polymer communications

The steady-state shear compliance of regular star polymers*

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Linear viscoelastic properties of concentrated solutions and melts of polymers are characterized by their zero-shear viscosity (η_0) and their steady-state recoverable shear compliance (J_e^0). The dependence of η_0 on molecular weight (M) and polymer concentration (c) of linear polymers was discovered sometime ago[1] and is well documented[2-4]. Similarly, much experimental evidence has now appeared on the molecular weight and concentration dependence of η_0 for regular star polymers[5-10]. When the product ($c.M$) is low, star polymers have lower η_0 than linear polymers. However, when cM is high, enhancement of η_0 over that for the linear polymer is observed. These observations are particularly well modelled by the tube theory which considers movements of polymer chains in tubes formed by their entanglements with surrounding chains[11].

Accurate measurements of J_e^0 of polymer solutions and melts have enabled elucidation of the dependence of J_e^0 on M and c for narrow molecular weight distribution linear polymers[2,4]. It is observed that for linear polymers

$$J_e^0 \propto c^{-1}M^1 \tag{1a}$$

and

$$J_e^0 \propto c^{-2}M^0 \tag{1b}$$

when cM is less than $(cM)_c'$ and greater than $(cM)_c'$ respectively[4]. The Rouse model for free-draining isolated polymer molecules predicts that[12]

$$J_e^0 = \frac{2}{5}\frac{M}{cRT} \tag{2}$$

an equation of the same form as equation 1a. The numerical coefficient in equation 2 was found to agree remarkably well with the experimental results on narrow molecular weight distribution polymers even in the melt[2,4]. A reduced compliance (J_{eR}) was therefore introduced to present data on linear polymers[4]

$$J_{eR} = J_e^0 \frac{cRT}{M} \tag{3}$$

The solid lines in *Figures 1* to *4* represent the data for linear polymers. Experimental points for linear polymers have been omitted for clarity unless newer data are different from those in ref. 4. The horizontal line at -0.4 (log 2/5) indicates the region of cM in which J_e^0 is Rouse-like. The lines with slope -1 represent the behavior according to equation 1b. The breakpoint $(cM)_c'$ is a characteristic of each polymer.

A theoretical extension of the Rouse model to branched polymers originally due to Ham[13] indicates that

$$(J_e^0)_{br} = g_2 (J_e^0)_{lin} \tag{4}$$

where $g_2 = 1$ for linear polymers and is smaller than unity for branched polymers. In the case of free draining regular star polymers with a constant number of arms (f) of equal length[13,14]

$$g_2 = \frac{15f-14}{(3f-2)^2} \tag{5}$$

$g_2 = 0.632$, 0.460, 0.297 for 3, 4 and 6-arm stars respectively. Combining equations 3 and 4 yields the general definition of J_{eR}

$$J_{eR} = J_e^0 \frac{cRT}{g_2 M} \tag{6}$$

The experimental data on the dependence of J_e^0 on M and c and on the architecture of the star polymers are equivocal. The earliest results indicated $(J_e^0)_{br} = 10 \times (J_e^0)_{lin}$ for four-arm polystyrene melts, independent of M[15].

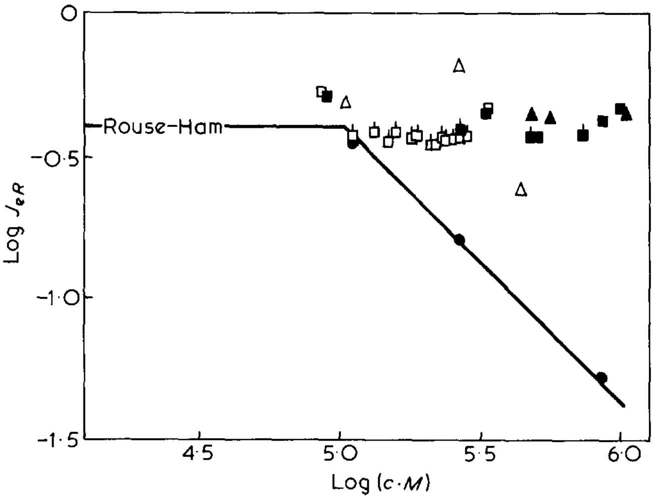

Figure 1 Dependence of J_{eR} on cM for polystyrene stars. Full symbols for melts. Open symbols for solutions. ○: linear polymers; □: four-arm stars; △: six-arm stars. Symbols without pips from refs. 10, 19. Symbols with pips from refs. 18 and 20

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However, results on 0.33 g cm^{-3} solutions of four- and six-arm polyisoprenes showed that J_e^0 varies linearly with M, over a wide range of M, in accordance with the Rouse-Ham model with the value of g_2 in agreement with equation 5[8]. The concentration dependent of J_e^0 for polyisoprene stars of very high M was found to be rather complex[8]. More recent results on star poly(α-methylstyrenes) have suggested that J_e^0 of star polymers changes from a c^{-1} to a c^{-2} dependence as do linear polymers[16].

