

# Stress relaxation of polymer melts subjected to large uniaxial tension

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The stress relaxation behaviour of two molten amorphous polymers (PMMA and PS), has been investigated. The range of draw ratios extends to about 3.5 for PMMA and 7 for PS. The results have been compared with a modification of the original reptation model. The experimental results are fitted rather well by the theoretical predictions in all the range of tested draw ratios for both the materials used.

(Keywords: polymer melts; stress relaxation; large uniaxial tension; reptation model; amorphous polystyrene; amorphous poly(methyl methacrylate))

## INTRODUCTION

One of the most useful experiments enabling the study of the mechanical behaviour of polymers above their glass transition, is the stress relaxation which follows the application of a fixed deformation. This is mainly due to the relative simplicity, of the experimental test, and the expressions to which proposed constitutive equations reduce.

In a previous work<sup>1</sup>, experimental data on the stress relaxation of an amorphous polymer (i.e. poly(methyl methacrylate)) have been discussed and the results interpreted in terms of a modification of the reptation model developed in recent years<sup>2</sup>. In the study by Marrucci and de Cindio<sup>1</sup> the attention was focused on the large deformation range where differences between models became more apparent. Nevertheless the range of deformation tested was not extended, and in order to confirm the proposed modification, a new series of experiments on two polymers; poly(methyl methacrylate) and polystyrene, (PMMA and PS) have been performed. The proposed theoretical modification deviates to a greater extent from the original model as the deformation increases, and consequently a range of draw ratios as large as possible have been investigated. However, it should be emphasized that the large deformation range is of importance from a technological point of view because the system is tested in conditions which are closer to the real operation.

It is worthwhile recalling the main features of the reptation model. In this theory the single macromolecular chain is assumed to move in a restricted volume due to the presence of the other macromolecules. The shape of this volume is tubiform, and the chain can diffuse longitudinally by reptating, while transversely a thermally controlled 'wriggling' motion is assumed to take place. In stress relaxation experiments, two relaxation mechanisms are predicted. The first is very fast and consists of a re-equilibration of the whole chain which has been subjected

to different tensions at the subchain level. The second relaxation mechanism has a longer time scale and is due to the deformation of the original interaction tube. The chain tends to create a new equilibrium, tubiform volume by reptating out of the initial deformed tube.

Here our attention is restricted to the second relaxation mechanism. The resulting equation for the relaxation stress is:

$$\underline{\underline{\sigma}} = \underline{\underline{Q}} \cdot G(t) \quad (1)$$

where  $G(t)$  has the usual meaning of shear modulus and  $\underline{\underline{Q}}$  is the tensor, which describes the dependency on the applied deformation. The main theoretical difference between reptation models essentially concerns the assumptions which lead to the expression of  $\underline{\underline{Q}}$ . The formal theoretical expression [equation (1)] is very simple because it refers to the case of stress relaxation, after a sudden deformation.

## EXPERIMENTAL

In the following experimental section, results obtained during the relaxation after the sudden imposition of an uniaxial tension are compared with theoretical predictions<sup>1</sup>.

### Materials

For this work two polymers were investigated, both are commercial products: poly(methyl methacrylate) manufactured by Montedison (PMMA, Vedril) and a polystyrene manufactured by DuPont (PS, Lacqrene 1531). PMMA was available as cast sheets, whilst PS was only available as pellets. The specimens were dumbbell shaped with standardized dimensions (see *Table 1*). For PMMA it was possible to mechanically machine the cast sheet in order to obtain the right shape and dimensions. However, the PS had been produced as sheets by compression moulding at 8 tons/inch<sup>2</sup> and 180°C, and this was followed

