

Isothermal relaxation of specific volume and density fluctuation in poly(methyl methacrylate) and polycarbonate

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Small-angle X-ray scattering (SAXS) was utilized to measure the density fluctuation, in two samples of poly(methyl methacrylate) and a sample of polycarbonate, as a function of temperature on a constant rate cooling and heating; and also as a function of time on isothermal annealing. For the purpose of comparison, measurements were also made on the specific volume of poly(methyl methacrylate) under comparable conditions. In the transition region of 20°–40° interval around T_g both the specific volume and the density fluctuation decreased with time on isothermal annealing. At temperatures below the transition region, however, the density fluctuation showed no observable change, while the specific volume continued to decrease linearly with the logarithm of time. In order to interpret the density fluctuation in terms of the concept of free volume, a simple model is presented in which holes of various sizes are randomly distributed in the continuous medium, and an equation is then derived to correlate the observed density fluctuation to the free volume fraction and the weight-average size of the holes.

(Keywords: density fluctuation; poly(methyl methacrylate); polycarbonate; glassy polymer; free volume)

INTRODUCTION

The concept of free volume has been used for a long time to understand better the behaviour of glassy polymers. Numerous studies have been made on the specific volume and the viscoelastic properties of glassy polymers as a function of temperature, pressure and thermal history. These observations have been rationalized fairly successfully in terms of the free volume concept. A number of theories^{1–6} provide a link between the free volume and the observable thermodynamic and mechanical properties.

Despite these successes, some shortcomings of the free volume concept have also been widely recognized. For example, the memory effect of volume recovery (first observed by Kovacs⁷) signifies that the properties of a glass are not uniquely determined by the current value of the specific volume (and hence the free volume) but are also determined in some way on the past history of the glass. Similarly two glass samples having the same specific volume but prepared through different processes (for example, isothermal ageing *versus* under elevated pressure) can exhibit very different behaviour. A way to reconcile these observations with the free volume concept is to postulate that not only the total amount of the free volume but also the state of its subdivision within the material may play a role in determining the properties. A measure of such a distribution of free volume can be obtained by determination of the density fluctuation by the small-angle X-ray scattering technique.

The density fluctuation is defined formally as follows: Consider a reference volume v of arbitrary shape and size.

As this reference volume is moved around in the sample, the number of electrons N falling within the volume fluctuates about the mean $\langle N \rangle$. The density fluctuation $\psi(v)$ is then given by the ratio of the variance $\langle (N - \langle N \rangle)^2 \rangle$ to the mean $\langle N \rangle$:

$$\psi(v) = \langle (N - \langle N \rangle)^2 \rangle / \langle N \rangle. \quad (1)$$

Statistical mechanics shows that, for a liquid in equilibrium, $\psi(v)$ in the limit of $v \rightarrow \infty$ (i.e., in the thermodynamic limit) is given by

$$\psi(\infty) = \rho k T \kappa_T \quad (2)$$

where ρ is the density (of electrons) and κ_T is the isothermal compressibility. Equation (2) shows that the density fluctuation is induced by the thermal motion of atoms, with energy kT , but is opposed by the bulk rigidity $1/\kappa_T$.

As the temperature of the liquid is lowered, the volume (and the free volume) decreases, and at the same time the density fluctuation also decreases. As the temperature is further lowered through the glass transition temperature, the free volume becomes frozen in and ceases to change any further, according to the traditional view of the free volume. (More recently the possibility of some further minor decrease in the free volume, either at lower temperatures or with prolonged annealing, is sometimes admitted.) The density fluctuation, present in the liquid, also becomes frozen in at T_g as the thermal motion required to redistribute the atoms becomes sluggish. Unlike the free volume fraction, however, not all the density fluctuation becomes frozen in. Below T_g there still remain many modes of atomic motion which are fast in

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comparison to the experimental time scale. Such fast modes are responsible for the finite (though much reduced) compressibility κ_T^g observable below T_g . The density fluctuation induced by these fast modes of motions is therefore still present and can change with further lowering of the temperature. Thus the density fluctuation ψ^{glass} observed with glassy polymers consists of two contributions^{8,9}

$$\psi^{\text{glass}} = \psi_{\text{dyn}} + \psi_{\text{qst}} \quad (3)$$

where the quasi-static contribution, ψ_{qst} , arises from the part frozen in at T_g , and the dynamic contribution, ψ_{dyn} , is related to the compressibility of the glass κ_T^g by:

$$\psi_{\text{dyn}} = \rho k T \kappa_T^g \quad (4)$$

A rigorous justification for equations (3) and (4) was given previously¹⁰ from a statistical mechanical consideration of an idealized model, 'theorist's ideal glass', which was originally proposed by Edwards¹¹.

