polymer papers

Orientation of polystyrene chains stretched above T_g as studied by fluorescence polarization

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Fluorescence polarization has been used to measure the orientation of polystyrene chains labelled by an anthracene group covalently bound in the middle of the chains and dispersed in atactic uncrosslinked polystyreme. Stretching is performed at constant strain rate and various temperatures above T_g using equipment which is described. The influence of strain rate and temperature on chain orientation is reported and leads to the conclusion that the orientation of the central part of the labelled chains is not related to the complete stress but is governed by the rubbery deformation. The occurrence of relaxation phenomena during stretching is demonstrated.

Keywords Fluorescence polarization; molecular orientation; stretched polymers; chain relaxation; stress–strain curves; polystyrene elongation

INTRODUCTION

The fluorescence polarization technique provides a means of measuring molecular orientation in stretched polymers[1] and yields second and fourth moments of the orientation distribution function. Several amorphous or semicrystalline polymers have been studied in this way using small fluorescent probes incorporated in the polymer matrix[2-4]. More recently, the fluorescence polarization technique has been extended[5] to oriented polymers in which molecular motions occur during the lifetime of the excited state. In such a case, a mean value of the motion amplitude can be obtained in addition to the second moment of the orientation distribution function. Particular optical equipment described elsewhere[6] is required for such measurements. The first studies have been performed on crosslinked elastomers[7] during stretching experiments.

It was of great interest to enlarge such measurements to uncrosslinked amorphous polymers stretched above T_g. For this purpose, it was necessary to develop a special stretching machine operating at constant strain rate and a very finely regulated oven. In the present paper, this apparatus will be described in the experimental part and orientation of atactic polystyrene during uniaxial stretching will be discussed as a function of strain rate and temperature in the second part. In order to get better information on chain orientation, instead of using fluorescent probes, a few polymer chains have been labelled by a fluorescent molecule.

EXPERIMENTAL

Sample preparation

The fluorescence polarization technique can be applied to polymers by incorporating 0.5–1% of fluorescent labelled chains in the material. Such labelled polymers have been synthesized in our laboratory[8] by the following procedure: monofunctional living anionic chains of polystyrene were deactivated by 9,10-bis(bromomethyl)anthracene such that the resultant polymer contained a centrally located fluorescent group in which the transition moment for absorption and emission is oriented along the local chain axis.

Anthracene-labelled polystyrene chains (called PAP) ($\bar{M}_n = 287\,000$) were mixed in a 10% solution in toluene with normal narrow disperse polystyrene (PS 200, $M_n = 191\,000$, $M_w = 207\,000$).* The mixture is dried in vacuum at 140°C in order to remove any solvent. The dried polystyrene is moulded under pressure and annealed to obtain transparent bubbleless samples and to avoid any birefringence. Sample size is 8 cm length, 2 cm width and 0.2 cm thickness. T_g of the resultant polymer blend, obtained using a Dupont 1090 Analyser differential scanning calorimeter at a heating rate 10°C min^{-1} is 107.5°C.

Fluorescence polarization equipment

The theory of fluorescence polarization, with the restricting assumption of uniaxial symmetry, has already

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been reported in a previous paper[5] and the particular optical equipment described in ref. 6 has been used to measure the orientation during stretching. Reference should be made there for further details. In the temperature range of the experiments, no molecular motion of labelled polystyrene chains occurs during the lifetime of the excited state (10^{-8} s), so that the second and fourth moments of the orientation distribution function can be derived. Hereafter, only the second moment will be considered

$$\overline{P_2(\cos\theta)} = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle$$

in which θ represents for one fluorophore the angle between the transition moment direction and the stretching axis, the brackets meaning an average over all the fluorescent molecules.

Stretching machine

The stretching machine represented in *Figure 1* has been designed and set up in our laboratory. The deformation is obtained by a double hydraulic plunger operating with a pump connected to a manometer, a pressure accumulator and a servovalve controlling the plunger displacement. The driving gear of the servovalve is essentially made up of a linear programmed electronic ramp receiving the required stretching conditions. At any time the signal delivered by a displacement collector is taken by a logarithmic amplifier and compared to the signal given by the ramp: the difference operates on the servovalve.

A stress sensor has also been fitted to this apparatus and allows recording of the stress during stretching. The stress range runs from 20 to 2000 N with a resolution of 0.1 N. This machine is able to perform stretching at constant strain rate $\dot{\varepsilon}$ (in a range from 2×10^{-3} to $2\times10^{-1}\,\mathrm{s}^{-1}$) up to 600% deformation for a sample of 6 cm length between jaws.

Temperature-controlled chamber

The study of a polymer in the glass transition zone and above T_g requires good thermal homogeneity all along the stretching axis.

