Mechanical relaxations in polybutene-1 and poly-4-methylpentene-1

C. L. Choy, W. K. Luk and F. C. Chen
Department of Physics, The Chinese University of Hong Kong, Hong Kong

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Dynamic mechanical measurements between −180°C and 180°C were made on both isotropic and drawn samples of polybutene-1 (PB-1) and poly-4-methylpentene-1 (P4MB1) over a wide frequency range by the use of a torsional pendulum (0.3–3 Hz), a viscoelastic spectrometer (5–90 Hz) and ultrasonic technique (3 MHz). The relaxation peaks were identified and the associated activation energies determined from Arrhenius plots. For PB-1 it was observed that orientation reduces the height and shifts up the temperature of the α_a-peak associated with large scale main-chain motion in the amorphous regions, but has little effect on the β-peak associated with side-group motion. In addition to the α_a and β relaxations a high-temperature crystalline relaxation (α_c) is also observed in P4MP1. For both the α_c and β relaxations the mechanical loss at 45° to the draw direction is much larger than that at 90°, which indicates that shear processes are involved in these relaxations.

INTRODUCTION

Of the series of polyolefins the mechanical relaxations of the first two members only, polyethylene and polypropylene, have been investigated extensively[1-3]. For polybutene-1 (PB-1) and poly-4-methylpentene-1 (P4MP1) dynamic mechanical studies[4-13] have been confined to narrow ranges in either frequency or temperature, which did not allow reliable estimates to be made on the activation energies of the various relaxations. Little work has been done on the effect of thermal treatment or orientation.

In this work we report on dynamic mechanical measurements of PB-1 and P4MP1 between −180°C and 180°C and over a wide range of frequency. A torsional pendulum has been used between 0.3 and 3 Hz while tensile measurements with a viscoelastic spectrometer cover the range of 5 to 90 Hz. Ultrasonic measurements at 3 MHz have also been made by the liquid-tank technique. In the above temperature–frequency range, two and three relaxations have been observed in PB-1 and P4MP1, respectively, and the activation energies for these relaxations have been evaluated. The effect of different degrees of crystallinity and orientation on these relaxations have also been studied. These results will be discussed in detail in later sections.

EXPERIMENTAL

Sample preparation and characterization

The starting material for PB-1 and P4MP1 were obtained in the form of pellets from Scientific Polymer Products Inc. The pellets were compression-moulded above their melting points into sheets of thickness 1–2.5 mm and then either quenched or slow-cooled (0.5°C min^{-1}) to room temperature. Oriented samples were prepared by drawing at 70°C quenched sheets of length 6 cm at a rate of 1 cm min^{-1} on an Instron tensile machine. PB-1 deforms homogeneously, so that a series of draw ratio λ between 1 and 3 can be attained. P4MP1 shows necking behaviour and so samples of only one draw ratio ($\lambda = 6$) were prepared. Since the crystalline phase of PB-1 can exist in a few forms[8,14] the PB-1 samples have been stored for six days at room temperature before measurements were undertaken, so that all the crystalline phase has already converted into a rhombohedric modification.

The densities of the samples of PB-1 were obtained by the flotation method, and their volume fraction crystallinities X were calculated from the observed values, the densities of the amorphous and crystalline phases taken to be 0.871 and 0.952, respectively[14]. Since the densities of the amorphous and crystalline phases of P4MP1 at room temperature differ only slightly[15] the density method is not reliable. Instead, the heats of fusion were measured on a Perkin-Elmer DSC II and the crystallinity calculated by taking the heat of fusion of the pure crystalline phase to be 29 cal g^{-1} (ref 16).

Mechanical measurements

Dynamic torsional measurements between 0.3 and 2.5 Hz were carried out on a torsional pendulum of the inverted type similar to that of Gray and McCrum[17]. Dynamic tensile measurements between 5 and 90 Hz were made on a viscoelastic spectrometer (Iwamoto Seisakusho Ltd). The procedure is standard[1]. Torsional measurements for oriented samples were made only about the draw axis whereas tensile measurements were made at 0°, 45° and 90° to the draw direction.

