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CHARACTERISATION OF INTERCHAIN ASSOCIATION IN POLYSACCHARIDE SOLUTIONS BY ULTRASONIC RELAXATION AND VELOCITY

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ABSTRACT

The amplitude of ultrasonic relaxation in aqueous solutions of disordered polysaccharides shows a marked increase with increasing degree of coil overlap and, at comparatively low concentrations, attains values comparable to those observed in polysaccharide gels. Mechanical spectroscopy studies indicate that, on the ultrasonic timescale, dynamic networks formed by polymer entanglement in solution are indistinguishable from true gels. In both cases the intense relaxations observed are attributed predominantly to motion of solvent within the polymer network. Due to the inherent stiffness of most polysaccharides, formation of a highly entangled network structure (with consequent enhancement of ultrasonic relaxation) occurs at much lower concentrations than for typical synthetic polymers. The onset of coil overlap (c transition) is accompanied by an abrupt change in the concentration dependence of ultrasonic velocity. Results for the conformationally rigid polysaccharide xanthan, suggest that velocity measurements may offer a convenient method for determination of c* in systems where the normal viscometric characterisation is impossible.*

INTRODUCTION

An ultrasonic relaxation is observed in liquids and solutions when the quantity α/f^2 decreases with increasing frequency (α being the sound absorption coefficient at

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frequency f). In chemical relaxation studies the ultrasonic method has been used extensively to investigate the kinetics of fast reactions in solution. The relaxation occurs as a result of the perturbation of rapid chemical or molecular equilibria by the incident wave. In solutions of synthetic polymers in organic solvents, extensive ultrasonic measurements (Cochran *et al.*, 1972, 1974; Pethrick *et al.*, 1974; Dunbar *et al.*, 1977) have shown that relaxation is associated with the perturbation of various conformational equilibria occurring in the macromolecule. An additional contribution to the relaxation process at high polymer concentrations has been attributed to polymer/polymer contact.

Recently (Gormally *et al.*, 1982) we presented evidence to show that a new, very intense, ultrasonic relaxation in polysaccharide gels crosslinked by aggregated double helices arises predominantly from the motion of solvent molecules within the polymer network. Since disordered polysaccharide chains, at sufficiently high concentrations, can also develop a network structure by interpenetration ('entanglement') of individual random coils (Graessley, 1974; Morris *et al.*, 1981) the possibility therefore exists that the ultrasonic relaxation technique can be used as a probe to monitor such entanglements.

Furthermore, since physical properties such as viscosity are known to be extremely sensitive to the development of structure in polymer solutions, one might expect other solution properties such as adiabatic compressibility to show a similar sensitivity. In this connection the sound velocity (C) in a solution is related to its adiabatic compressibility, β, through the Laplace equation

$$C^2 = 1/\rho\beta \tag{1}$$

where ρ is the density. In order to explore how various ultrasonic parameters are affected by polymer/polymer interactions, we have measured the ultrasonic absorption and velocity in some random coil polysaccharide solutions which have been characterised by rheological measurements. We report here a systematic study of these systems.

POLYMER ENTANGLEMENT

At sufficiently low concentrations disordered polymer chains exist in solution as isolated 'random coils' surrounded by solvent. With increasing concentration, however, a point is reached (Graessley, 1974) at which further molecules can be accommodated only by interpenetration of the polymer coils ('entanglement'). The concentration (c^*) at which this occurs is, of course, dependent on the volume occupied by each molecule.

A particularly convenient index of coil dimensions is intrinsic viscosity, $[\eta]$, defined as follows:

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_s}{\eta_s c} \tag{2}$$

where η is the solution viscosity, η_s is the solvent viscosity, and c is the concentration. For a disordered polymer of molecular weight M_r, intrinsic viscosity varies (Flory, 1969) with a radius of gyration (R) according to the Flory–Fox relationship:

$$[\eta] = \Phi 6^{3/2} R^3 / M_r \qquad (3)$$

where Φ is a constant ($\approx 2{\cdot}6 \times 10^{26}$ kg^{-1}). The volume of each coil will vary as R^3, and is therefore proportional to $[\eta]M_r$. Since the number of coils is proportional to c/M_r, the degree of occupancy of space may be characterised by the (dimensionless) 'coil overlap parameter' $c[\eta]$.

