Solvent dependence of the viscous and viscoelastic properties of a high molecular weight polystyrene in moderately concentrated solution

N. Hugo Ladizesky
Department of Physics, University of Leeds, Leeds LS2 9JT, UK

and John Lamb
Department of Electronics and Electrical Engineering, University of Glasgow, G12 8QQ, UK

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The steady-flow viscosity and viscoelastic behaviour of two solutions of a sensibly monodisperse polystyrene of high molecular weight ($M_w = 498\,000$) have been measured over a temperature range of 100°C for identical concentrations of 20.55 wt.%. Toluene and methyl ethyl ketone were chosen as the two low viscosity solvents having, respectively, good and marginal thermodynamic affinities. Dynamic viscoelastic measurements were made at a frequency of 41 kHz using travelling torsional waves. At this frequency, both solutions exhibit behaviour characteristic of the rubbery region, and the ratio of the dynamic viscosity normalised by dividing by the corresponding solvent viscosity is independent of the solvent until the onset of the glass transition region with decreasing temperature. The storage shear modulus of the toluene solution in the rubbery region is higher than for the MEK solution, indicating a higher entanglement density in the better solvent and a larger polymer radius. Some features of the results in the poor solvent (MEK) appear to indicate that, as the temperature decreases, partial exclusion of the solvent leads to the formation both of stronger entanglements and of macromolecular aggregates or bundles, as suggested by Dreval and others[6–8,11,22].

Keywords Viscoelastic properties; polymer solutions; viscosity; solvent dependence; polystyrene

INTRODUCTION

Extensive studies have been made of the viscous and viscoelastic behaviour of polystyrene solutions and of undiluted polystyrene melts. This polymer has been widely chosen because it exhibits a combination of desirable characteristics; it is available with narrow molecular weight distribution over a wide range of molecular weights; it is essentially amorphous with a glass transition temperature ($T_g \simeq 100°C$) which is not inconveniently high from an experimental point of view; it has an intermediate degree of backbone flexibility; it is free from hydrogen bonding with relatively weak intra- and intermolecular interactions and can be obtained as a linear molecule with negligible side branching. Solution studies of the viscoelastic properties have in the main been limited to moderately dilute solutions, although increasing attention has been paid to the behaviour of concentrated solutions of polystyrene and other polymers[1–5]. An important practical reason for this is that, in contrast with the undiluted polymer melt, an extended range of temperature over which measurements can be made is available in concentrated solutions, from T_g to the onset of degradation, due to the decrease of T_g with increasing amounts of diluent added to the initially undiluted polymer melt.

Riande *et al.*[4,5] have investigated the behaviour of different molecular weight polystyrenes in a single solvent, tri-*m*-tolyl phosphate, at concentrations from 1 to 100% and find that the shape and breadth of the retardation spectrum associated with the 'entanglement peak' do not change appreciably with increasing polymer concentration above about 25%. Properties of polymer solutions are, however, affected by the choice of solvent with differing thermodynamic affinities and the object of the present work has been to study the effect of the solvent for a given concentration of a selected high molecular weight polystyrene ($M_w = 498\,000$). A concentration of 20.55 wt% was chosen in order to be well within the entanglement region and the two solvents used were toluene and methyl ethyl ketone having, respectively, good and marginal thermodynamic affinities with respect to the polystyrene.

Salient features of the general background to this investigation concerning the effect of the solvent are as follows. Dreval *et al.*[6,7,8] have examined the flow of polydisperse polystyrene and other polymer solutions in various solvents and concluded that there is a tendency for macromolecular bundles to form in solvents of poor thermodynamic affinity. Graessley[2] attributed these results to the effect of the solvent on free volume. Vinogradov *et al.*[9] performed flow and creep measurements in various polymer/solvent systems, including a polydisperse polystyrene similar to that employed by Dreval *et al.*[6,7,8], and concluded that the nature of the solvent may

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affect the mechanical properties of the solution only when strong macromolecular interactions are present. For non-polar, fairly flexible polymers such as polystyrene the role of the solvent is manifested by a shift in the glass transition temperature of the solution arising from a difference in the associated free volume. This interpretation is broadly similar to that put forward by Graessley[2].

The above mentioned experiments were essentially carried out using solvents of relatively low viscosity. In contrast, Chapoy[10] performed differential thermal analysis and stress relaxation experiments on solutions of polydisperse polystyrene ($M_w = 266\,000$) in three highly viscous solvents having different thermodynamic affinities. He concluded that the results obtained were not incompatible with the formation of macromolecular aggregates or bundles in relatively poor solvents.

Quadrat and Podnecka[11] report the flow properties of a polydisperse polystyrene ($M_n = 270\,000$) in eleven solvents of low viscosity and interpret their results purely in terms of entanglements. However, Streeter and Boyer[12] made flow and specific volume measurements on polystyrene solutions of unidentified polydispersity ($M_w = 370\,000$) using fifteen solvents and concluded that macromolecular aggregates might exist in all solutions but that, under an applied stress, they will continue to exist only in poor solvents.

These different hypotheses advanced to explain the viscoelastic behaviour of polymer solutions are not necessarily mutually exclusive. Ideas are often speculative and the lack of more precise definition may reflect the paucity of data in certain regions of the mechanical spectrum. Moreover, most of the experiments have been made either at a constant temperature or within a narrow range of temperature. Although insufficient attention appears to have been given to the use of temperature as an important experimental variable when comparing the effect of the solvent on the mechanical properties of concentrated polymer solutions, it remains that this is only of real value in helping to elucidate the mechanisms responsible for the observed behaviour if the experiments are performed in a region where the nature of the mechanism itself is directly affected by change of temperature. For example, use of a wide temperature range adds little additional information about the operative polymer mechanism if measurements are confined either to the glassy or to the terminal zones of relaxation, although it does, of course, provide useful data on the temperature-dependence of the parameters involved; e.g., glassy modulus or steady flow viscosity and, to a limited extent, on the effect of temperature on the size of the polymer molecule.

In the present work, both steady-flow viscosity and dynamic viscoelastic measurements have been made over a temperature range of some 100°C (from −60°C to 40°C), the viscoelastic experiments being performed at a frequency of approximately 41 kHz. The aim of this work has been to study the behaviour over the 'rubbery plateau' between the terminal zone of relaxation and the glassy region—a part of the viscoelastic spectrum which has received little attention hitherto, apart from the extensive work of Plazek and collaborators[4,5] using a single good solvent of relatively high viscosity. Fixing the same concentration of polymer in each of the two solvents was intended to achieve approximately corresponding states of the two solutions with respect to their glass transition temperatures.

EXPERIMENTAL

Materials

The polystyrene was supplied by the Pressure Chemical Co. (Batch No. 5(a)) with a molecular weight designated by the manufacturers of $M_w = 498\,000$ and a ratio $M_w/M_n < 1.2$. Measurements by gel permeation chromotography confirmed this value of M_w to within $\pm 5\%$ but indicated a somewhat higher ratio $M_w/M_n = 1.6$. However, since g.p.c. measurements are known to show a broadening effect on samples of high molecular weight, the actual ratio is probably greater than 1.2 but somewhat less than 1.6.

