

The Newtonian Viscosity of Polymer Solutions: Over a Wide Range of Concentrations

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Summary: Viscosity of three polymers, namely polyisobutylene, cellulose acetate and polyschizophyllan, having different degree of flexibility is investigated over a wide range of concentrations and molecular weights. The data so obtained show a smooth variation in viscosity with respect to concentration of the polymers. The relationship between molecular weight of polymers and intrinsic viscosity or characteristic concentration, c_{ch} is obtained, by fitting the data to method of least squares. The c_{ch} values of the polymers were calculated using Graessley and Simha et al. models. $\log \eta$ vs c/c_{ch} or $c[\eta]$ were plotted to get the superposition curves for every polymer. Where η is the reduced viscosity of the polymers. The data show that the deviations from these curves increase with the increase in rigidity of the polymer and it was not possible to scale the polyschizophyllan data using either of the above mentioned models. The data further show that the Graessley model is better than the others.

Introduction

Zero shear viscosity η^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 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 neighbouring chains. At very high concentration the molecular dimensions remain unaffected by the nature of the solvent and approach to their unperturbed values [4,6]. The effect of concentration is reflected in viscoelastic behaviour. In dilute solutions the intrinsic viscosity depends directly on chain dimensions [3]. At moderate concentrations the viscosity is controlled primarily by the extent of

coils overlapping and is characterized by the product of concentration (c) and intrinsic viscosity $[\eta]$ [1,2,7,8] or by the characteristic concentration (c_{ch}) [2,5,9,10]. The c_{ch} 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, $\langle S^2 \rangle$ and N_A are the mean square radius of gyration and Avogadro number respectively. Generally c_{ch} varies as $[\eta]^{-1}$, the numerical proportionality constant being dependent on the chosen model and on the interactions. Simha et al. [9] suggested for hexagonal close packing, the relation

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

While Graessley [10], considering a closely packed random array of spherical impenetratable coils, proposed the relation:

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

Some of the investigators [12-15] concluded that the variation of $\log \eta_r$ vs $\log c$ can be represented by two intersecting straight lines and their point of intersection corresponds to the c_{ch} of the polymer in the solvent in question, while the others [16,17] observed as the 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 $\eta = \eta_{sp}/c$ $[\eta]$ and $c=c/v$ could be defined which result in a single curve for a given polymer series solvent combination [18]. Here v can be c_{ch} or $[\eta]^{-1}$ and is a function of molecular weight. Though the above discussed models give reasonably good results for flexible polymers or at theta conditions, but are not verified for rigid polymers. On the other hand these (rigid and semi rigid) type 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 degree of flexibility, with respect to their molecular weight and concentration and to test these models by plotting the data of these polymers for superposition curves.

Experimental

The polymers investigated in this report are polyisobutylene (PIB), cellulose acetate (CA) and Schizophyllan. The PIB was kindly supplied by BASF, W.Germany whereas CA by Ravi Rayon Ltd., Pakistan. The PIB and CA were fractionated with respect to their molecular weight by a 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 CA in acetone. Both the solvents were of E.Merck brand and were doubly distilled before use. The viscosity was measured by Ostwald type viscometer and concentric rotational type (HAAKE) viscometer. The temperature was kept constant at $25 \pm 0.02^\circ\text{C}$ and concentration was varied from 0.1g/dl-60g/dl for every fraction of both the polymers. The viscosity data for schizophyllan dissolved in water at 25°C are obtained from the literature [20].

Results and Discussion

The intrinsic viscosity of all the fractions of PIB and CA were determined using the Huggins equation:

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

and extrapolating to zero concentration. Here η_{sp} and k_1 are the specific viscosity and Huggins constant respectively. The intrinsic viscosity of schizophyllan is taken from the literature [20]. The c_{ch} of all the polymers were calculated using equations (2&3). $\log \eta_r$ of all the three

polymers is plotted vs log c and c in figures (1&2) respectively. The figures show that viscosity increases smoothly with concentration for every fraction of all the polymers. Therefore it is difficult to consider log η_r vs log c curves as two intersecting straight lines, as suggested by [12-15] and to find the c_{ch} values in this

way. These figures also show that the viscosity does not vary linearly with concentration except in very dilute region.