The onset of entanglement is accompanied by a dramatic increase in the concentration dependence of solution viscosity. For aqueous solutions of disordered polysaccharides (Morris *et al.*, 1981) this occurs when $c[\eta] \approx 4$, and the concentration dependence increases from $\sim c^{1.4}$ to $\sim c^{3.3}$.

At low rates of shear the observed viscosity of an 'entangled' solution remains constant, as interactions disrupted by the imposed flow are replaced by new entanglements, with no net change in 'crosslink density'. It is this fixed 'zero shear' or 'Newtonian' viscosity (η_0) which characterises the extent of coil overlap, and is therefore used in the viscometric determination of c^*. At higher shear rates, where the rate of disruption of existing interactions exceeds the rate of re-entanglement, the network is depleted, and viscosity falls. This is known as 'shear thinning', and occurs at progressively lower shear rates as the degree of coil overlap increases.

The same behaviour is evident in dynamic studies of solution viscoelasticity. At low frequencies of oscillation, where the timescale of the applied deformation is slow in comparison with the time required for disentanglement, the predominant response of an entangled network is by viscous flow, characterised by the loss modulus G''. At higher frequencies, however, where there is insufficient time for entanglements to break and reform within the period of one oscillation, the network accommodates the applied stress mainly by elastic deformation, characterised by the storage modulus G'. Under these conditions a dynamic entangled network will therefore show properties approaching those of a covalently crosslinked polymer network, or a 'permanent' polysaccharide gel, crosslinked by cooperative interchain junction zones (Gormally *et al.*, 1982; Rees, 1977; Morris *et al.*, 1977*a*).

EXPERIMENTAL

Lambda carrageenan (sample number Rex 5400) was prepared for us by Marine Colloids Inc., Rockland, Maine, USA. Guar gum and locust bean gum were commercial materials from the same supplier (samples Rex 5923 and 5924, respectively). Xanthan (Keltrol F) was kindly donated by the Kelco Division of Merck & Co., Inc., San Diego, California, USA. Solutions were prepared by dispersing the polysaccharides in distilled water and autoclaving (400 K; 30 min). In the case of the polyelectrolytes (lambda carrageenan and xanthan) a solution of the highest polymer concentration required was dialysed to equilibrium against an appropriate salt solution, and the dialysate was then used for subsequent dilutions, to ensure constant chemical potential.

'Zero shear' viscosities (η_0) of dilute solutions were measured on a low shear, concentric cylinder viscometer, after the design of Ogston & Stanier (1953). Extrapolation to intrinsic viscosity (see Morris & Ross-Murphy, 1981) was by a combined Huggins (eqn (4)) and Kraemer (eqn (5)) treatment, as illustrated in Fig. 1.

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \qquad (4)$$

$$(\ln \eta_{rel})/c = [\eta] + k''[\eta]^2 c \qquad (5)$$

where η_{rel} is the relative viscosity (η/η_s), and η_{sp} the specific viscosity ($\{\eta - \eta_s\}/\eta_s = \eta_{rel} - 1$). A Rheometrics mechanical spectrometer (Model RMS-605), with a 50 mm cone and plate assembly of cone angle 0·04 radians, was used to measure η_0 of more concentrated solutions, and for dynamic studies of storage and loss moduli (G' and G'').

Ultrasonic absorption coefficient (α) and velocity (C) were measured at different frequencies over the range 2-20 MHz using the resonance technique of Eggers (1968). The ultrasonic velocity was calculated from the frequencies of the resonance peaks,