Ultrasonic measurements at 3 MHz were carried out using a liquid-tank method similar to that of Waterman[18]. The procedure has been discussed in detail previously[19]. Two piezoelectric ceramic transducers, one acting as transmitter and the other as receiver, were bonded to buffer rods which were fixed in a horizontal line. The sample was placed between the rods with its plane normal to the axis of the rods. The free ends of the rods and the sample were immersed in a tank of liquid at a controlled temperature, the liquid being propanol and

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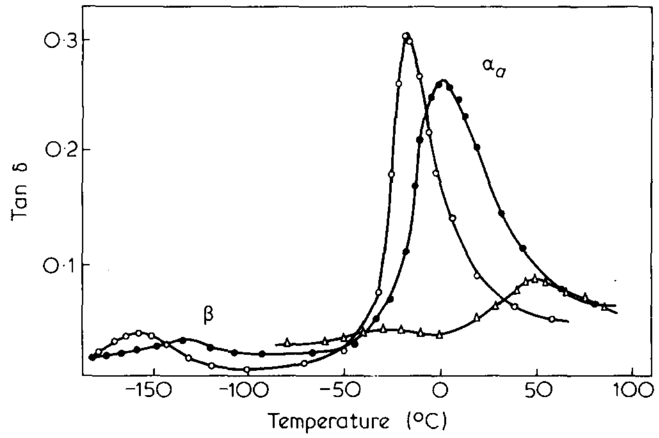

Figure 1 Temperature dependence of the loss tangent of PB-1. ○, 0.3 Hz torsional; ●, 90 Hz tensile; △, 3 MHz ultrasonic

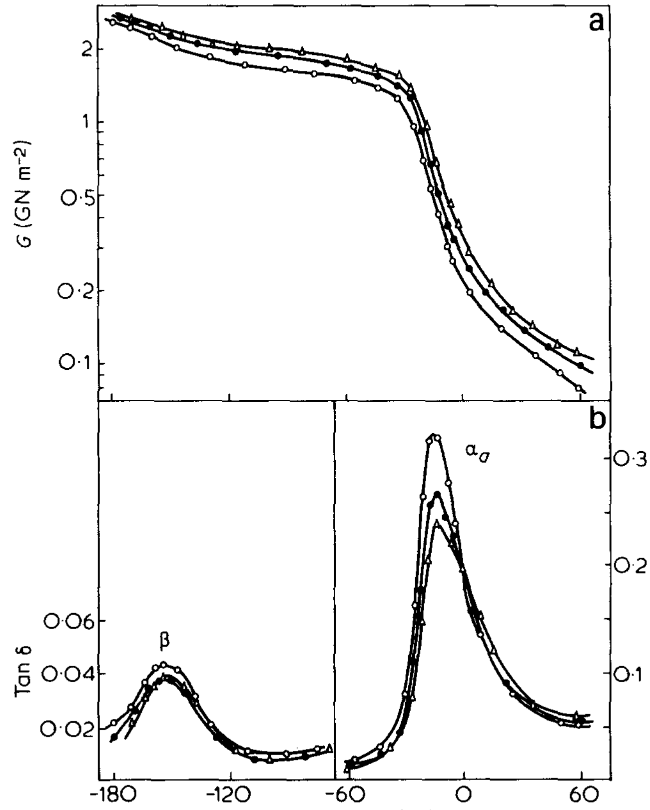

Figure 2 Temperature dependence of (a) the shear modulus *G* and (b) the loss tangent at 1 Hz for three samples of PB-1 with different degree of crystallinity *X*. ○, Quenched (*X* = 0.55); ●, slow-cooled (*X* = 0.6); △, quenched and then annealed at 100°C for 40 h (*X* = 0.66)

silicone oil for temperatures below and above room temperature, respectively. A pulsed 3 MHz longitudinal wave generated by the transmitter passed through the sample at normal incidence and was picked up by the receiver. The received signal and the attenuated driving pulse were observed on a Tektronix 7834 oscilloscope, and the transit time for the ultrasonic pulse to travel from one transducer to the other was measured on a gated interval-counter (Tektronix 7D15). Similar measurement was also made when the sample was removed and from these data the longitudinal wave velocity v and hence the modulus $M = \rho v^2$ were calculated; ρ being the density of the sample.

The attenuation coefficient α of the sample was determined by comparison of the amplitude of a pulse transmitted through the sample with that of the received pulse when the sample was removed. The loss factor $\tan\delta$ was calculated from

$$\tan\delta = \frac{\alpha\lambda'}{\pi}$$

where λ' is the wavelength of the ultrasonic wave in the sample. For oriented samples only the modulus and loss normal to the draw direction were measured.

RESULTS AND DISCUSSION

Polybutene-1

As shown in *Figure 1* PB-1 exhibits two relaxations for both low frequency (torsional and tensile) and ultrasonic measurements, in agreement with previous work[5,13]. The α_a relaxation at $-17°C$ (0.3 Hz) is associated with the micro-Brownian motion of the chain backbone while the β relaxation at $-158°C$ (0.3 Hz) has been attributed to the local motion of frozen side groups[5,13]. Our results are consistent with these assignments, since the α_a peak has a much larger magnitude and it shifts less in temperature than the β peak as frequency increases, indicating a higher activation energy for this relaxation process.

