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CONCENTRATION AND SHEAR RATE DEPENDENCE OF VISCOSITY IN RANDOM COIL POLYSACCHARIDE SOLUTIONS

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ABSTRACT

The concentration (c) and shear rate ($\dot{\gamma}$) dependence of viscosity (η) has been studied for a wide range of random coil polysaccharide solutions, and the following striking generalities are observed:

1. *The transition from dilute to concentrated solution behaviour occurs at a critical concentration $c^* \approx 4/[\eta]$, when 'zero shear' specific viscosity (η_{sp}) ≈ 10. η_{sp} varies as $c^{1.4}$ for dilute solutions, and as $c^{3.3}$ for concentrated solutions.*
2. *The shear rate dependence of viscosity, and frequency dependence of dynamic (oscillatory) viscosity are closely superimposable.*
3. *Double logarithmic plots of η/η_0 against $\dot{\gamma}/\dot{\gamma}_{0.1}$ (where η_0 is 'zero shear' viscosity, and $\dot{\gamma}_{0.1}$ is the shear rate at which $\eta = \eta_0/10$) are essentially identical for all concentrated solutions studied, and thus the two parameters η_0 and $\dot{\gamma}_{0.1}$ completely define the viscosity at all shear rates of practical importance.*

Departures from points 1 and 2, but not 3, are observed for concentrated solutions of locust bean gum, guar gum, and hyaluronate at low pH and high ionic strength and are attributed to specific intermolecular associations ('hyperentanglements') of longer timescale than non-specific physical entanglements.

1. INTRODUCTION

The rheological properties of polymer solutions and melts are of considerable technological importance in, for example, the plastics industry, and a number of sophisticated modern theories have been developed to relate flow properties to

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molecular behaviour (Flory, 1953; Ferry, 1980; De Gennes, 1971; Graessley, 1974, 1980). These theoretical treatments, however, normally relate to a narrow molecular weight distribution of polymer chains interacting only by topological entanglement, and experimental verification has been largely confined to synthetic polymers in non-aqueous solvents, or in the absence of solvent as polymer melts, although aqueous solutions of synthetic polyelectrolytes have also been studied extensively (Moan *et al.*, 1977).

In the present work a systematic investigation of the flow behaviour of naturally occurring or derivatised polysaccharides in aqueous solution is reported. These materials are extensively utilised in the food industry and elsewhere as thickeners, and, in comparison with typical synthetic polymers, impart unusually high solution viscosities at relatively low concentrations (e.g. ~1% w/v or less). Commercial polysaccharides are almost invariably highly polydisperse ($M_w/M_n \gtrsim 10$), and the significance of this for solution properties will be discussed.

Polysaccharides are also widely used as gelling agents, and it is now well established that in most cases the mechanism of gelation involves the formation of stable intermolecular 'junction zones' between structurally and conformationally regular chain sequences (Morris *et al.*, 1977a; Rees, 1977; Rees & Welsh, 1977). Under appropriate conditions of temperature, concentration, ionic strength and/or specific ionic environment, analogous rigid, ordered structures may be adopted in solution (Kohn, 1975; Morris *et al.*, 1977b, 1978a, 1980a; Darke *et al.*, 1978; Gidley *et al.*, 1979; Yanaki *et al.*, 1980). Such solutions often show unusual rheological properties (Morris, 1977), which will be discussed in more detail in future publications. The polysaccharides studied in this work, however, are known from spectroscopic criteria such as nmr relaxation times (Bryce *et al.*, 1974; Darke *et al.*, 1975), or optical activity (Morris *et al.*, 1973, 1977b, 1978a, 1980a) to be conformationally mobile, and would therefore be expected to adopt disordered or 'random coil' chain geometry, at least in dilute solution. Previous studies (Morris *et al.*, 1980c; Welsh *et al.*, 1980), however, indicate that specific interchain associations, analogous to those in polysaccharide gels, but of shorter timescale, may occur in concentrated solutions of otherwise disordered polysaccharides, and may substantially modify rheological properties. One of the objectives of this work has therefore been to explore the extent and implications of such interactions.

The present studies have been confined to flow behaviour under lateral shear, since this is by far the most widely utilised form of viscosity measurement, although other types of deformation, such as extensional flow, may be of technological importance for understanding the behaviour of polymer solutions under processing conditions in, for example, extruders and mixers. Shear viscosity (η) is defined, eqn (1), as the ratio of the applied shear stress (τ) to the resulting rate of shear ($\dot{\gamma}$), or equivalently of the stress generated in resisting deformation, to the shear rate imposed on the sample.

$$\eta = \tau/\dot{\gamma} \tag{1}$$

For many simple liquids (e.g. oils) and solutions of small molecules (e.g. sugar syrups) shear rate increases linearly with increasing stress, and such materials ('Newtonian' liquids) therefore have a single fixed viscosity. By contrast, almost all polymer solutions are 'shear thinning', so that, for example, doubling the applied stress normally produces more than twice the rate of flow. Thus, as illustrated in Fig. 1, apparent viscosity decreases with increasing shear rate, and Newtonian behaviour is observed only at low rates of shear, if at all. As illustrated in the following sections, however, the 'zero shear' or 'Newtonian' viscosity (η_0) of random coil polymer solutions is a particularly valuable index of molecular size and interactions. In particular the following points will be considered in detail:

1. The concentration dependence of η_0 for polysaccharides of different chemical type and different molecular weight.
2. The way in which apparent viscosity falls to values lower than η_0 with increasing shear rate.