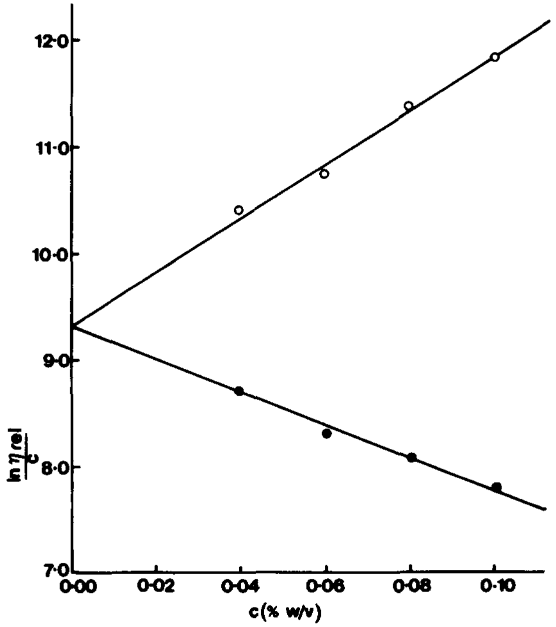

Fig. 1. Determination of intrinsic viscosity by the combined Huggins (o) and Kraemer (•) extrapolation technique (eqns (4) and (5)), illustrated for guar galactomannan.

and its magnitude quoted relative to the value (Barlow & Yazgan, 1966) for water: 1496·58 ± 0·04 ms^{-1} at 298 K. The accuracy of the velocity measurements is of the order 0·5 ms^{-1}.

POLYSACCHARIDE STRUCTURE AND CONFORMATION

Guar gum and locust bean gum are both members of the galactomannan family of plant polysaccharides (see Dea & Morrison, 1975) and are based on a linear 1,4-linked backbone of β-D-mannose residues, substituted to different extents by α-D-galactose residues, linked to position 6 of mannose. The average degree of substitution is about 1 galactose per 4 mannose residues in locust bean gum, while the galactose content in guar gum is about twice this. Both materials exist in solution in a disordered, 'random-coil' chain conformation, and interact predominantly by physical entanglement, although there is some evidence (Morris *et al.*, 1981) that at high polymer concentrations there may be some contribution to network formation from more specific segment–segment interactions (hyperentanglement).

Lambda carrageenan is based (Anderson *et al.*, 1968) on an alternating disaccharide repeating sequence of 1,4-linked α-D-galactose-2,6-disulphate and 1,3-linked β-D-galactose (some residues of which are also sulphated at position 2). It also adopts a disordered chain conformation in solution, irrespective of ionic environment (Morris *et al.*, 1978).

Xanthan is an extracellular bacterial polysaccharide with a linear backbone of 1,4-linked D-glucose (as in cellulose), solubilised by attachment of a charged trisaccharide sidechain on every alternate glucose residue (Jansson *et al.*, 1975). Under most conditions of temperature and ionic strength xanthan exists in solution in a rigid, ordered chain conformation (Morris *et al.*, 1977*b*), stabilised by non-covalent interactions between side chain and main chain (Moorhouse *et al.*, 1977).

ULTRASONIC RELAXATION IN ENTANGLED NETWORKS

An ultrasonic relaxation was observed in concentrated ($c \gg c^*$) solutions of all the disordered polysaccharides studied. As illustrated in Fig. 2 for guar galactomannan, the amplitude of the relaxation process shows a marked increase with increasing concentration of polymer. Indeed, one of the unusual features of this relaxation is the relatively high amplitude observed at comparatively low polysaccharide concentrations. Normally, for polymer solutions in which the ultrasonic wave perturbs various intramolecular conformational equilibria, comparable relaxation amplitudes are observed (Cochran *et al.*, 1972, 1974; Pethrick *et al.*, 1974; Dunbar *et al.*, 1977) at concentrations in the range 8–15% w/v. The significant size of the present relaxation amplitude

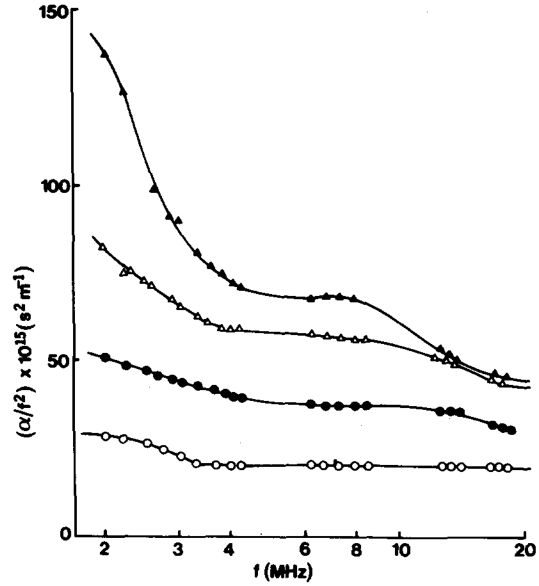

Fig. 2. Ultrasonic relaxation in aqueous solutions of guar galactomannan. The polymer concentrations shown are 0·25% w/v (○); 0·75% w/v (●); 1·5% w/v (△) and 2·0% w/v (▲).