The intensity $I(s)$ of X-rays scattered (per unit volume of sample) in the direction s ($s = 2 \sin \theta / \lambda$) is related to the density fluctuation by^{12,13}

$$\psi(v) = \int (1/\rho) I(s) (1/v) [\phi(s)]^2 ds \quad (5)$$

where $\phi(s)$ is the Fourier transform of the form factor representing the reference volume v . In particular, the thermodynamic limit $\psi(\infty)$ can be obtained from the observed intensity by

$$\psi(\infty) = \lim_{s \rightarrow 0} (1/\rho) I(s) \quad (6)$$

The small-angle X-ray scattering technique is therefore a convenient way of determining $\psi(\infty)$, and its utility in the study of glassy polymers was first demonstrated by Wendorff and Fischer¹⁴, and Ruland and coworkers^{15,16}. We earlier utilized the technique to correlate⁸ the change in the specific volume with that in the density fluctuation observed with polystyrene samples annealed isothermally below its T_g , and also to correlate⁹ the specific volume and the density fluctuation of polystyrene glasses formed under elevated pressures. In this work we investigated two other polymers, poly(methyl methacrylate) and polycarbonate with respect to the changes in the specific volume and the density fluctuation which occurred on constant rate cooling and heating and on isothermal annealing at temperatures around and below T_g .

EXPERIMENTAL

Two samples of PMMA were studied. One is a commercial material obtained from E. I. duPont Co. and had a viscosity-average molecular weight of 380 000. The other was a narrow molecular weight sample obtained from Pressure Chemical Co. who provided us with the following information: $M_n = 640\,000$ (osmometry) and $M_w/M_n = 1.16$ (g.p.c.). The polycarbonate sample was purchased from Aldrich Chemical Co.

The density measurement was performed by dilatometry. The details of the small-angle X-ray scattering measurements were described elsewhere⁸. In particular,

the stability of the incident X-ray beam power was monitored by means of a separate scintillation counter mounted to receive stray scattering from the collimating system. The intensity data obtained was scaled to absolute units by comparison with the scattering from a calibrated Lupolen sample¹⁷ kindly supplied by Prof. O. Kratky. Correction for slit-smearing effects was also applied in the manner described previously⁸.

RESULTS

Figure 1 shows the specific volume against temperature plots of the two PMMA samples determined on cooling at $0.3^\circ\text{C min}^{-1}$. From the intersection of the extrapolated liquid and glass lines, the T_g found to be 106°C for the commercial PMMA and 113°C for the narrow fraction of 640 000 MW. The X-ray intensity $I(0)$, obtained by extrapolation of the observed intensity $I(s)$ to $s \rightarrow 0$, is plotted against the temperature in Figure 2 for the same two polymers. Here for each data point the X-ray intensity was collected for 200–300 s while the sample was being cooled at a constant 0.3°C/min rate, and the point was plotted at the temperature corresponding to the average of the interval spanned. From the intersection of the extrapolated liquid and glass lines, the T_g is obtained to be 113° and 120°C for the commercial and narrow fraction samples. The extrapolation of $I(0)$ values below T_g to 0 K leads to the values -159 and -155 ($\text{electron}^2/\text{nm}^3$) for commercial and narrow fraction samples – a result which does not confirm the previous assertion¹⁴ that $I(0)$ values below T_g are proportional to the absolute temperature.

The $I(0)$ values obtained with the commercial sample on cooling (at 0.3°C/min) and on subsequent heating (at

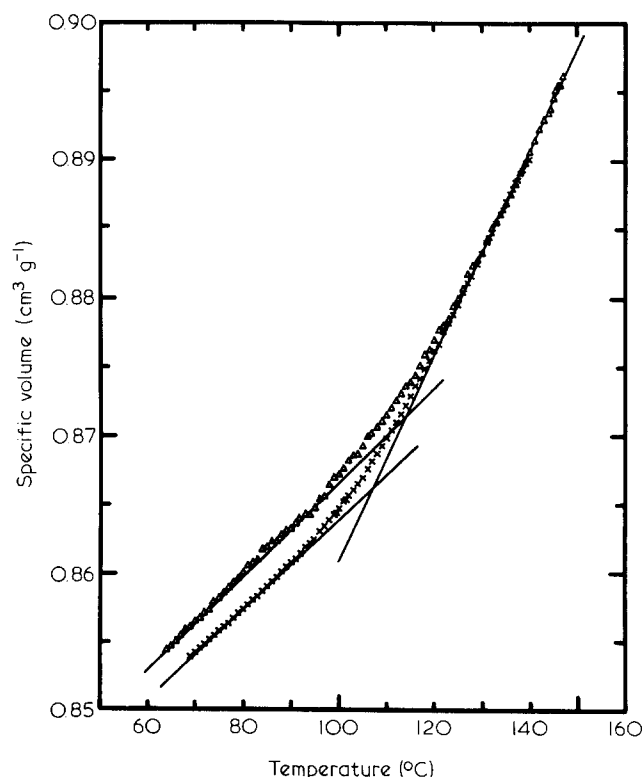


Figure 1 Specific volume of PMMA samples determined dilatometrically on cooling at $0.3^\circ\text{C min}^{-1}$. (Δ) narrow fraction of MW 640 000, (\times) commercial sample of viscosity average MW 380 000

