Determination of the glass–rubber transition of poly(vinyl chloride)and poly(ethylene terephthalate) by small-angle X-ray scattering

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Semicrystalline polymers can be regarded as systems of two phases, an amorphous and a crystalline phase, with different electron densities and different thermal expansion coefficients. The small-angle X-ray scattering of these systems is proportional to the square of the difference between the electron densities of the phases and so increases with temperature. As Fischer and Kloos have shown[1], this increase is discontinuous at the glass–rubber transition temperature, T_g, so providing a method for determining T_g and the difference $\alpha_{ar}-\alpha_{ag}$ between the thermal expansion coefficients of the amorphous phase above and below T_g. This method was applied to poly(vinyl chloride) (PVC) and poly (ethylene terephthalate) (PETP). For the latter, small-angle X-ray scattering in addition constitutes a method for following and interpreting physical aging.

INTRODUCTION

A classical method for determining the glass–rubber transition temperature, T_g, of polymers is based on the fact that the change in density as a function of temperature (thermal expansion) is discontinuous at T_g. In general, density changes in polymers are small, and so it would be advantageous to determine them by measuring the density difference with respect to that of a reference whose density is about the same as that of the material being investigated.

A suitable technique for measuring density differences in a sample is determination of the small-angle X-ray scattering (SAXS). The intensity of this scattering, when integrated over the entire small-angle scattering range (about 0.1 rad), is proportional to the mean-square electron density fluctuation in the material:

$$I \sim \overline{(\rho_{ei} - \bar{\rho}_e)^2} \qquad (1)$$

where ρ_{ei} is the electron density of a small volume v_i, and $\bar{\rho}_e$ is the mean electron density of the entire volume. For two-phase systems equation (1) takes the form:

$$I \sim x_1 x_2 (\rho_{e1} - \rho_{e2})^2 \qquad (2)$$

where x_1 and x_2 are the volume fractions of the phases, and ρ_{e1} and ρ_{e2} their electron densities. The electron density of a phase is proportional to its mass density, the proportionality factor being the ratio of the atomic numbers to the atomic weights of the atoms of which the material consists.

In general, the densities ρ_1 and ρ_2 will change almost linearly with temperature, but not to the same extent. The square root of I, which is proportional to the difference between the densities (see equation 2), will therefore change linearly with temperature and with the difference in the coefficients of thermal expansion of the phases. Determination of this difference from measurements of the scattering as a function of temperature would therefore seem to be a suitable method for determining the T_g of semicrystalline polymers. For these systems it can be assumed that the thermal expansion coefficient of the amorphous phase is only slightly larger than that of the crystalline phase below T_g, but considerably larger above T_g.

The slope of a scattering intensity vs. temperature plot will therefore increase discontinuously at T_g. Since the difference between the densities of the phases is small with respect to the densities themselves, even a small change in density of one phase will manifest itself in a marked increase in scattering intensity. Another advantageous circumstance is that for many semicrystalline polymers, the product of the volume fractions x_1x_2 is not far from 0.25, where it is a maximum. Finally, the difference in electron densities of the phases is simply proportional to the difference of their mass densities, because the two phases have the same chemical composition.

The method of determining glass–rubber transition temperatures from small-angle X-ray scattering was first applied by Fischer and Kloos, who investigated, e.g. linear and methyl-branched polyethylenes[1]. The present work gives some results of measurements on poly(vinyl chloride) (PVC) and poly(ethylene terephthalate) (PETP).

THEORY

In a small temperature range, the density of a polymer can be regarded as a linear function of temperature. If we as-

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sume that this also holds for the two phases of a semicrystalline polymer, we may write:

$$\rho_a = \rho_{a0}[1 - \alpha_a(T - T_0)]$$

$$\rho_c = \rho_{c0}[1 - \alpha_c(T - T_0)] \qquad (3)$$

where α is the coefficient of thermal expansion, the subscripts a and c referring to the amorphous and crystalline phases, respectively, and the subscript 0 to the state at a reference temperature T_0.

