Orientation and relaxation in uniaxially stretched atactic polystyrene

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Infra-red measurements of the dichroic ratio of atactic polystyrene absorption bands provide a valuable method of determination of orientation as well as relaxation of chains during stretching. Different strain rates and temperatures of stretching were used. Orientation relaxation was analysed using Lodge's constitutive equation and a master curve was obtained at a reference temperature $T_0 = 115°C$. Orientation relaxation behaves similarly to mechanical relaxation and a scaling factor of 3.6×10^{-8} m^2 N^{-1} holds between the two sets of results.

Keywords Orientation; relaxation; polystyrene; infra-red dichroism; birefringence; Fourier transform infra-red spectroscopy

INTRODUCTION

Molecular orientation is commonly used to improve the properties of polymeric materials. Thus there is a great deal of interest in knowledge at the molecular level of the phenomena occurring during stretching or any forming process. Several techniques have been proposed to measure orientation[1,2]: X-ray scattering, sonic modulus, broad-line n.m.r., polarized fluorescence and Raman spectroscopy, u.v. and visible birefringence and infra-red spectroscopy. Among all these techniques, vibrational spectroscopy represents a very valuable tool to get an insight into the processes occurring at the molecular level.

The present work deals with the influence of experimental conditions of stretching (temperature, strain rate, molecular weight) on orientation and relaxation in uniaxially stretched polystyrene (PS), using Fourier transform infra-red spectroscopy (*FT*i.r.). In addition orientational relaxation will be compared to mechanical relaxation.

EXPERIMENTAL

Three different PS samples were used: a commercial atactic and two monodisperse anionic polymers. Their characteristics are given in *Table 1*.

Sample preparation

Thin films suitable for infra-red spectroscopy were obtained by casting a 6% chloroform solution of PS on a glass plate. Subsequent annealing was done under vacuum for 24 h at 145°C, in order to remove any trace of solvent and internal stress. Samples for mechanical measurements (thickness: 1 to 2 mm) were compression moulded at 165°C and annealed for 4 h at 145°C.

Oriented samples from thin films were obtained on an apparatus developed in our laboratory[3], i.e. a stretching machine operating at constant strain rate and a special oven to obtain a very good stability of the temperature all over the sample (homogeneity is ~0.05°C). The same machine was used for mechanical extension and stress relaxation.

Infra-red dichroism

The polarized spectra were recorded using a Nicolet 7199 Fourier transform infra-red spectrometer. Single beam spectra were run and the absorbance calculated using the computer facility and a stored polarizer spectrum as reference. A gold wire-grid Perkin–Elmer polarizer set at a maximum transmission position was used and the samples rather than the polarizer were rotated 90° in order to obtain the two polarization measurements. Thirty-two co-added interferograms were scanned at 2 cm^{-1} resolution. Infra-red dichroism was calculated as $R = A_{\parallel}/A_{\perp}$ for $A_{\parallel}$ and $A_{\perp}$ the peak optical densities. Baseline determination was as in ref. 4.

Dynamic shear

A Rheometrics Weissenberg-type Rheometer RMS 605 fitted with a cone–plate system (25 mm diameter; angle 0.115 rad) was used. The frequency range was 10^{-2} to 10^{+2} rad s^{-1}.

RESULTS AND DISCUSSION

Orientation behaviour

Dichroic ratio measurements allow one to calculate the second-order moment of the orientation function according to the relation:

$$\langle P_2(\cos\theta)\rangle_{av} = \tfrac{1}{2}(3\langle\cos^2\theta\rangle_{av} - 1) = \frac{R-1}{R+2}\,\frac{R_0+2}{R_0-1}$$

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Table 1 Characteristics of PS samples

Polymer	M_n	M_w	M_w/M_n	T_g (°C)	Origin
PS 1	149 800	254 800	1.70	105	CdF Chimie C⁰
PS 100	105 000	118 000	1.12	105	EAHP*
PS 900	891 000	999 000	1.12	105	EAHP

* EAHP: Ecole d'Application des Hauts Polymères, Strasbourg, France

with $R_0 = 2\cot^2\alpha$ where α is the angle between the dipole moment vector of the considered vibration and the chain axis and θ is the angle between the chain axis and the draw direction[1]. The choice of chain axis and absorption bands suitable to measure orientation in PS has been discussed previously[4]. Similarly, the 1028 cm^{-1} and 906 cm^{-1} absorption bands were used.

