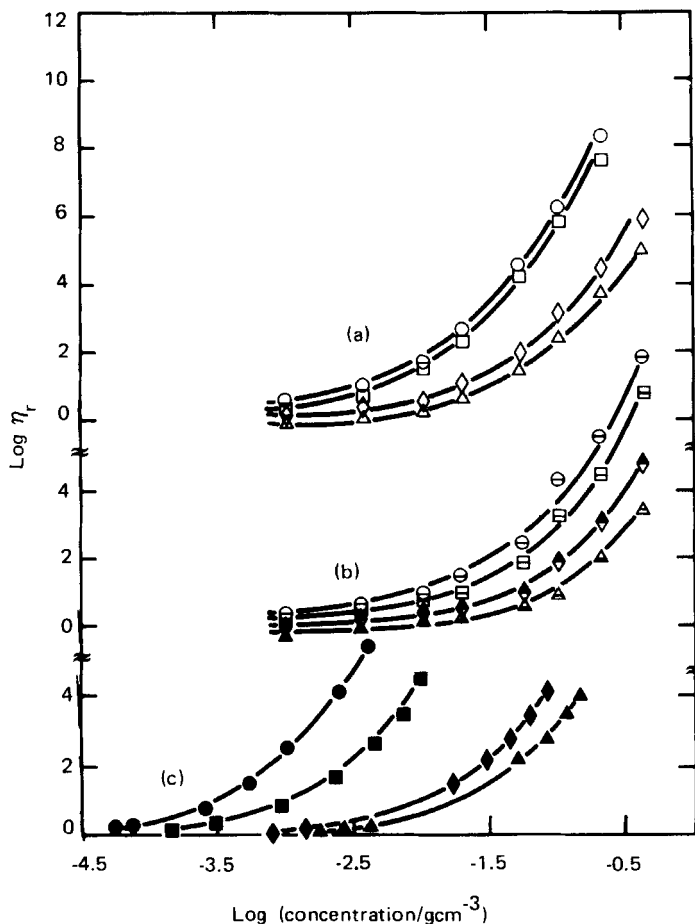


FIG. 1. Relative viscosity as a function of concentration for solutions of polymers of various molecular weights. (a) Polyisobutylene in cyclohexane:  $M$ : ( $\Delta$ )  $1.41 \times 10^5$ , ( $\diamond$ )  $2.82 \times 10^5$ , ( $\square$ )  $2.63 \times 10^6$ , ( $\circ$ )  $3.162 \times 10^6$ . (b) Cellulose acetate in acetone:  $M$ : ( $\Delta$ )  $2.2 \times 10^4$ , ( $\diamond$ )  $4.6 \times 10^4$ , ( $\square$ )  $1.12 \times 10^5$ , ( $\circ$ )  $1.55 \times 10^5$ . (c) Schizophyllan in water:  $M$ : ( $\blacktriangle$ )  $2.2 \times 10^5$ , ( $\blacklozenge$ )  $3.35 \times 10^5$ , ( $\blacksquare$ )  $1.73 \times 10^6$ , ( $\bullet$ )  $4.30 \times 10^6$ .



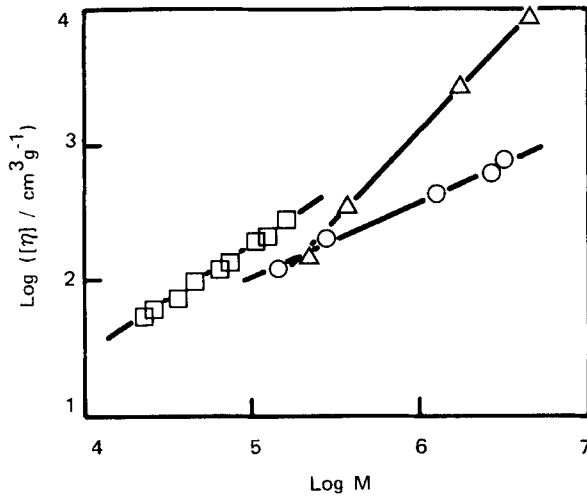


FIG. 2. Intrinsic viscosity as a function of molecular weight of polyisobutylene in cyclohexane ( $\circ$ ), cellulose acetate in acetone ( $\square$ ), and schizophyllan in water ( $\triangle$ ).