Before preparing the solutions, the polymer was dried overnight under vacuum at 90°C with no observable change in M_w or in the ratio M_w/M_n.

Both of the solvents used, toluene and methyl ethyl ketone, were of Analar grade and each was dried for at least 24 hours on an activated bed of molecular sieve, type 5A, and then poured through membrane filters of 5 μm pore size. The melting points are −95.0°C for toluene and −86.9°C for MEK[13].

The solutions were made to a concentration of 20.55 ± 0.05 wt%, which was checked again after the viscoelastic experiments had been performed and found to be unchanged within the above limits. Dilution was carried out at room temperature and a slow stirring with a magnetic stirrer was applied three or four times a day. The solutions were visually homogeneous within three days but were not used for experiments before a lapse of at least ten days. It was discovered that the polystyrene in MEK solution degrades significantly with the passage of time over several months[19] and, on account of this, no measurements were made on these solutions after a period of twenty days from initial commencement of the preparation of the solution. No such problems were encountered with the toluene solution, in which no perceptible degradation occurred over many months. All handling of dried polymers, solvents and solutions was carried out in a dry nitrogen gas atmosphere.

Viscoelastic measurements

The components of the complex shear modulus of the polymer solutions $G^*(j\omega) = G'(\omega) + jG''(\omega)$, were measured at a frequency of approximately 41 kHz, using a travelling torsional wave technique over the temperature range −60°C to 40°C. The transducer is a cylindrical quartz crystal of diameter 0.95 cm and axial length 4.80 cm. The crystal is cut with its length parallel to the X-axis of crystal quartz and is excited in torsional oscillation by four cross-connected quadrant electrodes extending over the length of the cylinder, which is equal to one-half the wavelength of shear waves propagated along the X-axis at the centre frequency of the resonant response. The transducer is fixed to the upper end of a nickel silver rod of length 0.9345 m held vertically and electrically excited to generate repeated pulses of torsional oscillations. Each pulse propagates along the length of the rod and, after reflection from the far end, returns to re-excite the transducer, where it is again reflected and the process repeated until the initial energy is sensibly dissipated. The transducer acts, therefore, as a common transmitter–receiver and, since it is heavily damped by attachment to the rod, operation is not solely confined to the resonant frequency of the crystal but is possible over a relatively wide bandwidth.

The theoretical analysis of this system is given by McSkimin[14], who was the first to employ this method for the measurement of the dynamic viscoelastic properties of relatively viscous liquids and polymer solutions having a steady-flow viscosity, η, greater than about 5P.

The experimental system employed in this work is basically similar to that described previously[15-17], although certain refinements were incorporated in order to improve the stability of the signal and hence the reproducibility and accuracy of the results. The repetition frequency of the pulsed oscillations applied to the transducer is conveniently 25 s^{-1} and the pulse duration is adjusted to contain at least 20 cycles of the exciting oscillations, which are derived from a high stability oscillator, the output of which is gated. Each received pulsed signal is added to an attenuated continuous wave from the oscillator prior to amplification and display on the oscilloscope. Any selected received pulse, after one or more double transits along the nickel rod, is then cancelled to within the noise level by adjustments of the attenuator setting and, independently, of the oscillator frequency. Measurements are made with the rod unloaded (in vacuum) and subsequently with the polymer solution introduced to cover a length, h, of the rod (approximately 0.7 m). At each temperature, the attenuation per trip is determined from the measured attenuation of seven echoes, (six trips or double transits). Thus if A' is the attenuation per trip for the loaded rod, A the corresponding value for the unloaded rod, f' and f the cancellation frequencies for the loaded and unloaded rod, respectively, n the number of the echo being measured and ΔF the difference between two successive cancellation frequencies for the unloaded rod (above and below f'), then in terms of nepers per metre and radians per metre, respectively:

$$\Delta\alpha = \frac{\Delta A}{2h} = \frac{A' - A}{2h} \text{ and for the } n\text{th echo,}$$

$$\Delta\beta = \frac{\Delta B}{2h} = \frac{\pi(f - f')}{hn\Delta F} \tag{1}$$

Neither $(f - f')$ nor $(n\Delta F)$ should change with echo number, n, and averages from the seven echoes are used. The complex cylindrical shear impedance of the liquid is then obtained from the equation[14]:

$$Z_C = R_C + jX_C = \frac{a\rho_a V_a}{2}(\Delta\alpha + j\Delta\beta), \tag{2}$$

where a is the radius of the rod, ρ_a the density of the rod material and V_a the velocity of propagation of torsional waves in the unloaded rod. Having in this way determined the real and imaginary components of the cylindrical shear impedance from measurement of the quantities in equation (2), the corresponding components of the plane shear wave impedance of the liquid, $Z_L = R_L + jX_L$, are calculated from[15]:

$$R_L = R_C - (3/\omega\rho a)R_C X_C$$

$$X_L = X_C + (3/\omega\rho a)(R_C^2 - X_C^2)/2 \tag{3}$$

where ρ is the density of the liquid.

The complex shear modulus of the liquid, $G^*(j\omega)$, is related to its shear impedance, Z_L, by[18]:

$$Z_L^2 = \rho G^*(j\omega) = \rho[G'(\omega) + jG''(\omega)] \tag{4}$$

Hence $G'(\omega)$ and $G''(\omega)$ are determined from:

$$G'(\omega) = (R_L^2 - X_L^2)/\rho\text{:}\quad G''(\omega) = 2R_L X_L/\rho \tag{5}$$

Elsewhere in this paper reference will be made to the complex dynamic viscosity, $\eta^*(j\omega) = \eta'(\omega) - j\eta''(\omega)$. The components are given by $\eta'(\omega) = G''(\omega)/\omega$ and $\eta''(\omega) = G'(\omega)/\omega$.

In practice, a set of measurements is made on the unloaded rod at suitable intervals over the whole temperature range, from which graphs are drawn of A *versus* T, f *versus* T and $(n\Delta F)$ *versus* T. The rod is then loaded with the liquid and recorded values of A' and f' are plotted *versus* temperature. Values of $\Delta\alpha$ and $\Delta\beta$ can then be derived from equation (1) at any chosen temperature.