**Table 1** Geometrical data of the specimens

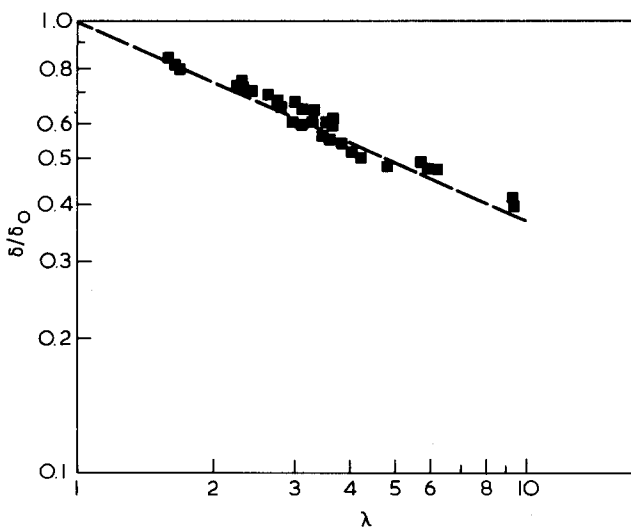
Material	Width (cm)	Length (cm)	Thickness (cm)
PMMA	1.40	12 and 16	0.20
PS	1.35	12 and 16	0.25

by annealing under pressure and slow pressure discharge. This was necessary in order to avoid any orientation (or frozen stresses) in the specimen. The pre-experimental stress-free state of all the samples was tested using a dark field polarization microscope.

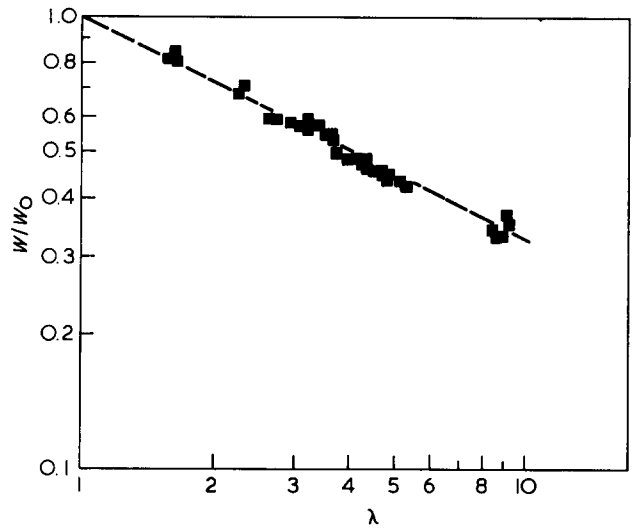
*Experimental procedure*

The materials were uniaxially stretched using a tensile Instron machine equipped with a thermostatically controlled chamber set at 140°C (for PMMA) and 125°C (for PS). Two crosshead speeds were used (100 cm min<sup>-1</sup> and 10 cm min<sup>-1</sup>). The experiment consisted of two parts: first after the specimen had reached the correct temperature, it was stretched for a fixed length of time, after the crosshead was stopped, the subsequent relaxation of the total force was recorded. At the end of the test the specimen was quickly quenched to room temperature. In order to attain the real draw ratio λ (final length/initial length) ink marks were drawn on the specimen. The initial distance between successive marks was 1 mm, after the elongation the final distance was measured and thereafter the real draw ratio was calculated. In the central part of the samples the spread of λ was contained within 10% (in the worst situation).

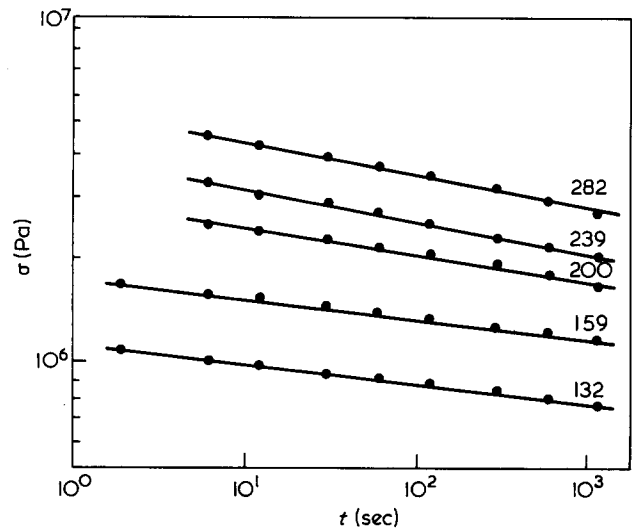
The width and the thickness of the cold specimens were measured; in order to verify the assumption of uniaxiality of elongation. The incompressibility of the material, and the uniaxial tension imply that both the ratios between the final and initial widths, and the final and initial thicknesses have to vary inversely proportionally as the square root of the draw ratio λ. All the samples were in good agreement with the assumption of uniaxial stretch. In Figures 1 and 2 typical plots of the ratios defined above are reported for the particular case of PS elongated at a crosshead velocity of 100 cm min<sup>-1</sup>. The experimental data fit well with the theoretical line (slope -0.5).