Let us consider the polydisperse sample PS 1. *Figure 1* illustrates the change of the second-order moment of the orientation function $\langle P_2(\cos\theta)\rangle_{av}$ as a function of draw ratio $\lambda = l/l_0$ (l_0 is initial length of the sample, l is the length after drawing) for a strain rate $\dot{\varepsilon} = 0.115\ \mathrm{s}^{-1}$ and different stretching temperatures. Up to $\lambda = 3.5$ this change approximates to a straight line, the slope of which decreases with increasing temperatures.

Figure 2 shows the influence of strain rate $\dot{\varepsilon}$ for a stretching temperature of 122°C. Similarly, a linear relationship holds for different strain rates between $\langle P_2(\cos\theta)\rangle_{av}$ *versus* draw ratio. For a given draw ratio, $\langle P_2(\cos\theta)\rangle_{av}$ increases with strain rate. Another way to illustrate the orientation behaviour is to plot the slope $d\langle P_2(\cos\theta)\rangle_{av}/d\lambda$ as a function of T and $\log(1/\dot{\varepsilon})$ as in *Figures 3* and *4*. The choice of $\log(1/\dot{\varepsilon})$ as variable was suggested by the fact that in our experiments, realized at constant strain rate, $1/\dot{\varepsilon}$ is similar to time.

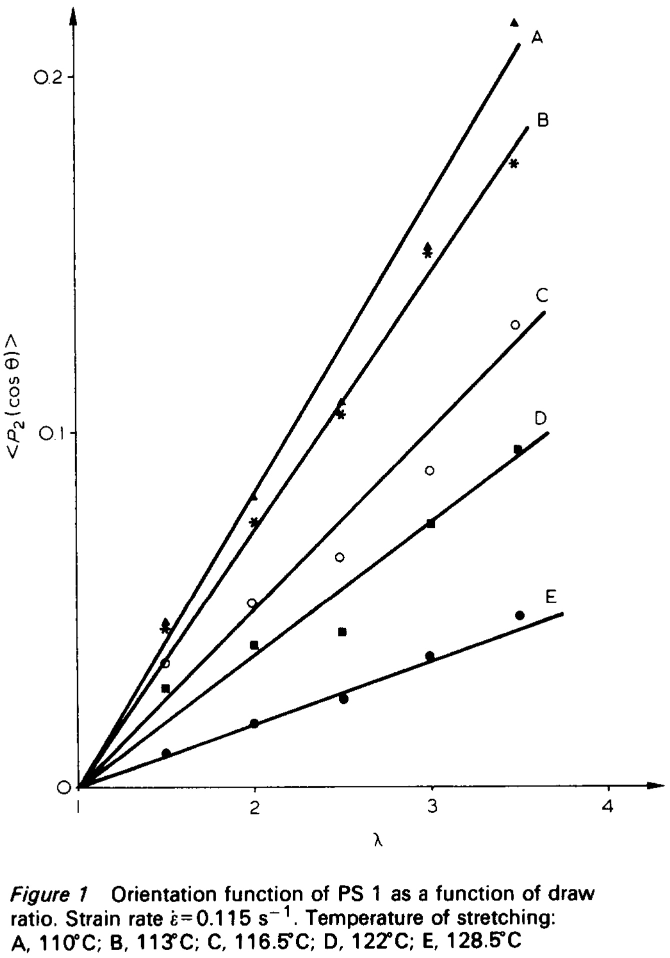

Figure 1 Orientation function of PS 1 as a function of draw ratio. Strain rate $\dot{\varepsilon}$=0.115 s^{-1}. Temperature of stretching: A, 110°C; B, 113°C; C, 116.5°C; D, 122°C; E, 128.5°C