For the density difference between the phases we then have:

$$\rho_c - \rho_a = (\rho_{c0} - \rho_{a0})\,[1 + (T - T_0)(\alpha_a\rho_{a0} - \alpha_c\rho_{c0})/(\rho_{c0} - \rho_{a0})] \qquad (4)$$

Since, in general, the changes in density with temperature are small with respect to the density difference at $T = T_0$, we may write:

$$\ln(\rho_c - \rho_a) = \ln(\rho_{c0} - \rho_{a0}) + (T - T_0)(\alpha_a\rho_{a0} - \alpha_c\rho_{c0})/(\rho_{c0} - \rho_{a0}) \qquad (5)$$

When the very small changes in the product x_1x_2 are neglected, equations (2) and (5) yield:

$$\tfrac{1}{2}\ln I = \tfrac{1}{2}\ln I_0 + (T - T_0)(\alpha_a\rho_{a0} - \alpha_c\rho_{c0})/(\rho_{c0} - \rho_{a0}) \qquad (6)$$

where I_0 is the scattering intensity at T_0 (which, for the sake of simplicity, is taken to be T_g). A plot of ½ ln I as a function of temperature consists of two straight lines with slopes H_g and H_r for temperatures below and above T_g, respectively:

$$H_g = (\alpha_{ag}\rho_{a0} - \alpha_c\rho_{c0})/(\rho_{c0} - \rho_{a0}) \quad T < T_g$$

$$H_r = (\alpha_{ar}\rho_{a0} - \alpha_c\rho_{c0})/(\rho_{c0} - \rho_{a0}) \quad T > T_g \qquad (7)$$

where g and r refer to the glassy and rubbery state, respectively. It is assumed that the coefficient of thermal expansion of the crystalline phase does not change at T_g. This transition temperature is found from the intersection of the straight lines, and the difference between the coefficients of thermal expansion is calculated for the difference in slopes above and below T_g:

$$\alpha_{ar} - \alpha_{ag} = (\rho_{c0} - \rho_{a0})(H_r - H_g)/\rho_{a0} \qquad (8)$$

EXPERIMENTAL

The scattering measurements were performed by means of a slit-collimated camera (Kratky) using CuKα radiation, which is monochromated by a nickel filter in the primary beam. The intensity of the scattered beam is measured as a function of the scattering angle, the number of pulses per unit time being counted by a proportional counter and a pulse height discriminator, which improves the monochromatization. For our purposes, we provided the instrument with a sample holder connected to a thermostat bath, so that the temperature of the sample could be kept constant to within 0.5K.

If intensities are to be measured accurately in a short time, the intensity of the beam should be high. To make it so, we used the widest available divergence of the beam (entrance slit 150 μm) and a wide counter slit of 375 μm; in spite of this, measuring times of at least 400 sec were needed.

In order to plot the straight lines ½ ln I vs. temperature, we had to measure at least six temperatures, three above and three below the expected T_g. For this reason we restricted ourselves to determining the intensity for two angles, namely the angle for which the intensity attains a maximum corresponding to the long-spacing reflection (often about 0.01 rad), and the angle for which the scattering is caused only by density fluctuations in the amorphous phase (about 0.1 rad). This restriction is allowed if no structural changes occur. Then the scattering due to the binary nature of the material (the difference between the scattering in the small-angle range and the amorphous scattering at large angles) changes with temperature by the same factor for all angles. An example of the scattering (although not corrected for the amorphous scattering) as a function of the angle at two different temperatures is given in *Figure 1.*

RESULTS AND DISCUSSION

Two polymers were investigated whose glass–rubber transition temperatures are supposed to be influenced by their content of stabilizers or plasticizers [poly(vinyl chloride), PVC], or by orientation and crystallization processes [poly(ethylene terephthalate), PETP]. The PVC samples were about 0.12 mm thick, and the PET samples about 1.1 mm. At these thicknesses the X-ray transmission equals $e^{-1} = 0.368$, giving the maximum scattering intensity.

PVC

The following samples were made.