for such low polysaccharide concentrations excludes the possibility of the perturbation of an intramolecular mechanism such as a conformational change. Rather the amplitude/concentration range found in the present work is comparable (Fig. 3) to that observed in recent studies of the 'permanent' network structure in polysaccharide gels (Gormally *et al.*, 1982).

To explore the origin of this behaviour, we have used mechanical spectroscopy to characterise the dynamic network structure of disordered polysaccharide solutions over the same range of concentration used in the ultrasonic relaxation studies. The 'solid-like' character of the entangled network (characterised by the storage modulus G') increases with increasing degree of coil overlap (i.e. increasing $c[\eta]$), as illustrated in Fig. 4 for aqueous solutions of guar gum. At sufficiently high concentrations (e.g. the 3% w/v solution shown) G' values at high frequencies become comparable to those observed for gelling polysaccharides such as agarose (Morris & Ross-Murphy, 1981). The frequencies accessed by the ultrasonic technique are between 5 and 6 orders of magnitude greater than the highest values shown in the mechanical spectra in Fig. 4. It is therefore clear that network re-arrangement in response to an applied perturbation (characterised by large values of G'' relative to G') cannot occur within the ultrasonic timescale.

On this evidence we consider that the most probable mechanism for ultrasonic relaxation in these solutions is similar to that observed (Gormally *et al.*, 1982) in long-

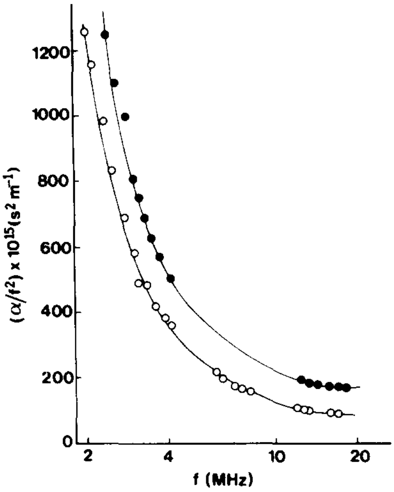

Fig. 3. Comparison of ultrasonic relaxation in a highly entangled aqueous solution of locust bean gum (○; 3% w/v; $c[\eta] \approx 28$) and in (Gormally *et al.*, 1982) an iota carrageenan gel (●; 10% w/v; 0·1 M KCl).

lived polysaccharide gel networks and arises predominantly as a result of the motion of solvent molecules within the network. Present results indicate that, on the timescale of the ultrasonic technique, an entangled network is essentially indistinguishable from a true gel network, and thus gives rise to analogous mechanisms of relaxation. Development of a cohesive gel network through cooperative interchain junction zones (Rees, 1977; Morris *et al.*, 1977*a*), however, can occur at concentrations considerably lower than those required for extensive coil overlap (Morris & Ross-Murphy, 1981), thus explaining the increase in relaxation amplitude which accompanies polysaccharide gelation (Gormally *et al.*, 1982).