This may be due to the fact that the interactions between the polymer molecules will increase with concent-

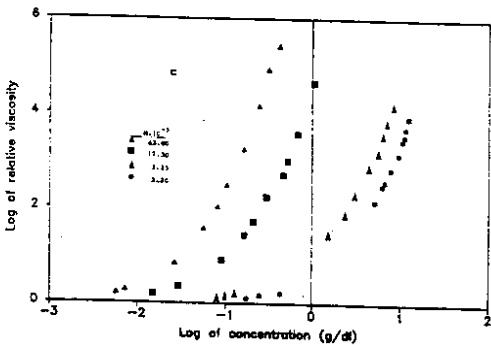
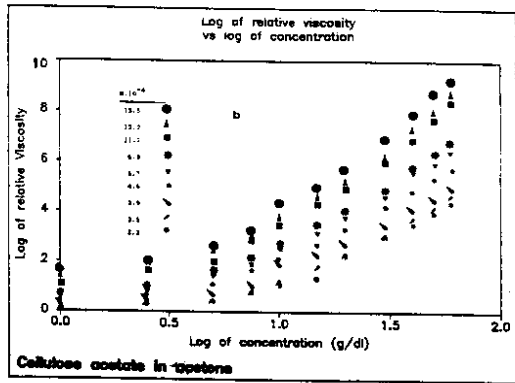
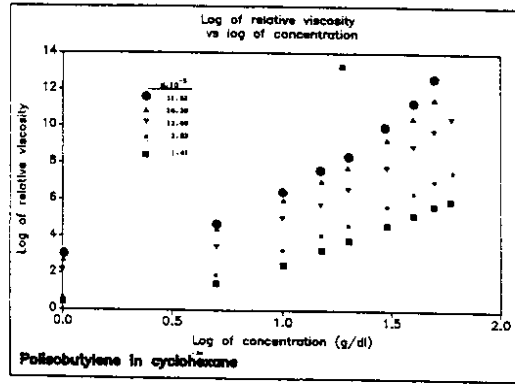


Fig.1: Log η_r as a function of log c of (a) polyisobutylene in cyclohexane (b) cellulose acetate in acetone (c) schizophyllan in water.

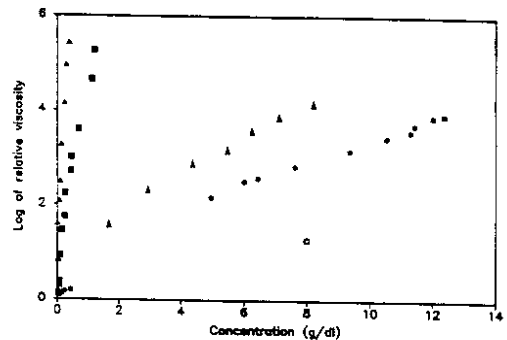
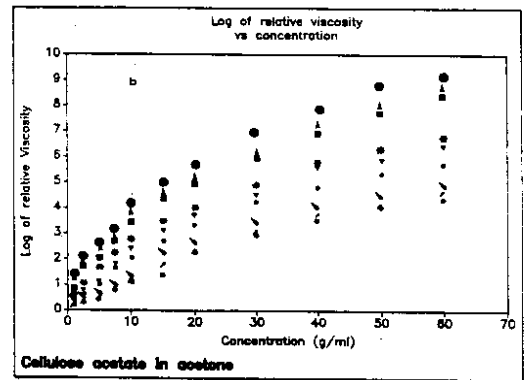
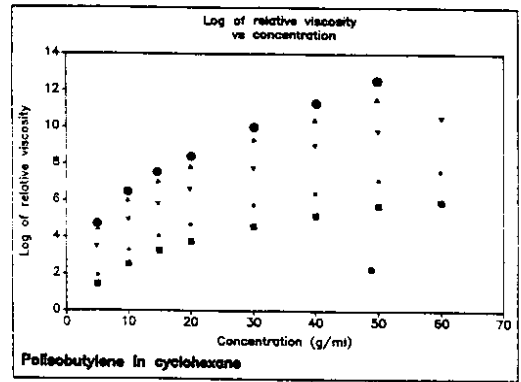


Fig.2: Log η_r as a function of concentration of (a) polyisobutylene in cyclohexane (b) cellulose acetate in acetone (c) schizophyllan in water. The symbols have the same meaning as in figure (1).