**Figure 1** Thickness ratio vs. drawing ratio for PS. Full line has -0.5 slope



**Figure 2** Width ratio vs. drawing ratio for PS. Full line has -0.5 slope



**Figure 3** Stress relaxation vs. time at different draw ratios for PMMA

*Experimental results*

The true stress exhibited by PMMA and PS has been obtained from the relationship:

$$\sigma(t) = \frac{F(t)}{S_0} \lambda \tag{2}$$

where  $F(t)$  is the total force recorded during the relaxation experiment,  $S_0$  is the initial area of cross section, and  $\lambda$  is the draw ratio. The relaxation was recorded for about 1000 s, and values of  $\lambda$  ranging from about 1.3 to 4 were used for PMMA (Figures 3 and 4). It was impossible to obtain higher values of  $\lambda$  because the specimens broke during the stretch. However, for polystyrene it was possible to obtain a wide range of  $\lambda$  starting from about 1.2 to about 7 (Figure 5). A log-log plot of the results show a linear decay and the resulting straight lines are very nearly parallel to each other.

It must be recalled that a stress relaxation experiment in principle requires the instantaneous application of the deformation. From a practical point of view, we applied the initial deformation in a finite time that is controlled by the crosshead speed of the tensile machine. Therefore at

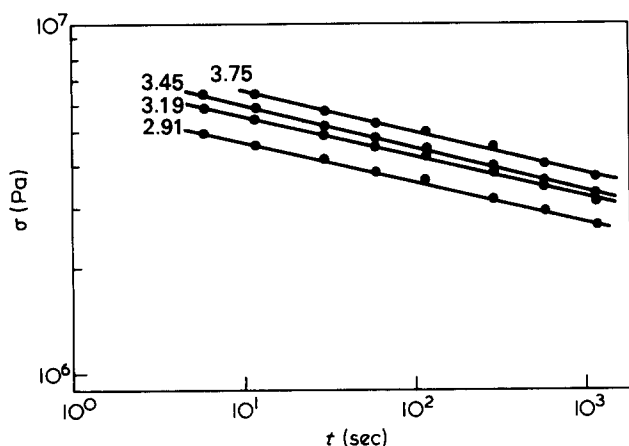


Figure 4 Stress relaxation vs. time at different draw ratios for PMMA

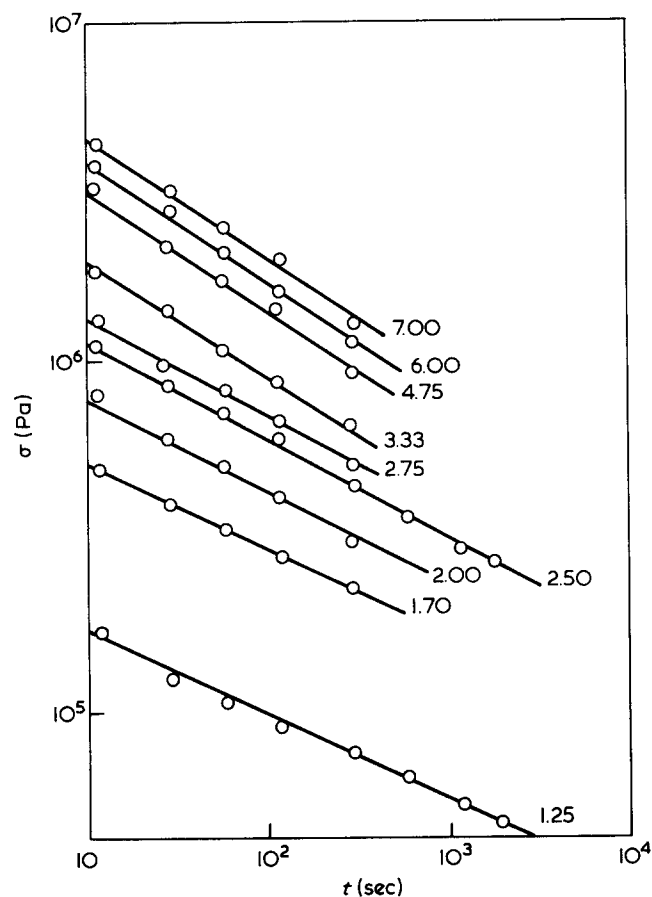


Figure 5 Stress relaxation vs. time at different draw ratios for PS

high draw ratios and short times the rate of deformation starts to be of some influence. This is revealed in our investigations by the spread in linearity and parallelism of the stress relaxation curves. The situation is, of course, more severe for the case of the lowest value of the cross head speed (i.e.  $10 \text{ cm min}^{-1}$ ): the linearity appears only at very high times for the largest values of  $\lambda$  and therefore the results cannot be used for the present study. In the following discussion we will refer only to data obtained at  $100 \text{ cm min}^{-1}$ .

## RESULTS AND DISCUSSION

In principle the stress relaxation of polymers depends