(a) A plate was pressed from 100 parts (by wt) of PVC (Solvic 229), 2 parts of a commercial tin stabilizer (Irgastab 17M), 1 part of glyceryl monostearate (Loxiol G12) and 0.5 part of paraffin wax (Irgawax 366). The components

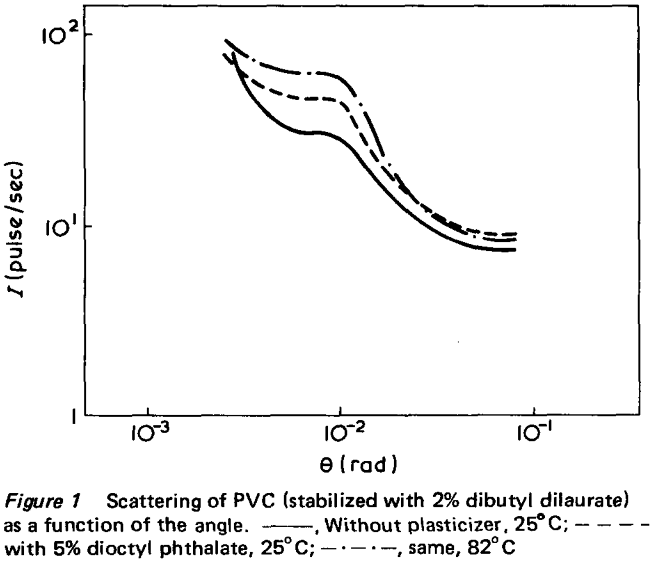

Figure 1 Scattering of PVC (stabilized with 2% dibutyl dilaurate) as a function of the angle. ———, Without plasticizer, 25°C; – – – – with 5% dioctyl phthalate, 25°C; —·—·—, same, 82°C

were mixed by hand, pressed at 200°C for 10 min and cooled to room temperature in 10 min.

(b) A plate was pressed from PVC (Carina 67–01) not containing any additives. The temperature of pressing was 100°C, and the time of pressing and cooling to room temperature 10 and 5 min, respectively.

(c) Four plates were pressed from 100 parts of PVC (Solvic 229), 2 parts of dibutyltin dilaurate and various quantities of plasticizer (dioctyl phthalate, DOP). The components were mixed by hand, rolled at 150°C for 5 min and pressed at 160°C for 8 min after which the sample was cooled to room temperature in 10 min.

Instead of a true maximum, the scattering intensities of these samples showed a shoulder at about 0.01 rad (*Figure 1*). The absence of a clear-cut maximum is due to the low degree of crystallinity of PVC, and perhaps also to the imperfect structure of the crystallites.

The measured scattering intensity at the maximum as a function of the temperature is given in *Figures 2–4*. For all samples, the relation between $\frac{1}{2}\ln I_{\max}$ and temperature

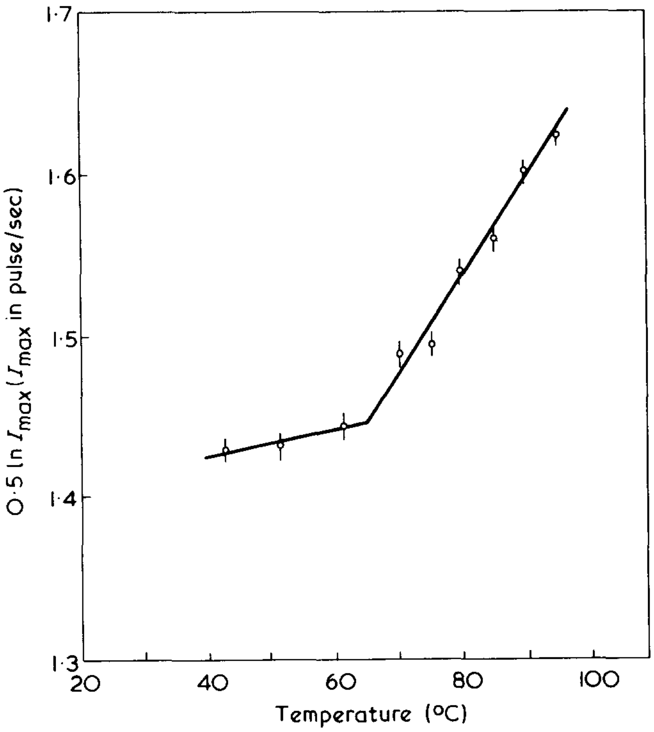

Figure 2 Scattering of PVC (Solvig 22 g, stabilized and plasticized, pressed at 200°C) as a function of temperature

