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Isothermal Relaxation of Volume and Density Fluctuation of Polystyrene Glass Prepared under Elevated Pressure

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ABSTRACT: Glasses having densities much higher than usual were prepared by cooling polystyrene from the liquid state under elevated pressure (up to 3 kbar) and then releasing the pressure at room temperature. Such densified glasses are unstable and in time undergo structural relaxation. The changes is specific volume and density fluctuation (measured by small-angle X-ray scattering) of these samples were determined at 25 and 50 °C. Both of these quantities show slow increase with time, the rate being higher with the samples prepared at higher pressures. Although the volume continues to expand throughout the period of observation, the density fluctuations of some of the samples (prepared under higher pressures and annealed at 50 °C) go through a maximum. The result of separation of the density fluctuation into its dynamic and quasi-static components, by an approximate method, suggests that the frozen density fluctuation eventually undergoes "healing" as the annealing progresses. The volume expansion can be considered analogous to the so-called memory effect and can be explained by a phenomenological model postulating a multiplicity of independent relaxation modes with distinct relaxation times. Anomalously intense scattering of X-rays at very low angles suggests the presence of microcavities formed during the pressure release. The existence of intrinsic heterogeneity in glassy polymers resulting from the frozen-in density fluctuation could be responsible for the creation of such microcavities, which were recognized by others as precursors to craze formation.

Introduction

The nonequilibrium nature of the glassy state is demonstrated, most clearly, by the slow changes occurring in the properties of the glass annealed below its glass transition temperature. Much study has been made on the sub-T_g relaxation of specific volume, enthalpy, mechanical properties, and other properties of polymeric and nonpolymeric glasses. The phenomenology of such "physical aging" is by now reasonably well understood, although molecular interpretation of the underlying process has yet to be achieved.

Glasses having unusually high densities can be prepared by applying elevated pressure to the material well above its T_g and then cooling to room temperature before releasing the pressure. Such pressure-densified glasses exhibit many unusual properties which, when studied in detail, provide additional insight into the molecular nature of the glassy state. Depsite the potential wealth of information obtainable, relatively little study has been made on them, and even less is reported about the relaxation of their properties below T_g.

In our previous paper[1] we reported the results of measurement of specific volume and density fluctuation of polystyrene glasses prepared under various elevated pressures. In this work we extend the study and report on the changes with time in the specific volume (determined by a density gradient column) and density fluctuation (determined by small-angle X-ray scattering). Such changes were observed with polystyrene glasses prepared under various pressures (up to 3 kbar) and annealed isothermally at 25 and 50 °C. The changes in these properties obtainable with pressure-densified samples are usually greater by nearly an order of magnitude than the corresponding changes achieved on physical aging of ordinary (atmospheric) glasses.

Scattering of X-rays by a single-component amorphous substance is caused by the presence of spatial electron-density fluctuation, which in turn is due to statistical variation of the local packing density of atoms through the material. Such density fluctuation arises by the thermal motion of atoms and molecules in the case of liquids and by the frozen-in disorder as well as the residual thermal motion in the case of glasses. If we regard the atoms to occupy well-defined, finite core volumes, then the presence of density fluctuation necessarily means the presence of fluctuation in the local free volume. Thus in any attempt to interpret the relaxation behavior of glasses through the concept of free volume, knowledge of free volume fluctuation and its change under various conditions should be important.

The electron-density fluctuation can be defined rigorously in the following manner. Consider a reference volume, v, of arbitrary size and shape. As this reference volume is moved around in the sample, the number, N, of electrons falling within the volume fluctuates about the mean $\langle N \rangle$. The extent of the fluctuation is expressed by the variance $\langle (N - \langle N \rangle)^2 \rangle$, where $\langle ... \rangle$ denotes a spatial average over the scattering volume. The electron-density fluctuation $\psi(v)$ is defined as

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

$\psi(v)$ can be determined from the knowledge of the intensity $I(s)$ of scattered X-rays as a function of scattering angle s ($s = (2 \sin \theta)/\lambda$). In particular, $\psi(\infty)$ can be related simply to the intensity $I(0)$ extrapolated to angle 0 by

$$\psi(\infty) = I(0)/\rho \qquad (2)$$

where ρ is the electron density (and $I(0)$ is given in electron units per unit scattering volume). $I(0)$ is thus related, strictly speaking, only to the density fluctuation among volumes of macroscopic sizes. However, as shown elsewhere in detail,[2] $\psi(v)$ is nearly independent of the size of the reference volume v so long as v is sufficiently larger than the atomic dimension, so that $I(0)/\rho$ in effect provides the information on the local density fluctuation that we are after. If the material consists of a single type of atoms, the atomic density fluctuation $\psi_{at}(v)$ can be related to the electron density fluctuation $\psi_{el}(v)$ considered above by

$$\psi_{at}(v) = \psi_{el}(v)/Z \qquad (3)$$

where Z is the atomic number.