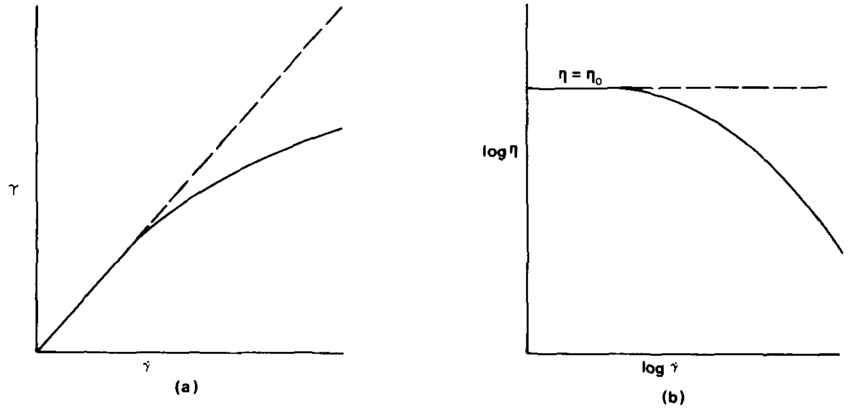

Fig. 1. Shear rate ($\dot{\gamma}$) dependence of (a) shear stress (τ) and (b) viscosity ($\eta = \tau/\dot{\gamma}$) for a Newtonian liquid (– – –) and a typical polymer solution (——).

2. EXPERIMENTAL

2.1. *Materials*

The following commercial polysaccharides were used: dextran (Pharmacia T2000); lambda carrageenan (Marine Colloids, Rex 5400); guar gum (Kobenhavns Pektinfabrik, purified grade); and locust bean gum (Marine Colloids, Rex 5924). Two commercial alginate samples (Alginate Industries F387 and SS/DJ) were used. These are identical to the materials whose block structure was characterised by Penman & Sanderson (1972) and by Morris *et al.* (1980b), and contain ~58% and ~29% mannuronate residues ('high mannuronate' and 'high guluronate') respectively. Carboxymethylamylose (degree of substitution 1·5) was prepared by a modification of the methods of

Brant & Min (1969) and Dubin & Brant (1975). Potato amylose (Avebe type V; 20 g) was dissolved in 0·5 M NaOH (600 ml) by mechanical stirring, and the solution was brought to 4 M wrt NaOH by addition of 10 M NaOH (350 ml). Sixty grammes of $ClCH_2COOH$ (1·5-fold molar excess per OH to be substituted) was added, and the reaction was allowed to proceed for 4 h on a water bath (55°C). To prevent oxidative degradation, all solutions were purged with nitrogen before and during use. The reaction was terminated by transferring the flask to an ice bath, and neutralising by gradual addition of 12 M HCl. The product was then dialysed exhaustively against distilled water until chloride free (3 days), and then freeze dried. Polystyrene of nearly monodisperse molecular weight distribution ($M_r \approx 6{\cdot}6 \times 10^5$) was a gift from Dr P. A. Irvine of the University of Essex Polymer Institute.

2.2. *Methods*

'Zero-shear' or 'Newtonian' viscosity (η_0) of dilute solutions was measured on a low shear, concentric cylinder, torsion wire viscometer, based on the design of Ogston & Stanier (1953). The maximum shear rate experienced by the sample was calculated from the relationship:

$$\dot{\gamma}_{\max} = 2\Omega R_2^2/(R_1^2 - R_2^2)$$

where R_1 and R_2 are the radii of the stator (6·37 mm) and rotor (7·97 mm) respectively, and Ω is angular velocity (rad s^{-1}). Measurements were made between 0·5 and 15·0 s^{-1}, and linearity of angular deflection of the bob versus speed of rotation of the cup (i.e. Newtonian behaviour) over this range was verified (e.g. Fig. 2). Most of the concentrated solution measurements were carried out on a Weissenberg Rheogoniometer (Model R18) using a 50 mm diameter cone and plate configuration with a cone angle of 2° (~0·035 rad). Some of the later studies, and in particular the comparison of shear rate dependence of viscosity, and frequency dependence of dynamic viscosity (e.g. Fig. 7) were made on a Rheometrics Mechanical Spectrometer (Model RMS-605), using a 50 mm cone and plate with cone angle 0·04 rad, or a 25 mm cone and plate with cone angle 0·10 rad, as appropriate. Shear rate ($\dot{\gamma}$) was calculated using the relationship $\dot{\gamma} = \Omega/\theta$, where Ω is angular velocity (rad s^{-1}) and θ is cone angle (rad). In studies of the concentration dependence of η_0, or the determination of intrinsic viscosity, polyelectrolyte solutions were dialysed to equilibrium against an appropriate salt solution, and the dialysate was then used for subsequent dilutions, in order to maintain constant conditions of ionic strength. All measurements were at 25°C.

