

New extensional rheometer for elongational viscosity and flow birefringence measurements: some results on polystyrene melts

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(Received 21 December 1984)

A new extensional rheometer allowing the simultaneous measurement of elongational viscosity and flow birefringence is described. Polystyrene melts have been tested at different temperatures and strain rates. It appears that the time-temperature superposition principle holds for elongational tests in the temperature range investigated, with the same shift factors as for linear shear experiments. It has been verified that the stress optical behaviour of the melts is linear for small values of the stress whereas significant deviations appear at higher stresses.

(Keywords: polymer melt rheology; elongational viscosity; polystyrene; flow birefringence; extensional rheometer; time-temperature equivalence)

INTRODUCTION

The rheological properties of molten polymers in elongational have been extensively studied in the last few years. Although this type of deformation occurs side by side with shearing in many methods of polymer processing and may even be predominant, most of the experimental studies in the field of elongational flows are relatively recent and few in number. This is due to the experimental difficulties encountered when a uniaxial stretching is performed on a liquid specimen (fastening of the specimen in clamps, flowing of the sample due to its own weight) and the special apparatus required.

In Meissner's apparatus¹ the specimen floats horizontally on the surface of an oil bath and the stretching is performed with rotary clamps; with this device one can reach a significant overall strain. More recently, Münstedt² has developed an apparatus in which the specimen is glued on the clamps and stretched vertically in an oil bath, allowing measurements to be taken with small quantities of material. The driving system of the upper clamp consists of a d.c. motor and a belt; the lower clamp is fixed and carries the transducer. In this case, the total strain is limited by the stroke of the upper clamp.

A number of studies^{3,4} have shown that the measurement of flow birefringence could be an important contribution to polymer melt rheology. Matsumoto and Bogue⁵ have designed an extensional rheometer equipped with a device for the measurement of birefringence, the specimen being heated in an air-oven. Therefore only high-viscosity samples can be tested. Moreover, the stretching is performed with one rotary clamp, one end of the specimen being attached to a fixed clamp. Thus, the light beam for the birefringence measurement shows a relative displacement with respect to the specimen during the deformation.

In this paper, a new rheometer for the measurement of elongational viscosity is described, the originality of which consists of a flow birefringence measurement on a specific point of the specimen which is fixed in space. The

use of an oil-bath environmental chamber and of specially designed clamps allows a wide range of polymers of highly different viscosity and chemical structure to be tested.

The results obtained on model polymers (anionic polystyrenes with narrow molecular weight distribution and a commercial polystyrene with a broad molecular weight distribution) are presented. The influence of temperature and strain rate on a measurement of elongational viscosity was carefully carried out and comparison made between the results and the predictions obtained from the linear viscoelastic behaviour. The values of birefringence and stress optical coefficient for these polymers were determined.

DESCRIPTION OF APPARATUS

The working of the apparatus is schematically described in *Figure 1*; two d.c. motors can be coupled to reducers with running screws; the nuts are connected to the clamps which are guided in translation. If the two screws are rotating at the same speed and in the opposite direction, the stretching will be symmetric with respect to the centre of the specimen which will not move with time.

In order to be able to interpret the uniaxial stretching test, it is necessary to work either at constant strain-rate or at constant true stress^{6,7}. In this case, the control system of the device allows a constant strain-rate deformation and the results are all relevant to this type of test. The elongational viscosity of the material is then defined as the ratio of the true stress to the strain rate and is generally a function of time or strain. When the deformation experienced by the specimen is not infinitely small, one can easily show that the velocity of the clamps must vary exponentially to reach a constant strain rate for the specimen⁸. The principle of the control system which leads to an exponential law for the position of the clamps is shown in *Figure 2*.