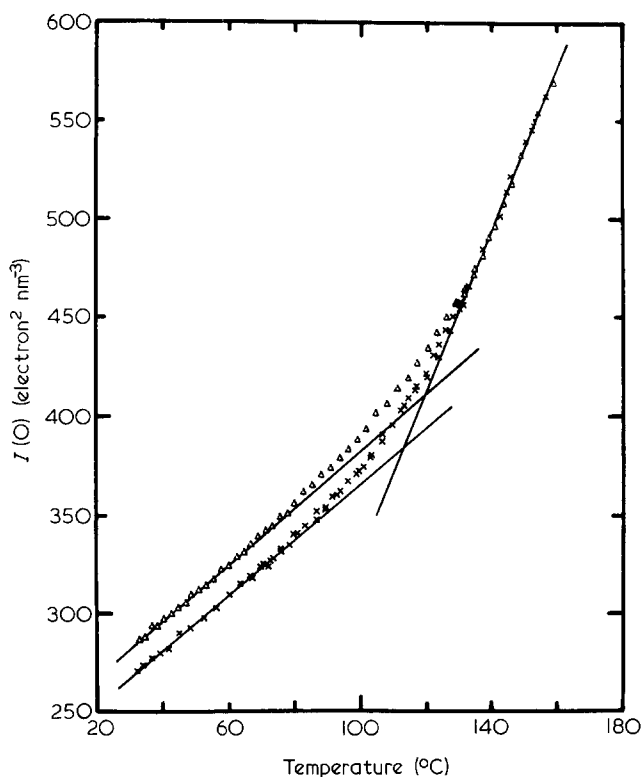


Figure 2 X-ray intensity $I(0)$, obtained by extrapolation of the observed intensity $I(s)$ to $s \rightarrow 0$, is plotted against temperature. The PMMA samples (triangles for the 640 000 MW fraction and crosses for the commercial sample) were cooled at a rate of $0.3^\circ \text{ min}^{-1}$ during the measurements

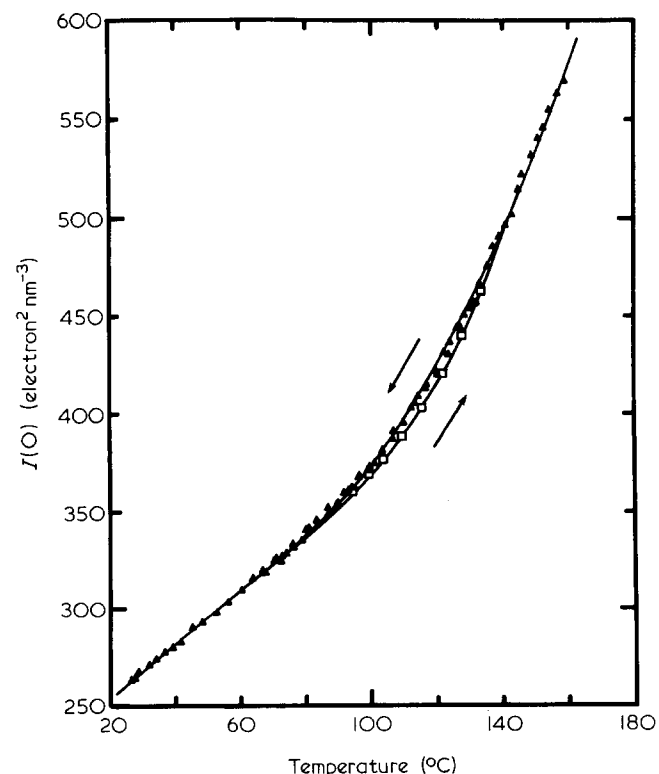


Figure 3 Comparison of $I(0)$ values obtained with the commercial PMMA on cooling at $0.3^\circ \text{ min}^{-1}$ (solid triangles) and on subsequent heating at $0.5^\circ \text{ min}^{-1}$ (open squares). Only a very slight hysteresis effect is noted

0.5° C/min) are compared in *Figure 3*. Only a very slight hysteresis effect is noted. This is to be contrasted with the very pronounced hysteresis effect previously observed with polystyrene⁸.

Figure 4 shows the isothermal volume relaxation of the commercial PMMA obtained with dilatometry. The excess specific volume (that is, the specific volume in excess of the extrapolated liquid line shown in *Figure 1*) is here plotted against the logarithm of the annealing time. At all temperatures below the glass transition temperature (106° C) the volume is seen to decrease linearly with $\log t$. Above T_g there is a temperature interval of about 20° in which an appreciable relaxation in volume is still noticeable. The shape of the volume relaxation curves