CONCENTRATION DEPENDENCE OF SOUND VELOCITY

The onset of coil entanglement with increasing concentration in solutions of disordered polymer chains is accompanied (Graessley, 1974; Morris *et al.*, 1981) by a pronounced increase in resistance to flow, and may be conveniently monitored by the change in gradient of a double logarithmic plot of 'zero shear' viscosity (η_0) against concentration. This is illustrated in Fig. 5 for lambda carrageenan under constant conditions of ionic environment. Figure 6 shows the concentration dependence of sound velocity for the same polymer–solvent system. Once more a marked change in gradient is observed at about the same degree of coil overlap. It would therefore appear that development of an entangled polysaccharide network affects the velocity

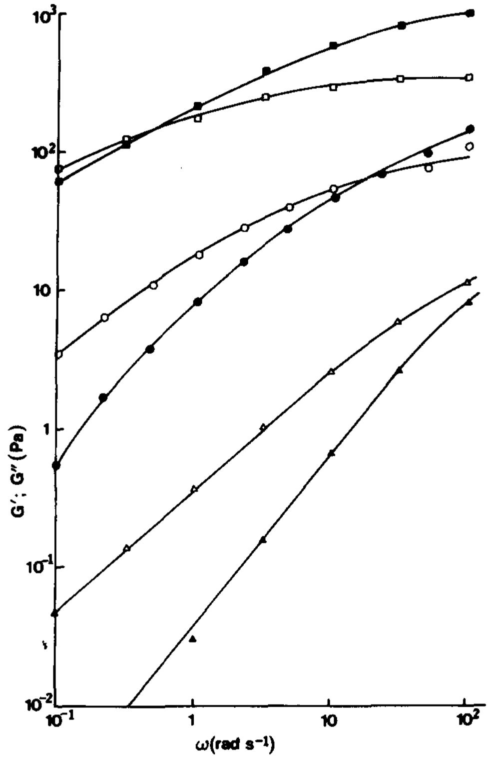

Fig. 4. Characterisation of interchain entanglement in aqueous solutions of guar galactomannan, by mechanical spectroscopy. The frequency (ω) dependence of storage (filled symbols) and loss (open symbols) moduli (G' and G'', respectively) is shown for polymer concentrations of 1% w/v (triangles), 2% w/v (circles) and 3% w/v (squares). The intrinsic viscosity of this sample is $\simeq$9·3 dl g^{-1} (Fig. 1), giving values for the coil overlap parameter $c[\eta]$ of 9·3, 18·6, and 27·9, respectively.

of propagation of sound waves, as well as their absorption, and that this offers a simple alternative method for characterisation of the c^* transition (onset of entanglement).

Solutions of xanthan, at concentrations in excess of $\simeq$0·5% w/v, appear to exhibit a 'yield stress' (i.e. a finite stress must be applied before flow is detected) and thus apparent viscosity tends to infinity with decreasing shear rate (Morris, 1977). A likely explanation of this behaviour (Frangou *et al.*, 1982) is that non-covalent interactions between the conformationally rigid chains lead to formation of a weak network structure, which must be disrupted before flow can occur. Under these conditions 'zero shear' or 'Newtonian' viscosity cannot be measured, and thus detection of the c^* transition from the concentration dependence of η_0 is impossible.

As shown in Fig. 7, however, a marked change in slope is once more observed in the concentration dependence of sound velocity. In contrast to the 'entanglement'

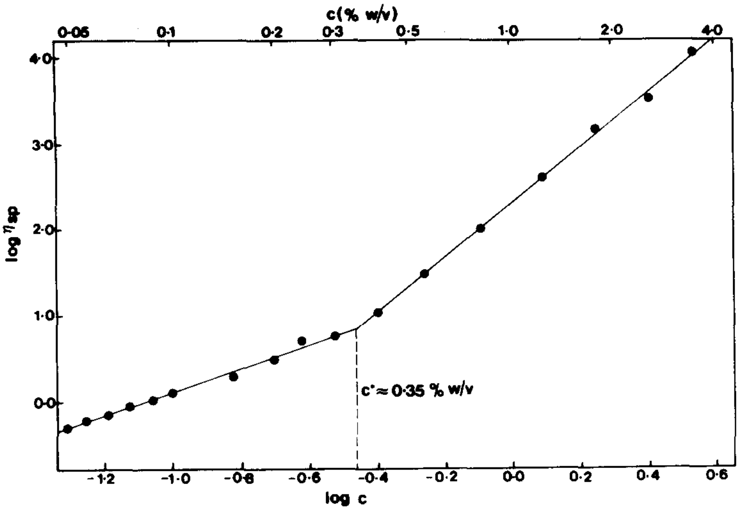

Fig. 5. Characterisation of the onset of coil entanglement by the concentration (c) dependence of 'zero shear' specific viscosity, η_{sp}, illustrated for lambda carrageenan (0·75 M NaCl; $[\eta] = 8 \cdot 6$ dl g^{-1}).