The vertical form of the oven impedes temperature homogeneity. The selected procedure is the following. Prewarmed air is blown into the oven through small holes in pipes, bringing horizontal homogeneity but an upward gradient. Vertical homogeneity is achieved, first, by rapid air circulation generated by a centrifuged electric fan and, secondly, by additional heating resistances located in the downward part of the air circulation. Temperature regulation is obtained through these resistances.

Such an oven can be regulated from room temperature up to 150°C. The temperature is controlled within ±0.02°C and is homogeneous along the stretching axis to at least 0.033°C. The main advantage of this equipment is the ability to get information about the molecular orientation, through fluorescence polarization measurements at every moment during the stretching at a given temperature and strain rate. The experiments have been performed in a temperature range from 116.5° to 135°C, and three different strain rates (0.029, 0.058 and $0.115\,\mathrm{s}^{-1}$) were used. The draw ratio was defined as $\lambda = l/l_0$ (l_0 is the initial length of the sample, l is the length after drawing).

Shrinking experiments

The deformed samples, with different initial draw ratio λ up to 6.0, were allowed to shrink at a temperature of 120°C for 24 h. Even at the highest temperature, the largest deformed samples returned to very nearly within less than 2% of their initial length.

RESULTS

In the following, the stress has to be understood as the nominal stress defined by $\sigma = F/S_0$ where F is the tensile strength and S_0 the initial section of the sample.

A typical example of stress–strain and orientation–strain curves is given in *Figure 2*. In this temperature range, polystyrene samples undergo a homogeneous deformation. The stress–strain curves show two main regions. The first, at small extension ratio, is characterized by a rapid increase of stress and is attributed to the glassy deformation. The second, at higher extension ratio, in

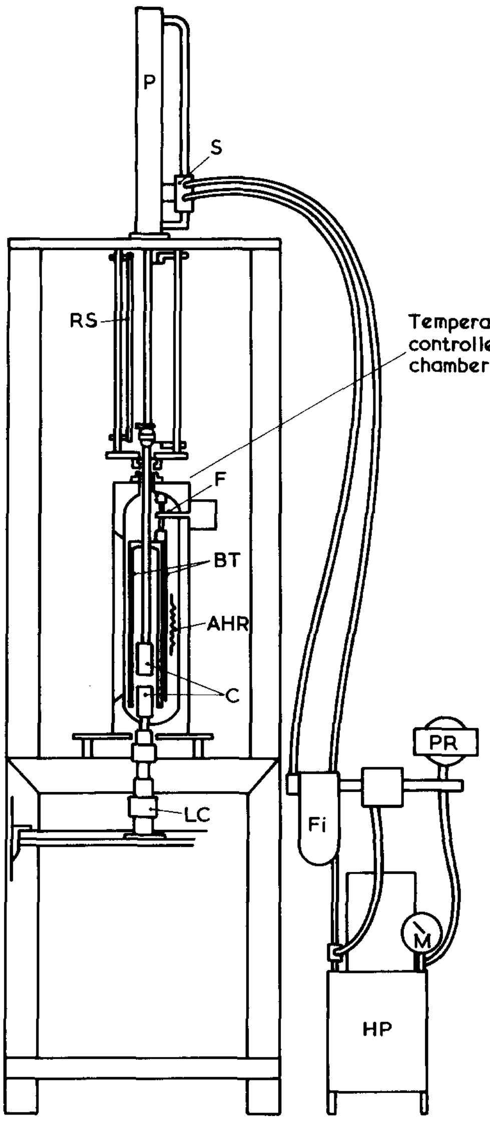

Figure 1 Stretching machine and temperature-controlled chamber: P, double hydraulic plunger; S, servovalve; RS, resisting sensor; C, clamps; PR, pressure reservoir; M, manometer; HP, hydraulic pump; LC, load cell; F, fan; BT, blowing tubes; AHR, additional heating resistances; Fi, filter