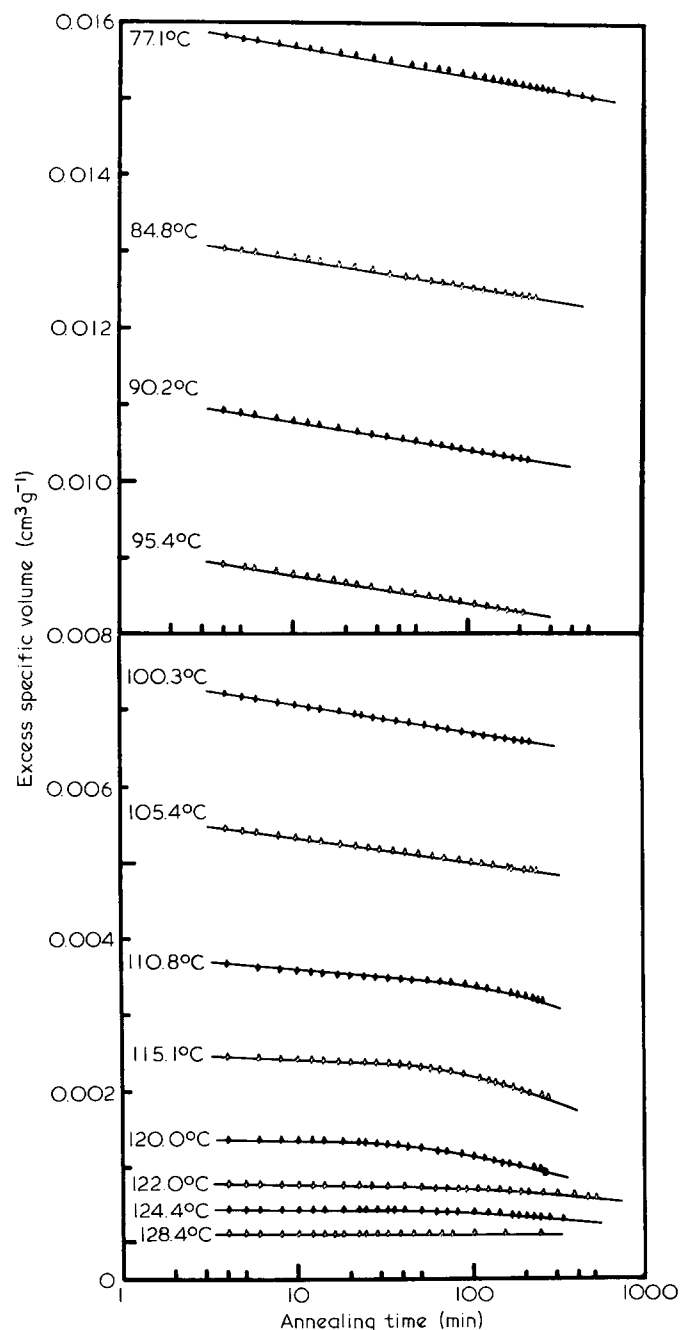


Figure 4 Isothermal volume relaxation of the commercial PMMA obtained by dilatometry. The ordinate shows the specific volume in excess of the extrapolated liquid line (see *Figure 1*). Note that below the glass transition temperature (106° C) the volume decreases linearly with the logarithm of time, and the slope remains approximately constant over the 30° interval shown

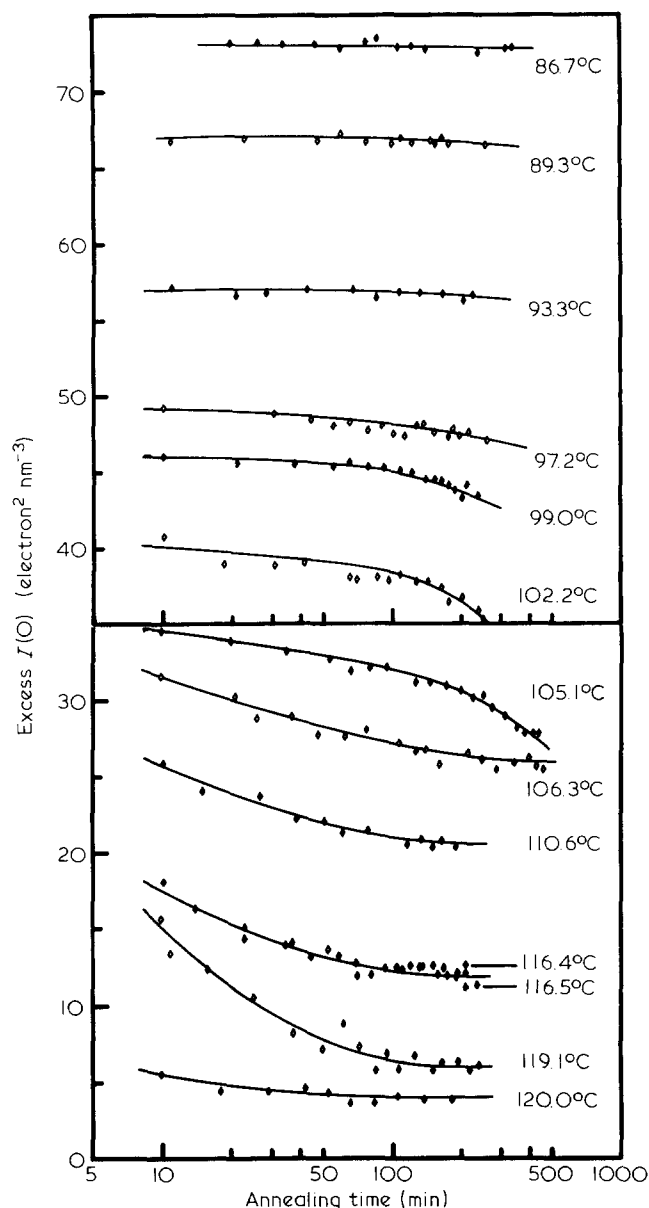


Figure 5 The change in the density fluctuation observed with the commercial PMMA sample upon isothermal annealing. The ordinate shows the excess of the observed $I(0)$ over the extrapolated liquid $I(0)$ values

exhibited in this interval is different from those observed below T_g . Instead of the steady decrease, linear with $\log t$, prevalent below T_g , the volume in this interval shows an initial period of 20–100 min with little change, which is then followed by a period of a more noticeable decrease. It does not seem possible to explain these differences in the shape of the relaxation curves as representing the different sections (of different mean relaxation times) of a single overall volume relaxation curve (the master curve).

