

RHEOLOGICAL STUDY OF AQUEOUS SOLUTIONS OF HYDROPHOBICALLY-ASSOCIATING DERIVATIVES OF PROPYLENE GLYCOL ALGINATE

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Studies on hydrophobically-associating water-soluble polymers have been, so far, mainly performed on the modification of maleic anhydride [1] or polyacrylic acid under various hydrophilic forms [2, 3, 4] (sodium acrylate, N-isopropyl acrylamide, etc.) as well as, to a lesser extent, on hydrophobic derivatives of certain polysaccharides [5, 6, 7] (hydroxyethyl cellulose, pullulan, etc.).

We report our results on the physicochemical study in aqueous solution of new amphiphilic polysaccharide derivatives, obtained by attachment of long-chain alkylamines (C_n-NH_2 $n = 8, 12, 14$) onto propylene glycol alginate (PGA), a partially esterified derivative of sodium alginate [8, 9, 10, 11]. The alginate salts differ from most other polysaccharides in that they exhibit a sol-gel transition when simply submitted to modifications of their ionic environment, e.g. substitution of Na^+ by divalent cations such as Ca^{2+} . Such a property is an additional motivation for the preparation of amphiphilic macromolecules and their study, not only in solution, but also in the near future in the gel state, both for theoretical reasons and because of the potential improvements they may bring to existing biomedical applications.

In aqueous solution, at low concentrations, intramolecular interactions are favoured [8] and [11]. These lead to more compact, shrunken conformations, resulting in lower intrinsic viscosities $[\eta]$, and higher Huggins coefficients k_H , when compared to those of the unmodified parent polymer.

Furthermore, in agreement with general principles governing the hydrophobic effect, the phenomena exacerbate as the ionic strength increases.

In semi-dilute regime, chains may overlap and thus associate via intermolecular hydrophobic associations. Solutions of parent PGA behave typically as non-Newtonian inelastic fluids, whereas those of hydrophobically-substituted polymers (PGA- C_n) are viscoelastic.

Alternating tests with different shear rates have shown that the intermolecular hydrophobic interactions can be quickly disrupted at high shear rates, whereas, once disrupted and suddenly submitted to low shear rate, they slowly build up [10]. The characteristic time for structure recovery, or in other terms for the re-establishment of hydrophobic interactions, was of the order of several hundred seconds, in agreement with reported values for other systems [7]. This time is much higher than that associated with the breaking down of the hydrophobic interactions. As suggested by Aubry and Moan [7], we determined a mean hydrophobic association lifetime as the inverse of the shear rate at which a catastrophic drop in viscosity is observed, as shown in Figure 1. We found a value of 0.08 s, which is consistent with other values reported in literature [7], [12] and [13].

We report in Figure 1 steady-state viscosity data obtained via a protocol similar to that used by Aubry and Moan [7]: in fact the sample was prestressed (4 Pa) during 600 seconds and then kept at rest for 300 seconds. When submitted to a particular stress after this prestress history, the shear viscosity response exhibits a large overshoot before reaching a steady-state value. This is also observed even when no prestress history has been imposed to the material, however the

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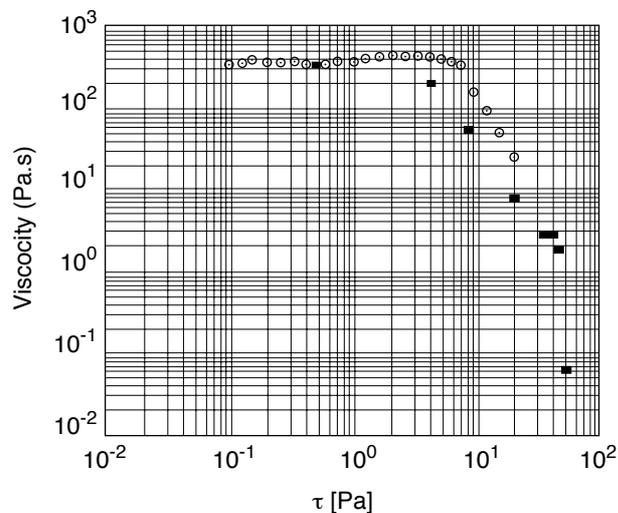


Figure 1

Steady-state viscosity as a function of imposed shear stress for PGA-C₁₂ (1.2 g.dl⁻¹), in pure water, (■) with prestress history, (O) without prestress history.

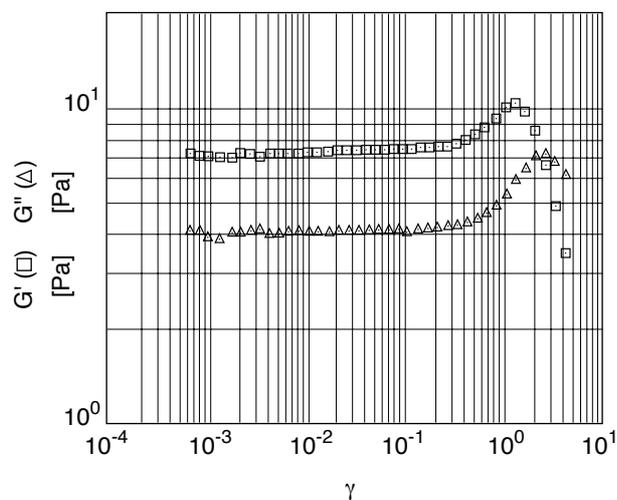


Figure 2

Strain sweep in oscillatory shear for PGA-C₁₂ in pure water (1.2 g.dl⁻¹).

steady-state data are not necessarily identical, particularly in a stress window between the Newtonian plateau ($\tau < 1$ Pa) and the critical stress value corresponding to the total destruction of the associating interaction junctions, i.e. $\tau \approx 40$ Pa.

When no prestress history has been imposed to the material, the viscosity curve exhibits a weak shear-thickening prior to a pronounced shear-thinning. Some authors have interpreted this behaviour in terms of a transition from a state of predominantly intramolecular associations to predominantly intermolecular associations [14] or in terms of a competition between rates of formation and disengagement of associations under the influence of shear [12]. In our particular case, polymer concentration is above the overlap concentration [10], then hydrophobic intermolecular interactions are more probable than intramolecular ones. Under shear, intramolecular interactions may be converted into intermolecular ones, giving rise to an increase in viscosity. This is further evidenced by large amplitude oscillatory experiments allowing to observe strain hardening at $\gamma \approx 1$ (Fig. 2).

When the previously described prestress has been imposed, this weak shear thickening is not observed. At this stage, the interpretation is probably difficulted by the fact that the rest period is of the order of the hydrophobic interaction restructuring time. Further work needs to be carried out in order to better understand these unusual rheological responses as well as to elucidate the underlying mechanisms.

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