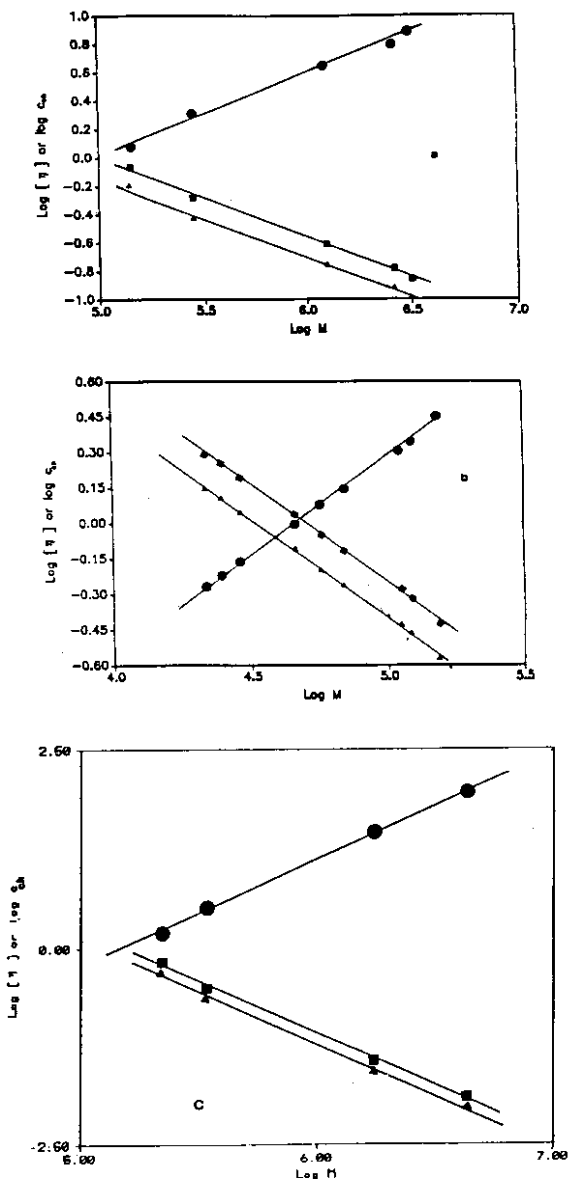


Fig.3: Variations in (●) $[\eta]$, (▲) $0.77/[\eta]$ and (■) $1.08/[\eta]$ as a function of molecular weight of (a) polyisobutylene, (b) cellulose acetate and (c) schizophyllan.

ration and will become more important after certain concentration. These interactions will then result to an additional increase in viscosity. Further increase in concentration will bring the polymer molecules closer and hence will result in overlapping of molecules, and ultimately the crowding limit will reach and viscosity will