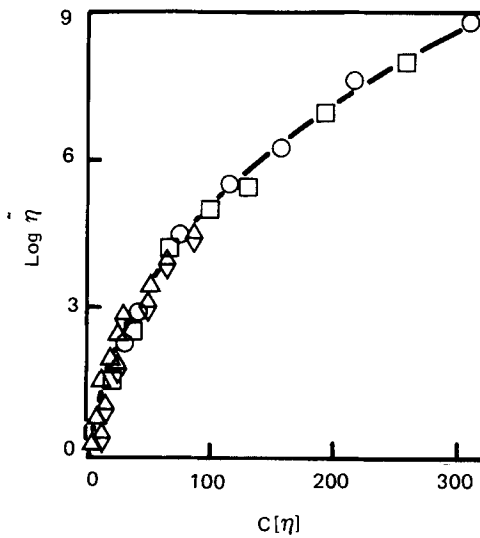


FIG. 3. Reduced viscosity as a function of reduced concentrations for polyisobutylene in cyclohexane. The symbols have the same meaning as in Fig. 1(a).

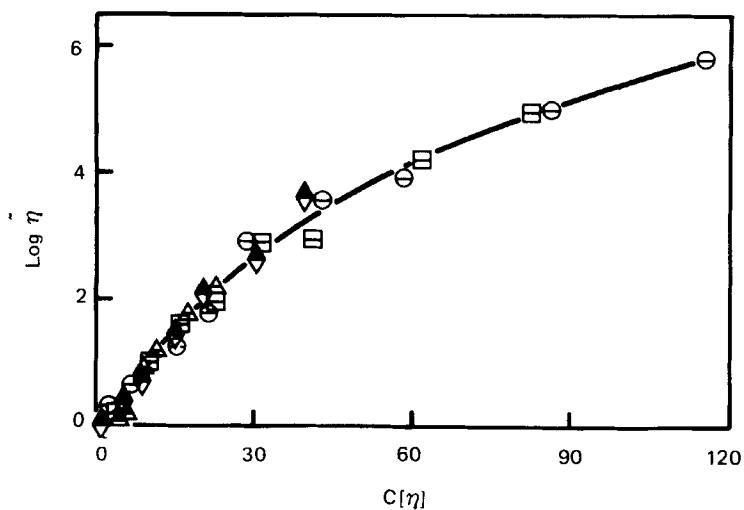


FIG. 4. Reduced viscosity as a function of reduced concentration for cellulose acetate in acetone. The symbols have the same meanings as in Fig. 1(b).

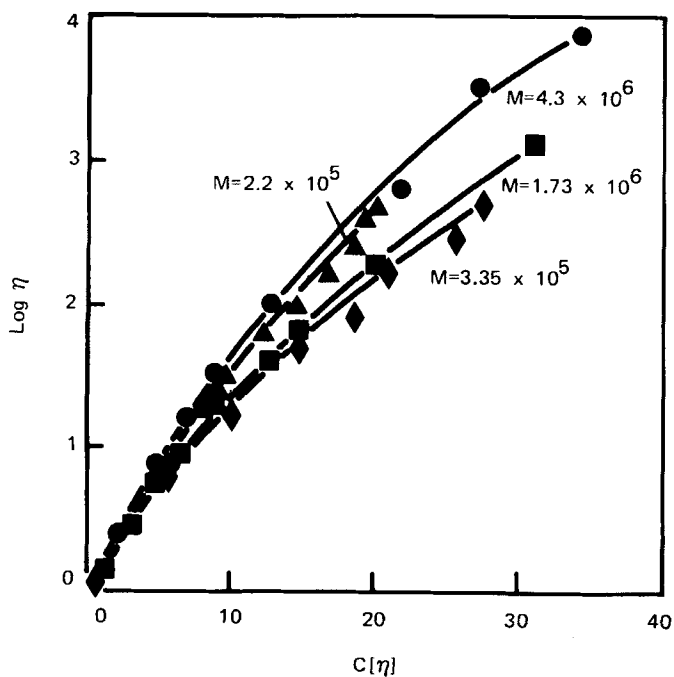


FIG. 5. Reduced viscosity as a function of reduced concentrations for schizophyllan in water. The symbols have the same meanings as in Fig. 1(c).

relations of viscosity may need revision when the polymers are stiff. These observations have inspired us to propose another model which can scale the viscosity data of rigid polymers as well, and which will be communicated in a subsequent paper.

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Received May 20, 1987

Revision received October 2, 1987