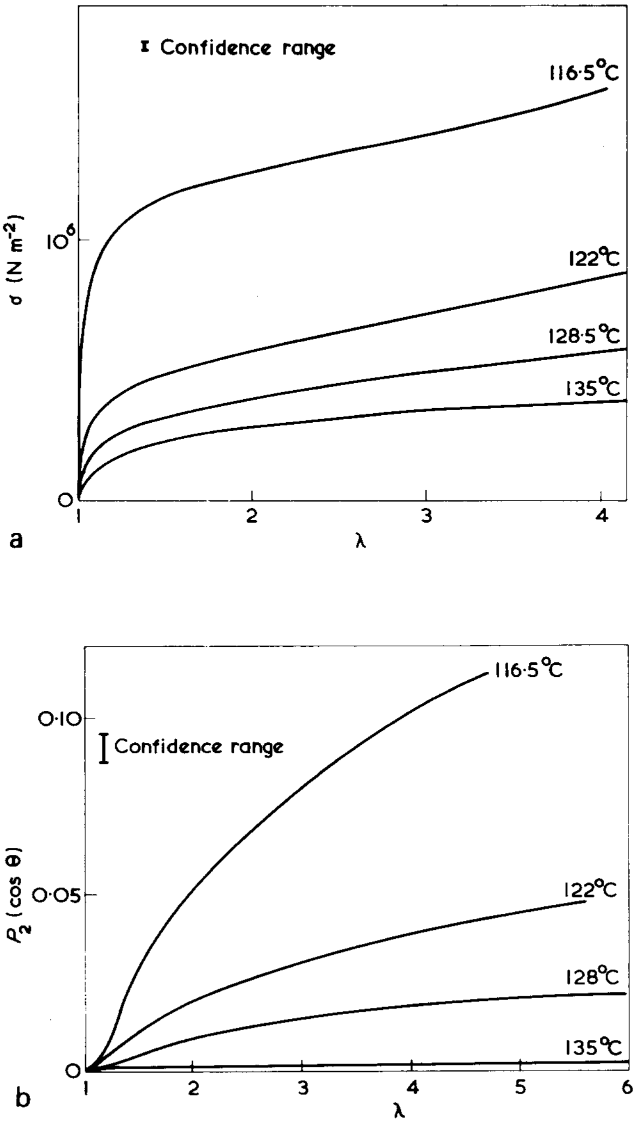

Figure 2 (a) Stress and (b) second moment *versus* elongation as a function of temperature. Strain rate, 0.115 s^{-1}

which the stress increases slowly with the deformation, reflects a rubber-like deformation, with a possible contribution from flow. In contrast, orientation curves, in which the second moment of the orientation distribution is plotted against the extension ratio λ, show a regular increase of orientation during stretching.

The influence of temperature appears clearly on these two plots. It can be seen that, at a given strain rate, the first part of the stress–strain curve is very sensitive to temperature whereas the slope of the second part decreases as temperature rises. It can also be noted that the orientation falls continuously and at 135°C is too low to be measurable.

Figure 3 shows the behaviour of stress and orientation at T_g+9°C for various strain rates. It is clearly seen that only the first part of the stress–strain curve is affected by the strain rate, but the orientation is not modified within the accuracy of our experiments. Comparison with *Figure 4* shows that at a higher temperature, at $T_g+14.5$°C, both the stress reflecting the rubber-like behaviour and the orientation are functions of the strain rate.

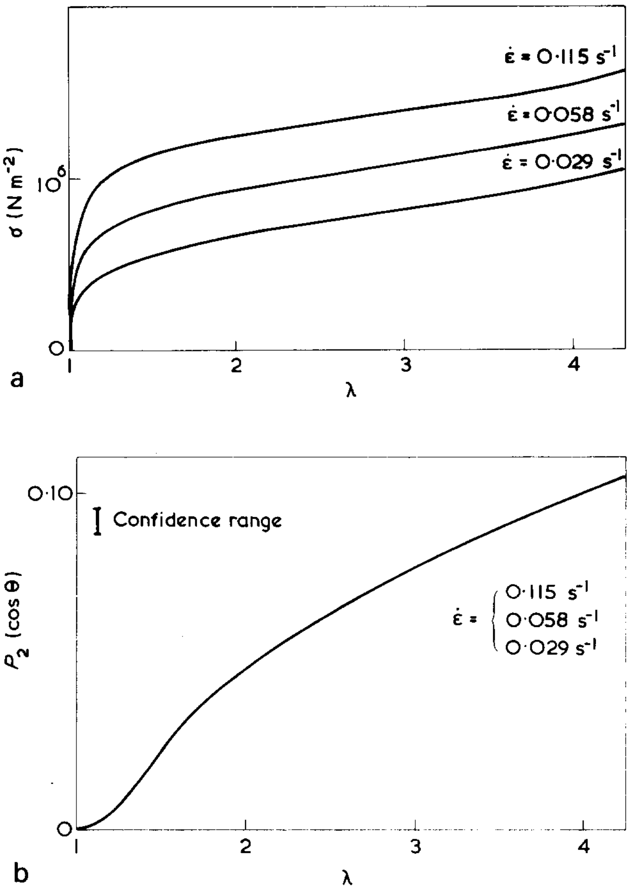

Figure 3 (a) Stress and (b) second moment *versus* draw ratio as a function of strain rate. Stretching temperature, 116.5°C