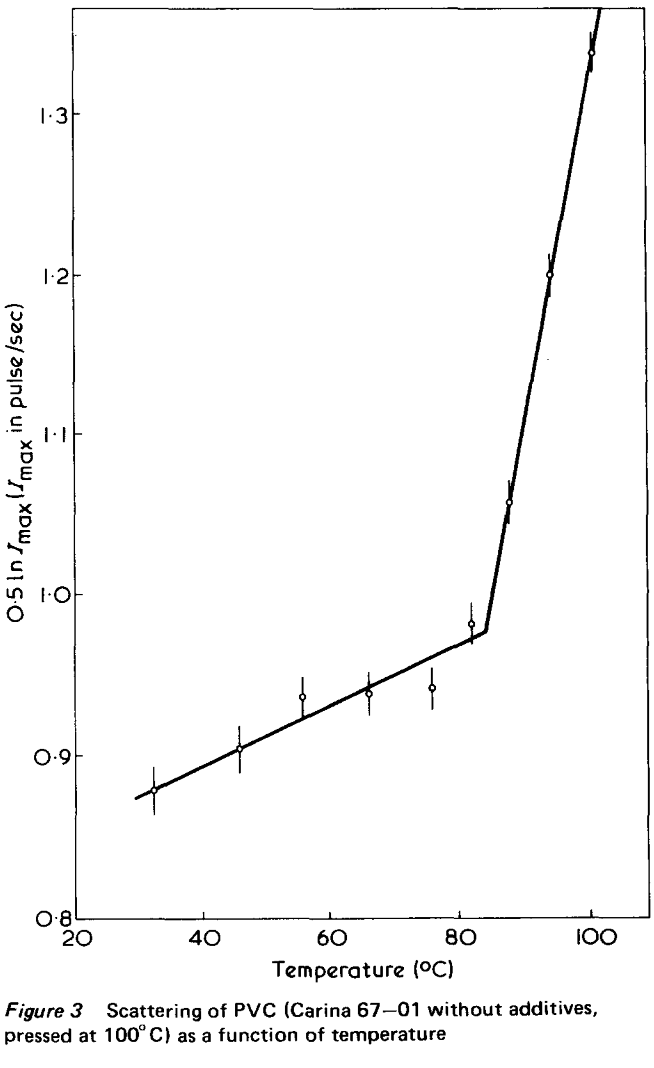

Figure 3 Scattering of PVC (Carina 67–01 without additives, pressed at 100°C) as a function of temperature