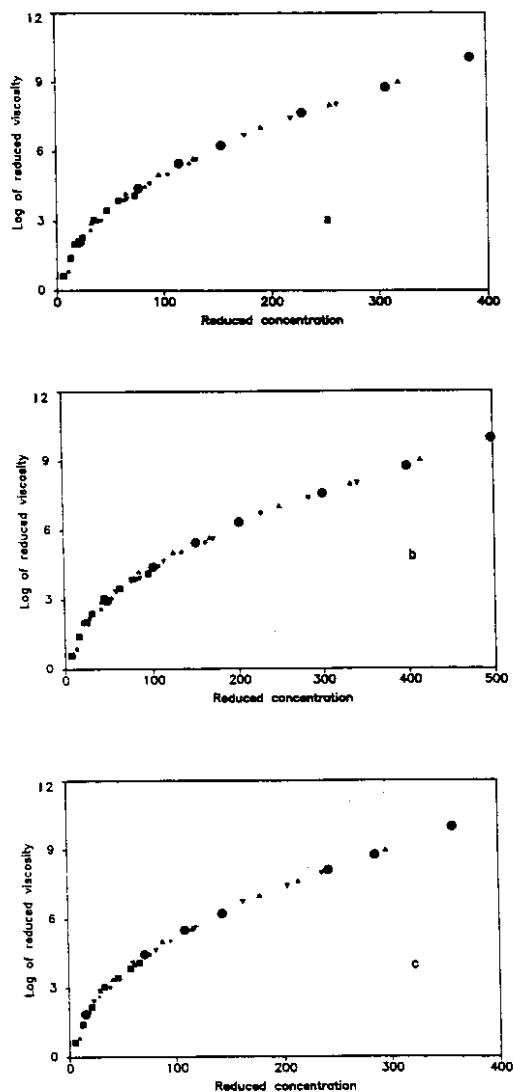


Fig.4: Reduced viscosity of polyisobutylene as a function of reduced concentrations defined as (a) $c[\eta]$, (b) $c[\eta]/0.77$ and (c) $c[\eta]/1.08$. The symbols have the same meaning as in figure (1a).

approach to infinity [3,4,6,9,10]. To establish a relationship between molecular weight and intrinsic viscosity or characteristic concentration the data were fitted to least squares method and the plots so obtained are shown in figure (3). It is clear from the figure that the deviations from the straight lines are under acceptable limit in either case. The relations

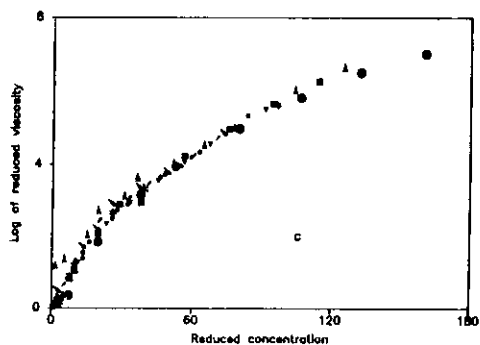
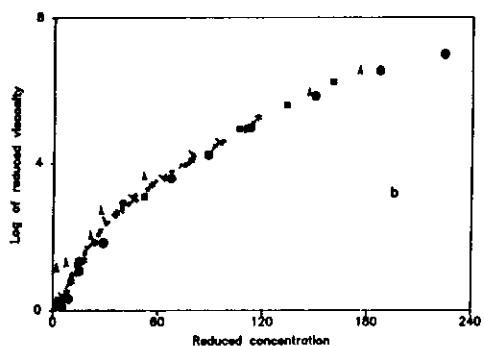
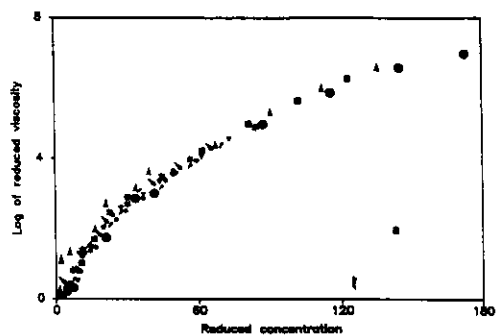


Fig.5: Reduced viscosity of cellulose acetate as a function reduced concentrations defined as (a) $c[\eta]$, (b) $c[\eta]/0.77$ and (c) $c[\eta]/1.08$. The symbols have the same meaning as in figure (1b).

so obtained for PIB, CA and schizophyllan are presented by equations (5-7) respectively.