A linear potentiometer delivers a voltage (u) pro-

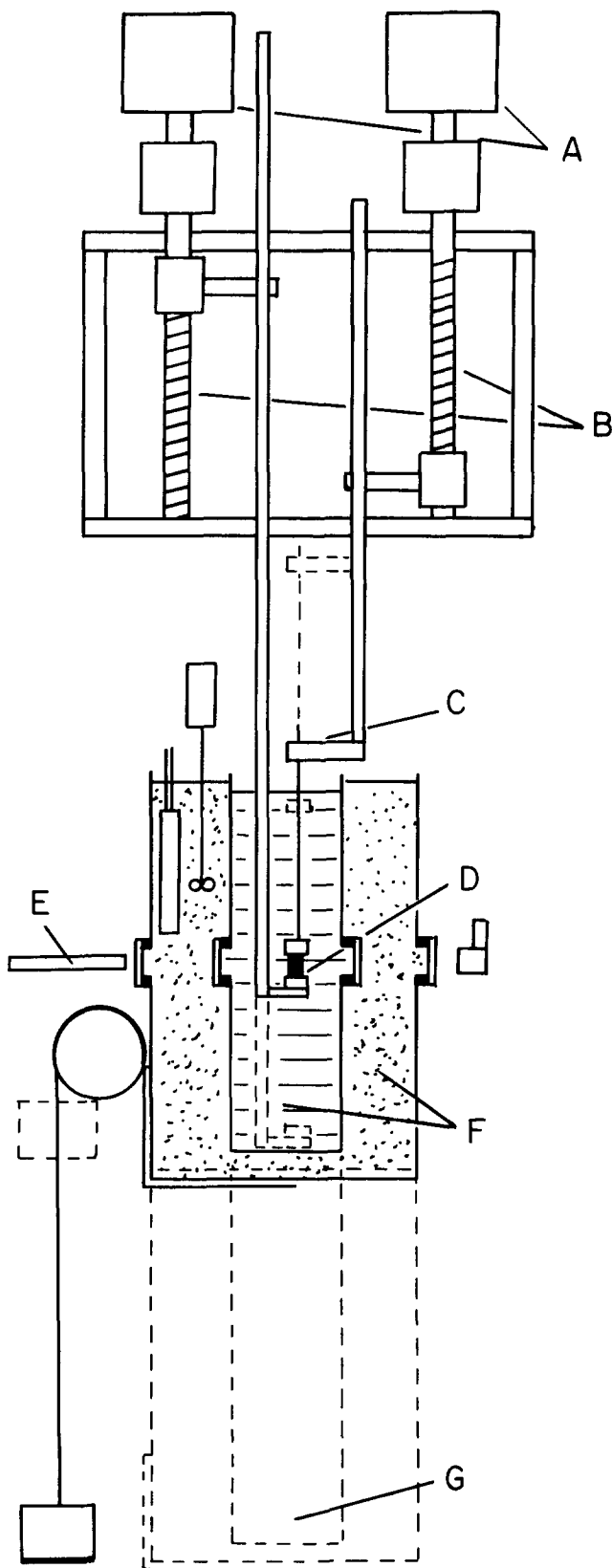


Figure 1 Schematic drawing of the apparatus: (A) d.c. motors, (B) screws, (C) transducer, (D) specimen, (E) laser, (F) silicone-oil bath, (G) lower position of the bath

portional to the position (x) of the upper clamp; this voltage is amplified and used as input-voltage of the servo-motors. In this way, one realizes a servo-system in which the velocity (v) of the clamps is proportional at every moment to their position (x); this means that an

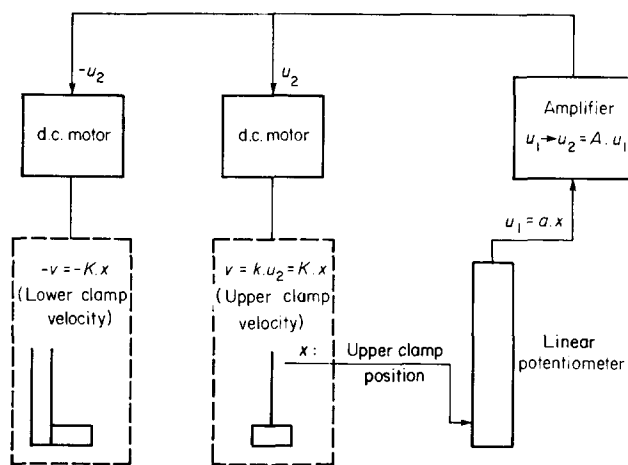


Figure 2 Block diagram of the electronic device. An exponentially increasing velocity of both clamps is obtained

exponential law is obtained for the length (L) of the specimen.

Each of the clamps has a stroke of 22.5 cm which represents 45 cm for the specimen and a Hencky strain ($\epsilon = \ln(L/L_0)$) of about 3.2 for an initial length of 2.5 cm. The strain-rate range accessible for the highest strain goes from $2 \times 10^{-4} \text{ s}^{-1}$ to $2 \times 10^{-2} \text{ s}^{-1}$ with the reducers and from $2 \times 10^{-2} \text{ s}^{-1}$ to 2 s^{-1} when the motors are running the screws directly.