Experimental Section

The polystyrene sample used was obtained from Monsanto Co., and was specially prepared to contain none of the additives usually present in commercial polymers. Its viscosity-average molecular weight is 215000. This is the same commercial polystyrene as

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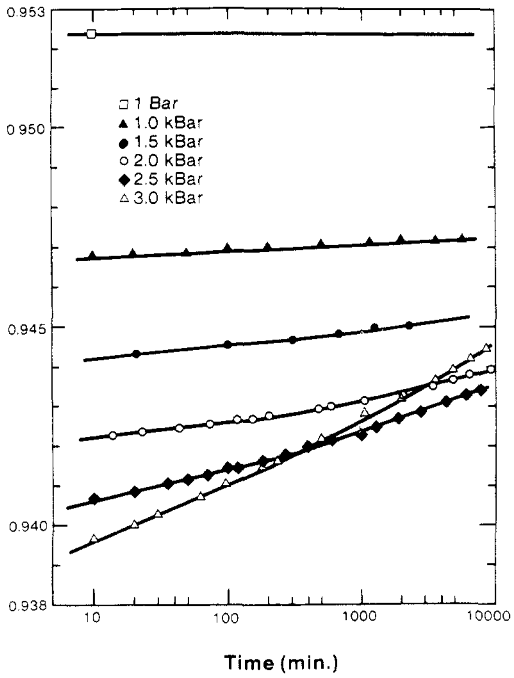

Figure 1. Change in specific volume of pressure-densified polystyrenes on annealing at 25 °C. The pressure employed during the preparation of the sample is indicated.

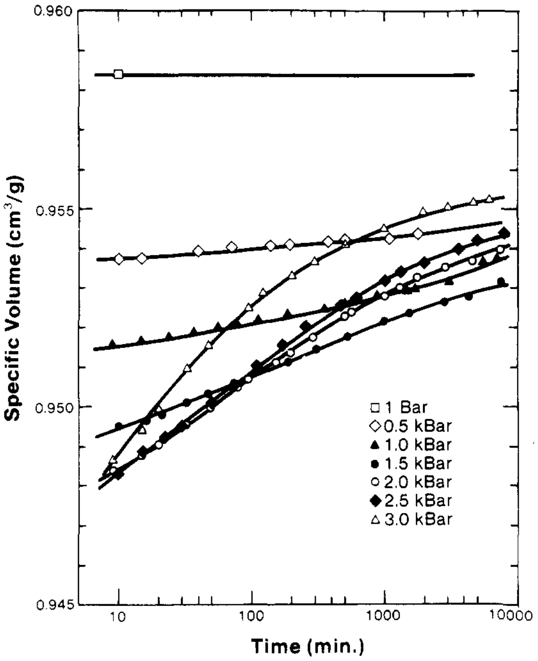

Figure 2. Change in specific volume of pressure-densified polystyrenes on annealing at 50 °C.

was studied in our previous work.[1,2] The polymer pellets were dried at about 100 °C under vacuum for 24 h just before use. The method of preparing the densified samples was substantially the same as described in the previous publication.[1] Briefly stated, the sample was initially heated to a temperature corresponding to about 30 °C above the anticipated T_g under the intended elevated pressure, assuming that dT_g/dP is equal to 30 °C/kbar.[3] After application of pressure, it was cooled at a rate of 3 °C/min to room temperature before the pressure was released.

Small-angle X-ray scattering measurements were performed with a Kratky camera coupled[1] to a Tennelec one-dimensional position-sensitive detector. The method of determingin $I(0)$ and scaling it to the electron units was described previously.[1,2] During the whole period of measurement of the change in $I(0)$ with time, lasting about a week, the sample was kept inside the Kratky camera undisturbed under vacuum, either at room temperature or at 50 °C. A separate scintillation counter, positioned to receive stray scattering from the collimating system, was utilized to monitor any variation in the incident X-ray beam power during the 1-week-long period, and a correction to the measured values of $I(0)$ was made accordingly.