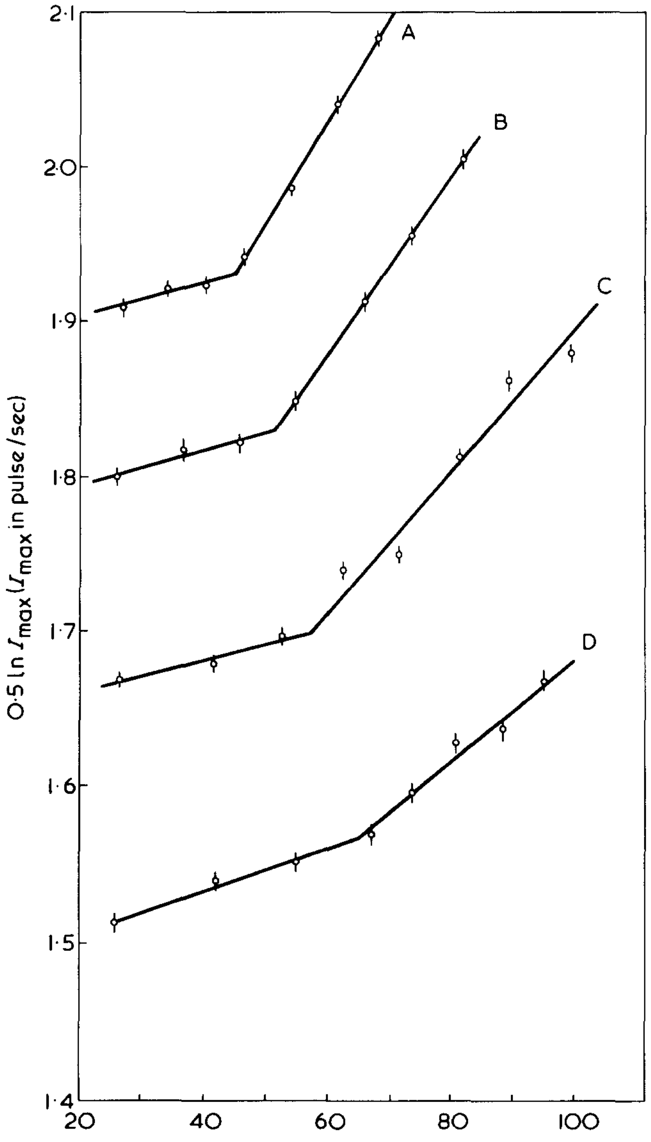

Figure 4 Scattering of PVC (Solvig 22 g stabilized, with different plasticizer contents, pressed at 160°C) as a function of temperature. A, 7.5% DOP; B, 5% DOP; C, 2.5% DOP; D, 0% DOP

consists of two straight lines, from whose intersection T_g can be determined.

The T_g of the sample without additive (b) was slightly higher than the reported value of 80°C[2]. After the experiment, the sample was cracked and had lost its transparency. It had apparently lost its coherence when heated – without external pressure being applied to it – to a temperature higher than that at which it was prepared. The loss of coherence increases the scattering, so that the slope of the $\frac{1}{2}\ln I_{max}$ vs. temperature plot no longer depends on the thermal expansion coefficients alone.

The sample with additives (a and c) retained their transparency upon being heated. Their T_g appeared to be at least 10K lower than that of pure PVC. This difference indicates that the additives are at least partly dissolved in the amorphous phase. *Figure 5* shows the T_g of PVC as a function of its plasticizer content. For every per cent (w/w) of DOP added to PVC, its T_g is lowered by about 2.6K, which is in reasonable agreement with the value given in the literature, viz. 2.1K[3]. The plasticizer influences the slope of $\frac{1}{2}\ln I_{max}$ vs. temperature only significantly at temperatures above T_g.

The results are summarized in *Table 1*. From the slopes above and below T_g, the difference between the thermal expansion coefficients, $\alpha_{ar} - \alpha_{ag}$, was calculated by means of equation (8), it being assumed that the densities of the amorphous and crystalline phases were $\rho_a = 1385$ and $\rho_c = 1530$ kg/m^3, respectively[4]. On these assumed densities the difference $\alpha_{ar} - \alpha_{ag}$ strongly depends, because it is proportional to $\rho_c - \rho_a$. The results agree roughly with the difference between the values $\alpha_r = 7.0 \times 10^{-4}$ K^{-1} and $\alpha_g = 2.2 \times 10^{-4}$ K^{-1}, reported in the literature[3].

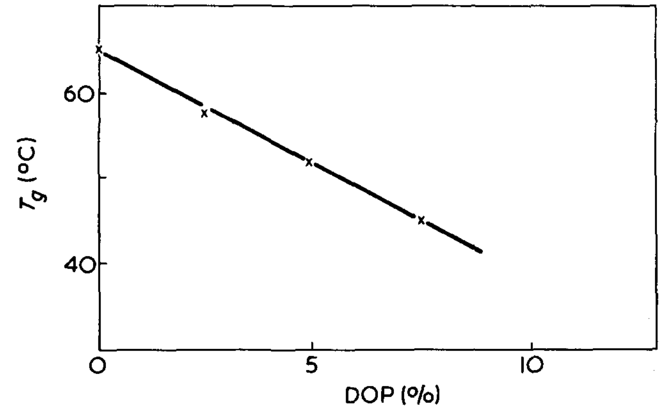

Figure 5 Glass–rubber transition temperature of PVC [PVC (Solvic 229)] as a function of the plasticizer content

A remark must be made on the effect of a possible small change in crystallinity x_1 during the heating of the samples. Since for PVC we have $x_1 \ll 0.5$, a change in x_1 would produce a non-negligible change the product x_1x_2, and entail a change in the scattering intensity leading to erroneous values of $\alpha_{ar} - \alpha_{ag}$ (equation 8). A decrease in x_1, due to melting of some crystallites during heating would in general cause the straight lines $\frac{1}{2}\ln I_{max}$ vs. T to bend downwards to the T-axis, but no such deviation was found. On the other hand, an increase in x_1 due to a further crystallization can be ruled out because the freshly prepared samples were cooled slowly enough to attain their equilibrium crystallinity; this was confirmed for sample (b), the scattering intensity of which at 27°C was remeasured and found not to have changed significantly.