3. RESULTS AND DISCUSSION

3.1. *Concentration Dependence of Zero Shear Viscosity*

Figure 3 shows the concentration (c) dependence of 'zero shear' specific viscosity (η_{sp}) (specific viscosity is defined in the footnote to Table 1) for some typical

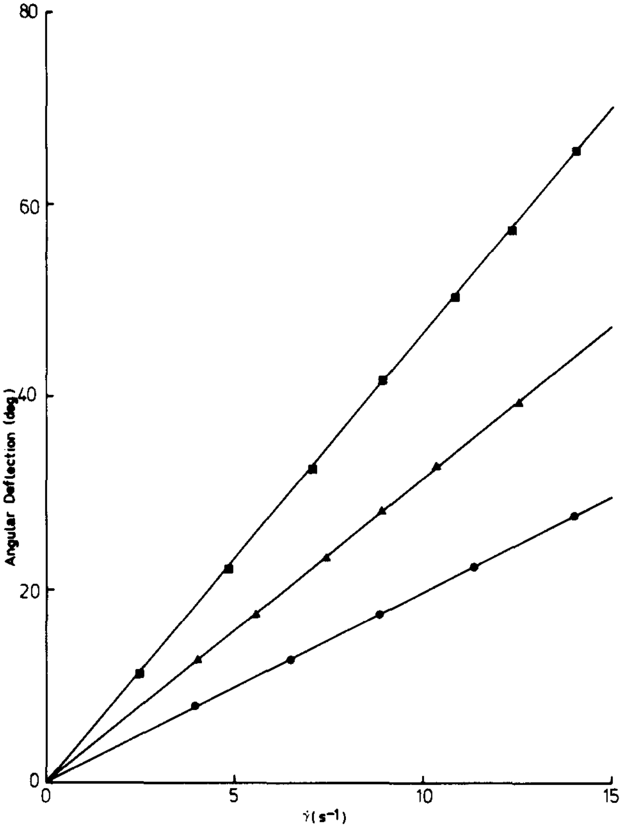

Fig. 2. Intrinsic viscosity determination using an Ogston–Stanier concentric cylinder, torsion wire viscometer, illustrated for lambda carrageenan (0·075 M KCl; pH 7·0; 25°C). The results shown are for polymer concentrations of 0·1 (■) and 0·05 (▲)% w/v, and for the dialysate against which the solutions were equilibrated (●). At each concentration the angular deflection (proportional to shear stress, τ) from an arbitrary null position is measured over a range of rotational speeds (proportional to shear rate, $\dot{\gamma}$). Linearity of τ versus $\dot{\gamma}$ shows Newtonian behaviour over the range of shear rates used, and thus 'zero shear' relative viscosity (η_{rel}) may be calculated from the ratio of slopes for the solution and solvent lines respectively, and intrinsic viscosity derived by extrapolation to infinite dilution, as illustrated in Table 1 and Fig. 4 for the above results, and other concentrations of the same polymer/solvent system.

'random coil' polysaccharide solutions. In each case, double logarithmic plots of η_{sp} against c show a pronounced increase in gradient above a specific critical concentration (c^*). Similar behaviour is well known for synthetic polymer solutions, and is attributed (Daoud *et al.*, 1975) to the transition from dilute solution conditions, where individual polymer molecules are present as isolated coils, to concentrated solutions where the total hydrodynamic volume of the individual chains exceeds the volume of the solution. Thus c^* marks the onset of significant coil overlap and inter-

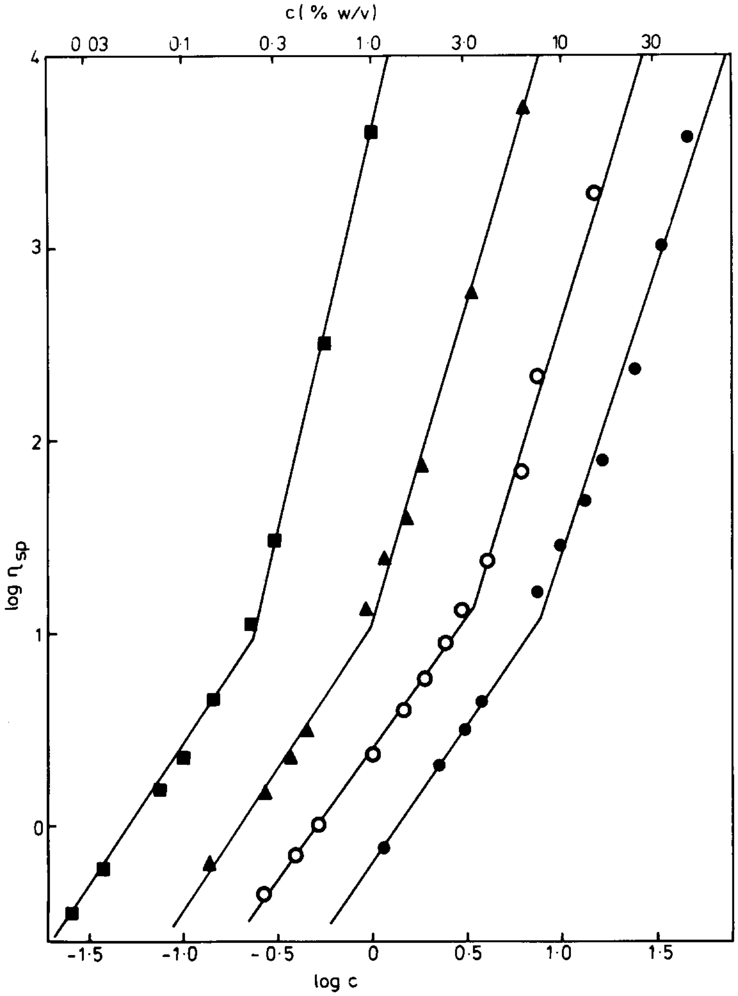

Fig. 3. Concentration dependence of 'zero shear' specific viscosity (η_{sp}) for guar gum (■), dextran (●), 'high guluronate' alginate, equilibrated against 0·2 M NaCl (▲) and polystyrene in toluene (○).

penetration. (In much of the literature on synthetic polymers, the term 'concentrated' is reserved for polymer melts, or solutions in which polymer predominates over solvent, and solutions of lower concentration, down to c^*, are referred to as 'semi-dilute'. Since for polysaccharides such extremes of concentration are experimentally inaccessible, however, the terms 'concentrated' and 'dilute' will be used to denote concentrations above and below c^* respectively.)