Figure 2 shows that as the crystallinity increases, the height of the α_a peak decreases quite significantly, again giving support to our previous assignment that this relaxation is associated with large scale motion in the amorphous phase. The height of the β peak also decreases

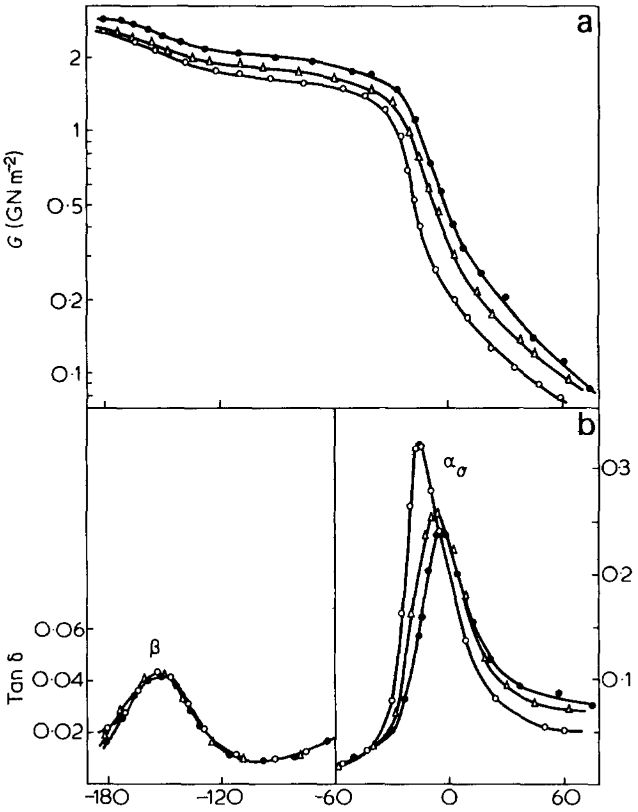

Figure 3 Temperature dependence of (a) the shear modulus *G* and (b) the loss tangent at 1 Hz for oriented samples of PB-1 with different draw ratios λ. ○, λ = 1; △, λ = 1.9; ●, λ = 3

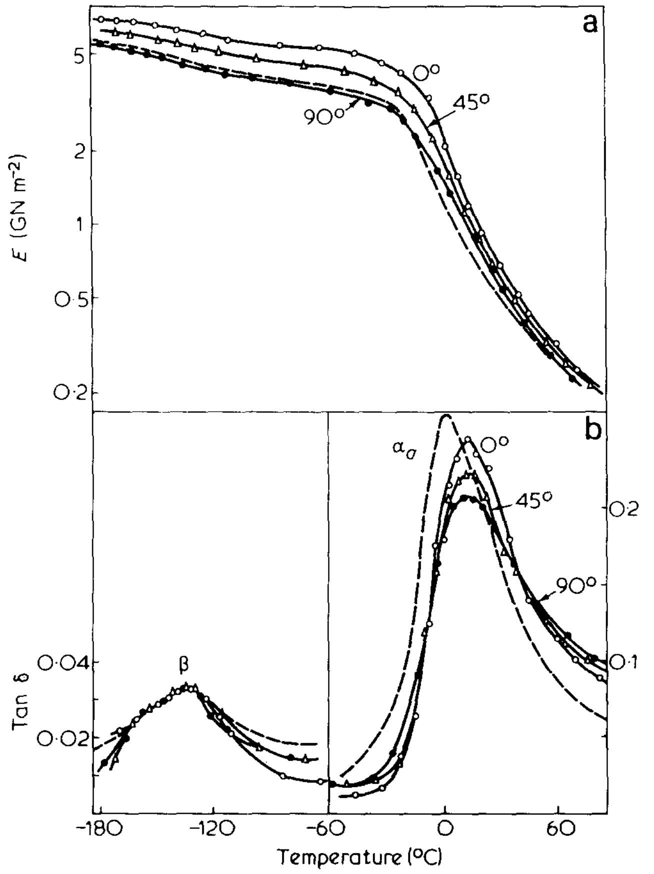

Figure 4 Temperature dependence of (a) the tensile modulus E and (b) the loss tangent at 90 Hz for oriented PB-1 with a draw ratio of 2.5. 0°, 45° and 90° denote the angle between the tensile axis and draw direction. The dotted curve represents the data for the isotropic sample