PETP

The following samples have been investigated.

(a) A plate of unoriented material (Arnite A200 of Akzo), which had been crystallized at 140°C. The density at room temperature was 1378 kg/m^3. The scattering of this sample was measured for increasing as well as for decreasing temperatures.

(b) A plate of the same material, to which a slightly higher degree of crystallinity was imparted by storage at 165°C for 1 day. The density at room temperature was 1380.5 kg/m^3. After being quenched to 25°C, the sample was kept at 25°C for 5 days, then heated rapidly to 108.5°C, and kept at this temperature for one day. Its scattering was measured at this temperature and during stepwise cooling to room temperature.

(c) A film was made by flat extrusion (Arnite A251 of Akzo), drawn at 90°C (draw ratio 1:3), then drawn at 150°C (draw ratio 1:2), and next allowed to relax at 200°C for 1 h (length reduction 10%). This sample was mounted with the machine direction perpendicular to the beam plane.

The scattering intensity of all PETP samples, measured at room temperature, showed a maximum at about 0.011 rad (*Figure 6*). This maximum was more marked for the drawn sample.

Figure 7 shows plots of $\frac{1}{2}\ln I_{max}$ vs. the temperature of the samples. The plots are linear, except where the tempera-

Table 1 Glass–rubber transition data of PVC: temperature T_g, slopes H_g and H_r of $\frac{1}{2}\ln I_{max}$ vs. temperature, $\rho_c - \rho_a$ as calculated from literature data, difference of thermal expansion coefficients $\alpha_{ar} - \alpha_{ag}$

Material	T_g (°C)	H_g (10^{-4} K^{-1})	H_r (10^{-4} K^{-1})	$H_r - H_g$ (10^{-4} K^{-1})	$\rho_c - \rho_a$ (kg/m^3)*	$\alpha_{ar} - \alpha_{ag}$ (10^{-4} K^{-1})
Solvic 229 + tin stabilizer + plasticizer	65	8	62	54	159	6.2
Carina 67–01	85	17				
Solvic 229 + dibutyltin dilaurate	65	14	32	18	152	2.0
Solvic 229 + 2.5% DOP	57.5	10	46	36	160	4.2
Solvic 229 + 5% DOP	51.5	11	57	46	168	5.7
Solvic 229 + 7.5% DOP	45.5	11	67	56	177	7.3

*ρ_a corrected for stabilizer and plasticizers (ρ = 1100 kg/m^3) and for dioctyl phthalate (ρ = 985 kg/m^3). All values refer to 25°C

ture decreases from some value above T_g to T_g. The glass–rubber transition temperatures found for unoriented and oriented PETP are quite different, namely 76° and 113°C. These temperatures are in fair agreement with those reported in the literature, viz. 81°C for unoriented PETP and 125°C for oriented PETP[6,7].

The results are summarized in *Table 2*. The difference $\alpha_{ar} - \alpha_{ag}$ was calculated for a ρ_a of 1335 kg/m^3 and for two rather different values ρ_c given in the literature, viz. $\rho_c = 1457$ kg/m^3 [8] and $\rho_c = 1495$ kg/m^3 [9].

If values of $\alpha_{ar} - \alpha_{ag}$ for the amorphous phase alone are to be compared with literature values of $\alpha_r - \alpha_g$ for the material as a whole, the former have to be multiplied by the factor $1 - x$ (x = the crystalline fraction). For sample *a*, this factor was calculated from the density of the material (1378 kg/m^3). The value $\rho_c = 1457$ kg/m^3 then yields $x = 0.35$ and $\alpha_r - \alpha_g = 1.6 \times 10^{-4}$ K^{-1}, while the value $\rho_c = 1495$ kg/m^3 yields $x = 0.27$ and $\alpha_r - \alpha_g = 2.3 \times 10^{-4}$ K^{-1}. The latter result is in good agreement with that obtained by Kolb and Izard[7] who found $\alpha_g = 1.71 \times 10^{-4}$ K^{-1} and $\alpha_r = 3.94 \times 10^{-4}$ K^{-1} for a sample of PETP whose density was slightly higher than that of sample *a*. It also agrees with results given by Petrukhov[10], viz. $\alpha = 1.6 \times 10^{-4}$ K^{-1} (30°–60°C) and 3.7×10^{-4} K^{-1} (90°–190°C). The difference $\alpha_{ar} - \alpha_{ag}$ appears to be less for oriented than for unoriented PETP.