The specific volume of the sample and its variation with time were determined by means of a density gradient column containing an aqueous solution of sodium chloride. The temperature of the column was maintained at 25 or 50 °C by circulating water through a jacket surrounding the column. A small piece of sample introduced into the column was left undisturbed, and the change in its position relative to those of calibrated glass beads was monitored over a period lasting a week or longer. Initially, it was noticed that even an ordinary sample prepared under atmospheric pressure exhibited a downward drift in the column, at first fairly rapidly and then at a gradually decreasing rate. For example, the apparent specific volume of a piece decreased at 25 °C from 0.95271 to 0.95246 cm^3/g in the first 200 min and then eventually to 0.95240 at the end of a week. We suspected this to arise from slow absorption of water into the polystyrene. We measured the rates of apparent density increase of several samples having different thicknesses and found their dependence on thickness to be consistent with a diffusion model. Thereafter, the thickness of all the samples prepared for density measurements was standardized to 0.06 cm, and the observed specific volume was corrected according to a calibration curve established with a sample of the same thickness prepared under atmospheric pressure. Modification of the rate of volume relaxation itself by the absorption of water, although conceivable, is probably negligibly small in view of the very small solubility of water in polystyrene.

Results and Discussion

The specific volume of pressure-densified samples expands rather appreciably as time elapses, as the results given in Figures 1 and 2 illustrate. Here the abscissa refers to the time in minutes from the moment of pressure release. The features exhibited at the two temperatures are qualitatively similar, except that the rate of volume expansion is higher at 50 °C. At any given temperature, the sample prepared under a higher pressure shows a smaller initial volume and a higher rate of volume expansion, so that the various curves for samples prepared under different pressures cross each other in time. Oels and Rehage[5] previously determined the volume change of pressure-densified polystyrene glasses at room temperature by dilatometry and obtained a similar result showing crossing relaxation curves. Volume expansion of pressure-densified polystyrene itself was noted even earlier by Weitz and Wunderlich.[6]

The change with time in the density fluctuation of pressure-densified samples shows overall features very similar to the expansion of specific volume. Figures 3 and 4 give the changes in $I(0)$ values observed at 25 and 50 °C, respectively, with samples prepared under various pressures. The curves depicting the behaviors of samples of different formation pressures are again seen to cross each other, although at 50 °C the crossover evidently occurred in some cases even before the measurement could be commended 10 min after the pressure release. One particular feature in the relaxation of $I(0)$, however, differs from the corresponding behavior in specific volume. For samples formed under pressures 2.0 kbar and higher the curves in Figure 4 show that the $I(0)$ values pass through a maximum and then decrease slowly even within the time period of our observation. No corresponding maxima could be observed with the specific volume shown in Figures 1 and 2. It is, however, probable that the specific volume may eventually go through a maximum at much longer time. Indeed, Weitz and Wunderlich[6] report that their polystyrene sample, prepared under 2.8 kbar, exhibited a

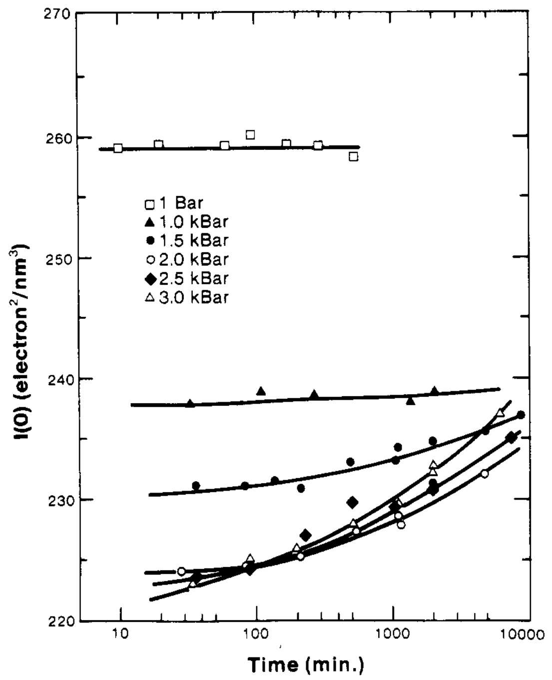

Figure 3. Change in the extrapolated intensity $I(0)$ of X-rays scattered from pressure-densified polystyrenes on annealing at 25 °C.