The effect of isothermal annealing on the density fluctuation was also measured with the commercial PMMA samples and the results are shown in Figure 5. Here again, the excess of the observed $I(0)$ over the extrapolated liquid $I(0)$ value is plotted against $\log t$. During these measurements the sample was always kept in the X-ray camera *in vacuum*. The sample was at first heated to temperatures 25°–30° above T_g and then was cooled rapidly to the desired annealing temperature. After the temperature jump it took about 2–3 minutes for the temperature to stabilize to within 0.1° of the desired temperature.

The shape of the curves in Figure 5 follows two distinct patterns. Below 106°C (which is the glass transition temperature obtained from the volume measurement) the curves show an initial period of a linearity with $\log t$, followed by a period of an 'apparently' more rapid decrease. (The absolute rate of change is not necessarily faster, and the apparent acceleration is the consequence of plotting against $\log t$.) The pattern of change exhibited by $I(0)$ immediately below 106°C is similar to the pattern of the volume change observed *above* 106°C. The slope of the initial section, linear with $\log t$, decreases as the temperature is lowered, and eventually below 90°C little change can any longer be detected over the period of observation extending to about 6 h. Above 106°C the $I(0)$ values show an initial rapid decrease followed by a levelling-off. The values to which it has levelled off at the end of the 5–10 h annealing period is, however, still far above the extrapolated liquid line and is rather close to the values obtained on a constant 0.3° min⁻¹ cooling, as is illustrated in Figure 6.

The results of $I(0)$ measurements on isothermal annealing with the narrow fraction PMMA sample are shown in Figure 7. Here again, the distinction between the two types of kinetic behaviour noted above is recognizable. The change-over in the behaviour occurs at about 108°C, which is a little higher than the 106°C found with the commercial PMMA sample. This difference probably reflects the higher T_g of the narrow fraction sample but is not as large as the difference in T_g suggests.

Figure 8 shows the $I(0)$ values obtained with the polycarbonate sample on cooling at a constant rate of 0.3°C/min. The intersection of the liquid and glass lines yields the T_g of 144°C, and the extrapolation of the glass lines gives the $I(0)$ value at 0 K equal to 94 electron²/nm³.

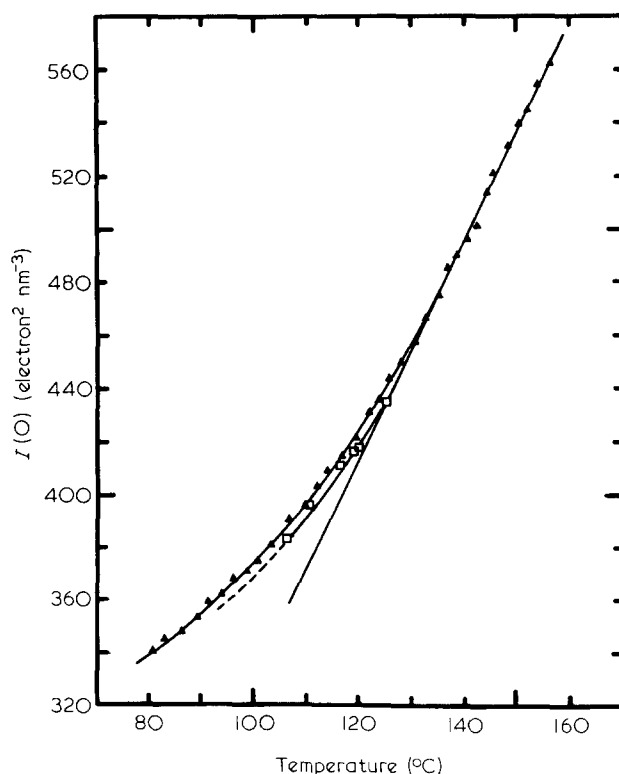


Figure 6 Values (□) to which the observed $I(0)$ has levelled off at the end of 5–10 h of annealing (see Figure 5) are compared with the $I(0)$ values (▲) directly observed on cooling at 0.3° min⁻¹. It illustrates that the extent of change in the density fluctuation on isothermal annealing is rather small

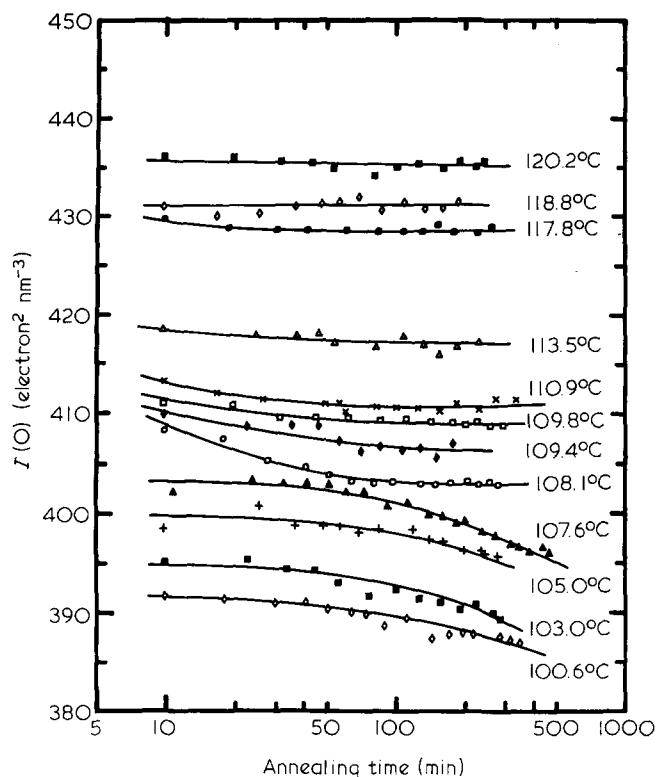


Figure 7 The $I(0)$ values observed on isothermal annealing of the narrow fraction PMMA sample