Figure 7 shows that the scattering intensity of the unoriented samples is subject to hysteresis when measured during heating and subsequent cooling. The hysteresis can be explained in terms of volume-relaxation[11,12]. The storage of 800 days at room temperature is long enough for the sample to set strongly. Upon being heated to a temperature far above T_g, the amorphous phase cannot recover its original volume, even when it is cooled at a moderate rate. At each temperature its density will therefore be lower, and its scattering higher, than when it is heated from the initial state. From the shift in $\frac{1}{2}\ln I_{max}$, which is equal to $\Delta\rho_a/(\rho_c - \rho_a)$ (cf. equation 10), it can be calculated that the density of the amorphous phase below T_g decreases by 4 or 5 kg/m^3, depending on the assumed value of ρ_c. This is more than the expected decrease of 1 kg/m^3 calculated from the volume relaxation rate given by Struik[12].

Volume relaxation may also be responsible for the non-linearity of $\frac{1}{2}\ln I_{max}$ vs. temperature shown by sample (b) above T_g. From his measurements of the increase with time elapsed after quenching in the density of semicrystalline polymers, of which our sample (b) was one, Struik[11,12] concluded that volume relaxation can also occur above T_g.

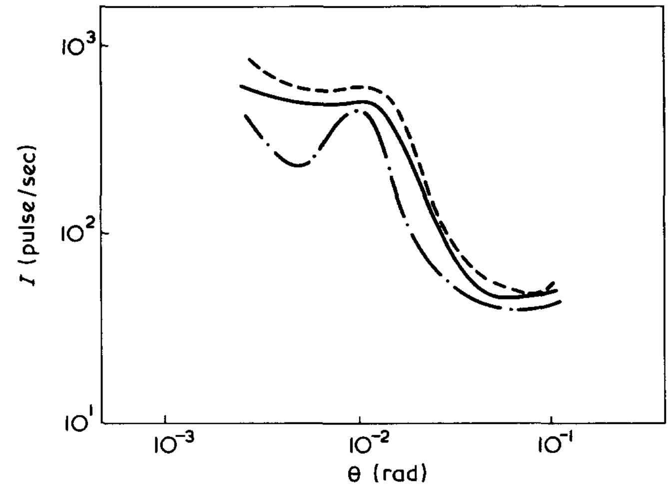

Figure 6 Scattering of PETP [PETP (Arnite)] as a function of the angle. – – – –, A200, unoriented, crystallized at 165°C; ———, same, crystallized at 140°C; —·—·—, A251, drawn and relaxed

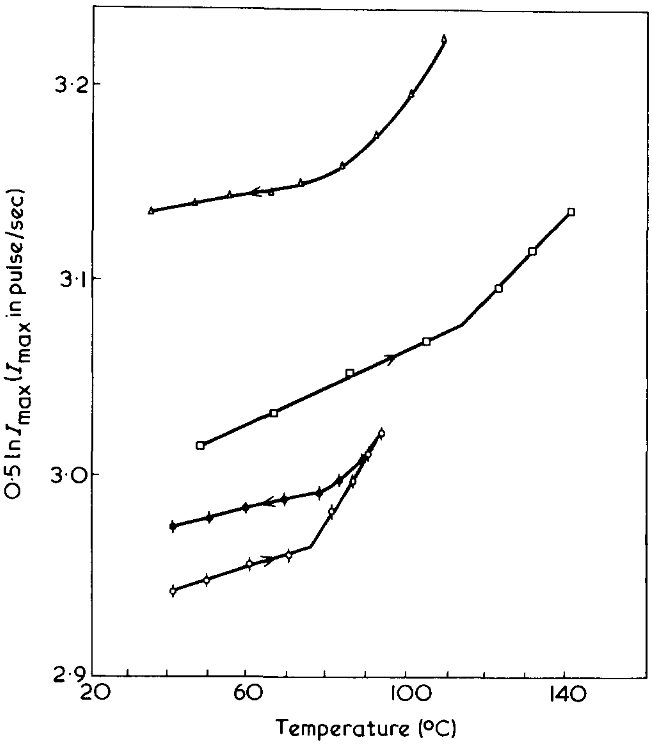

Figure 7 Scattering of PETP as a function of temperature. △, A200, crystallized at 165°C; □, A251, drawn and relaxed; ○, ●, A200, crystallized at 140°C