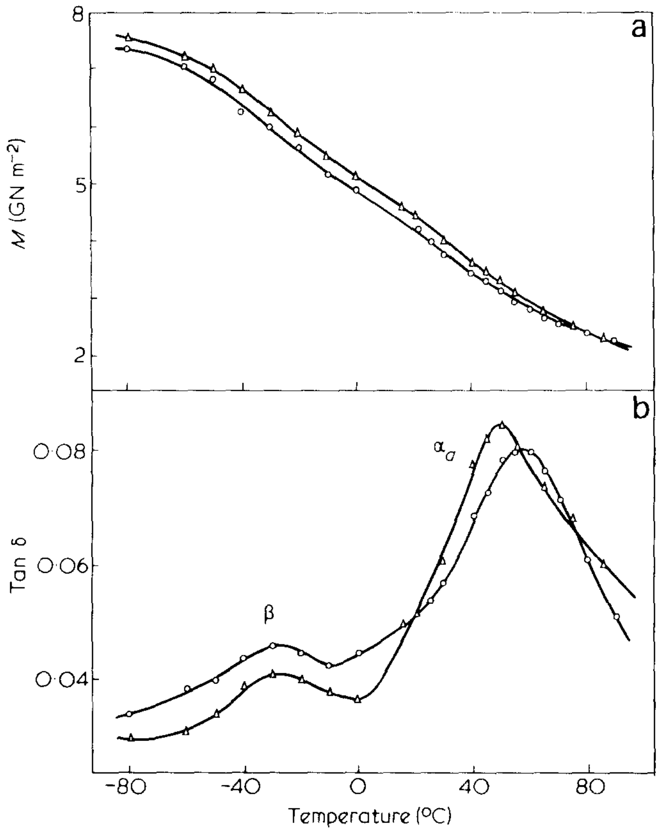

Figure 5 Temperature dependence of (a) the longitudinal modulus M and (b) the loss tangent at 3 MHz for isotropic and oriented samples of PB-1. For the oriented sample the measurements were made normal to the draw axis. △, isotropic; ○, oriented ($\lambda = 2.5$)

slightly with increasing crystallinity, so the localized motion of the side chains occurs at least partly in the amorphous regions.

The effect of orientation on the dynamic torsional measurements are shown in *Figure 3*. As the draw ratio increases the shear modulus increases, the effect being more significant above the α_a relaxation. Moreover, the α_a peak decreases in height and shifts to higher temperature. These results indicate that the chains in the amorphous regions of the oriented sample are under considerable constraint and large scale motion is impeded. In contrast, the limited motion of the side groups is not affected much, so the height of the β relaxation remains unchanged.

Figure 4 shows the tensile modulus and loss at 0°, 45° and 90° to the draw direction. The pattern of anisotropy for the tensile modulus is very simple, with $E_0 > E_{45} > E_{90}$. This merely reflects the greater strength of the convalent bonds along the chains which are now preferentially aligned along the draw direction. The α_a loss peak, located at ~ 10°C above that of the isotropic sample, also shows anisotropy but the β relaxation is not affected by orientation and exhibits isotropic behaviour. As illustrated in *Figure 5* the effect of orientation on the attenuation of ultrasonic longitudinal wave is quite similar to the low-frequency results, the difference being that the β peak is slightly enhanced after drawing.

The Arrhenius plots for both the α_a and β relaxations are shown in *Figure 6*. Since the location of the β peak is the same for both the isotropic and oriented samples only the data points for the former are shown. Although the

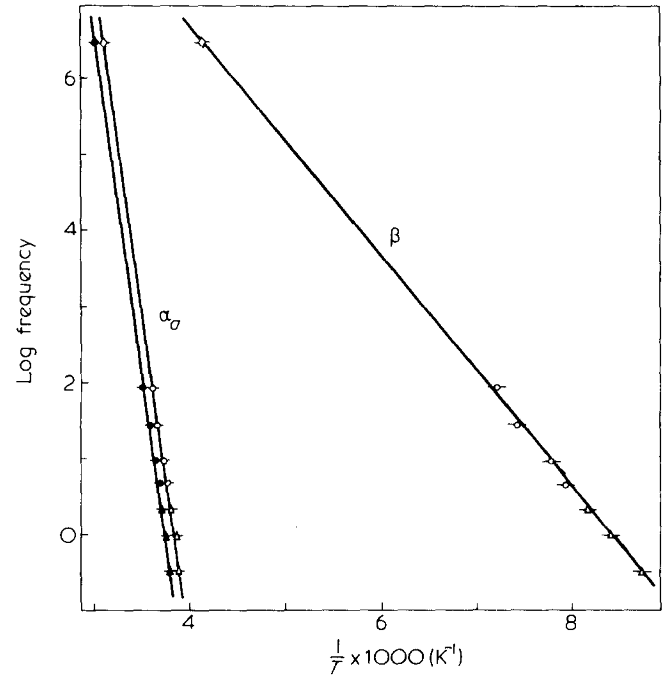

Figure 6 Plot of log frequency versus $1/T$ for isotropic and oriented PB-1. The open and closed symbols represent the data for the isotropic and oriented samples, respectively, and the bars denote possible errors. △, torsional; ○, tensile; ◇, longitudinal wave