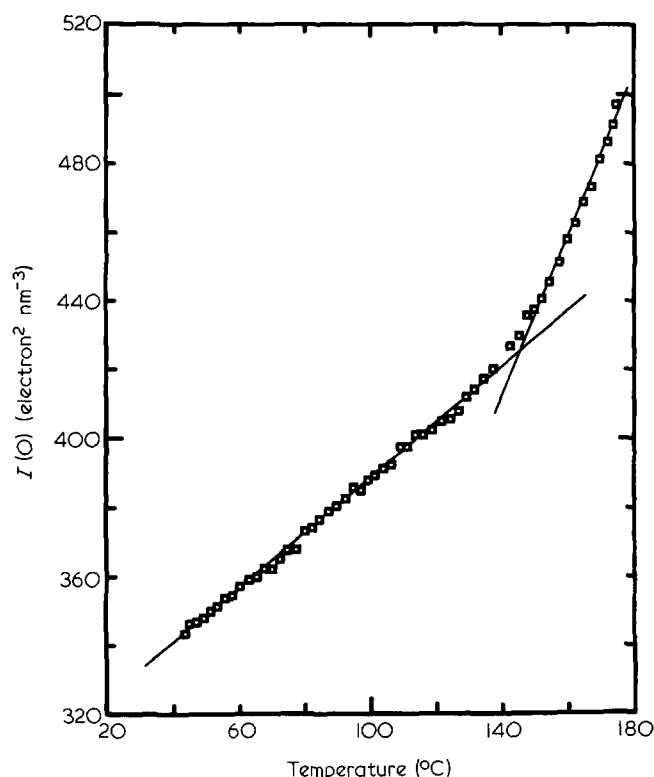


Figure 8 The $I(0)$ values observed with the polycarbonate sample on cooling at $0.3^\circ \text{ min}^{-1}$

Polycarbonate shows only a narrow temperature range around T_g ($\approx 130^\circ\text{--}152^\circ\text{C}$) in which the observed $I(0)$ values deviate from the extrapolated liquid or glass lines. This should be contrasted with the similar but broader transition regions, amounting to $\approx 93^\circ\text{--}121^\circ\text{C}$ for the commercial PMMA, $\approx 96^\circ\text{--}126^\circ\text{C}$ for the narrow fraction PMMA, $\approx 68^\circ\text{--}107^\circ\text{C}$ for the 133 000 MW polystyrene⁸ and $\approx 70^\circ\text{--}106^\circ\text{C}$ for the commercial polystyrene⁸.

The results of measurements of density fluctuation on isothermal annealing of polycarbonate are shown in Figure 9. The change in the pattern of kinetic behaviour is seen to occur at around 141°C , which is again close to the glass transition temperature. With polycarbonate the temperature range within which any change in the density fluctuation is observable at all is rather narrow – from about 130° to 147°C . This fact agrees with the rather narrow transition region around T_g noted in Figure 8. Earlier Wendorff¹⁸ measured the small-angle X-ray scattering from polycarbonate samples annealed at 124°C for up to 1000 h and could not detect any change in the density fluctuation. His data thus support our results and show that outside the narrow temperature range of $130^\circ\text{--}147^\circ\text{C}$ no measurable density fluctuation can be induced by annealing for even a substantially longer period of time than we employed.

DISCUSSION

The change in the density fluctuation with temperature and with annealing time has by now been observed with three polymers, polystyrene, PMMA, and polycarbonate, and the results can be summarized as follows. The plot of $I(0)$ versus T is qualitatively similar to the familiar V versus T plot and consists of three regions, the liquid region (approximately linear with T); the transition region of a 20° to 40° interval around T_g , and the glass region (approximately linear with T , at least in the limited temperature range studied). The hysteresis effect between cooling and heating can be observed *only* in the transition region. On isothermal annealing any change in the density fluctuation with time is also observable *only* in the transition region. Within this transition region, two distinct patterns of change in $I(0)$ with $\log t$ can be noticed and the change-over from one to the other occurs rather abruptly at a temperature close to T_g .