The available literature data are presented in *Figures 1* to *4* according to equation 6. It can be seen that J_{eR} of star polymers is always very nearly equal to the value predicted by the Rouse-Ham model. Both, the M and c dependences extend presently to about $10\times(cM)'_c$ at which point accurate zero-shear measurements on star polymers become very difficult. The best results are obtained with polystyrene[10,18-20] (*Figure 1*) and polybutadiene stars[21,11] (*Figure 2*). *Figure 3* shows the data on polyisoprene solutions[8]. The J_{eR} data of the six-arm stars lie systematically above those of the four-arm stars. The indicated oscillations in the J_{eR} dependence on c may well be of experimental origin. These features are not observed in the corresponding cM regions of polystyrene and polybutadiene stars. The poly(α-methylstyrene) data shown in *Figure 4* reveal a small drop in J_{eR} at high cM interpreted previously as a transition from c^{-1} to c^{-2} dependence for J_e^0[16]. Taking into account the possible experimental error in the data only two experimental points deviate significantly from Rouse-Ham behaviour.

In conclusion, the available data suggest that J_e^0 of star polymers follow the Rouse-Ham model to $cM = 10\,(cM)'_c$.

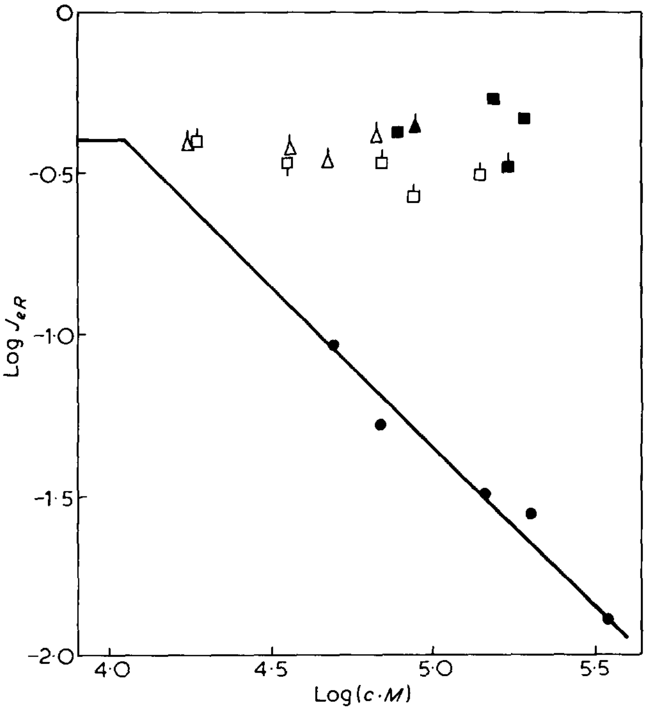

Figure 2 Dependence of J_{eR} on cM for polybutadiene stars. Full symbols for melts. Open symbols for solutions. ○: linear polymers, △: three-arm stars, □: four-arm stars. Data from refs. 21 (without pips) and 22 (with pips)

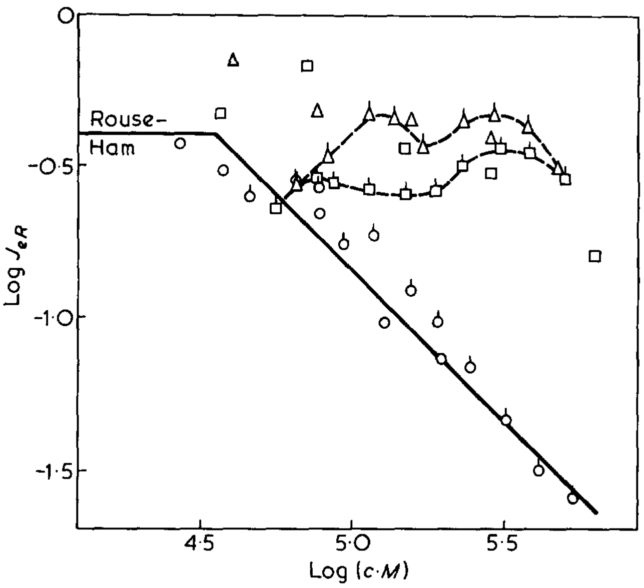

Figure 3 Dependence of J_{eR} on cM for polyisoprene star solutions. ○: linear polymers; □: four-arm stars, △: six-arm stars. Symbols without pips: dependence on M at c = 0.33 g/ml; with pips: dependence on c. Data from ref. 8