Among the parameters which determine the validity of measurements in an elongational flow, the homogeneity of deformation is of particular importance. Two main factors can affect the deformation homogeneity, which are due to the liquid state of the specimens:

(i) The weight of the specimen induces a stress which can bring about an important deformation of the specimen especially for low-viscosity samples.

(ii) The viscosity in the molten state of many polymers (particularly of amorphous polymers near T_g) is highly sensitive to temperature. A low temperature gradient in the oven will be a necessary condition for a homogeneous deformation.

A convenient method to overcome the first difficulty is to use a liquid of the same density as the polymer for the heating system^{1,2,9,10}. The silicone oils satisfy fairly well the conditions which this liquid has to fulfil (density equivalent to that of the polymer, transparency for the measurement of birefringence, good stability at high temperatures, absence of interaction with the polymer and low viscosity at the test temperature to avoid perturbations of the force measurement due to viscous friction of the upper clamp).

An oven schematically represented in Figure 1 with a double silicone oil bath has been designed in order to reduce, as far as possible, the gradient of temperature. The oil of the outer bath is heated up to the desired temperature and mixed vigorously. The oil in the inner bath is at rest so it does not disturb the geometry of the specimen, and is heated by conduction from the outer bath. The homogeneity of temperature one can obtain with this method is better than $\pm 0.2^\circ\text{C}$; it should be noted that the lower clamp guide had to be heated separately, as part of this guide enters the bath during stretching. Windows made of Pyrex with an accurately adjusted parallelism allow a laser beam to pass through the specimen.

Furthermore, the design of the apparatus permits a vertical displacement of the oven, which has the following advantages: the specimens are quick to heat up (about 10 min), an easy handling of the specimens, the possibility of quenching a stretched and partially relaxed sample just by moving down the oven. Thus the orientation of the polymer chains can be fixed at a given moment and further characterized at room temperature.

The fastening of the ends of the specimen becomes a difficult problem in cases where the stretching of the specimen is not performed with rotary clamps. Gluing onto a metallic clamp has shown to be a satisfactory solution in several cases^{7,11,12} especially for polystyrene. The use of conventional clamps has been possible in other studies, where the geometry of the specimens was a parallelepiped^{5,13} and the viscosity high enough.

In this laboratory, a correct measurement of birefringence implies a known thickness of material passed through by the light beam, which means a parallelepiped geometry of the specimens. However, gluing tests on polyethylene samples have not been conclusive. For this reason, self-blocking clamps were designed, specially adapted to the molten state which allow a satisfactory fastening of the specimens, whatever the chemical nature of the polymer and in a wide range of viscosities.

The parameters with physical meaning (true stress σ and birefringence Δn) are related to the experimentally measured parameters (force F and transmitted intensity I) by the relations¹⁴:

$$\sigma = F/S \quad (1)$$

$$I = I_0 \sin^2 \frac{\pi \Delta n e}{\lambda} \quad (2)$$

where S is the cross-section of the specimen,

e is the thickness crossed by the light beam,

λ is the wavelength of the light ($\lambda = 632.8$ nm).

A data-acquisition system connected to a micro-computer allows a rapid calculation of σ and Δn . To evaluate σ , it is supposed that the deformation occurs at constant volume, which leads to:

$$\sigma = \frac{FL}{V_0} \quad (3)$$

For the calculation of Δn , it will have to be further assumed that the deformation is isotropic in a plane perpendicular to the stretching in order to calculate the instantaneous thickness, given by the relation:

$$e = e_0 \frac{L_0}{L} \quad (4)$$

This assumption has been verified by measuring the final width and thickness on the stretched specimens.

The calculation of Δn from I according to relation (2) needs a programme which is able to identify and count the maxima and minima of the $I(t)$ curve.

EXPERIMENTAL RESULTS

Two anionic polystyrenes with a narrow molecular weight distribution were used for the measurements of elongational viscosity. They were synthesized at E.A.H.P.

with the following designations:

$$S\ 611\ (M_w = 115\ 000\ M_w/M_n = 1.04)$$

$$S\ 620\ (M_w = 170\ 000\ M_w/M_n = 1.05)$$

A commercial polystyrene with a broad molecular weight distribution whose designation is:

$$GEDEX\ 1801\ GA\ 100\ (M_w = 250\ 000\ M_w/M_n = 2.44)$$

was also used.