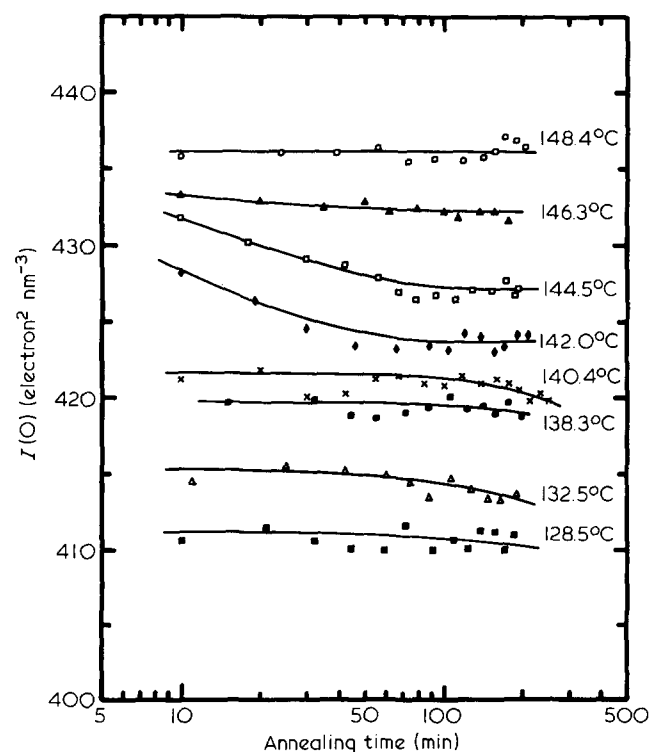


Figure 9 The changes in the $I(0)$ values observed with the polycarbonate sample on isothermal annealing

When these observations on the density fluctuation are compared with those on the corresponding changes in the specific volume, the following differences and similarities can be noted. On isothermal annealing, the change with time in the specific volume is observable both in the transition region and the glass region. The kinetic pattern of volume change observable above T_g is again fairly distinct from the one below T_g , and the latter (both in the transition region below T_g and in the glass region) can be described by a linear function of $\log t$. In Figure 4 it is seen that the slope of such linear plots for PMMA remains approximately constant between 77°C and 105°C. It was previously noted¹⁹ that the enthalpy change of polystyrene on isothermal annealing can also be described by a linear function of $\log t$ with an approximately constant slope over a similarly wide temperature range. In contrast to the behaviour of the specific volume and the enthalpy, the density fluctuation shows no observable change, outside the transition region, even on prolonged annealing.

Photon correlation spectroscopy performed on polystyrene^{20,21} and PMMA²² shows that the relaxation time spectra of these polymers near T_g are extremely broad and span several decades of time. Studies of mechanical properties and analysis²³ of volume and enthalpy relaxation data likewise reveal the existence of a wide distribution of relaxation times in glassy polymers. One may therefore attempt to explain the differences between the kinetic behaviour of the density fluctuation and the specific volume on the basis of the broadness of the relaxation time spectrum. One might, for example, argue that the density fluctuation depends more on those molecular motions having the longer of the relaxation times within the overall spectrum. One might then continue, that the failure to observe any change in the density fluctuation on annealing in the glass region could be a consequence of the much longer time necessary for the density fluctuation to change. On closer examination, however, it appears unlikely that the qualitative difference between the kinetic behaviour of the density fluctuation and of the specific volume can be explained on the basis of the difference in the effective time scale alone. Within the transition region the effective relaxation times of the density fluctuation and of the volume are apparently of the same order of magnitude, yet the kinetics of the two diverge enormously from each other as the temperature is lowered below the transition region.

As is well known, the success of the time-temperature superposition principle, which allows reduction of mechanical property data at different temperatures into a single master curve, arises from the fact that essentially the same activation energy is shared by all the relaxation modes represented in the relaxation time spectrum. In contrast to this, the density fluctuation and the specific volume exhibit very different temperature dependences and certainly do not share the same activation energy. Thus these two properties are unlikely to be explainable by the same relaxation spectrum in which all modes have the same activation energy. A difference in the temperature dependencies was also noted earlier²⁴ when we compared the change in creep properties on isothermal annealing with the corresponding change in enthalpy. It was then suggested that the relaxation time spectrum representing the molecular motions responsible for the creep has to be very different from the spectrum which governs the enthalpy relaxation. Similarly, it appears as

though we may have to assume two distinct spectra to explain the temperature dependence of the density fluctuation and of the specific volume.

The definition of the density fluctuation $\psi(v)$, formally given by equation (1) in terms of the number of electrons N in a volume v , does not immediately reveal its relation to the specific volume or the free volume. In order to gain some intuitive understanding of its physical meaning, we now seek to establish a link between $\psi(v)$ and the distribution of free volume. Although the free volume concept is widely discussed on an intuitive basis, it usually lacks a detailed definition. A more specific model of free volume is, however, required for the purpose of calculating the density fluctuation. We therefore adopt the following heuristic model. The free volume consists of a collection of holes of various sizes dispersed randomly in the continuous material medium. The average number of holes (of all sizes) per unit volume is n , and the electron density in the continuous medium surrounding the holes is ρ_0 . The holes are classified according to their sizes; there are s different sizes available; the volume per hole of the j -th size is equal to f_j ($j = 1 \dots s$); and the number fraction of the holes of the j -th size is equal to q_j ($\sum q_j = 1$). The moments of the distribution of the hole volumes f_j is given by

$$\langle f^m \rangle = \sum_{j=1}^s f_j^m q_j \quad (7)$$

Let us consider a reference volume v within this material studded with holes. The probability that it contains k holes is specified by $P(k)$, and the probability that l_j holes out of these k are of size j ($j = 1 \dots s$) is specified by $Q_k(l)$, where $l = (l_1, l_2, \dots, l_s)$, and $\sum l_j = k$. The number of k of holes in the volume v varies of course as v is taken elsewhere in the sample. The moments of the distribution of k are given by

$$\langle k^m \rangle = \sum_k k^m P(k) \quad (8)$$

If $P(k)$ and $Q_k(l)$ are statistically independent, that is, if the size distribution among the holes found within the volume v is not influenced by the number of the holes in v , then it follows that

$$Q_k(l) = k! \sum_{j=1}^s q_j^{l_j} / l_j! \quad (9)$$

The number of electrons N within the volume v is given by

$$N(k, l) = \rho_0(v - lf) \quad (10)$$

where $f = (f_1, f_2, \dots, f_s)$. By multiplying $N(k, l)$ with $P(k)Q_k(l)$ and summing for all values of k and l we obtain

$$\langle N \rangle / \rho_0 = v - \langle k \rangle \langle f \rangle. \quad (11)$$