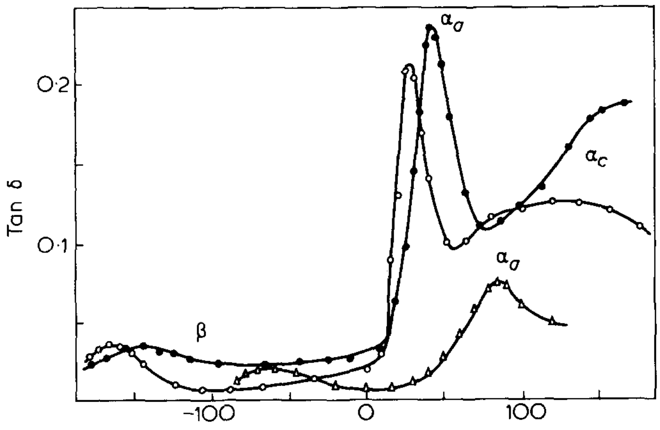

Figure 7 Temperature dependence of the loss tangent of P4MP1. ○, 0.3 Hz; ●, 90 Hz; △, 3 MHz

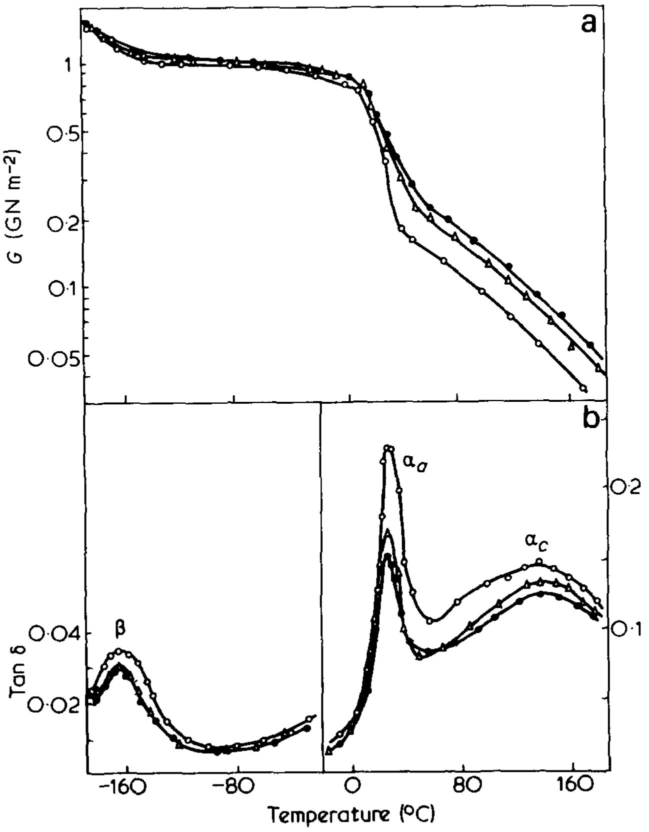

Figure 8 Temperature dependence of (a) the shear modulus G and (b) the loss tangent at 1 Hz for three samples of PB-1 with different degree of crystallinity X. ○, quenched (X = 0.23); △, slow-cooled (X = 0.29); ●, quenched and then annealed at 205°C for 20 h (X = 0.31)

plot for the α_a relaxation should in general obey the WLF equation[20], it is approximately linear within the limited frequency range of 0.3–3 × 10^6 Hz. After drawing, the α_a peak shifts upwards in temperature and yet the activation energy remains unchanged. The fact that the activation energy of the α_a process (40 kcal mol^{-1}) is much larger than that of the β process (7 kcal mol^{-1}) is consistent with our previous conjecture that the α_a and β relaxations are associated with the large scale motion of the main-chains and localized motion of the side groups, respectively.