For PIB:

$$[\eta]=1.638 \cdot 10^{-3} M^{0.563} \quad (5a)$$

$$c_{ch}=0.77/[\eta]=4.66 \cdot 10^2 M^{-0.562} \quad (5b)$$

$$c_{ch}=1.08/[\eta]=6.59 \cdot 10^2 M^{-0.563} \quad (5c)$$

For CA:

$$[\eta]=1.302 \cdot 10^{-4} M^{0.833} \quad (6a)$$

$$c_{ch}=0.77/[\eta]=6.03 \cdot 10^3 M^{-0.835} \quad (6b)$$

$$c_{ch}=1.08/[\eta]=8.375 \cdot 10^3 M^{-0.835} \quad (6c)$$

For schizophyllan:

$$[\eta]=1.306 \cdot 10^{-7} M^{1.335} \quad (7a)$$

$$c_{ch}=0.77/[\eta]=5.85 \cdot 10^6 M^{-1.334} \quad (7b)$$

$$c_{ch}=1.08/[\eta]=8.07 \cdot 10^6 M^{-1.333} \quad (7c)$$

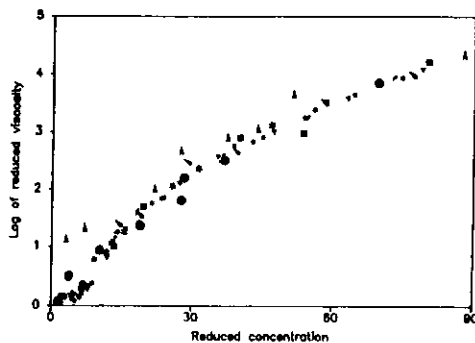


Fig.6: The same data as in figure (5b) for lower range of concentration.

To get the superposition curves, the log of reduced viscosity ($=\eta_{sp}/c$ $[\eta]$) is plotted versus reduced concentration ($=c/c_{ch}$ or $c[\eta]$). The superposition curves so obtained for PIB, CA and schizophyllan are shown in figures (4-6). The figures show that the data of PIB show almost no deviations from the superposition curve. The deviations are noticeable in case of CA especially in lower range of concentration (figure 6) and these are minimum in case of $c_{ch}=0.77/[\eta]$.

On the other hand it is not possible to get the superposition curve for schizophyllan by using either of the

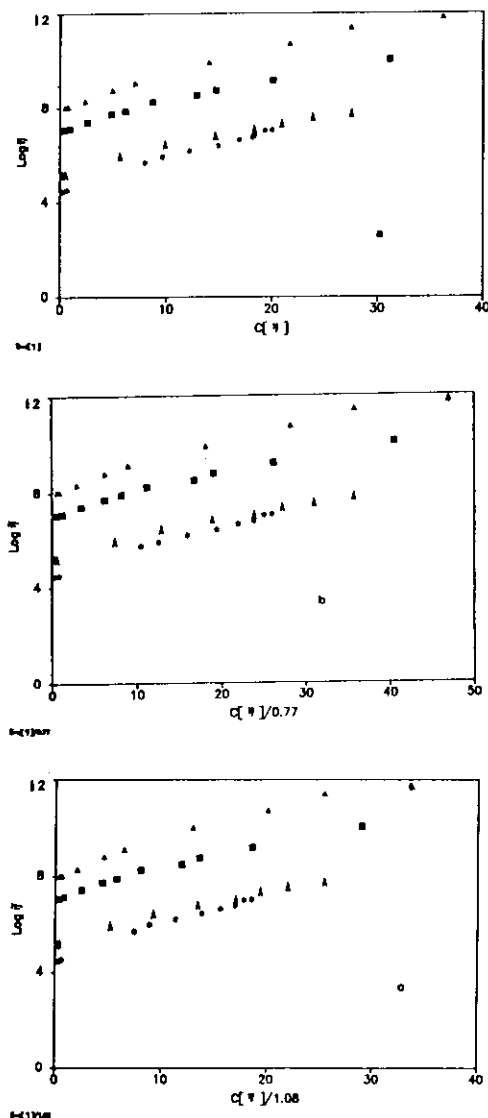


Fig.7: Reduced viscosity of schizophyllan as a function of reduced concentrations defined as (a) $c[\eta]$, (b) $c[\eta]/0.77$ and (c) $c[\eta]/1.08$. The symbols have the same meaning as in figure (1c).

above discussed three models or plotting $\log \eta^0$ vs $c[\eta]$ [20]. 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. These observations have inspired us

to propose an other model which can scale the viscosity data of rigid polymers as well, which will be communicated in next article.

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