Similarly, for the variance of N we obtain

$$\langle \delta N^2 \rangle / \rho_0^2 = \langle f \rangle^2 \langle k^2 \rangle - \langle k \rangle^2 + \langle k \rangle \langle f^2 \rangle - \langle f \rangle^2. \quad (12)$$

From the ratio of equations (12) and (11), the density fluctuation $\psi(v)$ can be evaluated. To obtain an expression of any utility, a further knowledge on the distribution of k is required. We now make the assumption that the locations of the holes are entirely random in space. When holes are created and annihilated dynamically and the

holes are separated far from each other, the creation of a hole at a given site may be considered an even independent of the presence of other nearby holes. If such an assumption is justified, then the distribution of k is given by the Poisson distribution with

$$\langle k^2 \rangle = \langle k \rangle^2 + \langle k \rangle, \quad (13)$$

and the density fluctuation becomes

$$\psi(v) = \rho \langle f \rangle_w \phi / (1 - \phi)^2 \quad (14)$$

where ϕ is the free volume (or hole volume) fraction

$$\phi = \langle k \rangle \langle f \rangle / v, \quad (15)$$

ρ is the apparent (or overall) electron density

$$\rho = \rho_0 (1 - \phi), \quad (16)$$

and $\langle f \rangle_w$ is the weight-average volume of a hole

$$\langle f \rangle_w = \langle f^2 \rangle / \langle f \rangle. \quad (17)$$

To see whether equation (14) presents a physically plausible picture, we can make the following simple numerical calculation. The WLF equation is known to be consistent with the value of 0.025 for the free volume fraction ϕ at T_g for a large number of polymers^{25,26}. For the commercial PMMA sample at 106°C, the observed specific volume and $I(0)$ value are 0.8675 cm³ g⁻¹ and 386 electron² nm⁻³, respectively. From these it follows that the electron density ρ equals 374.4 electrons nm⁻³ and the density fluctuation $\psi = I(0)/\rho$ equals 1.031 electrons. Substitution of these values in equation (14) leads to the value of the weight-average hole volume $\langle f \rangle_w$ equal to 0.105 nm³ = (0.47 nm)³, which corresponds to a volume of 0.74 monomers. We further calculate the average number n of holes per unit volume by the relation

$$\phi = n \langle f \rangle_n = n \langle f \rangle_w \langle f \rangle_n / \langle f \rangle_w \quad (18)$$

where $\langle f \rangle_n$ ($\equiv \langle f \rangle$) is the number-average hole volume. With the numerical values employed above, it turns out that $n = 0.239 \text{ nm}^{-3} \times \langle f \rangle_w / \langle f \rangle_n$. No information about the hole size distribution is available, but if we assume an exponential distribution, then we find $\langle f \rangle_w / \langle f \rangle_n = 2$ and $n = 0.478 \text{ nm}^{-3} = 1/(1.28 \text{ nm})^3$.

On the basis of the data on the positronium annihilation and ultrasonic velocity, Malhotra and Pethrick^{27,28} estimated the size of free volume cavities following the analysis of Ujihira *et al.*²⁹ They estimated the cavities in polycarbonate, polysulphone and polyether-sulphone to be between 0.17 and 0.26 nm in radius and those in polydimethylsiloxane to be around 0.7 nm in radius. Thus, their estimate of the cavity size in glassy polymers agrees reasonably well with our estimate ($\approx 0.5 \text{ nm}$ in diameter) based on the density fluctuation data.

Equation (14) shows that a change in the density fluctuation ψ arises essentially from two sources, the changes in the free volume fraction ϕ and in the size of the holes. At temperatures below the transition region, the experimental results show that the specific volume decreases while the density fluctuation remains virtually unchanged on isothermal annealing. In terms of equation

(14) it then means that while the free volume fraction decreases with time, the average hole size has to increase. The increase in the weight-average hole volume can result either from a coalescence of holes or from a preferential elimination of smaller ones while the larger ones remain unchanged.

The purpose of the above derivation of equation (14) in terms of the distribution of holes is to provide an aid for visualizing the concept of density fluctuation through a concrete physical picture. The numerical values of the average size and density of holes evaluated above are in the realm of plausibility. The agreement of our estimate with those based on the positronium annihilation and ultrasonic data lends further support to the plausibility. There is, however, at present no way of justifying all the assumptions employed in the derivation of equation (14). It remains to be seen whether the model is successful in correlating other types of data which might be obtained in the future. For the present it should prove useful in stimulating further thoughts on the relationship between the density fluctuation and free volume.

ACKNOWLEDGEMENTS

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