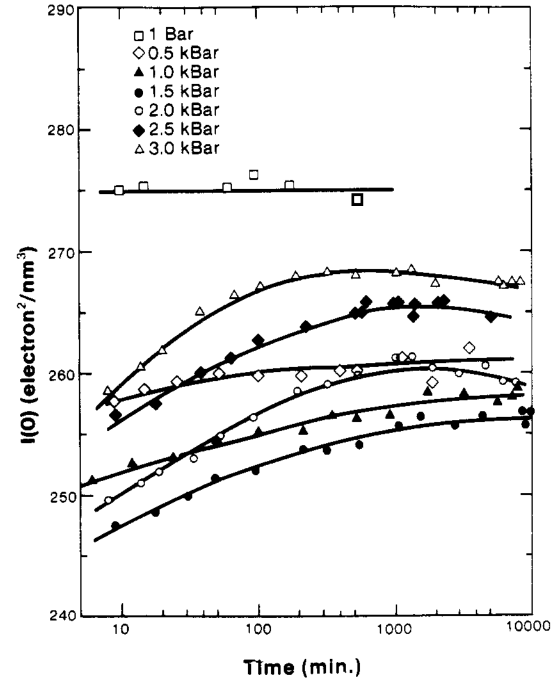

Figure 4. Change in the extrapolated intensity $I(0)$ of X-rays scattered from pressure-densified polystyrenes on annealing at 50 °C.

maximum in volume after 5 h at 70 °C.

The magnitudes of changes obtained here in both specific volume and density fluctuation are very large in comparison to the corresponding changes that can be induced on physical aging of atmospheric samples (that is, those prepared under atmospheric pressure). For example, with an atmospheric polystyrene sample[2] at 90 °C the specific volume might decrease by 0.001 cm^3/g and $I(0)$ by 7 electron^2/nm^3 from 10 to 1000 min of annealing. In contrast, in Figures 1–4 it is seen that in the same time period the specific volume of pressure-densified samples increases by as much as 0.007 cm^3/g and $I(0)$ by 20 electron^2/nm^3.

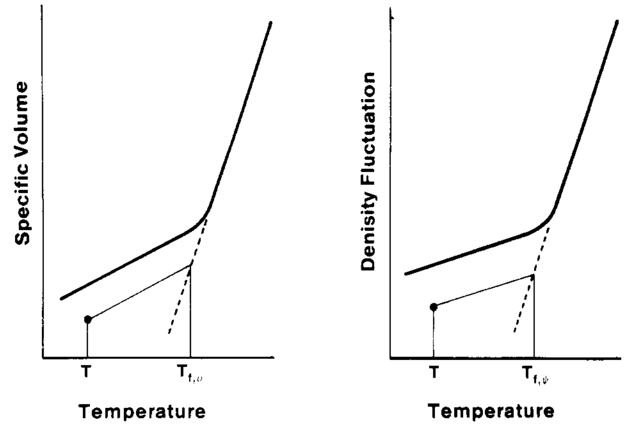

Figure 5. Schematics to illustrate the definition of (left) fictive temperature $T_{f,v}$ based on volume and (right) fictive temperature $T_{f,\psi}$ based on density fluctuation.

The change of 0.007 cm^3/g amounts to a less than 1% change in the total specific volume, while the change of 20 electron^2/nm^3 amounts to a nearly 10% change in the density fluctuation. It thus appears, at first sight, that a much larger change in density fluctuation accompanies a relatively smaller change in specific volume. Such a comparison is, however, somewhat misleading, and a more rational way would be to look at the relative change in free volume rather than in total volume. A convenient way of making the comparison on this basis is to utilize the so-called "fictive temperature". Figure 5 illustrates the definition[7] of fictive temperature, T_f, of a glassy sample either with respect to its specific volume or with respect to its density fluctuation. The difference $T_f - T$, where T is the actual temperature of observation, gives a direct measure of the departure of the internal structure of the sample from equilibrium as it is perceived through the particular property considered (specific volume, density fluctuation, etc.). If it turns out, as is often the case,[8] that three thermodynamic variables (T, p, and v) are not sufficient to describe the nonequilibrium state of the glass uniquely, then two fictive temperatures defined in reference to two different properties may differ from each other, that is, $T_{f,v} \neq T_{f,\psi}$, where $T_{f,v}$ and $T_{f,\psi}$ are the fictive temperatures based on specific volume and density fluctuation, respectively.