Table 2 Glass–rubber transition data of PETP: temperature T_g, slopes H_g and H_r of $\frac{1}{2}\ln I_{max}$ vs. temperature, difference of thermal expansion coefficients $\alpha_{ar} - \alpha_{ag}$

Material	T_g (°C)	H_g (10^{-4} K^{-1})	H_r (10^{-4} K^{-1})	$H_r - H_g$ (10^{-4} K^{-1})	$\alpha_{ar} - \alpha_{ag}$ (10^{-4} K^{-1})	
					ρ_k = 1457 kg/m^3	ρ_k = 1495 kg/m^3
A200, unoriented	76	6.5	32.5	26	2.4	3.1
A200, unoriented, crystallized at 165°C	75–80	3.6	≃39*	≃35	≃3.2	≃4.2
A251, drawn and relaxed	113	9.6	20.7	11	1.0	1.3

*H_r determined from the scattering intensities at the two highest temperatures

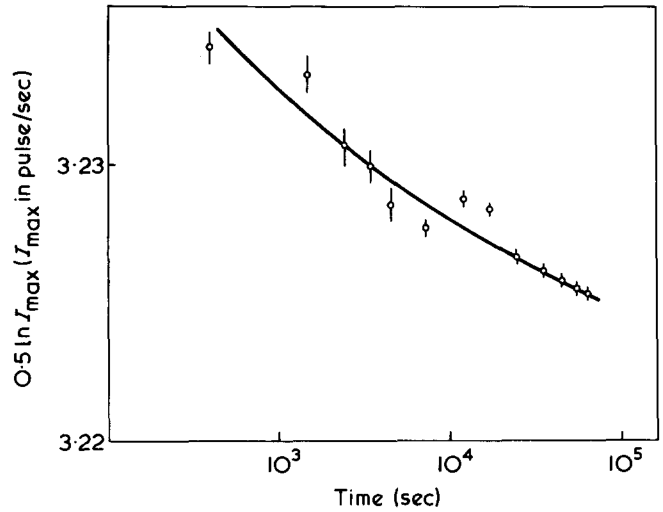

Figure 8 Scattering of PETP, crystallized at 165°C, quenched at 25°C, as a function of the time elapsed after heating to 108.5°C

As far as our sample is concerned, a different explanation in terms of continued crystallization can be rejected in view of the observation that the scattering intensity of the sample gradually decreased with time when it was stored for 1 day at 108.5°C. Since the proportion of crystalline material x is less than 0.5, an increase in x would entail an increase in the product $x(1-x)$, and therefore an increase in the scattering intensity. The observed intensity decrease can only be explained by a decrease in $\rho_c - \rho_a$ and hence, since ρ_c is constant, by an increase in ρ_a.

Equation (2) yields:

$$\tfrac{1}{2}\ln I(t) \sim \tfrac{1}{2}\ln x_1 x_2 + \ln(\rho_c - \rho_a) \qquad (9)$$

Therefore, with constant values of $x_1 x_2$ and ρ_c, we obtain:

$$\frac{d\rho_a}{d\log t} = -(\rho_c - \rho_a)\frac{d[\tfrac{1}{2}\ln I]}{d\log t} \qquad (10)$$

If it is assumed that $\rho_c = 1495$ kg/m^3 and that $\rho_a = 1335$ kg/m^3, it follows from the slope in *Figure 8* that:

$$\frac{d\rho_a}{d\log t} \simeq 0.7 \text{ kg/m}^3$$

With a degree of crystallinity of 0.27, this yields:

$$\frac{d\rho}{d\log t} = 0.5 \text{ kg/m}^3$$

which is of the same order of magnitude as the value found by Struik[12], viz. 0.3 kg/m^3. It follows, that the measurement of small-angle X-ray scattering also affords a simple method for investigating and interpreting volume-relaxation phenomena.

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