A convenient index of the size (hydrodynamic volume) of isolated polymer coils is the limiting viscosity number or 'intrinsic viscosity', $[\eta]$. Experimentally this is

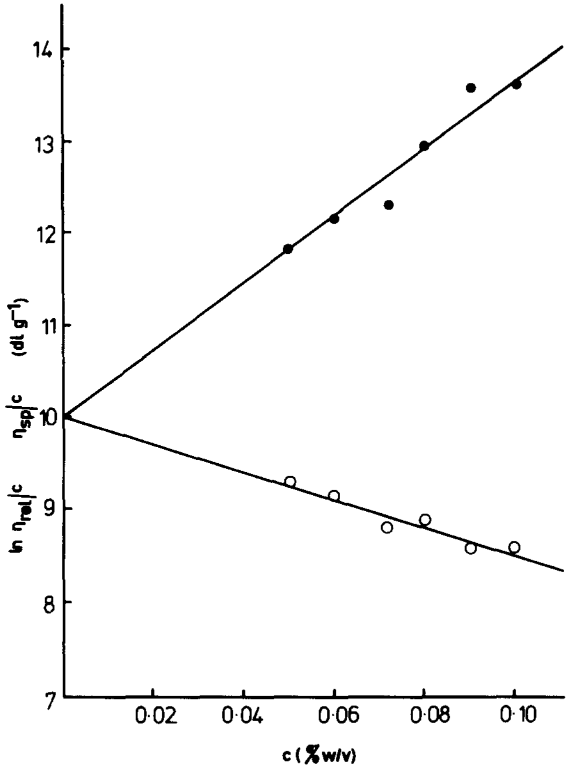

Fig. 4. Combined Huggins (●) and Kraemer (○) extrapolation to intrinsic viscosity (see eqns (2) and (3)) for the data shown in Fig. 2 and Table 1.

determined by direct comparison of solution viscosity with that of the solvent over a range of low concentrations, and then extrapolating to infinite dilution, as illustrated in Figs 2 and 4 and in Table 1 for a typical 'random coil' polysaccharide. In this work a double extrapolation procedure has been used, based on the Huggins (eqn (2)) and Kraemer (eqn (3)) relationships:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \tag{2}$$

$$(\ln \eta_{rel})/c = [\eta] + k''[\eta]^2 c \tag{3}$$

where the symbols have their conventional meaning, as defined in the footnote to Table 1. For all the samples studied in this work both extrapolations showed good linearity up to relative viscosities of ~2·5. Theoretically (for a derivation see for example Morris & Ross-Murphy (1981)) $k' + k'' = 0{\cdot}5$, and values within ±10% of this figure were found in all cases.

TABLE 1
Intrinsic Viscosity ($[\eta]$) Determination from Shear Stress–Shear Rate Plots Such as Those Shown in Fig. 2 (Illustrated for Lambda Carrageenan; 0·075 M KCl; pH 7·0; 25°C)

Concentration (c) (% w/v)	*Slope of viscometer plot*	η_{rel}[a]	η_{sp}[b]	*ln* η_{rel}/c *(dl* g^{-1}*)*	η_{sp}/c *(dl* g^{-1}*)*
0	0·990	–	–	–	–
0·05	1·577	1·593	0·593	9·3	11·9
0·06	1·713	1·730	0·730	9·1	12·2
0·072	1·870	1·889	0·889	8·8	12·3
0·08	2·019	2·039	1·039	8·9	13·0
0·09	2·187	2·209	1·209	8·8	13·4
0·10	2·339	2·363	1·363	8·6	13·6

[a] Relative viscosity (η_{rel}) is the ratio of solution viscosity (η) to that of the solvent (η_s).
[b] Specific viscosity (η_{sp}) is the fractional enhancement of viscosity due to the solvent, i.e. $\eta_{sp} = (\eta - \eta_s)/\eta_s = \eta_{rel} - 1$.
Extrapolation to infinite dilution (Fig. 5) is by a combined Huggins (eqn (2)) and Kraemer (eqn (3)) method.

For random coil polymer solutions, intrinsic viscosity varies with coil dimensions according to the Flory–Fox relationship:

$$[\eta] = \Phi 6^{3/2} R^3/M_r \tag{4}$$

where R is radius of gyration, M_r is molecular weight, and Φ is a constant (Flory, 1953). Thus treating each coil as a sphere of radius R, hydrodynamic volume is proportional to $[\eta]M_r$. Since the total number of coils is proportional to c/M_r, the degree of occupancy of space may therefore be characterised by the dimensionless 'coil overlap parameter', $c[\eta]$. When the concentration dependence of zero shear viscosity (e.g. Fig. 3) is replotted using this parameter in place of concentration alone, a striking generality of behaviour is evident for most of the polysaccharides studied. Thus as shown in Fig. 5, the c^* transition occurs at a value of $c[\eta]$ close to 4 (i.e. $c^* \approx 4/[\eta]$), and the specific viscosity at this degree of coil overlap is invariably close to 10. Since the viscosity of water at 25°C is 0·891 mPa s, this corresponds to a solution viscosity of ~ 10 mPa s (or in older nomenclature ~ 10 cP).