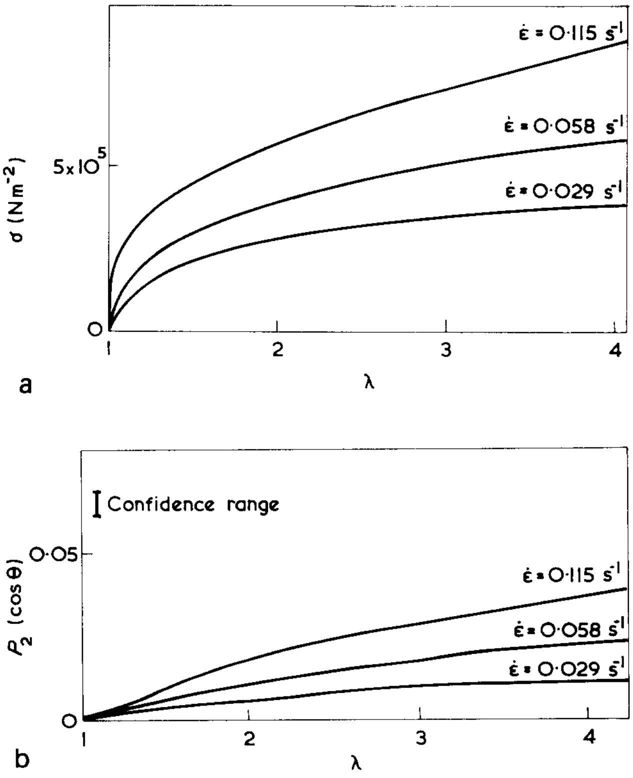

Figure 4 (a) Stress and (b) second moment *versus* draw ratio as a function of strain rate. Stretching temperature, 122°C

DISCUSSION

First, it must be noted that the orientation given by our fluorescence polarization measurements refers to the anthracene group, the transition moment of which lies along the chain axis and is located in the middle of the chain. This particular position implies that the measured orientation reflects the orientational behaviour of statistical chain segments of the central part of the chain. It seems difficult to state the size of this central part precisely. Owing to the molecular weight of the labelled chain ($M_n = 287\,000$), it is reasonable to assume that the orientation of the chain-end segments is not taken into account by this method.

Comparison between *Figures 2a* and *2b* seems to indicate that orientation does not originate from the glassy part of the stress but is related to the rubber-like component. At a given temperature, the slope of the rubbery part of the stress–strain curve and its dependence on the strain rate governs the orientation behaviour. The shrinking experiments show that, within our experimental conditions (strain rate, temperature, molecular weight), the contribution of the terminal flow zone is negligible.

Thus, in our experiments, the orientation observed through fluorescence polarization is not directly related to the complete true stress, but depends on the deformation in the rubbery plateau zone. This result is rather different from that which is obtained with birefringence measurements in which stress and orientation are related through a constant coefficient. Also, infra-red dichroism measurements performed in our laboratory with films issued from the same polystyrene batch lead to the conclusion that stress and orientation obtained by i.r. dichroism are identical[9]. Such a discrepancy could originate from the fact that birefringence as well as i.r. dichroism measurements reflect an average over all the chain segments, whereas in our case the fluorescence polarization measurements are only sensitive to the central part of the chain.

From results presented in *Figures 2b* and *4b* it can also be noted that an increase in temperature may have the same effect on orientation as a decrease of strain rate, so that time and temperature seem to affect the system in the same way. Such a behaviour must be attributed at a molecular level to the participation of relaxation phenomena during stretching. At the present stage it is not possible to evaluate precisely the relaxation times. In fact, according to the Doi–Edwards model[10,11], the relaxation of the chain in a step strain experiment is described through three different relaxation processes, each one occurring in a different time scale. At short times a local re-equilibration of the strength is predicted (state A), followed by a retraction of the chain inside its deformed tube in order to equilibrate the stretch along itself and to recover the equilibrium curvilinear monomer density (stage B). Then, the chain disengages itself from the original deformed tube by a reptation process in order to reach the isotropic configuration (stage C).

Within our experimental conditions, the deformation is recoverable by an annealing treatment above T_g. Thus it means that the disengagement time is not reached. The first relaxation motion does not create a change in the orientation since the vector joining to consecutive entanglement points of the labelled chain is not affected. Hence, the relaxation motion observed should be the shrinking of the chain into its deformed tube.

From our experiments we can only get an order of magnitude of the involved relaxation time. It has been shown that, at $T_g + 9$°C, orientation does not depend on the strain rate. This means that the relaxation mechanism which affects the central part of the chain has a characteristic time which is longer than the longest stretching time (i.e. 60 s for a 600% deformation). By increasing the temperature, relaxation times decrease and chain relaxation mechanisms can take place during stretching; this happens at $T_g + 14.5$°C.

Further developments like the influence on the orientation of a labelled chain of molecular parameters such as the molecular weights of the labelled chain or of the matrix are presently in progress in our laboratory.

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