both on time and on the applied deformation (i.e. the draw ratio  $\lambda$ ). Very often it is possible to factorize, in two terms this dependency: assuming that the stress depends on the product of two separate functions of time and deformation respectively. Thus:

$$\sigma(t, \lambda) = G(t) \cdot f(\lambda) \quad (3)$$

$G(t)$  coincides with the relaxation modulus if  $f(\lambda)$  is properly defined. It should be noted that  $f(\lambda)$  depends on the model used. For instance the classical rubber elasticity theory<sup>3</sup> would require (for the case of uniaxial tension) that:

$$f(\lambda) = \lambda^2 - \lambda^{-1} \quad (4)$$

However, equation (3) coincides with classical linear viscoelasticity<sup>4</sup> in the range of small deformations, if  $f(\lambda)$  is assumed to be proportional to the strain. Further, it is also obvious that in equation (3), we refer to an idealized experiment in which the time required to apply the given deformation is zero. This implies the absence of a deformation rate dependence.

In order to theoretically interpret our data, we first verified if the separability of time and the applied deformation effects was valid i.e. equation (3). We therefore plotted isochronous values of the modulus  $G(t)$  versus the draw ratio  $\lambda$  at different times. The results are shown in Figures 6 and 7. It appears that it is possible to assume that separability occurs five minutes after relaxation, for both the materials tested. Finally, the stress is plotted versus the draw ratio  $\lambda$  at a given time (300 s for PS and 20 min for PMMA). The relative plots are shown in Figures 8 and 9. A comparison between the two materials shows a higher value for PMMA than that for PS (at a relaxing time that is four times larger). This was expected due to the larger 'rubber-like' nature of PMMA compared with PS. Further the values of  $G$  obtained from the data (see Figures 8 and 9) are  $1.122 \times 10^5 \text{ Pa}$  and  $5.964 \times 10^5 \text{ Pa}$  for PS and PMMA respectively; these values are in agreement with the values found in current literature.

Finally, we tried to find the expression of  $f(\lambda)$  enabling correlation of our data, by plotting the experimental value