For the polymer solutions investigated the quantity $(f - f')$ appearing in equation (1) varies from 1 Hz to 18 Hz, depending upon experimental conditions. Accurate temperature control of the system is therefore essential, since a temperature error of 0.1°C gives rise to an error of 0.5 Hz in $(f - f')$. As described previously[15,16], the rod is placed in an insulated double-walled jacket through the outer portion of which circulates a liquid which is pumped from a constant temperature bath. The temperature inside the jacket was measured by two thermocouples placed approximately 0.15 m from each end of the rod. These were inserted through the double walls and sealed with Araldite. In order to remove any soluble impurity, the system was left for one week filled in turn with each of the pure solvents to be used subsequently in the solutions to be measured. The temperature stability was found to be better than ±0.05°C over the whole range of measurement. From determinations made with the two thermocouples, it was found that a small temperature gradient existed along the length of the rod amounting to a maximum difference of 0.4°C at −60°C. Since the rod has a relatively high heat conductivity, this gradient was unaffected by introduction of the solution: unloaded and loaded conditions were essentially the same and negligible error was introduced into the quantities $(f - f')$ on this account. The cancellation frequencies varied from 41.7 kHz at −60°C to 40.6 kHz at 40°C.

In previous work, the quartz crystal was bonded to the metal rod with Araldite, but visible shearing faults occurred in the bonded end of the crystal due to shrinkage of the material over the wide temperature range of the present measurements: this problem was overcome by using a filled Araldite as the bonding agent.

Considerable care was taken to prevent contamination of the solutions by moisture and to keep the rod itself dry. The inner tube of the glass jacket containing the rod was vacuum sealed at both ends. Electrical contacts to the gold electrodes on the lateral surface of the crystal were made *via* glass-metal sealings with the upper end of the rod resting on a PTFE neck sitting firmly on the inside of the glass jacket. The unloaded rod was kept under vacuum for at least 24 hours before measurements began. When these were completed no air was allowed to enter the system which was flushed several times with dry

Table 1 Parameter values for density and steady state viscosity equations

	Density parameters† $\rho(T)$ (kg m^{-3})			Steady state viscosity parameters*					
Material	ρ_0 ($T = 0°$C) (kg m^{-3})	a (kg m^{-3} (°C)$^{-1}$)	b (kg m^{-3} (°C)$^{-2}$)	D	F	η	K	H	T_0 (°C)
Toluene	887	–0.9	0	1.035	104.4	1.5488	–	–	–
MEK	826	–1.0	0	0.669	121.8	1.4981	–	–	–
Ethyl alcohol	806	–0.8	0	–	–	–	–	–	–
Toluene solution	915	–0.8	1	–	–	–	–2.67	595	–144.5
MEK solution	866	–0.9	0	–	–	–	–3.37	461	–130.9

† $\rho(T) = [\rho_0 + aT + 10^{-3} bT^2]$ (kg m^{-3}) (6)

* $\ln[\eta(\text{Pa s})] = K + H/(T - T_0)$ (8)

$\eta_s/(\text{Pa s}) = D/(F + T)^\eta$ (7)

nitrogen gas and the solution was then introduced into this atmosphere.

Since the penetration depth of the torsional wave in the polymer solution is less than 100 μm, any wetting of the rod above the liquid column would contribute significantly to the measurements. Hence, solution measurements were commenced at the lowest temperature, with the solution being introduced at a temperature of 5°C below this value. This required some forcing pressure (dry nitrogen) since the viscosity of the solutions was between 30 and 100 Pa s at these lower temperatures.

The attenuation of each echo was measured to within $\pm 5 \times 10^{-3}$ neper. Since determination of $\Delta\alpha$ involved interpolation, the error in this quantity was estimated to be $\pm 10^{-3}$ neper m^{-1}. Cancellation frequencies were measured to within 0.5 Hz, which gives an error of $\pm 2.5 \times 10^{-3}$ rad. m^{-1} in $\Delta\beta$. Errors for the derived viscoelastic quantities are shown in the corresponding graphs (*Figures* 5 to 9). These were calculated according to the general formulae:

$$\Delta A = \Delta B + \Delta C \quad \text{for } A = B \pm C$$

$$\frac{\Delta A}{A} = \frac{\Delta B}{B} + \frac{\Delta C}{C} \quad \text{for } A = B \times C \text{ or } A = B/C$$

The magnitude of the multiplying factor $(a\rho_a V_a/2)$ in equation (2) was 3.555×10^{-4} kg m^{-1}.

Measurement of steady-flow viscosity

Steady-flow viscosities of solvents and solutions were measured using suspended-level capillary viscometers in accordance with British Standard Specification No. 188. Precautions were taken to eliminate humidity and to reduce evaporation as described elsewhere[19]. The bath temperature was maintained constant during measurements to within ± 0.07°C and viscosity values were reproducible to within $\pm 0.7\%$ for solutions and $\pm 0.2\%$ for the solvents. The absolute errors of the viscometers are estimated to be $\pm 1\%$.

Measurement of density

Measurement of the absolute value of density is not required to significantly greater precision than that which pertains to the determination of the viscoelastic quantities. Interest centres, however, on the accuracy of the relative change of density with temperature, which was conveniently measured as follows.

The length, h, of the rod which is covered by the solution is measured as a function of temperature, as an integral part of the procedure for determining the quantities $\Delta\alpha$ and $\Delta\beta$ as functions of temperature (equation (1)). Hence, if the volume of the inner jacket containing the rod is known as a function of h, the density of the solution can then be determined if the mass of solution inside the jacket is known: this mass remains unchanged over the whole temperature range. In the first place, the volume of the inner jacket was calibrated as a function of h, using known volumes of ethyl alcohol, for which the density as a function of temperature is given by[13]:

$$\rho(T) = [\rho_0 + aT + 10^{-3} bT^2](\text{kg m}^{-3}) \qquad (6)$$

where T is in °C and the parameters ρ_0, a and b are given in *Table 1*. In view of the scarcity of the experimental polymer sample and the exposure to room atmosphere of solutions used for density determination, the strategy adopted to relate the mass of solution to the volume determined as a function of h, as described above, was to prepare two new solutions of a commercial polystyrene ($M_w = 150\,000$) in analar grades of toluene and MEK. The polymer concentration was identical within experimental error to the concentration of the solutions studied in this work and the assumption was made that their respective densities were also identical. Room temperature densities of the commercial polystyrene solutions were measured using calibrated weighing bottles and this provided the necessary data from which the mass of the solutions of interest could be evaluated. Hence, the density was thereby determined as a function of temperature. Reproducibility of the room temperature measurements of density was $\pm 0.5\%$ and it is estimated that the values obtained with the commercial polystyrene solutions agree to better than 3% with the corresponding room temperature densities of the solutions studied in this work. The volume of the jacket was calculated with an error of $\pm 0.4\%$ and h was measured to within $\pm 0.1\%$. Using h *versus* T graphs obtained from several runs of the viscoelastic measurements gave density *versus* temperature curves for the solutions, which were reproduced with a maximum scatter of $\pm 0.15\%$.

Calibrated weighing bottles were also used to measure the room temperature densities of the pure solvents with an accuracy of $\pm 0.2\%$.

