The onset of entangled behaviour in amylose solutions

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The variation of η_0 with amylose fraction is analysed, separating the effect of the polymer concentration from the effect of temperature. This gives a critical amylose volume fraction $\varphi_2^* = 0.14$ for the onset of entanglements. The corresponding critical molecular weight, $M_c = 29\,400$ fulfils correlations recently presented in the literature, in particular the correlation between critical end-to-end distance and molecular chain diameter.

(Keywords: amylose; entanglements; critical end-to-end distance; chain diameter)

INTRODUCTION

The properties of amylose in H_2O and dimethyl sulfoxide have been widely studied[1–6], but the molecular mechanism involved in gelation is a subject of controversy. Some authors suggest that gels are only formed from entangled solutions, whereas Gidley[6] has shown that gelation is also possible from dilute, non-entangled solutions.

In this context, however, the critical molecular weight for the onset of entanglements has not yet been established. Studies[7–10] that have analysed the correlation between critical molecular weight, M_c, and structural parameters for more than 70 flexible, semi-flexible and rigid polymers, do not envisage the case of amylose, due to the lack of experimental data.

In this paper we examine the dynamic viscoelastic properties of stable solutions of amylose in dimethyl sulfoxide, at concentrations ranging from 1 to 30%. The aim of the study is to deduce the critical molecular weight of amylose from viscoelastic results and to correlate it with structural parameters of the polymer.

EXPERIMENTAL

Amylose V obtained by fractionation of potato starch (AVEBE, Veendam, Holland) and dried dimethyl sulfoxide (DMSO; Panreac, Spain) are used in this work.

The intrinsic viscosity, determined at 25°C in an Ubbelohde viscometer, is $[\eta] = 78\ \mathrm{ml\,g^{-1}}$. Using the equation proposed by Everett and Foster[1]:

$$[\eta] = 3.06 \times 10^{-2}\, M_v^{0.64} \tag{1}$$

we obtain a molecular weight $M_v = 210\,000$, corresponding to a degree of polymerization, $DP = 1300$. In the discussion of the results we include a correction for the polydispersity effect.

Solutions of amylose in DMSO were prepared taking special care to avoid the presence of water, which can cause gelation even at low concentrations of polymer. All solutions were clear and no signs of aggregation were found, since viscosities measured 2 months after preparation of the solutions gave identical results to the initial experiments.

Viscoelastic measurements were carried out at temperatures ranging from 5 to 65°C on a Carri-Med CSL-100 rheometer. Cone–plate geometry and oscillatory shear mode were used to determine the storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$, over the range of frequencies $10^{-2}\ \mathrm{Hz} \leqslant \omega \leqslant 10\ \mathrm{Hz}$. The linear viscoelastic region was located by the aid of a torque sweep. The rheometer was also used in steady flow and creep mode.

RESULTS

Figure 1 is the experimental trace of G' and G'' *versus* frequency, for two amylose solutions at a temperature, $T = 35$°C. The rest of the solutions give rise to similar plots, which allow the Newtonian viscosity, η_0, and the steady-state recoverable compliance, J_e^0, to be obtained from the linear viscoelastic relations:

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{2}$$

$$J_e^0 = \frac{1}{\eta_0^2} \lim_{\omega \to 0} \frac{G'(\omega)}{\omega^2} \tag{3}$$

η_0, obtained for each sample from equation (2), can be considered to be the product of two factors[11], a structure-sensitive factor, $F(x)$, and a temperature-dependent friction factor, ξ:

$$\eta_0 = F(x)\xi(T) \tag{4}$$

Generally a Vogel-type equation for the temperature dependence of the viscosity is used:

$$\ln \eta_0 = \ln A + \frac{1}{\alpha(T - T_0)} \tag{5}$$

where A, α and T_0 are constants.

Best fits of our experimental data, shown in *Figure 2*, are obtained using equation (5) with $T_0 = 0$ K, which transforms this equation into an Arrhenius-like equation.