The density fluctuation of an atmospheric polystyrene sample above and below T_g was previously determined,[2] using the same polystyrene as used here to make the sample. From this result the following empirical equation can be derived to give an approximate value of $T_{f,\psi}$ from the knowledge of $I(0)$.

$$T_{f,\psi} = 0.700I(0) - 0.1926T - 98.5 \qquad (4)$$

where both $T_{f,\psi}$ and T are in °C and $I(0)$ is in electron^2/nm^3. Similarly, utilizing the data for the specific volume of polystyrene above and below T_g given by Richardson and Saville,[9] the following equation can be derived to calculate $T_{f,v}$ from the knowledge of the specific volume v.

$$T_{f,v} = 2849v - 0.5869T - 2614 \qquad (5)$$

The values of v and $I(0)$ at 10 and 5000 min of annealing, read off from Figures 1–4, were converted into the corresponing fictive temperatures by means of eq 4 and 5, and the results are listed in Table I. The following remarks can be made about the features revealed in Table I. (1) In all cases, $T_{f,v}$ and $T_{f,\psi}$ are both larger than T. This means that the specific volume and density fluctuation of

Table I
Changes in Fictive Temperature with Time

prep press, kbar	anneal temp, °C	anneal time, min	$T_{f,v}$, °C	$\Delta T_{f,v}$, °C	$T_{f,\psi}$, °C	$\Delta T_{f,\psi}$, °C
1.0	25	10	68.8		62.9	
		5000	69.6	0.8	63.6	0.7
1.5	25	10	61.4		58.3	
		5000	64.1	2.7	61.9	3.6
2.0	25	10	55.7		52.2	
		5000	59.6	3.9	59.6	7.4
2.5	25	10	51.4		52.3	
		5000	58.2	6.8	60.1	7.8
3.0	25	10	48.5		51.5	
		5000	60.5	12.0	61.7	10.2
0.5	50	10	73.8		72.3	
		5000	76.0	2.2	75.1	2.8
1.0	50	10	67.5		68.1	
		5000	72.9	5.4	72.1	4.0
1.5	50	10	61.2		65.1	
		5000	71.2	10.0	71.2	6.1
2.0	50	10	58.4		67.1	
		5000	73.9	15.5	73.5	6.4
2.5	50	10	58.4		71.5	
		5000	75.2	16.8	77.0	5.5
3.0	50	10	59.5		73.5	
		5000	77.7	18.2	78.9	5.4

our densified samples are always higher than the values expected of an (extrapolated) equilibrium liquid. It is therefore interesting to note that both v and $I(0)$ increase with time, that is, change in the direction away from the equilibrium liquid. Moreover, the rate of increase is not related, in any obvious way, to the magnitude of $T_{f,v} - T$ or $T_{f,\nu} - T$. (2) In the case of the data obtained at 25 °C, $T_{f,v}$ is approximately equl to $T_{f,\psi}$ with all the samples, both at 10 and at 5000 min of annealing. With the data obtained at 50 °C even closer agreements between $T_{f,v}$ and $T_{f,\psi}$ are observed at 5000 min of annealing. At 10 min of annealing at 50 °C, on the other hand, there are substantial differences between them, especially with those samples prepared under pressure higher than 1.5 kbar. It shows that, in these latter cases, $T_{f,\psi}$ increases much more rapidly than $T_{f,v}$ in the first few minutes after the pressure release, but eventually $T_{f,v}$ and $T_{f,\psi}$ attain comparable values at longer times. (3) The changes, $\Delta T_{f,v}$ and $\Delta T_{f,\psi}$, in the fictive temperatures in the time period between 10 and 5000 min of annealing increase with increasing formation pressure, reflecting that both the volume and density fluctuations expand more rapidly when the sample was initially more highly densified. At 25 °C $\Delta T_{f,v}$ and $\Delta T_{f,\psi}$ are fairly comparable. At 50 °C $\Delta T_{f,\psi}$ is much smaller than $\Delta T_{f,v}$ at higher formation pressures. This is because, as remarked above, much of the increase in $T_{f,\psi}$ evidently has already occurred in the first 10 min and also because $T_{f,\psi}$ goes through a maximum whereas $T_{f,v}$ continues to increase monotonically.

Earlier we reported[2] that on annealing atmospheric polystyrene samples at temperatures moderately below T_g, both the volume and density flucutation decreased approximately linearly with the logarithm of time (except that at temperatures below about 80 °C the density fluctuation no longer showed any change with time). In the present work it is found that with pressure-densified samples both the volume and density fluctuation increase with time. On a qualitative level, therefore, these observations suggest that the changes in these two properties in most cases proceed in the same direction under different conditions. Robertson[10] earlier proposed a model to explain the kinetics of volume contraction of polymer glasses on annealing. He postulates that a change in the local conformation of polymer chains requires a region of a certain small volume V, and the rate of conformational relaxation in such a region of volume depends on the fractional free volume available in it. He then calculates the distribution of free volume among the regions of volume V by comparison with the observed density fluctuation and on this basis explains the existence of a broad relaxation time spectrum for volume contraction observed experimentally. Since the model assumes a higher relaxation rate in a region having higher free volume, it leads to the conclusion that when the overall volume contracts, the distribution of free volume among different regions should become narrower and the density fluctuation decrease. This is qualitatively in accord with our observation that the density fluctuation, in general, decreases when the volume contracts and increases when the latter expands. A much more detailed comparison would be required to see whether the model can explain the main features of our observations in quantitative terms. It is, however, clear that the model cannot explain some detailed features among our observations, especially the fact that at temperatures below 80 °C no change in density fluctuation accompanies volume contraction of atmospheric polystyrene samples and that density fluctuation goes through a maximum when the volume continues to expand with pressure-densified samples.