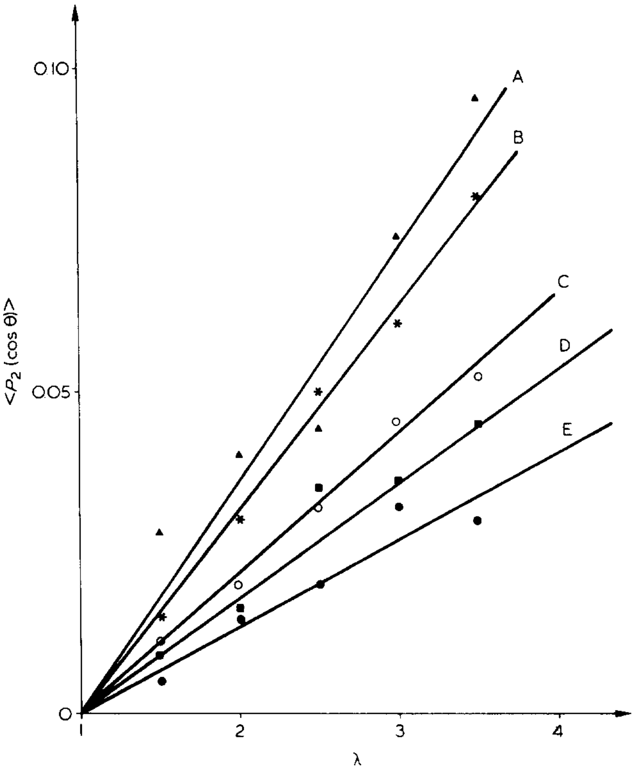

Figure 2 Orientation function of PS 1 as a function of draw ratio. Temperature of stretching T=122°C. Strain rate: A, 0.115 s^{-1}; B, 0.086 s^{-1}; C, 0.059 s^{-1}; D, 0.026 s^{-1}; E, 0.008 s^{-1}

These results suggest that relaxation of orientation occurs during stretching. In order to get a more quantitative analysis of these relaxation phenomena, the results obtained by infra-red dichroism were analysed according to the method developed by Lodge[5] for birefringence. The question is to describe the orientation of a polymer during deformation by a constitutive equation, analogous to stress. Among the different constitutive equations that have been proposed to describe the viscoelastic properties of polymers, we chose the equation corresponding to the Lodge model. In this model, which is the simplest for nonlinear viscoelasticity, an amorphous polymer is considered during deformation as a network of elastic chains, the density of links of which changes with time.

As far as stretching at constant strain rate is concerned, the second-order moment of the orientation function $\langle P_2(\cos\theta)\rangle_{av}$ will be given by the constitutive equation:

$$\langle P_2(\cos\theta)\rangle_{av} = \sum_i \theta_i \left(\frac{3\dot{\varepsilon}\tau_i}{(1-2\dot{\varepsilon}\tau_i)(1+\dot{\varepsilon}\tau_i)} - \frac{2\dot{\varepsilon}\tau_i e^{2\dot{\varepsilon}t} e^{-t/\tau_i}}{1-2\dot{\varepsilon}\tau_i} - \frac{\dot{\varepsilon}\tau_i e^{-\dot{\varepsilon}t} e^{-t/\tau_i}}{1+\dot{\varepsilon}\tau_i} \right)$$

where θ_i and τ_i originate from a decomposition of the orientation relaxation function $\theta(t)$ into a sum of exponentials:

$$\theta(t) = \sum_i \theta_i e^{-t/\tau_i}$$

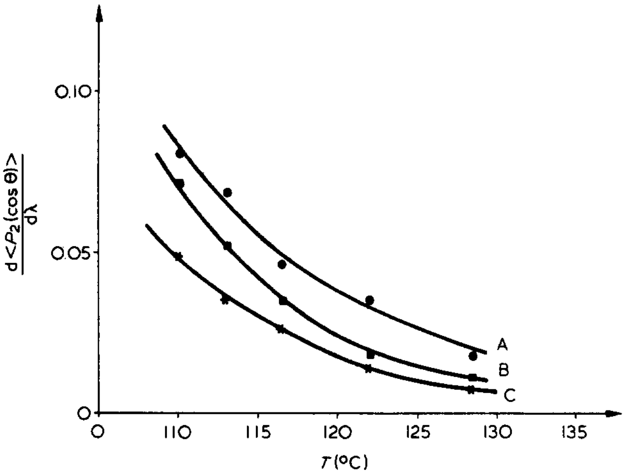

Figure 3 Slope of $\langle P_2(\cos\theta)\rangle = f(\lambda)$ as a function of temperature of stretching. Strain rate: A, 0.115 s^{-1}; B, 0.026 s^{-1}; C, 0.008 s^{-1}