The specimens were obtained by freeze-drying and vacuum moulding at 150°C for 30 min. Removal of all the solvent is obtained by heating the polymer before moulding at 70°C under vacuum for 1 h. The specimens have the form of parallelepipeds with a total length of between 4 and 7 cm (which corresponds to a useful length of 2 to 5 cm), a width between 1 and 2.5 cm and thickness between 0.1 and 0.5 cm.

It must be noted that the initial shape of the specimen and especially the ratio of length to width (L/l) may influence the validity of the measurements. The deformation is not homogeneous near the clamps and this effect is amplified when the ratio L/l decreases. By repeating the same measurement on the same polymer it could be shown that no significant changes take place in the elongational viscosity measurements when the ratio L/l was higher than 1.5. For all the results shown in this paper, a typical value of L/l equal to 2.5 was chosen.

When the elongational viscosity of a polymer above T_g is measured, two different behaviours may be observed depending on the value of the strain rate:

(1) For low enough strain rates, the flow reaches a steady-state regime after a stress growth period; the equilibrium stress σ_0 obeys Trouton's relation^{15,6}

$$\sigma_0/\dot{\epsilon} = 3\eta_0 \quad (5)$$

where η_0 is the Newtonian viscosity in shear.

Moreover, if the ratio of stress to strain rate (elongational viscosity) is plotted against time during the stress growth period, the curve obtained is independent of strain rate.

(2) For higher strain rates, a more complex behaviour is observed; the elongational viscosity increases more rapidly than for the first case and exceeds Trouton's limiting value (in some cases, a maximum followed by a decrease of $\sigma/\dot{\epsilon}$ has been observed, but for much higher values of the total strain than those accessible with the apparatus described in this article ($\epsilon \sim 7$)¹⁶). Moreover the curve representing the elongational viscosity as a function of time now depends on the strain rate.

Both types of behaviour have been observed for the monodisperse polystyrenes. The steady state regime has been observed at 142°C for a strain rate of 0.02 s⁻¹. A valuable test for the apparatus was to compare the value of the elongational viscosity in the steady state regime to the Newtonian viscosity in shear measured at the same temperature with a cone and plate rheometer (Rheometrics RMS 605). It can be noticed in *Figure 3* that Trouton's relation is fairly well verified for the two monodisperse polymers (S611 and 620).

Curves characteristic of the second type of behaviour have been obtained on the polydisperse polystyrene (GEDEX 1801) for different temperatures and strain rates.

Figures 4 and 5 show the elongational viscosity as a

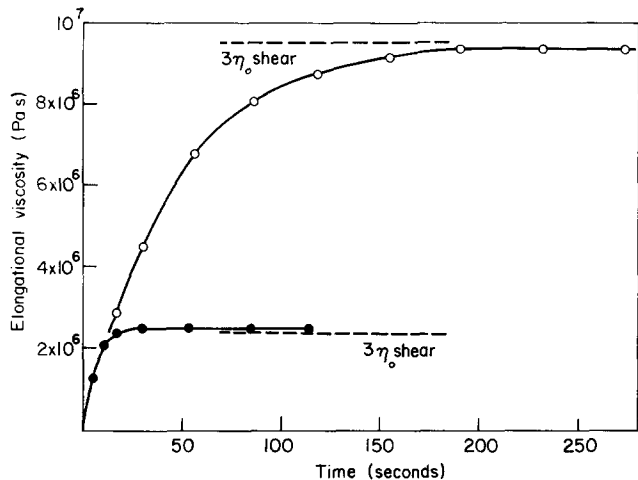


Figure 3 Elongational viscosity as a function of time for two monodisperse polystyrene melts at a temperature of 142°C and a strain rate of $\dot{\epsilon} = 0.02 \text{ s}^{-1}$. (●) S611, (○) S620

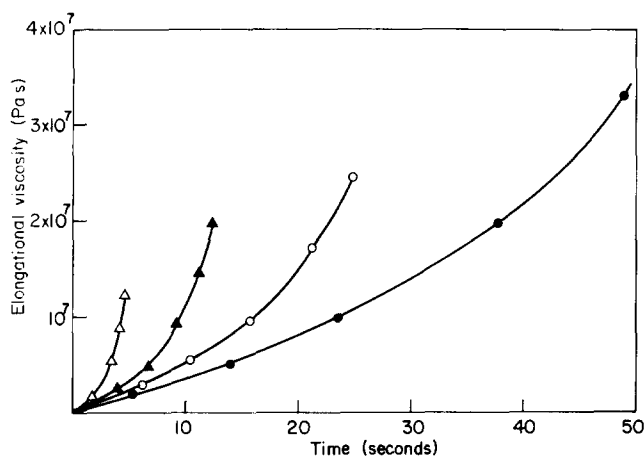


Figure 4 Elongational viscosity as a function of time for the GEDEX 1801 melt at a temperature of 136°C and at different strain rates. (●) 0.05 s^{-1} , (○) 0.1 s^{-1} , (▲) 0.2 s^{-1} , (△) 0.5 s^{-1}