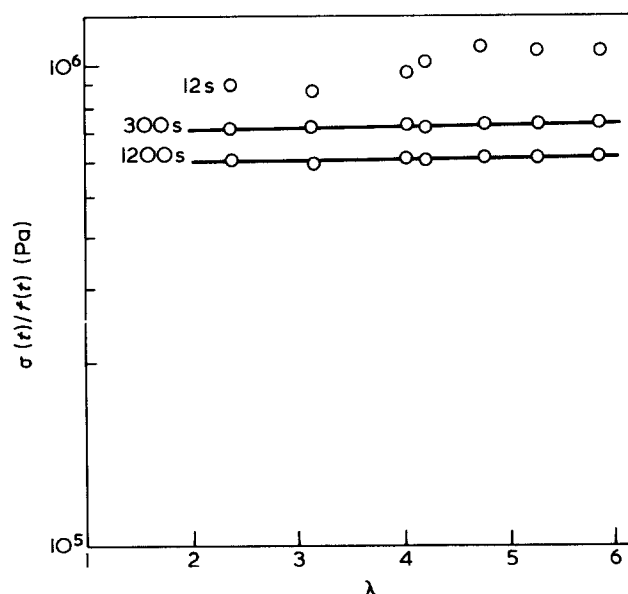


Figure 6 Stress relaxation modulus vs. draw ratio for PMMA at different times

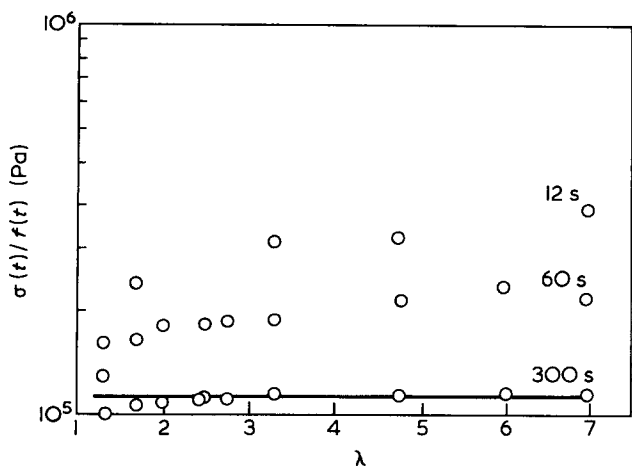


Figure 7 Stress relaxation modulus vs. draw ratio for PS at different times

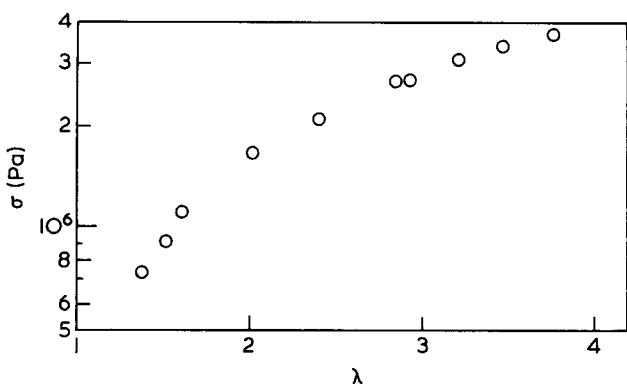


Figure 8 Stress vs. draw ratio for PMMA after 1200 s of relaxation

of the ratio between the stress and the modulus *versus*  $\lambda$ . No significant difference between the two tested materials was found. This was not completely unexpected and to some extent confirms the idea of substantially amorphous polymer behaviour. Therefore the only real difference is a scaling factor modifying the value of the modulus.

As discussed above, attention was focused on the reptation model. It can be used very successfully to describe the viscoelastic behaviour of polymers and concentrated solutions of macromolecules<sup>1,2,5</sup>. A modification of the original model has been used in previous work<sup>1</sup> in order to interpret the stress relaxation of PMMA. The main object was how to obtain an expression for  $f(\lambda)$ , which was able to correlate the polymer melts data. A fit could only be obtained with the original model for the lower range of the draw ratio. In ref. 1 it is assumed that the tube-like region in which the polymeric chain becomes trapped, deforms affinely to the applied deformation. An approximate expression can then be derived for the case of uniaxial tension

$$f(\lambda) = \frac{\lambda^2 - \lambda^{-1}}{\sqrt{(\lambda^2 - 2\lambda^{-1})/3}} \quad (5)$$

In Figure 10 a comparison is shown between experimental values of  $f(\lambda)$  and the corresponding theoretical predictions. The average fitting is very good in all the tested range of draw ratios.