Determination of concentration after viscoelastic measurements

The concentration of the solutions was checked after the viscoelastic measurements, both to verify the initial

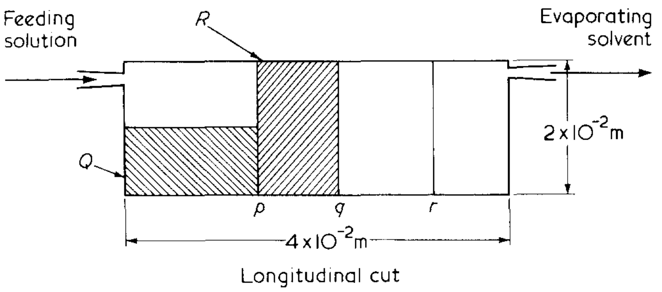

Figure 1 Longitudinal section of the glass container used to measure the concentration of the solutions after the viscoelastic experiments

concentration, as prepared, and to confirm that no significant evaporation had occurred.

When transferring the solution from the measuring system containing the rod back into its original container, a small volume of the solution (approximately 2×10^{-6} m^3) near the top of the liquid column was diverted into a small cylindrical vessel, of which a longitudinal section is shown in *Figure 1*. *p*, *q* and *r* are three internal glass walls: *p* and *r* have holes at the top, while *q* has holes at the bottom. The space, *R*, is filled with glass wool and *Q* is the volume of solution introduced. The weight of solution is known by weighing the container before and after introducing the solution. The container is then heated under vacuum at a temperature between 115°C and 125°C, keeping the aperture on the solution side, *Q*, closed and the opposite one open. Thus the solvent evaporates with negligible loss of polymer. Heating is continued for several days until no further change in weight of the container is observed. Final weighing gives the weight of the polymer after subtracting the weight of the empty vessel. Hence the concentration of the solution in weight % is determined. By suitable handling of the vacuum and of the temperature, the solution could be made to bubble in the initial stages of evaporation. This increased the rate of evaporation but had no significant effect on the final value of the concentration.

RESULTS

In the following description, the superscripts 'Tol' and 'MEK' designate quantities referring to toluene and methyl ethyl ketone respectively, whether pure solvents or solutions. The subscript '*s*' refers to pure solvent and the absence of a subscript indicates a solution value.

Density

The density of the solvents as a function of temperature is given by equation (6)[20] with the values of the parameters given in *Table 1*. Published data[13,20] and results obtained by the authors agree with this expression to within ±0.2%.

The densities of the two solutions also agree with equation (6) and agreement between calculated values using the parameters of *Table 1* and the measured values is well within experimental error over the whole temperature range (−60° to 40°C).

Steady-flow viscosity

The steady-flow viscosity of the two solvents was determined over the temperature range −50°C to 30°C. Results are fitted to within a maximum error of ±0.11% by the equation:

$$\eta_s(\text{Pa s}) = D/(F+T)^n \qquad (7)$$

T is in °C and values of the parameters *D*, *F* and *n* are given in *Table 1*. Other published data[13] agree with the present results to better than 1%, although older data quoted in the International Critical Tables are somewhat at variance and different values are quoted there for the parameters *D*, *F* and *n*, from those used by the authors.

Steady-flow values of the viscosity of the solutions were determined over the temperature range −58°C to 20°C and the results are shown in *Figure 2*. A least squares fit of the data to the modified free volume equation gave a maximum scatter of 3.3%.

$$\ln[\eta/(\text{Pa s})] = K + H/(T - T_0) \qquad (8)$$

T and T_0 are in °C and the values of the parameters *K*, *H* and T_0 are given in *Table 1*.

Over the temperature range covered in the present experiments η_s^{Tol} is 50 to 100% higher than η_s^{MEK}. Making the usual assumption that the viscosity reaches 10^{12}Pa s at the glass transition temperature we obtain:

$$T_g^{\text{Tol}} = -124.8^\circ\text{C} \;:\; T_g^{\text{MEK}} = -116.0^\circ\text{C}$$

Figure 3 shows the variation with temperature of the steady-flow viscosity of the solutions, each normalized with respect to the steady state viscosity η_s of the corresponding solvent. The curve for the toluene solution is significantly higher than that for MEK. Viscosity ratios for solutions and solvents are shown in *Figure 4*. In particular, the ratio $(\eta/\eta_s)^{\text{Tol}}/(\eta/\eta_s)^{\text{MEK}}$ is approximately constant over the temperature range 0° to 40°C but decreases with decreasing temperature below 0°C.

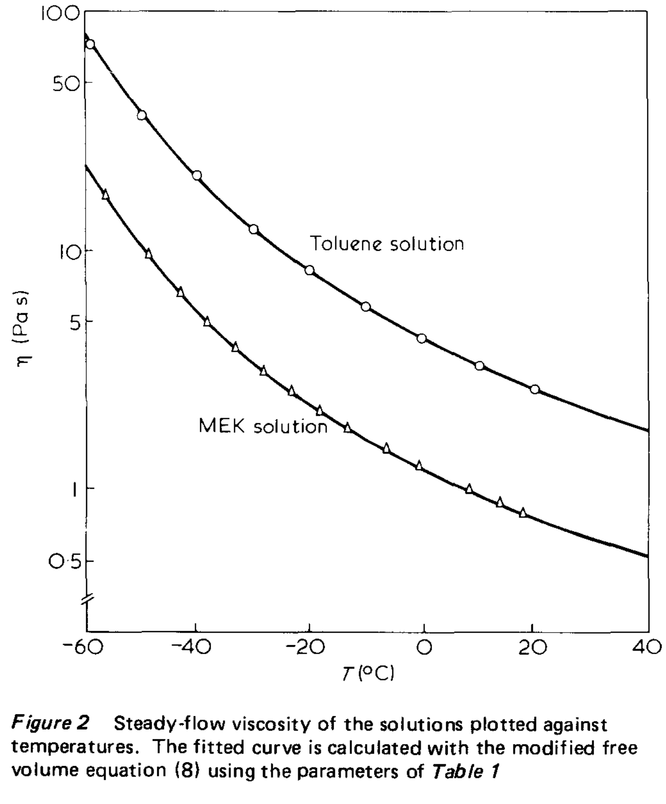

Figure 2 Steady-flow viscosity of the solutions plotted against temperatures. The fitted curve is calculated with the modified free volume equation (8) using the parameters of *Table 1*

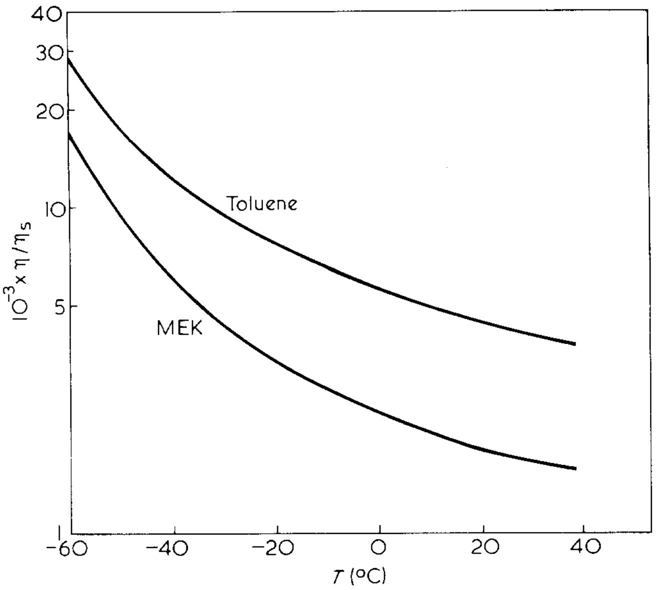

Figure 3 Steady-flow viscosity of the solutions normalized with respect to the steady-flow viscosity of the respective solvent (equation (7) and *Table 1*), plotted against temperature