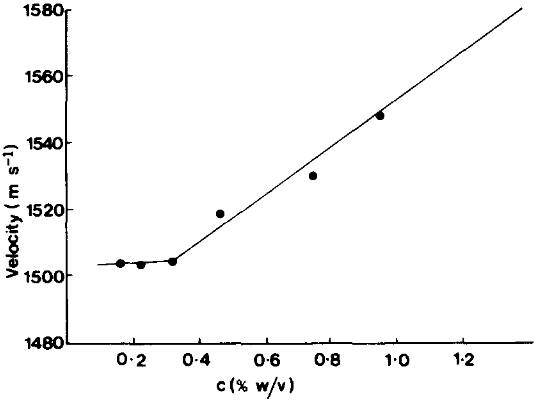

Fig. 6. Concentration dependence of sound velocity (2 MHz) in aqueous solutions of lambda carrageenan (0·75 M NaCl; $[\eta] = 8 \cdot 6$ dl g^{-1}).

coupling illustrated in Fig. 6, the concentration dependence for xanthan decreases at higher polymer concentrations, indicating a different mechanism of intermolecular interaction. Similar behaviour has, however, been observed for sound velocity in detergent solutions above and below the critical micelle concentration (Bloor, 1981), and supports the above suggestion that conformationally rigid chain sequences in xanthan

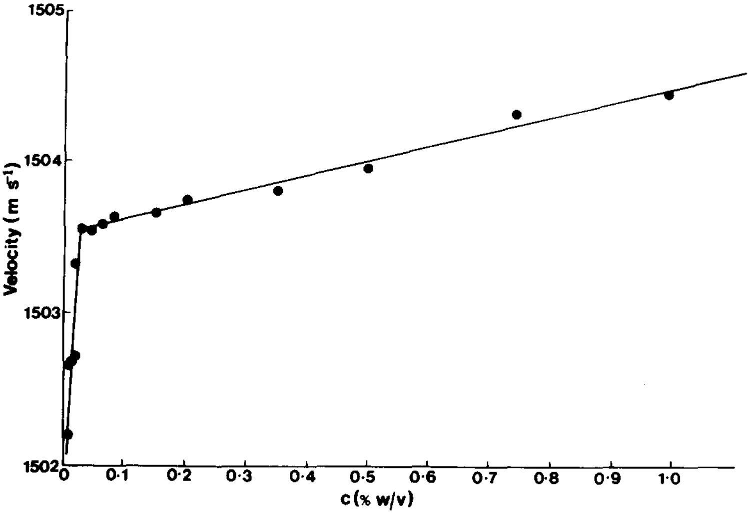

Fig. 7. Concentration dependence of sound velocity (2 MHz) in aqueous solutions of xanthan (0·10 M KCl; $[\eta] = 40$ dl g^{-1}).

may associate by weak non-covalent interactions rather than by physical entanglement. The break in the plot of sound velocity versus concentration (Fig. 7) occurs at a $c[\eta]$ value of about 1·0, rather than the somewhat higher values (typically $c[\eta] \approx 4$) observed for entanglement of disordered polysaccharides, again indicating the involvement of a different mechanism of interchain association.

CONCLUSIONS

Our present results indicate that sound velocity measurements may provide a simple and convenient method for characterisation of the onset of intermolecular association in polysaccharide solutions, including systems where viscometric characterisation is impossible. For solutions of disordered polysaccharides in which there is substantial overlap of individual coils, the response of the resulting dynamic, entangled network is indistinguishable on the ultrasonic timescale from that of a 'permanent' polysaccharide gel. In both cases we attribute the very intense ultrasonic relaxation observed, to motion of solvent molecules within the network. Due to the inherent stiffness (and hence large coil dimensions) of most polysaccharide chains (Morris & Ross-Murphy, 1981) this new relaxation process occurs at very much lower concentrations than it would in solutions of typical synthetic polymers.

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