Poly-4-methylpentene-1

As seen in *Figure 7* three relaxations α_c, α_a and β, are observed in the low-frequency torsional and tensile measurements. Ultrasonic measurements reveal only the latter two relaxations since the α_c relaxation has been shifted to above our temperature range. The α_a relaxation is associated with the glass transition, since there is a significant decrease in tan δ with increasing crystallinity as shown in *Figure 8*. The β relaxation, which is associated with the localized motion of the side chains, has been studied in detail by Takayanagi and Kawasaki[12]. By studying various kinds of samples they have shown that the β relaxation is composed of two overlapping peaks: a higher-temperature β–A peak associated with the frozen amorphous chains and a β–C peak associated with the defect regions within the crystalline phase. However, for the samples studied in the present work a single β peak only is observed and the slightly smaller peak height of the slow-cooled sample is a reflection of the lower amorphous fraction in this sample.

Little is known about the broad α_c relaxation except that it is also observed in single-crystal mats of P4MP1, and is probably associated with the crystalline phase[12]. Similar high-temperature crystalline relaxations have also been observed in polyethylene and polypropylene[1–3]. It is seen from *Figure 8* that the α_c relaxation is only slightly affected by change in crystallinity.

The effect of drawing is shown in *Figures 9–11*. For both low and high frequency measurements the α_a relaxation is reduced in height and shifted to higher temperature. The drop in modulus in the relaxation region is also smaller for the oriented sample. This reflects

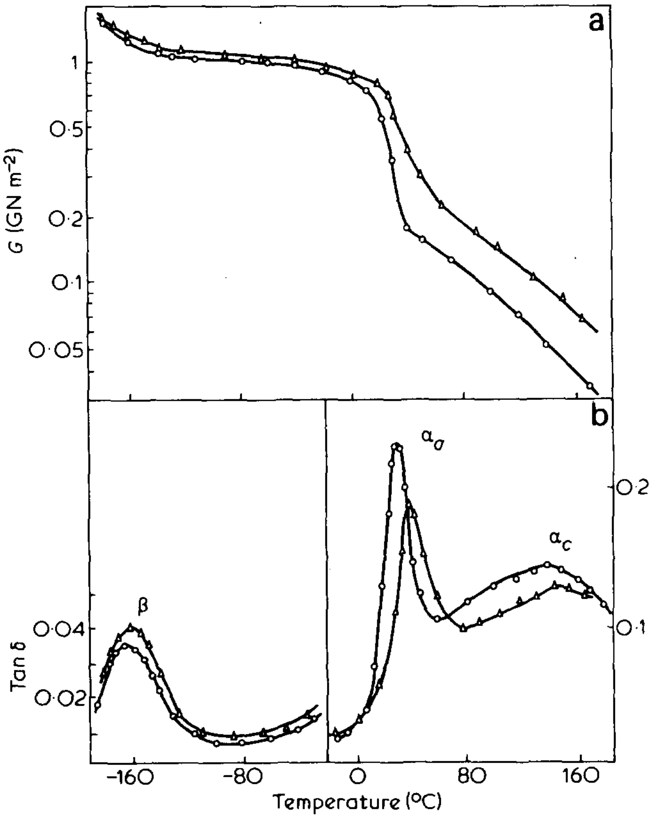

Figure 9 Temperature dependence of (a) the shear modulus G and (b) the loss factor of 1 Hz for isotropic and oriented samples of P4MP1. ○, isotropic; △, oriented (λ = 6)