## CONCLUSIONS

The results obtained from the work presented in this paper seem to confirm the applicability of a 'topological constant volume' (introduced in ref. 1). However, this means that the assumption of a constant equilibrium tension<sup>2</sup>, is not applicable for amorphous polymer melts in the large deformation range. It should be recalled that in the small deformation range there is no difference between the two hypotheses. From the data presented in current literature, it would appear that the assumption of constant equilibrium tension, can only be applied successfully to concentrated solutions of polymers.

An attempt to treat the two contrasting assumptions as limiting cases of a more general theory, have been presented<sup>5</sup>. In principle the introduction of a constitutive parameter should enable distinction to be made between different systems (melts and concentrated solutions). It has been noticed<sup>5</sup>, that this parameter is not sensitive enough to discriminate between systems which (as in the case presented here) are not very different. At this stage of the development of the theory it is only possible to

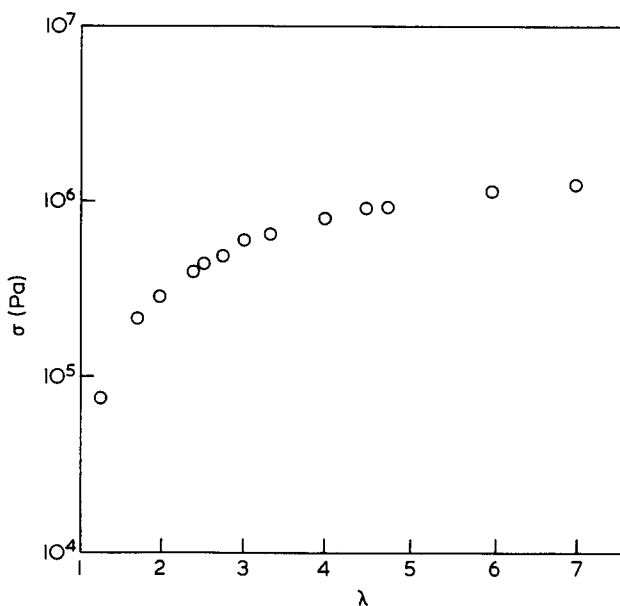


Figure 9 Stress vs. draw ratio for PS after 300 s of relaxation

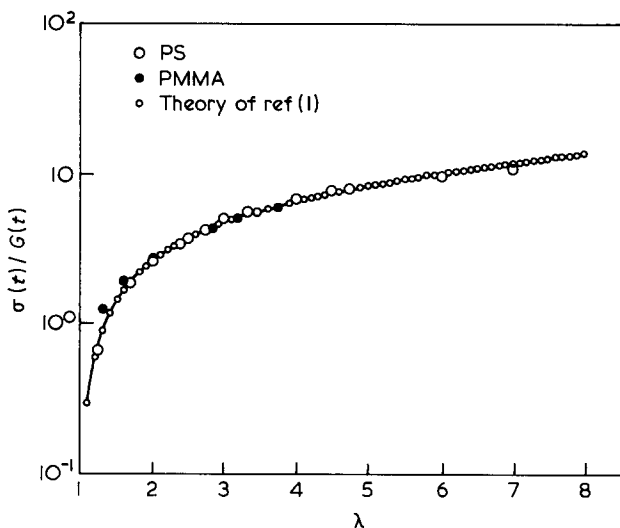


Figure 10  $f(\lambda)$  vs. draw ratio

discriminate between amorphous polymers and concentrated solutions, but not between different concentrations or different polymers. It has been suggested<sup>5</sup> that at higher deformation levels, these differences should be more relevant. However, we should remark that, somewhat unexpectedly, increasing the deformation values ( $\lambda \sim 7$ ), it was possible to obtain a good fit with a simple modification of ref. 1.

A more thorough theoretical study is necessary, in order to clarify the fit obtained, in view of the fact that the theoretical modification of ref. 1, is less consistent at high deformations where it diverges.

In conclusion, the data presented here, supports the modification of the original reptation model (for amorphous polymers) proposed in ref. 1.

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