In liquids, the density fluctuation is determined by the balance of two opposing effects: the randomizing effect of thermal motions of atoms and molecules, and the ordering effect due to the repulsive force between atoms (which in turn leads to the finite compressibility of liquids). For equilibrium liquids the following relationship holds:

$$\psi(\infty) = \rho k T \beta_T \tag{6}$$

As the temperature is lowered, both the thermal energy kT and the isothermal compressibility β_T decrease, leading to reduced density fluctuation. As the temperature is lowered further through T_g, the compressibility is reduced discontinuously to a much smaller value β_T^g. Because of the greatly reduced mobility below T_g, the density fluctuation cannot be reduced suddenly as eq 6 suggests. Instead, the density fluctuation which has prevailed just above T_g is now partially frozen in and, consequently, at T_g one merely observes a discontinuity in the rate of change with temperature. For samples below T_g one can therefore write[2,11]

$$\psi(v) = \psi_{\mathrm{dyn}}(v) + \psi_{\mathrm{qst}}(v) \tag{7}$$

where the quasi-static component $\psi_{\mathrm{qst}}(v)$ represents the part that was frozen in at T_g, while the dynamic component $\psi_{\mathrm{dyn}}(v)$ is the part that arises from the residual atomic and segmental mobility remaining in glasses. The latter can be related to the compressibility β_T^g of the glass by

$$\psi_{\mathrm{dyn}}(v) = \rho k T \beta_T^g \tag{8}$$

The sharp division of the density fluctuation into a dynamic and a quasi-state component is of course an idealization, and in reality there would be a spectrum of components of density fluctuation that differ in their relaxation times. Also, eq 8 would be valid only if the density fluctuation and the glass compressibility are measured on a comparable time scale.

In order to be able to decompose our observed density fluctuation values into their dynamic and quasi-static components, we need information on the compressibility of the sample in the various stages of volume relaxation. No such information is available at this time. In our desire to achieve the decomposition even very approximately, we instead adopt the crude assumption that the volume of a

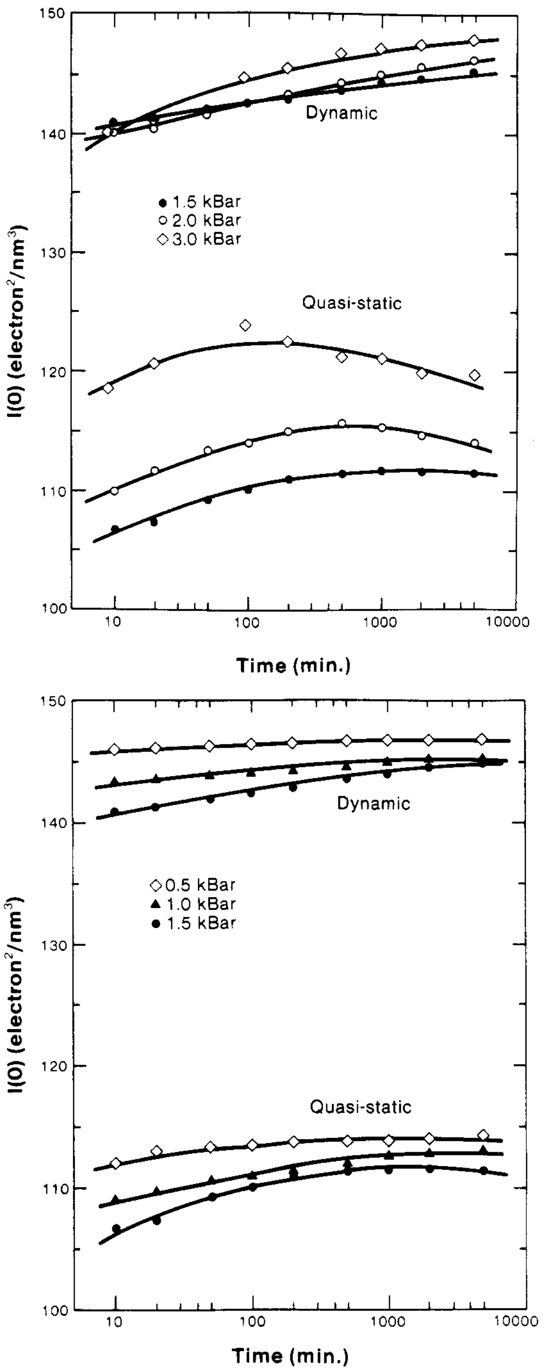

Figure 6. The observed change in $I(0)$, representing the density fluctuation, is decomposed into its dynamic and quasi-static components by an approximate method described in the text.