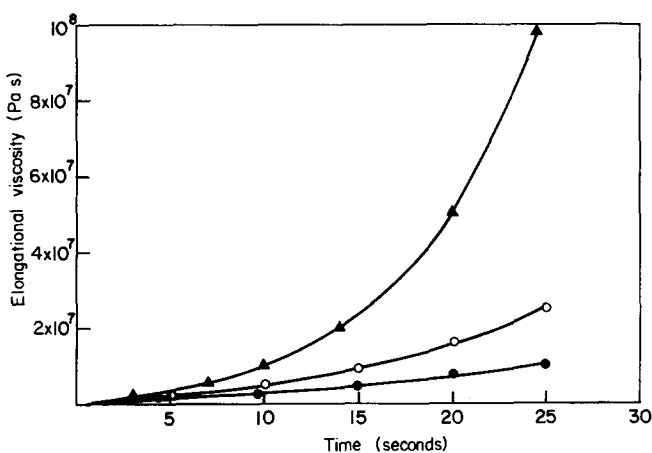


Figure 5 Elongational viscosity as a function of time for the GEDEX 1801 melt at a strain rate of 0.1 s^{-1} and at different temperatures. (●) 146°C, (○) 136°C, (▲) 126°C

function of time for this polymer. In the first case (Figure 4) the strain rate was varied at constant temperature; in the second case the temperature was varied at constant strain rate. It can be noticed that the effect of a temperature

decrease is similar to that of a strain rate increase. The quantitative interpretation of this observation will be examined later in this paper.

The flow birefringence has been calculated during stretching at different temperatures and strain rates for the commercial polystyrene (GEDEX 1801). The results are shown in Figure 6 where the birefringence has been plotted as a function of true stress during the experiment. Apart from small experimental errors, the birefringence depends only on stress (at equivalent stress it does not depend on temperature or on strain rate).

For values of stress lower than $2 \times 10^6 \text{ Pa}$, a linear relation between stress and birefringence is seen. The value of the stress optical coefficient that can be derived ($C = 4.7 \times 10^{-9} \text{ m}^2/\text{N}$) agrees rather well with the published values for polystyrene^{3,4}; one can also remark that for higher stress values the birefringence increases more slowly than the stress, which corresponds to a decrease of the stress optical coefficient. A similar result has been obtained by Retting³, who showed that the stress optical coefficient decreases with a decrease in temperature. This phenomenon can be qualitatively accounted for by noting that the orientation for a chain (and hence the observed birefringence) has a finite limiting value when the maximum extension of the chain is approached, whereas the associated stress tends theoretically towards infinity.

DISCUSSION

From the results obtained, two particular points were further examined. It has been seen that for a steady state regime, Trouton's relation was well verified, which means that the value of the steady-state elongational viscosity is equal to that which can be calculated from a linear equation (7). From this, it can be checked (in the case where a steady state flow is reached) whether the linear theory applies to the whole curve representing elongational viscosity as a function of time, including the stress growth period. It is also interesting to compare the results to the prediction of Lodge's constitutive equation.

The experiment has been realized on one of the monodisperse polystyrenes (S611, $M_w = 115\,000$) at 142°C and for a strain rate of 0.02 s^{-1} . After a stretching of 80 s, when the steady state is reached, the stress relaxation