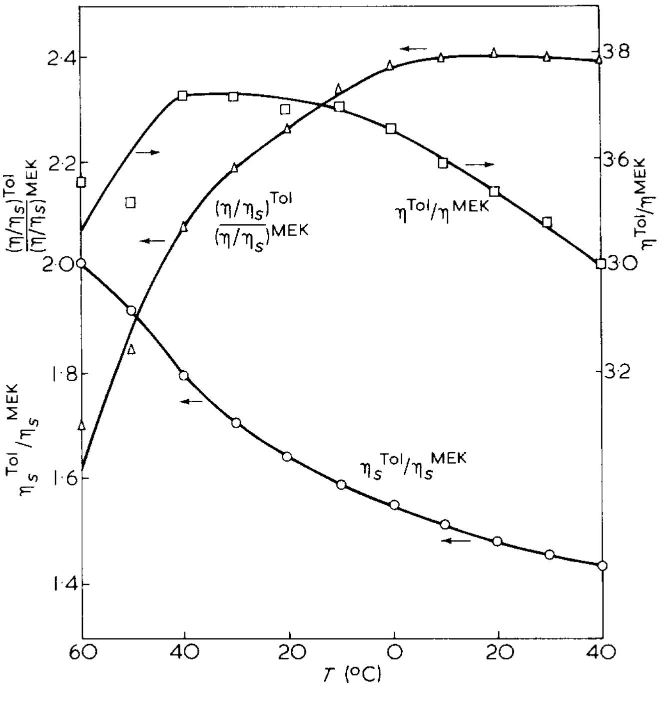

Figure 4 Ratios of steady-flow viscosities of solvents and solutions, plotted against temperature

Viscoelastic behaviour

Experimental results for $\Delta\alpha$ and $\Delta\beta$ as functions of temperature are shown in *Figure 5*. $\Delta\alpha$ is consistently larger than $\Delta\beta$ in order to yield a positive value for G', the values of which are plotted *versus* temperature in *Figure 6*. $(G')^{Tol}$ has a constant plateau value within experimental error over the temperature ranges −20°C to 40°C but increases with decreasing temperature below −20°C, as the observed behaviour, at constant frequency, passes from the 'rubbery plateau' into the 'liquid-like' region associated with motions of short elements of the polymer chain[21,22] (see *Figure 10*). However $(G')^{MEK}$ is sensibly constant over the whole range of temperature with a slight

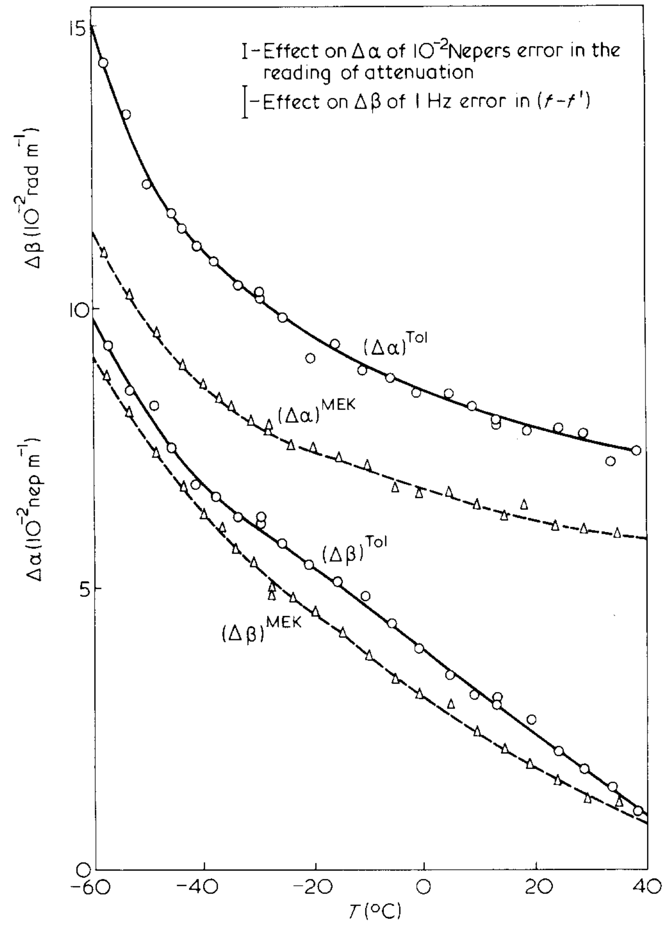

Figure 5 Measured attenuation and phase data used to calculate the viscoelastic properties of the solutions. The double points at the same temperature give the results obtained with the last measurement of the day, and the first measurement on the following morning, after leaving the solution-rod system at constant temperature overnight. The errors shown apply over the whole temperature range

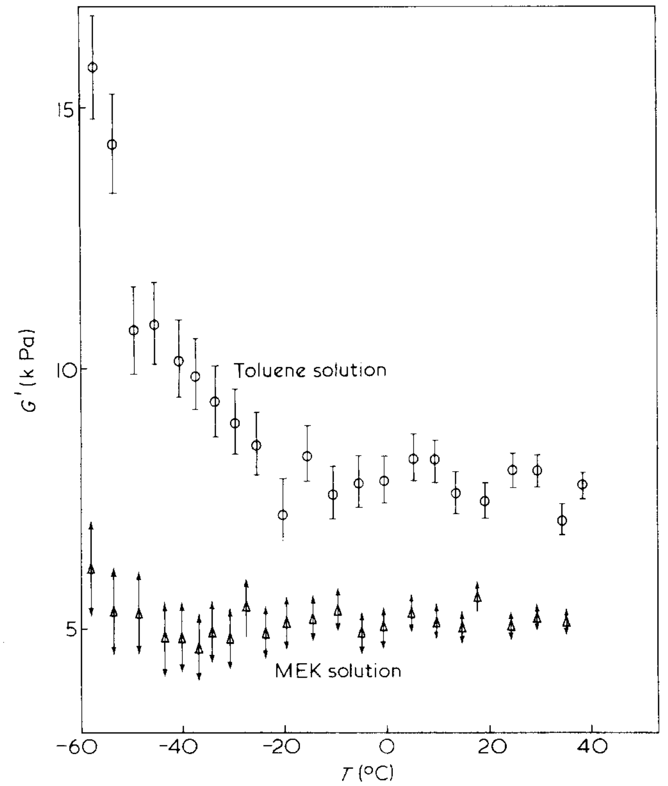

Figure 6 Measured values of the storage shear modulus, G', for the two solutions, plotted against temperature