At lower degrees of coil overlap (dilute solutions), the slope of double logarithmic plots of η_{sp} against $c[\eta]$ are close to 1·4 for all samples studied, while at higher values (concentrated solutions) this increases to 3·3 ± 0·3. This value is close to that observed for the molecular weight dependence of zero shear viscosity in monodisperse polymer melts (Graessley, 1974), where η_0 typically varies as $M_r^{3{\cdot}4}$. A somewhat greater concentration dependence ($c^{3{\cdot}75}$) has been predicted theoretically (De Gennes, 1979) using the so-called 'scaling argument', although this conclusion applies strictly only to polymers of very high molecular weight (i.e. low c^*). The authors have also obtained results (Fig. 6) for solutions of a typical synthetic polymer (polystyrene, $M_r \approx 6{\cdot}6 \times 10^5$) in a non-aqueous solvent (toluene), which are closely similar to the polysaccharide data shown in Fig. 5.

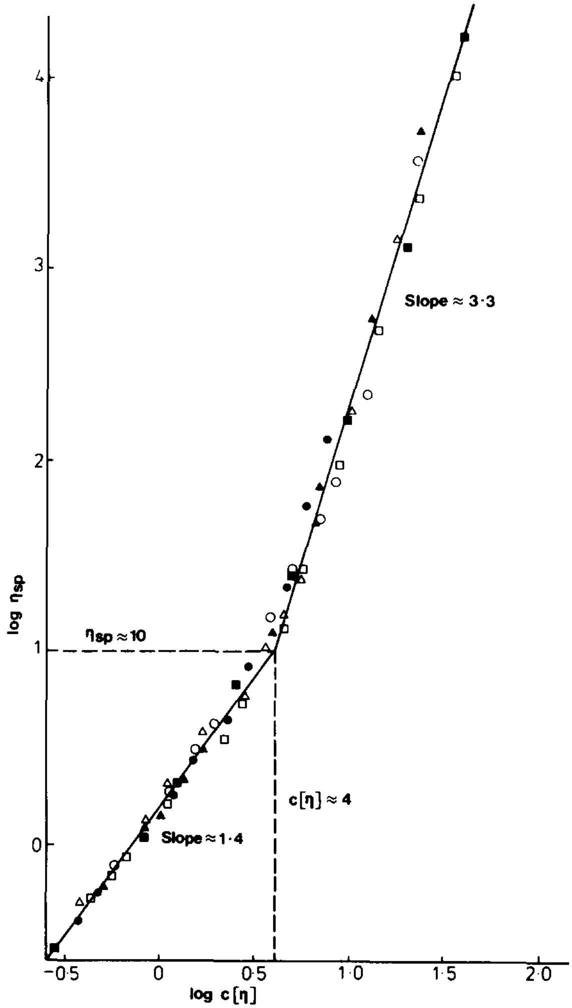

Fig. 5. Variation in the 'zero shear' viscosity of polysaccharide solutions with the degree of occupancy of space by the polymer coils (characterised by the coil-overlap parameter $c[\eta]$). The results shown are for: (○) dextran; (●) carboxymethylamylose (0·5 M NaCl; pH 7); (△) 'high mannuronate' alginate (0·2M NaCl; pH 7); (▲) 'high guluronate' alginate (0·2M NaCl; pH 7); (□) lambda carrageenan (0·075 M KCl; pH 7); and (■) hyaluronate (0·015M NaCl; pH 7; from Morris *et al.* (1980c)).

The only departures from this generalised behaviour which the authors have observed are, as previously reported, for aqueous solutions of the plant galactomannans locust bean gum and guar gum (Doublier & Launay, 1977) and for hyaluronate under conditions of low pH and high ionic strength where intermolecular electrostatic repulsions are suppressed (Morris *et al.*, 1980c). These systems show the onset of

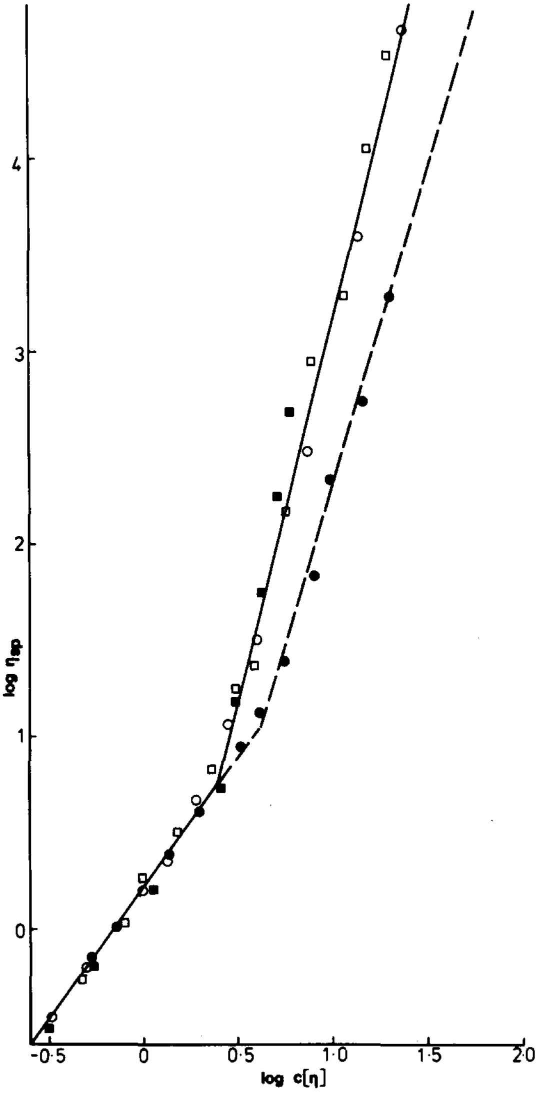

Fig. 6. Comparison of the generalised concentration dependence of polysaccharide specific viscosity (— — —) from Fig. 5, with results for: (●) polystyrene in toluene; (○) guar gum; (□) locust bean gum; and (■) hyaluronate (pH 2·5; 0·15 M NaCl; from Morris *et al.* (1980c)).

concentrated solution behaviour at somewhat lower values of $c[\eta]$ (~2·5), and substantially greater concentration dependence thereafter, so that by values of $c[\eta]$ of ~15 for example, they have attained zero shear viscosities at least an order of magnitude greater than would be expected from the generalised behaviour shown in Fig. 5.