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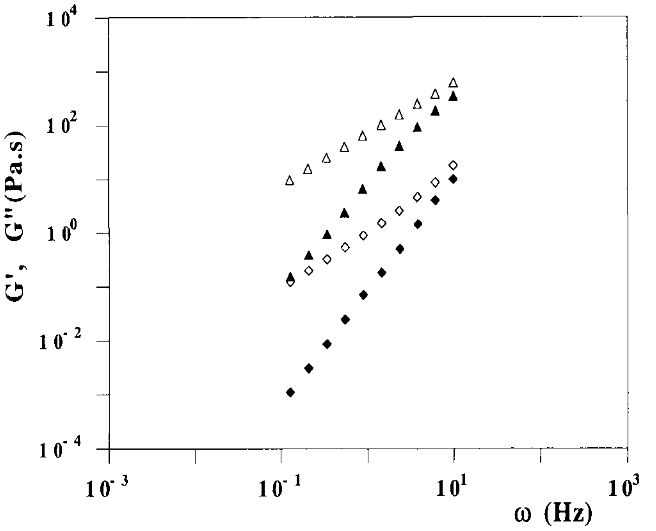

Figure 1 Frequency behaviour of storage and shear moduli for 0.09 and 0.25 amylose volume fraction. Temperature 35°C. Open symbols, G'; filled symbols, G''

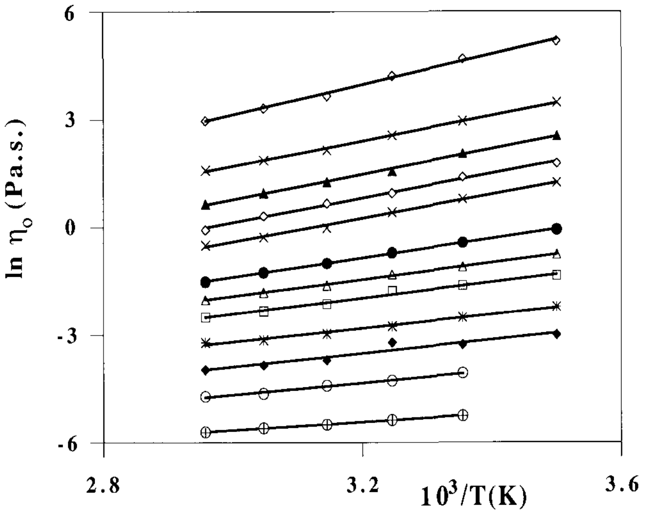

Figure 2 Arrhenius plots of the Newtonian viscosities η_0. Amylose volume fraction φ_2 (from top to bottom): 0.28, 0.25, 0.23, 0.20, 0.18, 0.14, 0.11, 0.09, 0.06, 0.04, 0.03, 0.01

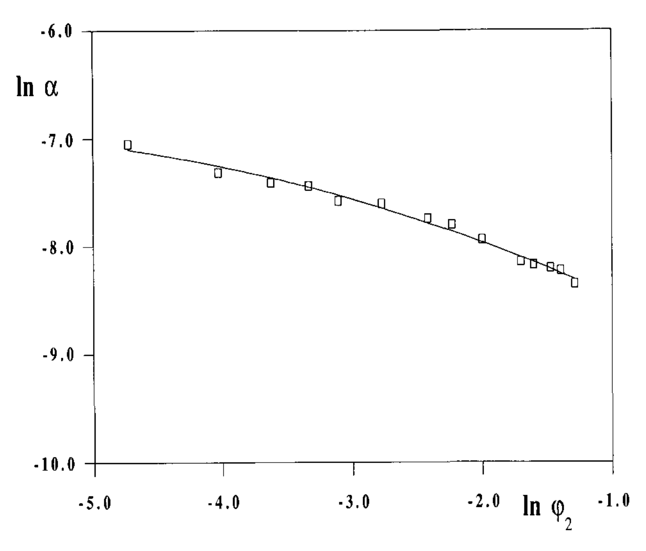

Figure 3 The parameter α of equation (5) as a function of the amylose volume fraction, φ_2

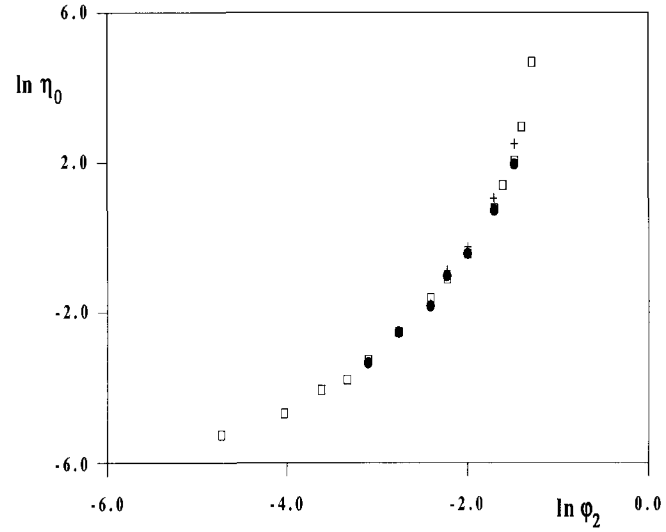

Figure 4 Variation of Newtonian viscosity of solutions with amylose volume fraction at T=25°C. □, Oscillatory data; +, steady shear flow data; ●, data from terminal slope of creep measurements