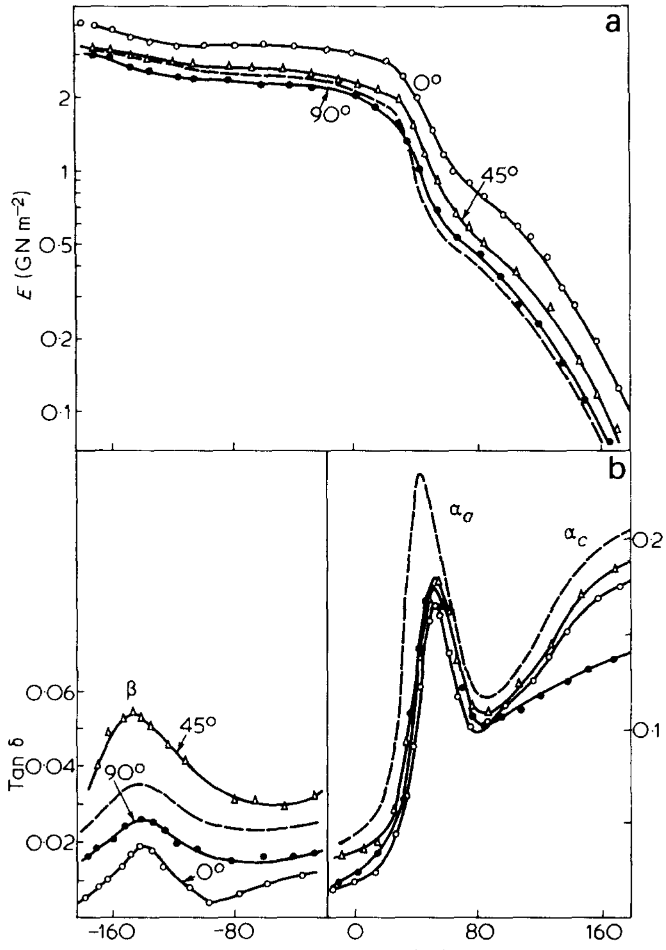

Figure 10 Temperature dependence of (a) the tensile modulus E and (b) the loss tangent at 90 Hz for oriented P4MP1 with a draw ratio of 6. 0°, 45° and 90° denote the angle between the tensile axis and draw direction. The broken curve represents the data for the isotropic sample

the decrease in mobility in the amorphous regions as a result of chain orientation and the increase in tautness of the intercrystalline tie molecules. In contrast, the low frequency torsional measurements (*Figure 9*) and the ultrasonic results (*Figure 11*) reveal that the α_c and β loss peaks are little affected by drawing.

The dynamic tensile measurements in *Figure 10* also show that there is a large anisotropy in tan δ at both the α_c and β relaxations, with the loss at 45° to the draw direction being the largest. These results suggest that shear processes are operating at these two relaxations. In fact, closer examination of the β-relaxation in *Figure 10* reveals that the peak of tan δ_{45} lies at $\sim 10°$C below those of tan δ_0 and tan δ_{90}. This seems to indicate that tan δ_{45} is associated with a shear process in the defect regions within the crystalline phase, which may be identified with the β–C process proposed by Takayanagi and Kawasaki[12], while tan δ_0 and tan δ_{90} are largely associated with the β–A process.

Similar anisotropy in tan δ has also been observed for the α-relaxation in drawn low-density polyethylene (LDPE) and it was shown[21] that the relaxation is related to the crystalline regions and involves shear deformation in the direction of drawing in planes containing the draw axis (c/c shear process). It seems possible that both the β and α_c relaxations in P4MP1 are also associated with this process.

The relaxation maps for the isotropic and oriented samples of P4MP1 are shown in *Figures 12* and *13*, respectively. Upon orientation the activation energy H of the α_a relaxation remains essentially unchanged at 60 kcal mol^{-1}. Since the α_c relaxation is very broad and is

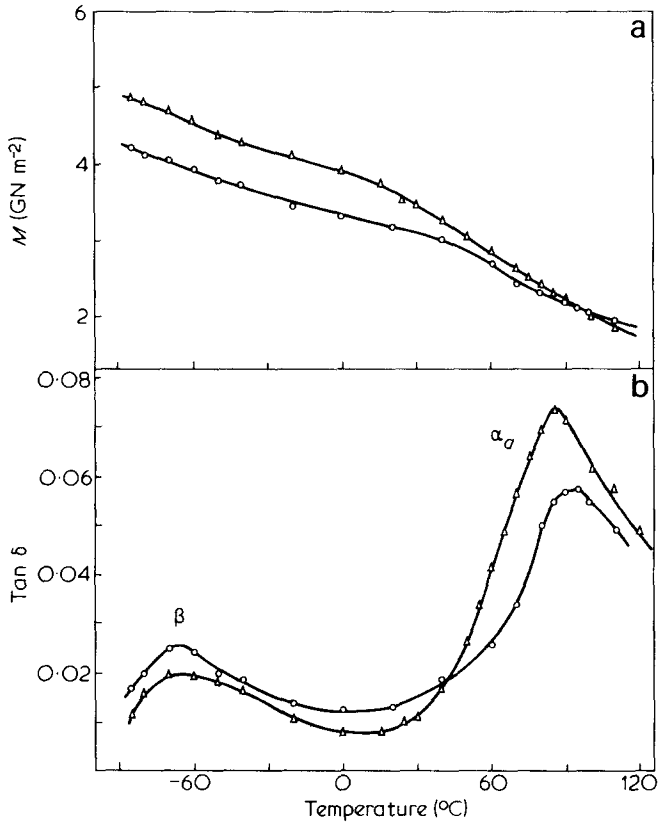

Figure 11 Temperature dependence of (a) the longitudinal modulus M and (b) the loss tangent at 3 MHz for isotropic and oriented P4MP1. For the oriented sample the measurements were made normal to the draw axis. △, isotropic; ○, oriented ($\lambda = 6$)