A common feature of these three anomalous systems, which is not shared by the other polysaccharides studied, is that on limited reduction of water activity they form gels or precipitates (Balazs, 1966; Gibbs *et al.*, 1968; Dea *et al.*, 1977; Morris *et al.*, 1980c). From systematic comparison of changes in the tendency to interchain association with variation in primary structure or solvent environment, this behaviour can be traced to the formation of specific junctions between stiff, structurally regular chain sequences. A likely explanation of the enhanced viscosity of these materials might therefore be that similar, though less stable, interactions occur in solution, in addition to physical entanglement of overlapping coils. The extent of specific chain-chain association of this type would be expected to increase with increasing concentration, thus in effect raising the average molecular weight of the polymer, and hence the viscosity. Similar effects have been observed in some synthetic polymers, e.g. poly(n-butyl methacrylate) solutions (Newlin *et al.*, 1962), where entanglement coupling is intensified by specific attractive forces ('hyperentanglement').

For the majority of disordered polysaccharides, however, where there is no evidence of any such specific interactions, the generalised concentration dependence in Fig. 5 allows the maximum or 'zero shear' viscosity (η_0) at every concentration to be expressed with reasonable accuracy in terms of a single parameter, $[\eta]$, irrespective of chemical type, chainlength, or solvent environment (provided that changes in the latter do not lead to departures from random coil chain geometry). Thus for all such solutions, $\eta_0 \approx 10$ when $c = 4/[\eta]$, and at higher or lower concentrations, may be calculated from eqns (5) or (6) respectively:

concentrated solution: $$\eta_0 \approx \eta_s (c[\eta])^{3 \cdot 3}/10 \qquad (5)$$

dilute solution: $$\eta_0 \approx \eta_s \{1 \cdot 5 (c[\eta])^{1 \cdot 4} + 1\} \qquad (6)$$

These equations are derived directly from the linear equations for the double logarithmic plot in Fig. 5. The '+ 1' term in eqn (6) takes account of solvent viscosity which is essentially negligible for concentrated solutions. η_0 is expressed in mPa s. η_s is solvent viscosity, which for water at 25°C is 0·891 mPa s.

The two principal factors which determine the magnitude of $[\eta]$ are chainlength (i.e. molecular weight), and chain stiffness. While the average molecular weights of typical commercial polysaccharides are not unusually high in comparison with synthetic polymers, carbohydrate chains are in general far less flexible (Rees, 1975; Morris & Ross-Murphy, 1981), and therefore adopt considerably more expanded coil geometry than most other random coil polymers, with correspondingly larger values of $[\eta]$ for comparable molecular weights. This in turn implies (eqns (5) and (6)) unusually high solution viscosities at relatively low concentrations (compare for example the viscosity shown in Fig. 3 for alginate and guar gum with those of polystyrene at the same concentrations).

The origin of the restricted flexibility of carbohydrate chains may be traced (Cleland, 1971; Rees & Scott, 1971; Whittington, 1971; Rees, 1975; Rees & Smith, 1975; Morris *et al.*, 1978b) to steric crowding and other local interactions which severely limit the range of possible relative orientations of adjacent residues (although for polyelectrolytes coil dimensions may be further expanded by long range electrostatic repulsions). A notable exception is dextran, where linkage is predominantly through O(6) rather than through an oxygen atom attached directly to the sugar ring, thus conferring additional conformational freedom by rotation about the C(5)-C(6) bond. As illustrated in Fig. 3, dextran therefore shows much lower solution viscosities than most other polysaccharides. The transition from dilute to concentrated behaviour also appears less pronounced for dextran and carboxymethylamylose than for other chains.

3.2. *Shear Rate Dependence of Viscosity*

So far results have been confined to 'Newtonian' viscosity behaviour at low rates of shear. For dilute solutions reduction in viscosity from this maximum value with increasing shear rate is relatively minor (typically less than a factor of 2 over the entire range of experimentally accessible rates of shear), and arises from alignment of transiently elongated coils in the direction of flow. For concentrated solutions, however, shear thinning is much more dramatic, as illustrated in Fig. 7, and arises from