The activation energy of flow is $E_a = R/\alpha$. The parameter α as a function of the amylose volume fraction φ_2 is presented in *Figure 3*. It is seen that α decreases as φ_2 increases, in agreement with the variation observed for the activation energies of flow of polymer solutions[12].

The variation of η_0 with amylose volume fraction, at constant temperature T=25°C, is shown in *Figure 4*; an increase of the dependence of η_0 on φ_2 is observed as the latter increases. The figure also includes η_0 obtained from steady flow and creep measurements. The data agree fairly well and although at high concentrations oscillatory data fall below those measured in steady shear, this does not affect the interpretation of the results.

In order to analyse the data shown in *Figure 4* and to separate the effect of the polymer concentration on $F(x)$ from the effect of temperature on the friction factor ξ, we express $F(x)$ of equation (4) in the form[11]:

$$F(x)=\left(\frac{N_0}{6}\right)\frac{\langle s^2\rangle_0\varphi_2^*}{V_0}\left(\frac{\varphi_2}{\varphi_2^*}\right)^a \qquad (6)$$

where $a = 3.4$ for $\varphi_2 \geqslant \varphi_2^*$ and $a = 1$ for $\varphi_2 < \varphi_2^*$; $\langle s^2\rangle_0$ is the unperturbed radius of gyration, V_0 the volume per chain atom and φ_2^* the critical volume fraction of polymer for the onset of entanglements. On the other hand, taking into account the results of *Figure 2*, we can express the friction factor as:

$$\ln\xi=\ln\xi_0+\frac{1}{\alpha T} \qquad (7)$$

where both ξ_0 and α are functions of φ_2.

Combining equations (4), (6) and (7) and differentiating η_0 with respect to φ_2 at constant T and molecular weight, we obtain:

$$\frac{\partial\ln\eta_0}{\partial\ln\varphi_2}=a+\frac{\partial\ln\xi_0}{\partial\ln\varphi_2}-\frac{1}{\alpha T}\left[\frac{\partial\ln\alpha}{\partial\ln\varphi_2}\right] \qquad (8)$$

From *Figures 3* and *4*, respectively, the left-hand side and the third term of the right-hand side of equation (8) are obtained, which allows $a+\partial\ln\xi_0/\partial\ln\varphi_2$ to be represented as a function of $\ln\varphi_2$, as shown in *Figure 5*. In this figure the variation of a is also presented, as

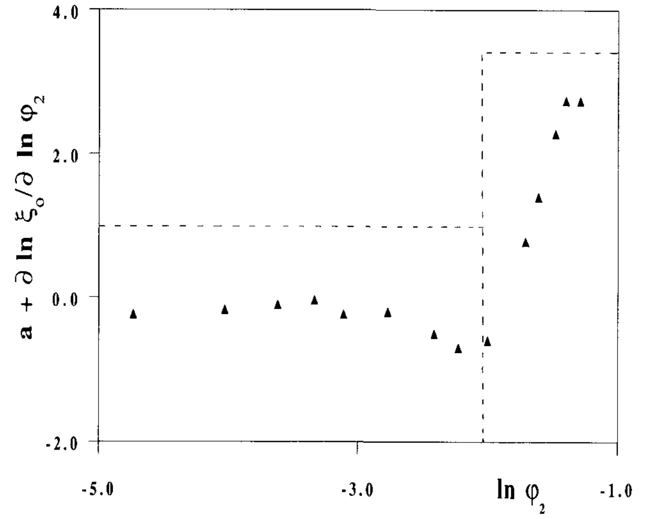

Figure 5 Plot of $a+\partial \ln \xi_0/\partial \ln \varphi_2$ (equation (8)) as a function of $\ln \varphi_2$. Dotted lines represent the variation of a as established in equation (6)

Table 1 Values of structural parameters described in the text

l_0 (Å)^a	m_0 (g mol^{-1})	N	$C_\infty{}^a$	$\langle R_c \rangle$ (Å)	D (Å)^b
4.4	162	181	5.7	141	10.8

^{a} Value obtained assuming that amylose has a distribution of molecular weights governed by the Schulz relation (reference 2, p. 147)
^{b} Value obtained from reference 16

established in equation (6). It is generally accepted that polydispersity does not affect α and consequently the third term of equation (8) does not need to be modified to include a heterogeneity correction.