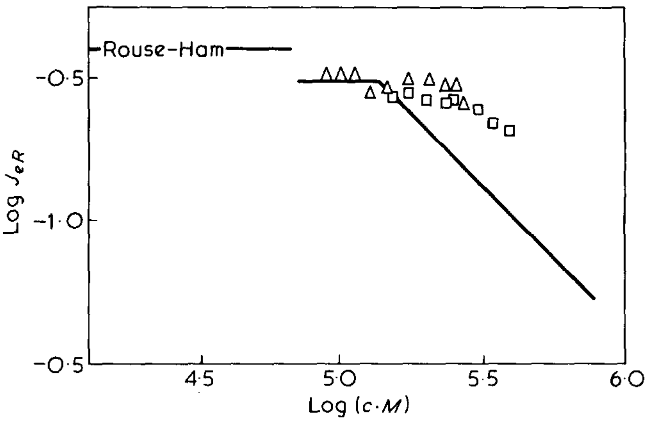

Figure 4 Dependence of J_{eR} on cM for poly(α-methylstyrene) three-arm star solutions in α-chloronaphthalene[16]. □: S26; △: S21. Lines based on data for linear polymers of ref. 24

The modern theory, based on the polymers-in-a-tube idea, provides a mechanical model and predicts the Rouse dependence of J_e^0 on M and c^{-1} over the whole range of c and M[11]. It is left to the future to elucidate the details of the more complex viscoelastic properties of star polyethylenes[23]. A dependence of J_e^0 on $c^{-2.25}$ rather than c^{-2} (equation 1b) observed in some linear polymer systems[8,22] may have corollaries for the depenendence of J_e^0 on c for stars. However, none of the present data on stars seem extensive or accurate enough to elucidate this point.

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Synthesis and e.p.r. studies of polyacetylene hydrogen sulphate $|CH(HSO_4)_y|_x$

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Introduction

Sulphuric acid, H_2SO_4, is known to react with graphite and other macromolecular systems like polyacetylene $(CH)_x$. In the first case reaction occurs only after electrochemical oxidation of graphite[1]. In the latter case reaction occurs directly between the H_2SO_4 vapour and polyacetylene[2]. In a previous study we found[2,3,4] that nitryl and nitrosyl ions (NO_2^+ and NO^+) are excellent species for oxidizing π-systems of graphite and polyacetylene concomitantly introducing anions (e.g. BF_4^-, PF_6^-, SbF_6^-) which stabilize the polycation formed. Recently we have established that a similar reaction can occur between graphite and nitrosyl hydrogen sulphate[5] ($NOHSO_4$). In this communication we want to present recent results concerning the interaction between polyacetylene and nitrosyl hydrogen sulphate.

Experimental and Results

The polyacetylene used in all experiments was prepared by a modification of the method of Ito *et al.*[6]. All-*trans* films of thickness $\sim 100\ \mu$ were used in the experiments. The doping reaction was carried out in the following manner: $NOHSO_4$ (Alfa-Ventron) was placed in the side arm of the reactor and pumped overnight in order to remove the volatile products of the hydrolysis. Then, rigorously dry nitromethane was vacuum distilled into the side arm. The suspension of $NOHSO_4$ in nitromethane was then discharged over the polyacetylene film. The reaction was complete when the characteristic golden colour of the doped polyacetylene could be observed. The excess salt was removed by washing with pure nitromethane and then the film was dried by dynamic pumping.

For the samples doped to saturation the *RT* conductivity measured by a 4-probe, pressure contact, method was 430 $\Omega^{-1}\ cm^{-1}$. The results of elemental analysis, of the same sample, were as follows: $\%C = 46.47$; $\%H = 5.44$; $\%S = 14.29$; $\%N = 1.01$; $\%O$ (by difference) $= 32.79$.

They agreed with the following empirical formula

$$|CH(HSO_4)_{0.12}(CH_3NO_2)_{0.02}|_x$$

The samples for e.p.r. studies (~ 2 mg) were placed in vacuum sealed tubing equipped additionally with a side arm allowing the cryogenic pumping. The e.p.r. spectra were recorded using a conventional X-band spectrometer working at a low hyperfrequency power level (< 1 mW). The temperature of the sample was varied in the range 20°C to 160°C.

For all measurements above room temperature the samples were cryogenically pumped while in the cavity.

Figure 1a presents a typical spectrum obtained at room temperature for an all-*trans* film. The observed symmetric shape as well as the values $g \sim 2.0026$ and $\Delta H_{pp} \sim 1$ G, respectively for the position and the width of the line, agree with standard results[8].

After doping to saturation the observed e.p.r. spectrum has a position which is roughly unchanged, but the line becomes strongly non symmetric (*Figure 1b*). This last property can be characterized by the ratio A/B of the amplitudes A and B measured on the low and high magnetic field sides of the line respectively. After the doping A/B is in the order of 6 and remains constant with time.

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