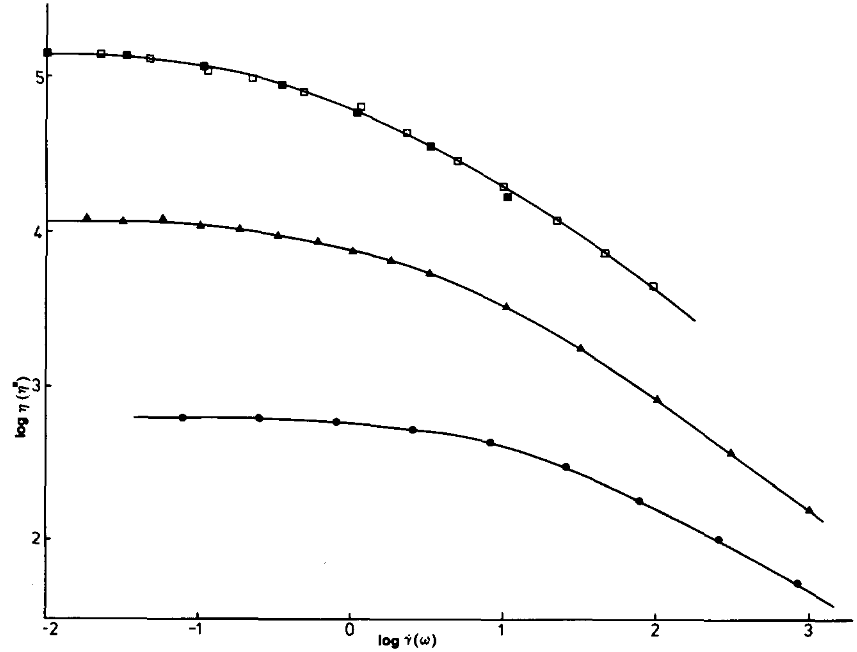

Fig. 7. Shear thinning of concentrated polysaccharide solutions, illustrated for lambda carrageenan (0·1 M NaCl; pH 7) at concentrations of 1·5 (●), 2·75 (▲) and 5·0 (■) % w/v. The frequency (ω) dependence of dynamic viscosity (η^*) is also shown (□) for the 5% w/v solution. η and η^* are in units of mPa s, $\dot{\gamma}$ is in s^{-1} and ω is in rad s^{-1}.

an entirely different mechanism. Interpenetration of polymer coils in concentrated solutions rise to a dynamic 'entangled' network structure (Graessley, 1974). At low rates of shear, those entanglements which are disrupted by the imposed deformation are replaced by new interactions between different partners, with no net change in the extent of entanglement, and hence no reduction in viscosity. This situation corresponds to the horizontal 'Newtonian plateau' in viscosity-shear rate plots such as those shown in Fig. 7. The onset of shear thinning occurs when the rate of externally imposed movement becomes greater than the rate of formation of new entanglements, and thus the 'crosslink density' of the network is depleted, and viscosity is reduced.

For many polymer solutions the shear rate dependence of viscosity is closely superimposable (Cox & Merz, 1958) upon the frequency (ω) dependence of dynamic viscosity (η^*), the ratio of total stress to frequency of oscillatory deformation. Most of the solutions studied follow this generality, which is illustrated in Fig. 7, but at high extents of coil overlap the galactomannan samples which showed (Fig. 6) departures from the generalised concentration dependence of η_0 also failed to obey the Cox-Merz rule, particularly at low frequencies and low shear rates. Such a departure from Cox-Merz superimposability has recently been reported for polyacrylamide solutions (Kulicke & Porter, 1980), and was attributed to the making and breaking of non-covalent (hydrogen) bonds.

As the degree of coil overlap (characterised by $c[\eta]$) increases, the freedom of movement of individual chains is progressively restricted, with consequent increase in the time required to form new entanglements to replace those disrupted by externally imposed deformation. Thus, as illustrated in Fig. 7, the shear rate (or frequency) at which Newtonian behaviour is lost moves to lower and lower values with increasing concentration (Graessley, 1974). Doi & Edwards (1978) explain this same effect by considering the relaxation of stress in the 'tube' model (de Gennes, 1971) of a concentrated polymer system. To quantify and characterise this effect, a 'shear thinning parameter' ($\dot{\gamma}_{0.1}$), the shear rate at which apparent solution viscosity is reduced to one tenth of the maximum 'Newtonian' value η_0 is defined (Fig. 8). To compare directly the form of shear thinning for different solutions, applied shear rates have been expressed as a fraction of this value (i.e. as $\dot{\gamma}/\dot{\gamma}_{0.1}$), and observed viscosities as a fraction of η_0.

When the shear rate dependence of concentrated solution viscosity is plotted in this way for all the polysaccharides studied in this work, another striking generality of behaviour is evident (Fig. 9). Thus irrespective of chemical type, molecular weight, solvent environment, or concentration (above c^*), concentrated polysaccharide solutions all show essentially the same shear thinning profile (Table 2), and differ only in the values of η_0 and $\dot{\gamma}_{0.1}$. With knowledge of the generalised form of shear thinning in Table 2, therefore, these two parameters are sufficient to characterise completely the solution viscosity at all shear rates of practical interest.

This generalisation applies equally to the systems (locust bean gum, guar gum, and

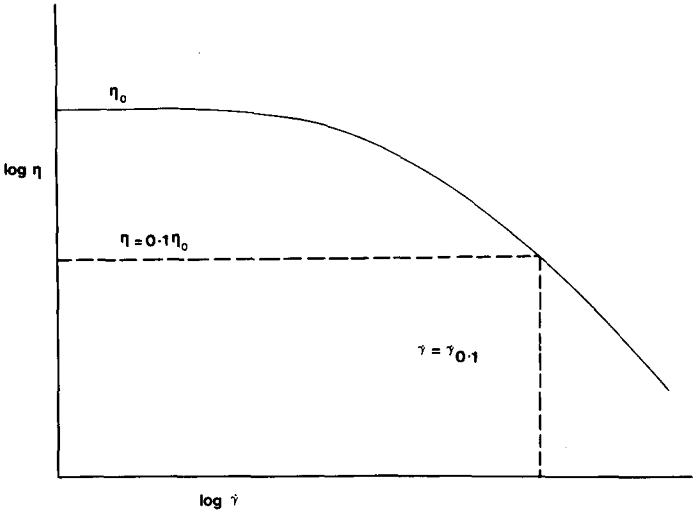

Fig. 8. Characterisation of shear thinning in concentrated polysaccharide solutions by the two parameters η_0 ('zero shear' viscosity) and $\dot\gamma_{0\cdot1}$ (the shear rate at which $\eta = \eta_0/10$).