glass sample is uniquely related to the pressure, irrespective of the thermal history, according to the Tait equation

$$V/V_0 = 1 - C \ln (1 + p/B) \tag{9}$$

Quach and Simha[12] showed earlier that eq 9 is a reasonably good approximation within limited ranges of V and p and evaluated the values of the temperature-dependent constants B and C for polystyrene below T_g. By utilizing the value of $\beta_T{}^g$ evaluated by differentiation of (9), we can then decompose the observed $I(0)$ into its components as indicated by eq 7 and 8, and the result is given in Figure 6 (shown only for the case of 50 °C). It shows that changes in both the dynamic and quasi-static components are responsible for the overall change observed. It also shows that the quasi-static part, i.e., the frozen-in fluctuation, goes through a maximum followed by a "healing" process, whereby some of the frozen-in fluctuation is gradually eliminated. The dynamic component simply increases with time, in parallel to the expansion of volume. The maxima observed in the overall density fluctuation therefore arises mostly from the quasi-static component. More detailed interpretation of Figure 6, however, may have to wait until the uncertainties concerning the use of the Tait equation are resolved.

With ordinary glass samples prepared under atmospheric pressure the volume decreases with time when annealed below T_g, and this is understood to reflect the relaxation of the nonequilibrium glass structure toward the equilibrium liquid structure occupying a smaller volume. All our densified samples have $T_{f,v} > T$, indicating that their volume is larger than the equilibrium liquid volume at the same T, and yet they all exhibit spontaneous expansion of volume with time. This is, at first sight, rather surprising, but one may explain it in qualitative terms as follows. When the volume of a liquid is reduced either by lowering the temperature or by application of pressure, not only the average interatomic distances are reduced but also the mode of interatomic (and intermolecular) packing is altered. The latter aspect is evidenced in the change in the radial distribution function and the spatial density correlation function observed experimentally. During the process of preparing a pressure-densified sample, when the temperature is lowered through T_g, the mode of interatomic packing becomes frozen in. At room temperature the immediate volume expansion accompanying pressure release is accomplished mostly through a scale enlargement without rearrangement, that is, through a more or less uniform increase in the interatomic distances involving only extremely local motions of atoms and with no appreciable rearrangement of the mode of packing. Subsequently, in seeking the lowest free energy state appropriate to the temperature and pressure, the atomic packing has to go through a series of intermediate configurational states of local free energy minimum. Such states of local free energy minimum may happen to have a volume higher than the initial or the final state has, especially when these two temrinal states are very far apart in the "configurational phase space". In other words, two glasses having the same volume but prepared through different thermal histories may have very different modes of atomic packing, and the passage from one of these states to the other may be achieved through a series of intermediate state of higher volume. Such intermediate states, although of lower free energy than the initial state, may even contain higher enthalpy. Such a possibility is suggested by the observation of an endothermic peak frequently obtained[6] below T_g on DSC scan of pressure-densified polymer glasses.

This phenomenon of volume expansion bears some resemblance to the so-called "memory effect" observable on isothermal annealing of glass at two successive temperatures. The memory effect[13] can be demonstrated as follows. With an atmospheric glass sample isothermal volume contraction at T_1 ($<T_g$) is interrupted and it is brought quickly to a higher temperature T_2, for which $T_{f,v} < T_2 < T_g$. Then the initial rapid expansion of the volume due to the temperature rise $T_2 - T_1$ is followed by a continued slow increase in volume (and $T_{f,v}$) for some time, before eventually the more normal process of volume contraction toward the equilibrium ensues. In the phenomological model advances by Kovacs[14,15] and by others,[16,17] such meory effect is explained by assuming the presence of a spectrum of relaxation modes, each mode decaying exponentially with a different relaxation time. The volume