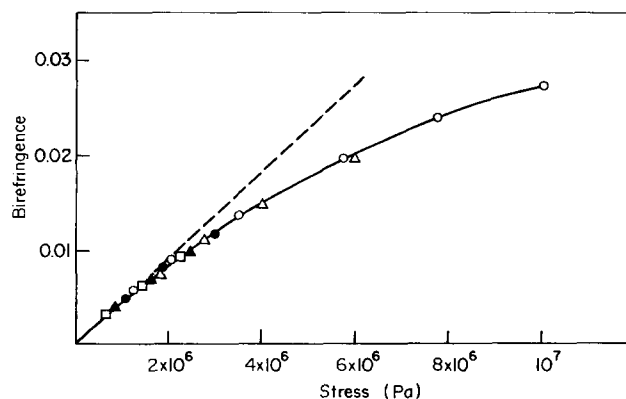


Figure 6 Birefringence of the GEDEX 1801 melt as a function of elongational stress at various temperatures and strain rates. (○) $T = 126^\circ\text{C}$ $\dot{\epsilon} = 0.1 \text{ s}^{-1}$, (●) $T = 126^\circ\text{C}$ $\dot{\epsilon} = 0.01 \text{ s}^{-1}$, (△) $T = 136^\circ\text{C}$ $\dot{\epsilon} = 0.5 \text{ s}^{-1}$, (▲) $T = 136^\circ\text{C}$ $\dot{\epsilon} = 0.1 \text{ s}^{-1}$, (□) $T = 146^\circ\text{C}$ $\dot{\epsilon} = 0.5 \text{ s}^{-1}$. The slope of the broken line corresponds to a stress optical coefficient of $4.7 \times 10^{-9} \text{ m}^2/\text{N}$

at constant strain at the same temperature can also be measured. The stress as a function of time has been plotted in Figure 7 for this test.

The theory of linear viscoelasticity applied to an elongational flow at a constant strain rate yields the following expression for the true stress¹⁸:

$$\sigma(t) = 3\dot{\epsilon} \int_0^t \int_{-\infty}^{+\infty} H(\tau) e^{-u/\tau} d \ln \tau du \quad (6)$$

$$= 3\dot{\epsilon} \int_0^t G(t-u) du \quad (7)$$

whereas the stress relaxation after cessation of a steady-state flow obeys the relation:

$$\sigma(t) = 3\dot{\epsilon} \int_t^{\infty} G(u) du = 3\dot{\epsilon} \eta_0 - 3\dot{\epsilon} \int_0^t G(t-u) du \quad (8)$$

where η_0 is the Newtonian shear viscosity.

The relaxation curve is symmetric to the stress growth curve with respect to a horizontal line ($\sigma = 3\eta_0/2$).

In order to calculate the stress from equation (6), the relaxation spectrum H of the considered polystyrene had to be determined. Tschoegl's method was applied to values of the dynamic moduli G' and G'' measured in shear in the linear field¹⁹. A double integration using Simpson's rule yields values of stress during stretching and relaxation. Figure 7 shows a good agreement between the experimental curve and the prediction from the linear theory, both for the flow at constant $\dot{\epsilon}$ and for the stress relaxation.

Lodge's equation applied to uniaxial deformation at constant strain rate yields:

$$\sigma(t) = \int_0^t m(s)(e^{2\dot{\epsilon}s} - e^{-\dot{\epsilon}s}) ds + (e^{2\dot{\epsilon}t} - e^{-\dot{\epsilon}t}) G(t) \quad (9)$$

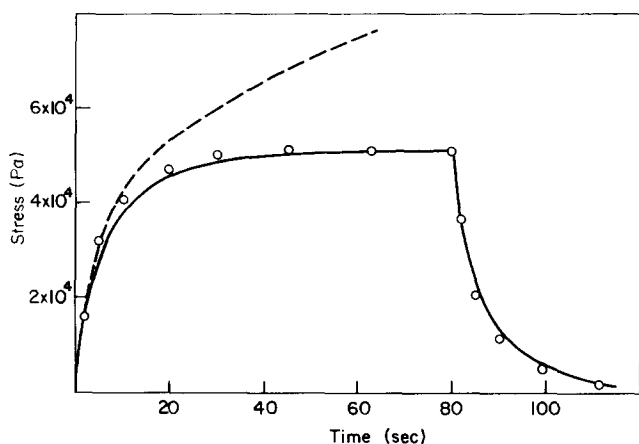


Figure 7 Elongational stress as a function of time for the S611 melt at 142°C. For times less than 80 s, a constant strain rate of 0.02 s^{-1} is applied. For times longer than 80 s the total strain is kept constant and the relaxation of stress is measured. (○) Experiment, (—) linear viscoelastic behaviour, (---) Lodge's equation

where $m(s) = -\frac{dG(s)}{ds}$ is the memory function of the material.

It should be noted that if $\dot{\epsilon}$ tends towards 0, one finds the linear expression (7). Figure 7 shows that Lodge's equation gives much higher values of stress than the experiment²⁰. In particular, it does not predict the steady state regime during the time of the experiment.

One form of the time-temperature superposition principle states that it is equivalent to measure the relaxation modulus at a reference temperature T_0 after a time t_0 or at a temperature T_1 after a time t_0/a_T , where a_T is a numerical factor depending only on temperatures T_0 and T_1 and not on time t_0 . This principle has been well proven in the range of linear viscoelasticity for a great number of amorphous polymers above T_g .