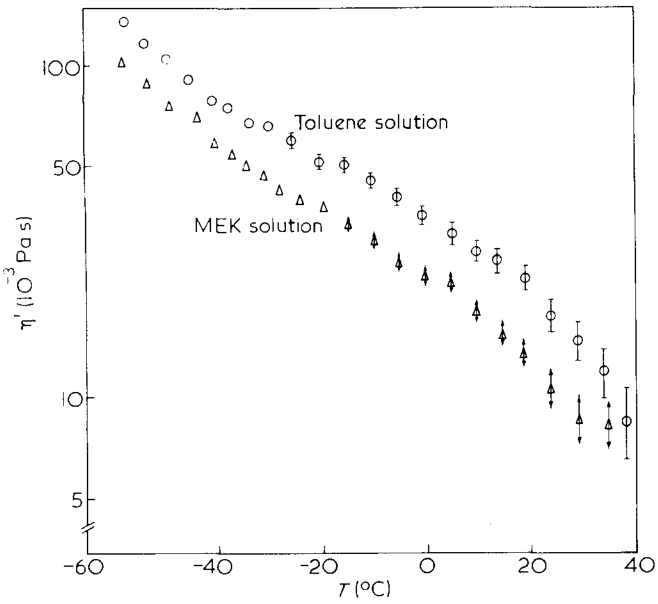

Figure 7 Measured values of the dynamic viscosity, plotted against temperature

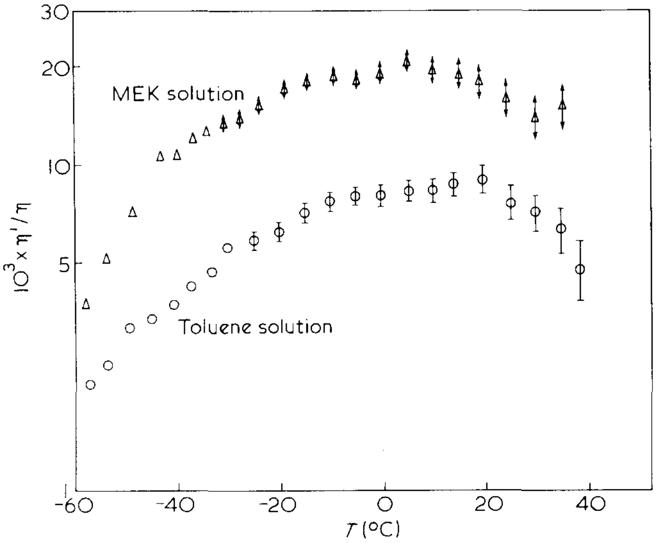

Figure 8 Dynamic viscosity of the solutions normalized with respect to the corresponding steady-flow viscosity and plotted against temperature

indication that its value might begin to increase with decreasing temperature below −60°C. The constant plateau value of G' is some 45% higher for the good solvent, toluene, than for the relatively poor MEK solvent.

Figure 7 shows the dynamic viscosity, η', *versus* T for both solutions, $(\eta')^{\mathrm{Tol}}$ being consistently higher than $(\eta')^{\mathrm{MEK}}$. There are two alternative ways in which these results can be normalized in an attempt to seek an understanding of the observed behaviour:

(1) values of the dynamic viscosity of the solution can be normalized by dividing by the corresponding value of the steady flow viscosity, as in *Figure 8*. In both solutions (η'/η) passes through a maximum at a temperature in the region of 15° to 20°C. Although $(\eta')^{\mathrm{Tol}}$ is greater than $(\eta')^{\mathrm{MEK}}$, $(\eta'/\eta)^{\mathrm{MEK}} > (\eta'/\eta)^{\mathrm{Tol}}$ since $(\eta)^{\mathrm{Tol}}$ is significantly greater than $(\eta)^{\mathrm{MEK}}$.

(2) η' can be normalized by dividing by the corresponding value of the steady flow viscosity of the respective solvent as in *Figure 9*, akin to the usual procedure for dilute solutions. At temperatures higher than about −20°C, the results for both solutions, cast in this way, are indistinguishable, (η'/η_s) increasing with decreasing temperature.

Below −20°C, $(\eta'/\eta_s)^{\mathrm{Tol}}$ becomes constant whereas $(\eta'/\eta_s)^{\mathrm{MEK}}$ continues to increase with decreasing temperature.

A minor detail of the results shown in *Figure 9* is the semblance of a small plateau in the plot of $(\eta'/\eta_s)^{\mathrm{MEK}}$ in the region of −17°C to −27°C. Since a similar feature was found in two other sets of experimental results—one with the same solution and the other with a different solution made to the same concentration—it would appear that this is an effect to be distinguished from statistical scatter.

DISCUSSION

The radius of gyration expansion coefficient, $\alpha_\eta^3 = [\eta]/[\eta]_\theta$, for solutions of polystyrene in toluene and MEK at 25°C is 2.17 and 1.30[11], respectively, thus indicating a considerably better thermodynamic affinity for the former. The melting points of the solvents are close to each other as are the calculated values of the glass transition temperatures for both solutions. These are well below the lowest temperature of measurement so that, in comparing the normalized relative viscoelastic behaviour of the two solutions, it is possible to ignore any shifts along the temperature scale to account for effects due solely to differences in the free volume of the solutions.

Steady-flow viscosity

We visualize the mechanism responsible for the viscous drag on a polymer molecule in solution under an applied stress as being mainly due to shearing effects between molecules of the solvent which, in turn, are responsible for

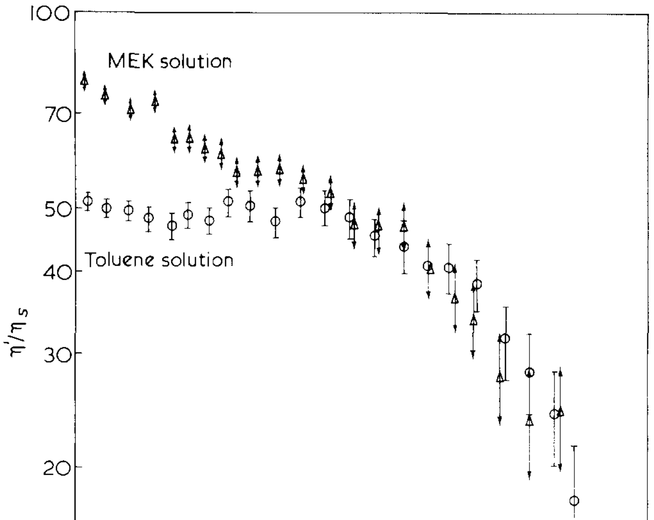

Figure 9 Dynamic viscosity of the solutions normalized with respect to the steady-flow viscosity of the solvent, plotted against temperature