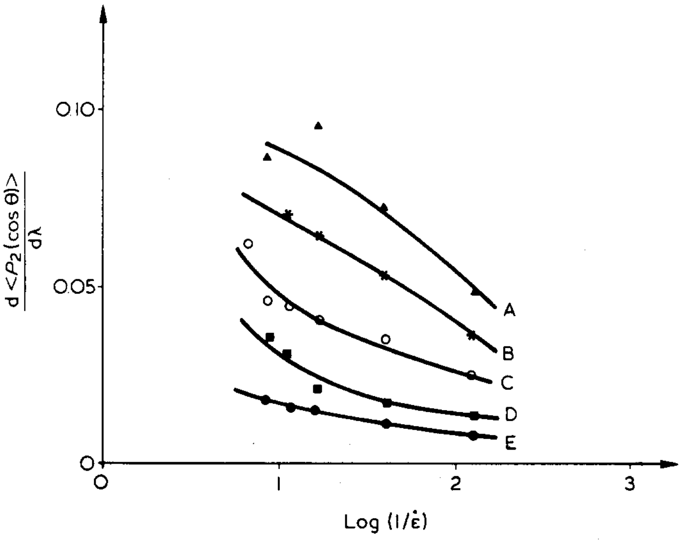

Figure 4 Slope of $\langle P_2(\cos\theta)\rangle = f(\lambda)$ as a function of strain rate. Temperature of stretching: A, 110°C; B, 113°C; C, 116.5°C; D, 122°C; E, 128.5°C

In order to perform the calculation we arbitrarily chose the relaxation function as

$$\theta(t) = \sum_{i=-1}^{+3} \theta_i e^{-t/10^i}$$

For each stretching temperature, five draw ratios and five strain rates have been used to calculate the θ_i. The change of $\log\theta_i$ as a function of $\log t$ for the five temperatures used is shown in *Figure 5*. From these results, it is possible to get a master curve for the orientation relaxation function; curves from *Figure 5* shifted using the WLF coefficients previously obtained by Plazeck[6]

$$\log a_T = -\frac{10.04(T-115)}{62.6+(T-115)}$$

gave the curve shown in *Figure 6* for a reference temperature of 115°C.

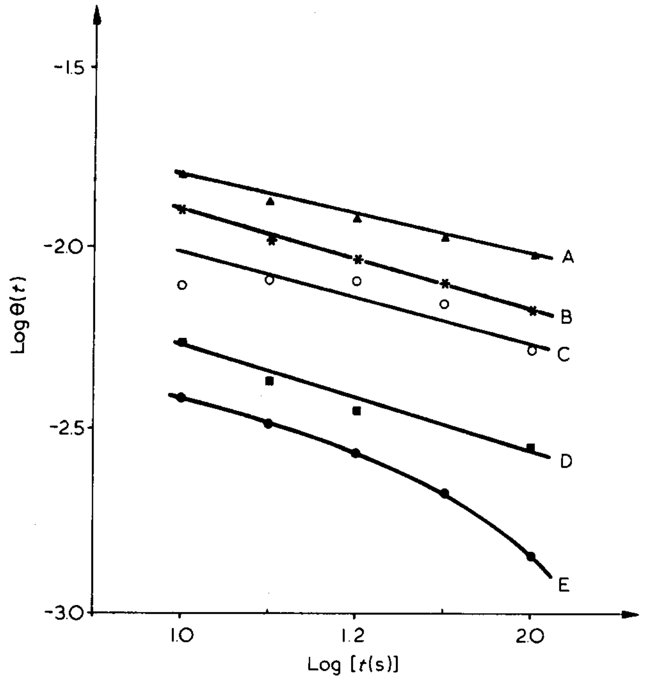

Figure 5 Log $\theta(t)$ vs. log t for PS 1: A, 110°C; B, 113°C; C, 116.5°C; D, 122°C; E, 128.5°C

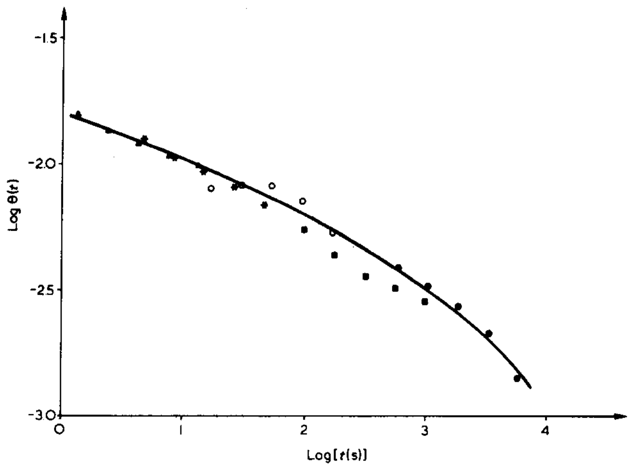

Figure 6 Master curve log $\theta(t)$ vs. log t for PS 1 between 110° and 128.5°C. Reference temperature $T_0 = 115$°C

The influence of PS molecular weight on the change of $d\langle P_2(\cos\theta)\rangle_{av}/d\lambda$ as a function of temperature and strain rate is illustrated in *Figure 7*. For a temperature of stretching close to the glass transition temperature, the two polymers behave in the same way. An increase of temperature results in a greater level of orientation for the higher molecular weight. The corresponding orientation relaxation functions are given in *Figure 8*. Under the experimental conditions used the two samples behave in the same way for short relaxation times. For longer relaxation times, the orientation relaxation function $\theta(t)$ decreases faster for PS 100. The behaviour of the polydisperse sample (PS 1) was found to be similar to PS 100, pointing out the great influence of the low molecular weight chains on the orientation and relaxation of polydisperse PS.