One can easily show that if the behaviour of a polymer in a uniaxial stretching test satisfies a Wagner-type single integral constitutive equation (from which Lodge's equation is a particular case) and if the time-temperature superposition principle is verified in the linear domain, then this principle also applies in a somewhat different form to a measurement of elongational viscosity.

Wagner's constitutive equation for an elongational flow can be expressed at temperature T_0 , time t_0 and for a strain rate $\dot{\epsilon}_0$:

$$\sigma(t_0, T_0, \dot{\epsilon}_0) = \dot{\epsilon}_0 \int_0^{t_0} h(\dot{\epsilon}_0 s) (2e^{2\dot{\epsilon}_0 s} + e^{-\dot{\epsilon}_0 s}) G(s, T_0) ds \quad (10)$$

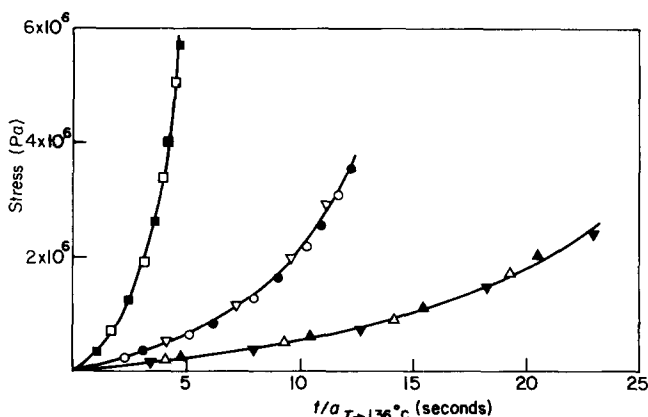


Figure 8 Elongational stress of the GEDEX 1801 melt as a function of reduced time $t/a_{T \rightarrow 136^\circ\text{C}}$ at temperature and strain rates listed in Table 1. (▲) $T = 126^\circ\text{C}$ $\dot{\epsilon} = 0.011 \text{ s}^{-1}$, (△) $T = 136^\circ\text{C}$ $\dot{\epsilon} = 0.095 \text{ s}^{-1}$, (▼) $T = 146^\circ\text{C}$ $\dot{\epsilon} = 0.5 \text{ s}^{-1}$, (●) $T = 126^\circ\text{C}$ $\dot{\epsilon} = 0.021 \text{ s}^{-1}$, (○) $T = 136^\circ\text{C}$ $\dot{\epsilon} = 0.19 \text{ s}^{-1}$, (▽) $T = 146^\circ\text{C}$ $\dot{\epsilon} = 1 \text{ s}^{-1}$, (■) $T = 126^\circ\text{C}$ $\dot{\epsilon} = 0.056 \text{ s}^{-1}$, (□) $T = 136^\circ\text{C}$ $\dot{\epsilon} = 0.5 \text{ s}^{-1}$

Table 1 Values of the strain rates at different temperatures calculated from $\dot{\epsilon}_1 = \dot{\epsilon}_0/a_{T_1 \rightarrow T_0}$ and experimentally determined shift factors so that three series of comparable elongational tests are obtained. Reference temperature is $T_0 = 136^\circ\text{C}$

T ($^\circ\text{C}$)	$a_{T \rightarrow T_0}$	$\frac{\rho_0 T_0}{\rho T}$	$\dot{\epsilon}$ (s^{-1})	$\dot{\epsilon}$ (s^{-1})	$\dot{\epsilon}$ (s^{-1})
			(1st series)	(2nd series)	(3rd series)
126	8.9	1.02	0.011	0.021	0.056
136	1	1	0.095	0.19	0.5
146	0.19	0.98	0.5	1	—

The non-linearity function h depends only on the strain $\dot{\epsilon}_0 s$. One can retrieve Lodge's equation by putting $h(\epsilon) = 1$. As it has been assumed that the time-temperature superposition principle was valid for the linear relaxation modulus G , $G(s, T_0)$ can be replaced in relation (10) by $(\rho_0 T_0 / \rho_1 T_1) G(a_T s, T_1)$ where ρ_0 and ρ_1 are the specific weights of the polymer at temperatures T_0 and T_1 respectively. Expression (10) then becomes:

$$\sigma(t_0, T_0, \dot{\epsilon}_0) = \frac{\rho_0 T_0 \dot{\epsilon}_0}{\rho_1 T_1 a_T} \int_0^{t_0 a_T} h\left(\frac{\dot{\epsilon}_0}{a_T} \cdot u\right) (2e^{(2\dot{\epsilon}_0/a_T)u} + e^{-(\dot{\epsilon}_0/a_T)u}) G(u, T_1) du \quad (11)$$