the viscosity, η_s, of the solvent itself. Using the values of the parameters given in *Table 1*, it follows from equation (7) that $(n_s)^{\mathrm{Tol}} > (n_s)^{\mathrm{MEK}}$ over the temperature range of the measurements. Hence , on a qualitative basis, we would expect $(\eta)^{\mathrm{Tol}}$ to be greater than $(\eta)^{\mathrm{MEK}}$, as is evident from *Figure 2*. However, if no other factor were involved, we would then expect that $(\eta/\eta_s)^{\mathrm{Tol}}$ would equal $(\eta/\eta_s)^{\mathrm{MEK}}$. This is clearly not the case, as can be seen from the results plotted in *Figure 3*. Since the relative steady-flow viscosity (η/η_s) in toluene is greater than the corresponding value in MEK solution at all temperatures, it is suggested that the polymer molecule adopts a more open configuration in toluene with an associated higher density of entanglement than in the MEK, which has a poorer thermodynamic affinity. Thus, the contribution of the macromolecular entanglements to the steady state viscosity is the greater for the toluene solution, implying larger units of flow than in MEK. Quadrat and Podnecka[11] concluded from a study of the relative viscosity of a polydisperse polystyrene sample in moderately concentrated solutions that the effect upon the viscosity of the thermodynamic quality of the solvent is due to a superposition of two counteracting contributions—a weakening of the strength of mutual contacts between the polymer molecules and an increase in the radius of gyration of the polymer chain by extension in a thermodynamically better solvent. The authors' explanation that the expansion of the polymer chain in the better solvent (toluene) produces an increased density of entanglement causing the higher value of relative viscosity (η/η_s) receives further support from the dynamic viscoelastic results, as discussed subsequently.

An increase in viscosity of the solvent due either to a change of solvent or to a decrease in temperature will increase the amount of viscous drag on the polymer molecule. In addition, the stiffening effect produced by a decrease in temperature should be greater for a polymer network with a relatively higher density of entanglements, i.e., in the better solvent, toluene. Since $(\eta_s)^{\mathrm{Tol}}/(\eta_s)^{\mathrm{MEK}}$ increases with decreasing temperature (*Figure 4*), we would therefore expect $(\eta)^{\mathrm{Tol}}/(\eta)^{\mathrm{MEK}}$ to do likewise but, as seen from the results plotted in *Figure 4*, this occurs only over the temperature range 40°C to -40°C. Moreover, the differential rate of increase of $(\eta)^{\mathrm{Tol}}/(\eta)^{\mathrm{MEK}}$ with decreasing temperature is less than that of $(\eta_s)^{\mathrm{Tol}}/(\eta_s)^{\mathrm{MEK}}$—at variance with the previous hypothesis associated with the increasing stiffening effect due to higher entanglement density in the toluene solution. The fact that an additional mechanism is operative can be demonstrated by examining the behaviour of the quantity $(\eta/\eta_s)^{\mathrm{Tol}}/(\eta/\eta_s)^{\mathrm{MEK}}$, shown also in *Figure 4*. In this ratio, the effect of the solvent drag on the polymer molecules has been removed in both numerator and denominator, leaving only the stiffening effect produced by a change of temperature on the two entanglement networks. We would, therefore, on these grounds, expect the ratio to increase with decreasing temperature due to the enhanced entanglement stiffening in the toluene solution, whereas the opposite behaviour is found, at least below 10°C since this ratio remains approximately constant from 10°C to 40°C.

It is concluded that there is a further mechanism in the MEK solution which increases the size of the unit of flow with decreasing temperature to a greater extent than is the case for the toluene solution, and this is attributed to partial exclusion of solvent within the entanglement regions, where the macromolecular packing is more efficient than in regions between the entanglements. Because of the entropy associated with thermal motions the tendency for solvent molecules to be excluded from the entanglement regions in the MEK solution will be more pronounced as the temperature decreases, and the entanglements will therefore become more stable compared with those in the toluene solution where, owing to the volume and high mobility of the solvent molecules, their presence within entanglements will decrease the entanglement stability. During the time required for steady-flow viscosity measurements above the glass-transition temperature the entanglements are destroyed and re-formed but, as the temperature decreases, the unit of flow in the MEK solution increases to a greater extent than in the toluene solution. Hence $(\eta/\eta_s)^{\mathrm{Tol}}/(\eta/\eta_s)^{\mathrm{MEK}}$ decreases with decreasing temperature (*Figure 4*).

Over the whole temperature range studied, the density of entanglements in the toluene solution remains higher than in the MEK solution, and this is responsible for the result that $(\eta/\eta_s)^{\mathrm{Tol}} > (\eta/\eta_s)^{\mathrm{MEK}}$, as seen in *Figures 3* and *4* and additionally $\eta^{\mathrm{Tol}}/\eta^{\mathrm{MEK}} > \eta_s^{\mathrm{Tol}}/\eta_s^{\mathrm{MEK}}$ (*Figure 4*). However, the results shown in *Figure 4* suggest that at some temperature below -60°C, $\eta^{\mathrm{Tol}}/\eta^{\mathrm{MEK}}$ will fall below $\eta_s{}^{\mathrm{Tol}}/\eta_s{}^{\mathrm{MEK}}$, indicating that the density of entanglements will then become larger in the MEK solution. This conclusion is supported by the value of T_g for these solutions, calculated from the values of the parameters shown in *Table 1* for a viscosity of 10^{12} Pa s. Although the viscosity of the toluene solution is greater than that of the MEK solution over the temperature range of the measurements, the value of T_g for the MEK solution is some 9°C higher than for the toluene solution. Hence, at some temperature below -60°C, η^{MEK} will overtake η^{Tol}, and this tendency is exhibited by the results plotted in *Figures 2*, *3* and *4*. Thus, the arguments based upon the value of T_g support the conclusion that, with decreasing temperature, partial exclusion of solvent from the entanglement regions will lead eventually to stronger entanglements, and larger units of flow, in MEK than in toluene—in line with the conclusion reached on the basis of the variations of steady-flow viscosity.

It should be noted that Quadrat and Podnecka[11] have already advanced the hypothesis that in a polymer solution lower thermodynamic affinity of the solvent leads to stronger entanglements.

Viscoelastic behaviour

Measurements reported here have been made as a function of temperature, over a range of 100°C, at sensibly constant frequency. Since only a part of the viscoelastic relaxation is thereby covered, it helps to place these in context by considering schematically the variations in η' and G' to be expected for a polystyrene solution with a substantial density of entanglements, as sketched in *Figure 10*. At sufficiently low temperatures approaching the glass transition temperature the elastic modulus approaches the glassy modulus, G_∞; the entanglement network is essentially frozen within the time-scale of the measurement and, additionally, both segmental motions of the parts of this polymer chain between entanglement points and the 'liquid-like' motions of small sections of the polymer backbone are likewise rendered inactive[21]. The dynamic viscosity will be close to that of the solvent with a small addition due to the inclusion within the solvent of an essentially rigid polymer network[23–25].