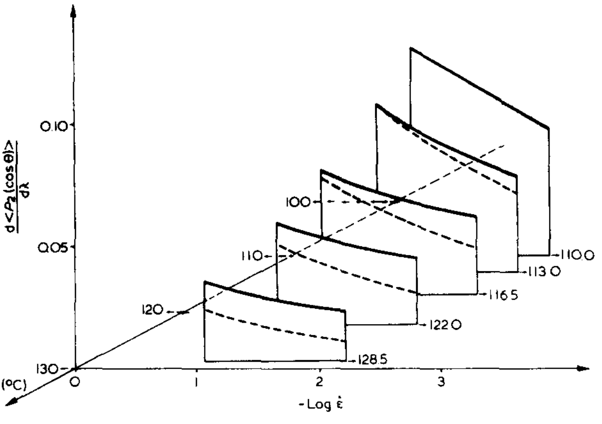

Figure 7 Slope of $\langle P_2(\cos\theta)\rangle = f(\lambda)$ as a function of temperature and strain rate for monodisperse samples: ---, PS 100; ——, PS 900

Mechanical relaxation

On the other hand, it is interesting to compare the orientation relaxation function with the mechanical relaxation modulus. Experiments were made on PS1, using three different techniques:

(a) Dynamic shear experiments allow one to observe the response in phase $G'(\omega)$ and in quadrature of phase $G''(\omega)$ at a dynamic shear oscillation of frequency ω. The relaxation modulus, according to Ninomiya and Ferry[7] is then given, with a good approximation, by:

$$E(t)=G'(\omega)-0.40G''(0.40\omega)+0.014G''(10\omega)|_{\omega=1/t}$$

(b) Stress relaxation also allows one to obtain the relaxation modulus[8-12]:

$$E(t)=\sigma(t)/\lambda^2-\lambda^{-1}$$

σ being the true stress in the drawing direction. Experiments were done using a 70 mm s^{-1} linear speed. In order to consider the initial deformation as a step deformation, a 10–10^3 s time range was used for each temperature.

(c) Extension at constant strain rate $\dot{\varepsilon}$ for which $l=l_0e^{\dot{\varepsilon}t}$ allows one to evaluate the relaxation modulus from the experimental stress–strain curve, using the Lodge constitutive equation[5] written as:

$$\sigma(t)=\sum_i E_i\left(\frac{3\dot{\varepsilon}\tau_i}{(1-2\dot{\varepsilon}\tau_i)(1+\dot{\varepsilon}\tau_i)}-\frac{2\dot{\varepsilon}\tau_i e^{2\dot{\varepsilon}t}e^{-t/\tau_i}}{1-2\dot{\varepsilon}\tau_i}-\frac{\dot{\varepsilon}\tau_i e^{-\dot{\varepsilon}t}e^{-t/\tau_i}}{1+\dot{\varepsilon}\tau_i}\right)$$

the relaxation modulus being a finite sum of exponentials

$$E(t)=\sum_i E_i e^{-t/\tau_i}$$

Calculation was made as described before.

Results are shown in *Figure 9*. Reasonable agreement is observed between the three methods. For short relaxation times a rubbery region exists, while for longer relaxation times a decrease of $E(t)$ corresponds to the beginning of the terminal zone. In *Figure 10*, relaxation modulus and orientation relaxation are compared. The two curves are very similar, indicating that the relaxation of the orientation is also linked to the plateau region and the beginning of the terminal zone. Furthermore, a scaling factor $\theta(t)/E(t)=3.6\times10^{-8}\,\mathrm{m^2\,N^{-1}}$ holds between the two sets of results. This factor is similar to the 'stress optical coefficient' or $SOC=\Delta/\sigma=-5200$ Brewster between birefringence (Δ) and stress (σ) measured by Jones[13].