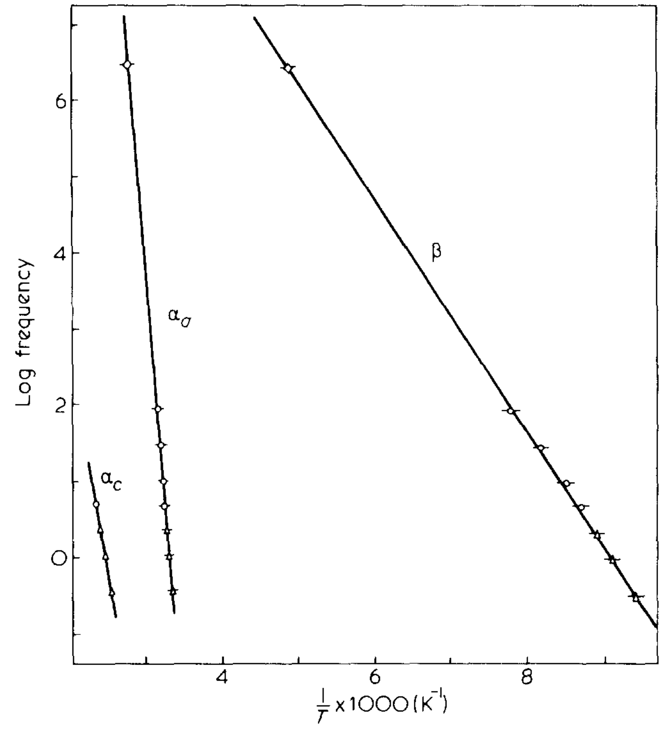

Figure 12 Plot of log frequency versus $1/T$ for isotropic P4MP1. The bars denote possible errors. △, torsional; ○, tensile; ◇, longitudinal wave

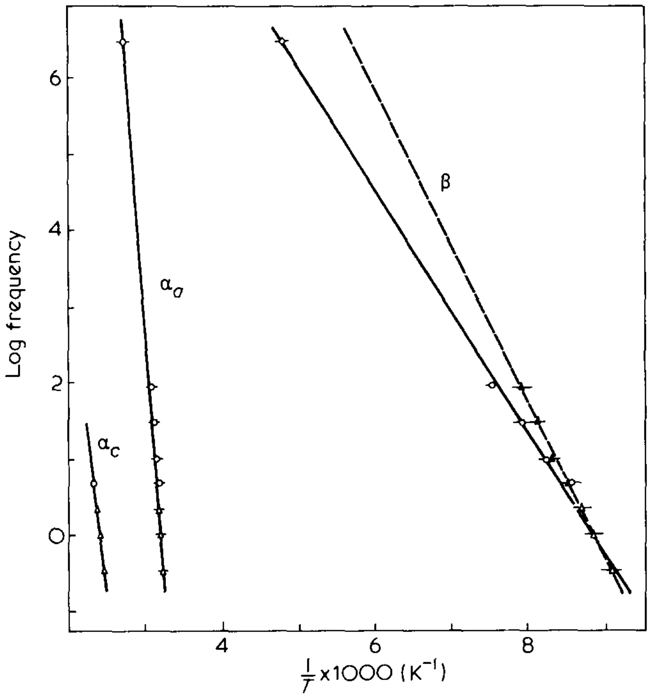

Figure 13 Plot of log frequency versus $1/T$ for oriented P4MP1. The bars denote possible errors. △, torsional; ▲, tensile tan δ_{45}; ○, tensile tan δ_{90} and tan δ_0; ◇, longitudinal wave

observed only in a narrow frequency range, the activation energy is estimated to be accurate to 40% only. Thus the observed increase in H from 25 kcal mol^{-1} ($\lambda = 1$) to 35 kcal mol^{-1} ($\lambda = 6$) upon orientation may not be genuine. For the β relaxation, all the data of the isotropic sample fall on a straight line giving an activation energy of 7 kcal mol^{-1} (*Figure 12*). However, for the oriented sample, the tan δ_{90} (and tan δ_0) data in low frequency tensile measurements lie on the same straight line as the ultrasonic loss data while the tan δ_{45} and the torsional data lie on another straight line with a larger slope (*Figure 13*). The activation energies corresponding to these two Arrhenius plots are 7.3 and 9.3 kcal mol^{-1}, respectively. We have tentatively associated the latter Arrhenius plot with a shear process in the crystalline phase of the polymer, but the observed activation energy of this process would not be accurate because of the limitation on frequency range.

In conclusion, our preliminary work on oriented P4MP1 has revealed some interesting features. Further mechanical studies, together with structural measurements such as wide-angle X-ray diffraction, would be useful in elucidating the underlying mechanisms.

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