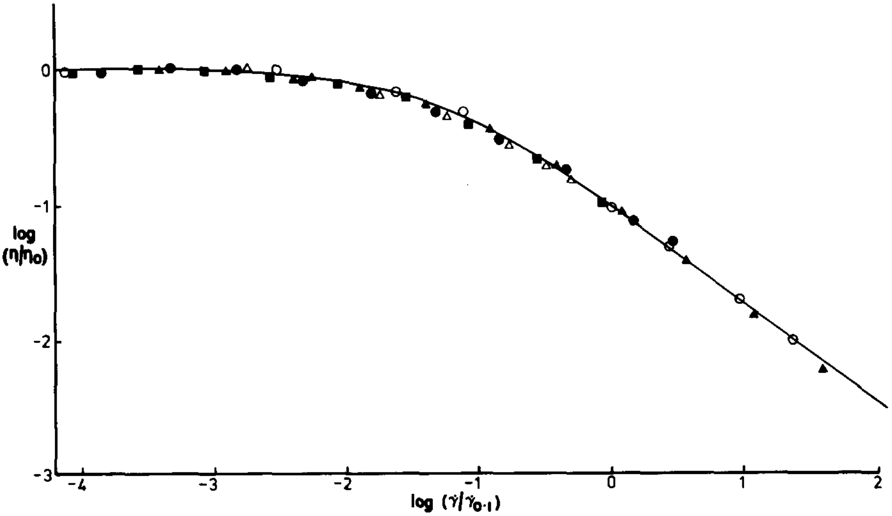

Fig. 9. Generalised shear thinning behaviour for concentrated solutions of disordered polysaccharides illustrated for: (△) guar gum; (▲) lambda carrageenan; (●) locust bean gum; (■) 'high mannuronate' alginate; and (○) hyaluronate (representative values taken from Fig. 3 in Morris *et al.* (1980c)).

TABLE 2

Generalised Shear Thinning Behaviour of Concentrated Solutions of Disordered Polysaccharides

log $(\dot{\gamma}/\dot{\gamma}_{0\cdot 1})$	*log* (η/η_0)	$(\eta/\eta_0) \times 100$
−4·0	0·00	100
−3·5	0·00	100
−3·0	0·00	100
−2·8	0·00	100
−2·6	−0·02	95
−2·4	−0·04	91
−2·2	−0·07	85
−2·0	−0·10	79
−1·8	−0·14	72
−1·6	−0·18	66
−1·4	−0·24	58
−1·2	−0·32	48
−1·0	−0·40	40
−0·8	−0·49	32
−0·6	−0·60	25
−0·4	−0·72	19
−0·2	−0·85	14
0·0	−1·00	10
0·5	−1·36	4·37
1·0	−1·73	1·86
1·5	−2·11	0·78
2·0	−2·48	0·33

hyaluronate at low pH and high ionic strength) which showed (Fig. 6) evidence of concentration-induced intermolecular association, as well as to the other systems (Fig. 5) where such effects were absent. From this it is concluded that the timescale of specific segment–segment interaction must be long in comparison with the lifetime of non-specific physical entanglements, since the generality of shear thinning implies a common mechanism of response (rearrangement of the entangled network) to applied deformation.

For solutions where η_0 is not experimentally accessible (i.e. shear thinning has begun at the lowest available shear rate), or where $\dot{\gamma}_{0.1}$ cannot be determined directly, because η still exceeds $\eta_0/10$ at the highest available shear rate, the two parameters may still be estimated from the generalised shear thinning profile shown in Fig. 9. The most satisfactory method is to use an iterative computer program, with standard minimisation routine, to vary both parameters until no further improvement can be obtained in the root-mean-square deviation between the observed shear thinning behaviour of the sample, and the 'standard' values listed in Table 2. Where computer facilities are not available, however, a reasonable alternative procedure is to construct on translucent graph paper the 'master curve' shown in Fig. 9 (using the tabulated values from Table 2), and a plot of log η versus log $\dot{\gamma}$ for the solution, drawn to the same scale. The two graphs may then be superimposed, and moved relative to each other along both axes, until the best visual fit is obtained. Approximate values of η_0 and $\dot{\gamma}_{0.1}$ may then be calculated directly from the relative positions of their respective co-ordinate frames.

Previous studies (Graessley, 1974) of the shear rate dependence of viscosity for synthetic polymer solutions and melts showed variations in shear thinning behaviour, particularly with changes in the degree of polydispersity, the greatest changes being observed on going from nearly monodisperse distributions to M_w/M_n of ~ 2, with progressively smaller changes thereafter. It seems likely, therefore, that a factor contributing to the generality which the authors have observed is the extreme polydispersity of commercial polysaccharides, which will in general be so great that differences in detailed molecular weight distribution become insignificant.

4. CONCLUSION

The concentration and shear rate dependence of viscosity in a variety of different random coil polysaccharides has been demonstrated to follow a general form quite similar to that found for synthetic polymers in organic solvents. In some cases, however, particularly for locust bean gum, guar gum and hyaluronic acid at low pH and high ionic strength, systematic deviations occur, and these can be rationalised in terms of the extra, specific segment-segment interactions which are known to occur in these systems.

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