As the temperature increases the first motions to be liberated within the experimental time scale will be those

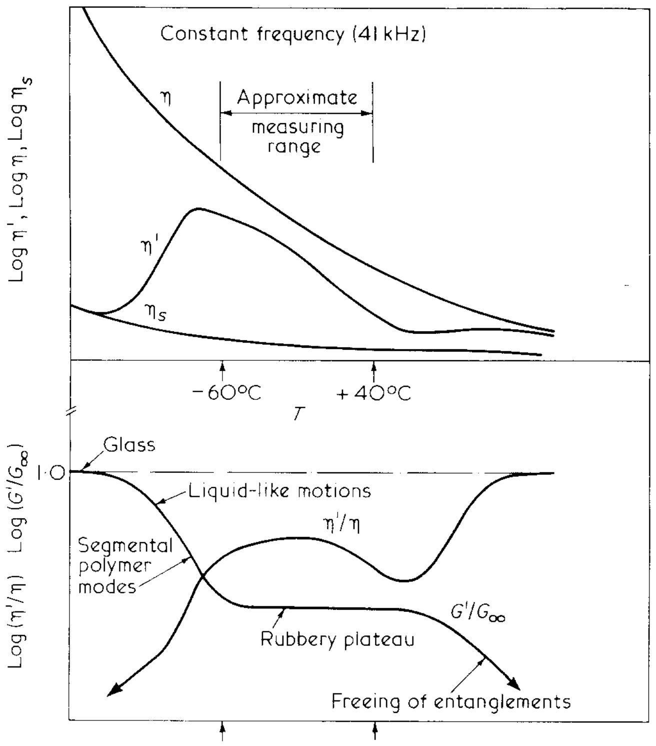

Figure 10 Predicted forms of the temperature dependence of the viscoelastic properties of an entangled polystyrene solution. It is assumed that the experiments are carried out at a fixed frequency over a range of temperature sufficiently wide to take the solution from the "glassy" to the viscous Newtonian states

associated with small elements of the backbone — akin to the viscoelastic relaxation in a supercooled non-polymeric liquid. Hence G' begins to fall and η' to increase with increase of temperature. In this region the segmental motions of the lengths of polymer chain between successive entanglement points will be driven by the applied stress but, as these become increasingly free to participate with increasing temperature, they are then thermally driven with the applied stress merely acting as a perturbation. η' therefore reaches a maximum and then decreases whilst G' continues to decrease until it reaches the rubbery plateau where all modes of motion between entanglements are operational.

Motions of the entanglement network itself remain frozen or inoperative over the temperature span covering the rubbery plateau but, at higher temperatures, the entanglements begin to break up and to reform during the time scale of the experiment. G' then decreases rapidly with increasing temperature and η' increases until the entanglement motions come to be fully driven by the thermal energy so that η' becomes asymptotic to the value of the steady-flow viscosity of the solution, η, which is a decreasing function with increasing temperature, although still numerically some three orders of magnitude greater than the solvent viscosity. The steady-flow viscosity, η, decreases from its value of 10^{12} Pa s at T_g to approximately 1 Pa s at the highest temperature of measurement.

The results of *Figures 6*, *7* and *8* show that the measurements fall in the region of the rubbery plateau with an incursion into the region of relaxation of the segmental modes at the lower temperatures. The salient feature is that overall motions of the entanglement network are inoperative over the 100°C temperature range of these measurements. In discussing the features of the steady-flow viscosity results, it was suggested that the differing thermodynamic affinities of the two solvents are responsible for a higher entanglement density in the toluene solution over the whole of the temperature range of measurement. A similar reasoning explains all the features of the storage modulus, G', depicted in *Figure 6*. Only the stiffness of the chain lengths between entanglements is relevant to the behaviour in this region. Thus, a higher entanglement density gives rise to a higher value of G' in the rubbery plateau for the toluene solution. Moreover, as the temperature decreases, this more entangled network becomes stiffer and the onset of the glass transition region is evident at a higher temperature (−15°C) than for the less entangled network in the MEK solvent.

Both the dynamic viscosity, η', and the solvent viscosity, η_s, decrease with increasing temperature over the region of the rubbery plateau. However, the drag which the solvent molecules exert on relative motions of the segments of the polymer molecules between entanglements can be taken into account by considering the ratio (η'/η_s). If the steady-flow viscosity is the only solvent property affecting the polymer relaxations, we would expect η'/η_s to be independent of the solvent for equal concentrations of the same polymer in the different solvents. The results in *Figure 9* show that this is indeed the case for temperatures above −15°C, where both solutions are in the rubbery region. Although the MEK solution remains in the rubbery region at temperatures below −15°C, and at least down to −55°C, the temperature of −15°C marks the onset of the glass transition region in the toluene solution as is evident from the behaviour of G' *versus* temperature discussed above (see *Figure 6*). At temperatures below −15°C $(\eta'/\eta_s)^{\mathrm{Tol}}$ becomes sensibly independent of temperature suggesting that, at the onset of the glass transition region with decreasing temperature, the toluene molecules become intimately associated with the smaller moving polymer segments; thus the viscoelastic behaviour in this region is essentially controlled by the viscous drag between solvent molecules, that is, by the viscosity of the solvent. Again, it must be emphasized that in the rubbery region the molecular weight of the polymer segments which are able to contribute to viscous loss is of the order of the molecular weight of the lengths of polymer chain between entanglements.

Attention was drawn previously to the semblance of a small plateau in the plot of $(\eta'/\eta_s)^{\mathrm{MEK}}$ *versus* T in the region of −17°C to −27°C, which would appear to be a real feature of the behaviour in this solution. A possible explanation is that macromolecular aggregates are formed at temperatures below about −27°C due to the poor thermodynamic affinity of the solvent and the resulting coiling of the polymer, which would lead to a partial exclusion of solvent from the moving segments. Viscous losses in this low temperature region would therefore be less than those attributed to the full drag of the solvent molecule on the segmental motions. There is, therefore, a reduction of $(\eta')^{\mathrm{MEK}}$ which is evident both in *Figure 7* and in *Figure 9*. It is implied that, as the temperature increases above −27°C, increasing thermal energy counteracts the tendency for aggregates to form, until above −17°C all segments contributing to the viscous losses experience the full drag of the solvent molecules with negligible effect of partial solvent exclusion. In this connection, it is noteworthy that Streeter and Boyer[12] were led to speculate that poor thermodynamic affinity favours an increased degree of polymer–polymer contact in solutions of moderate concentration.

It is concluded that an understanding of processes involving partial exclusion of solvent from moving segments can only be achieved by obtaining data over a wide range of temperature, which is also required in order to understand the effect of the thermodynamic affinity of the solvent on the mechanical behaviour of polymer solutions with an entangled network.

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