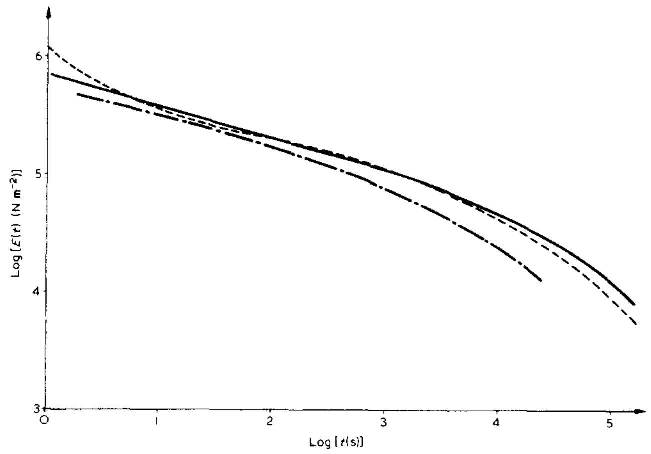

Figure 9 Master curves log $E(t)$ vs. log t for PS 1. Reference temperature T_0=115°C. ---, dynamic shear; ——, tress relaxation; —·—·—, extension at constant strain rate

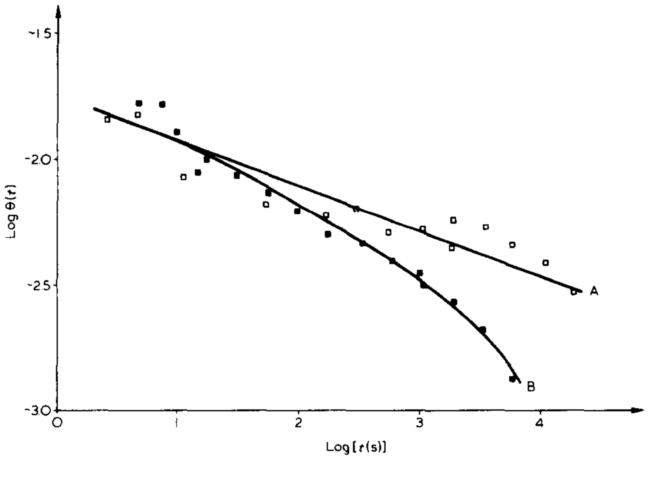

Figure 8 Master curve log $\theta(t)$ vs. log t for monodisperse samples between 110° and 128.5°C. Reference temperature T_0 =115°C. A, PS 900; B, PS 100

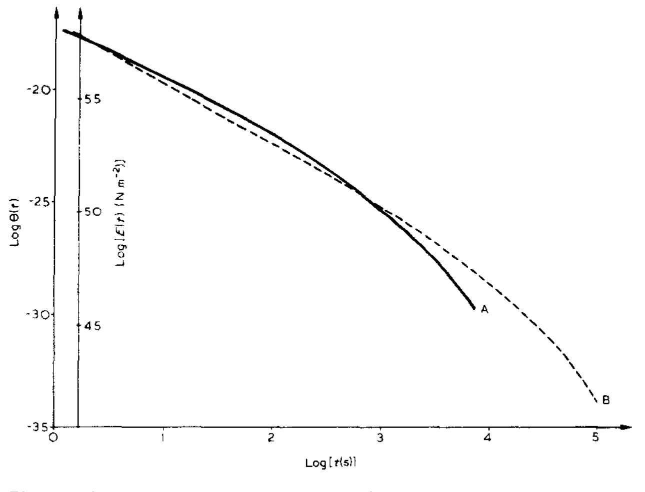

Figure 10 Comparison between log $\theta(t)$ and log $E(t)$ vs. log t for PS 1. Reference temperature T_0=115°C. A, Infra-red orientation relaxation; B, mechanical relaxation

From the relation

$$\Delta = \Delta^\circ \langle P_2(\cos\theta)\rangle_{av}$$

where Δ° represents the intrinsic birefringence[14] of PS ($\Delta^\circ = -0.10 \pm 0.05$), one obtains

$$\langle P_2(\cos\theta)\rangle_{av}/\sigma = \theta(t)/E(t) = 5.2 \times 10^{-8}\,\mathrm{m^2\,N^{-1}}$$

The experimental value of $3.6 \times 10^{-8}\,\mathrm{m^2\,N^{-1}}$ obtained in this work is in reasonable agreement with the *SOC* value, considering the uncertainty on Δ°. This simple relation between second-order moment of the orientation function and stress is explained[13,15,16] by the fact that infra-red as well as birefringence are two techniques measuring the mean orientation of monomer units averaged all over the different chains.

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