By putting $\dot{\epsilon} = \dot{\epsilon}_0/a_T$ and $t_1 = t_0 a_T$, it becomes:

$$\sigma(t_0, T_0, \dot{\epsilon}_0) = \frac{\rho_0 T_0}{\rho_1 T_1} \sigma(t_1, T_1, \dot{\epsilon}_1) \quad (12)$$

It should be noted that, except for the factor $(\rho_0 T_0 / \rho_1 T_1)$, which remains close to 1, the same value of elongational stress must be found at temperature T_0 after a time t_0 and at temperature T_1 after a time $t_1 = t_0 a_T$ providing that the strain rate is also modified in the ratio $1/a_T$ ($\dot{\epsilon}_1 = \dot{\epsilon}_0/a_T$).

For the elongational viscosities, the relation corresponding to equation (12) becomes:

$$\eta_e(t_0, T_0, \dot{\epsilon}_0) = \frac{\rho_0 T_0}{\rho_1 T_1} \frac{1}{a_T} \eta_e(t_1, T_1, \dot{\epsilon}_1) \quad (13)$$

An experimental verification has been carried out by measuring the elongational viscosity of the GEDEX 1801 polystyrene at three different temperatures. The shift factors a_T with respect to the reference temperature have been determined with shear tests in the linear regime on a cone and plate geometry.

Table 1 summarizes the different strain rates chosen to obtain comparable experiments. Figure 8 shows that the experimental curves of stress versus reduced time t/a_T can be superposed (except for small experimental errors) for

the three experimental series.

CONCLUSION

It was possible to show on a molten polystyrene that the time-temperature superposition principle could be applied to a uniaxial stretching test at constant strain rate, while the behaviour of the material for the considered strain rates is typically non-linear.

The shift factors a_T obey the WLF relation since they are identical to those determined in shear in the linear range.

This result is implicitly contained in a Wagner type single integral constitutive equation where the integrand is the product of the memory function of the material which is characteristic of the linear viscoelastic behaviour and of an arbitrary function of deformation.

REFERENCES

- 1 Meissner, J. *Rheol. Acta* 1969, **8**, 78
- 2 Münstedt, H. *J. Rheol.* 1979, **23**, 421
- 3 Retting, W. *Colloid Polym. Sci.* 1979, **257**, 689
- 4 Janeschitz-Kriegl, H. 'Polymer Melt Rheology and Flow Birefringence', Springer, Berlin, 1983
- 5 Matsumoto, T. and Bogue, D. C. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 1663
- 6 Wagner, M. H. *Rheol. Acta* 1979, **18**, 681
- 7 Münstedt, H. *Rheol. Acta* 1975, **14**, 1077
- 8 Bird, R. B., Armstrong, R. C. and Hassager, O. 'Dynamics of Polymeric Liquids', Wiley, New York, 1977
- 9 Cogswell, F. N. *Rheol. Acta* 1968, **8**, 187
- 10 Vinogradov, G. V., Fikhman, V. D. and Radushkevich, B. V. *Rheol. Acta* 1972, **11**, 286
- 11 Laun, H. M. and Münstedt, H. *Rheol. Acta* 1976, **15**, 517
- 12 Laun, H. M. and Münstedt, H. *Rheol. Acta* 1978, **17**, 415
- 13 Kamei, E. and Onogi, S. *Appl. Polym. Symp.* 1975, **27**, 19
- 14 Ward, I. M. 'Structure and Properties of Oriented Polymers', Applied Science, London, 1975
- 15 Everage, A. E. and Ballman, R. L. *J. Appl. Polym. Sci.* 1976, **20**, 1137
- 16 Raible, T., Demarmels, A. and Meissner, J. *Polym. Bull.* 1979, **1**, 397
- 17 Lodge, A. S. 'Elastic Liquids', Academic Press, London, 1964
- 18 Ferry, J. D. 'Viscoelastic Properties of Polymers', Wiley, New York, 1980
- 19 Tschoegl, N. W. *Rheol. Acta* 1971, **10**, 582
- 20 Wagner, M. H. and Meissner, J. *Makromol. Chem.* 1980, **181**, 1533