Taking into account these results we envisage that although generally ξ_0 is taken to be independent of φ_2, in the case of amylose/DMSO solutions $\xi_0 \propto \varphi_2^{-1}$. We also deduce a critical volume fraction for the onset of entanglements, $\varphi_2^* = 0.14$.

DISCUSSION

Gidley[6] has investigated the variation of specific viscosity with concentration for solutions of amylose in DMSO and H_2O. Using his experimental data and those of Miles *et al.*[4] he concluded that a discontinuity occurs at $c[\eta] \approx 5.5$ and that straight lines constructed for high and low concentration give gradients of 1.28 and 3.33, respectively.

These results were taken to show that entanglements take place at $c[\eta] > 5.5$, a conclusion which applied to the amylose ($[\eta] = 78$ ml g^{-1}) would give a critical volume fraction, $\varphi_2^* = 0.07$. However, our rheological results, in particular *Figure 5*, lead to a higher critical volume fraction for the onset of entanglements, $\varphi_2^* = 0.14$. We attribute this difference to the scatter of the data presented by Gidley and to the oversimplification of the analysis of $\log \eta_{sp}$ *versus* $\log c[\eta]$ data by two straight lines (figure 1 of reference 6).

In order to justify our $\varphi_2^* = 0.14$ result we have related the critical molecular weight M_c for entanglements to structural parameters of the amylose.

The critical volume fraction and critical molecular weight M_c for the onset of entanglements are related by the equation:

$$\varphi_2^* = \frac{M_c}{M} \tag{9}$$

where M is the molecular weight of the polymer. In our case we deduce a value of $M_c = 29\,400$ for amylose. The critical end-to-end distance for entanglements, which is taken to be equal to tube diameter of the reptation model[13], can be calculated from M_c through the following relations[14]:

$$\langle R_c \rangle = M_c^{1/2} (\langle R^2 \rangle_0 / M)^{1/2} \tag{10}$$

and

$$\langle R^2 \rangle_0 = C_\infty N l_0^2 \tag{11}$$

with C_∞, N and l_0 being respectively the characteristic ratio, the number and the average length of main chain bonds. *Table 1* gives the values of these and other parameters for amylose.

Graessley and Edwards[7] have proposed the following expression for M_c:

$$M_c = \frac{\rho N_A}{K(\nu L)^2 l} \tag{12}$$

where ν is the number of chains per volume unit, L the chain length, l the Kuhn step length, ρ the density of the undiluted polymers, N_A the Avogadro number and K a constant. The variables ν, L and l can be expressed as:

$$\nu = \frac{N_A \rho}{M} \tag{13}$$

$$L = \frac{M l_0}{m_0} \tag{14}$$

$$l = C_\infty l_0 \tag{15}$$

in which l_0, m_0 and C_∞ are given in *Table 1*.

Using our experimental $M_c = 29\,400$ value in equation (12), we obtain $K = 2.5 \times 10^{-3}$, a value slightly lower than the values presented in reference 7 for 12 polymers, which vary from 7.8×10^{-3} for poly(n-octylmethacrylate) to 3.2×10^{-3} for polyisoprene.

Recently Zang and Carreau[10] have studied the critical molecular weight, M_c, of 36 flexible and semi-rigid polymers. They found the following correlation between the critical end-to-end distance, $\langle R_c \rangle$, for entanglements and the average polymer chain diameter, D[15]:

$$\langle R_c \rangle = 13.6D \tag{16}$$

where 13.6 is an average value, with a minimum of 10.6 for poly(2-ethylbutyl methacrylate) and a maximum of 15.8 for hydrogenated polubutadiene. This relation is discussed by the authors in the light of reptation theory.

In the case of amylose the values of $\langle R_c \rangle$ and D presented in *Table 1* give the relation:

$$\langle R_c \rangle = 13.1D \tag{17}$$

Therefore we can deduce that the value $M_c = 29\,400$, obtained from viscosity *versus* concentration data, fulfils the relation proposed in reference 10.

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