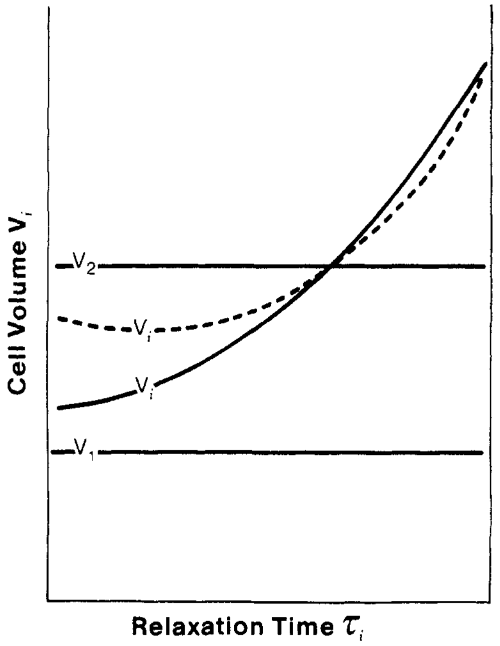

Figure 7. Schematic diagram to explain the volume expansion of pressure-densified glasses in terms of a simple phenomenological model in which the material consists of independent cells having different relaxation times τ_i. V_1 is the equilibrium volume per cell before pressure release (at room temperature) and the solid curve labeled V_i depicts the actual volume per cell before pressure release. V_2 is the equilibrium volume per cell after pressure release, and the broken curve labeled V_i depicts the actual volume per cell some time interval after the pressure release.

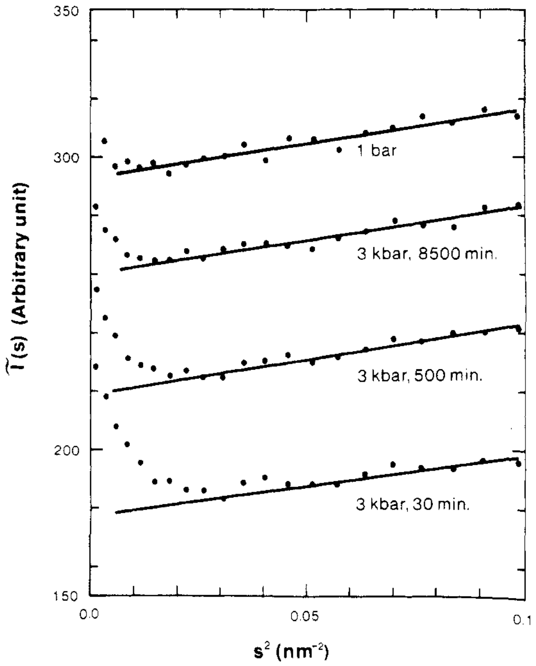

Figure 8. Change in the scattered X-ray intensity $\tilde{I}(s)$ of polystyrene prepared under 3 kbar on annealing at 50 °C. The numbers on the curves represent the annealing time. For comparison, the intensity scattered from an ordinary sample prepared under atmospheric pressure is also shown. The curves are shifted vertically by arbitrary units for the sake of clarity. Note that the anomalously intense scattering observed with the pressure-densified sample at very low angles gradually diminishes with prolonged annealing.

expansion of pressure-densified glasses can be explained on essentially the same scheme with some minor modifications. Here, without going into the details, we demonstrate the salient feature of the argument briefly as follows.

As an aid in the description of the basic idea, we adopt the following heuristic model. Suppose our glassy material is divided into a large number of cells, each assuming an identical volume under equilibrium condition. At any T below T_g, cell i undergoes a structural relaxation at a rate characterized by a single relaxation time τ_i. The relaxation time spectrum of the material is then specified by giving the number g_i of cells having relaxatin time τ_i. At any moment of time the volume of cell i is equal to V_i, which depends on the thermal history, and the total volume of the ample is given by $\sum g_i V_i$. During the preparation of the densified glass, just before the pressure release at room temperature, volume V_i of each cell is larger than the corresponding equilibrium volume V_1 at the same p and T. The deviation $V_i - V_1$, however, is not the same for different cells. Bdcause of the relaxation process which has been proceeding during the cooling below T_g under pressure, $V_i - V_1$ is smaller for those cells having shorter relaxation times τ_i (see Figure 7). Now when the pressure is relieved abruptly, the equilibrium volume of all of the cells is suddenly raised to V_2. As a result, for some of the cells having shorter τ_i the current volume V_i turns out to be smaller than V_2, while for others having longer τ_i, $V_i > V_2$. The total volume of the sample, given by $\sum g_i V_i$, can still be larger than the equilibrium volume $V_2 \sum g_i$ by an amount depending on the spectrum g_i and the exact crossover point of the curve V_i and the line V_2 in Figure 7. Now those cells having $V_i < V_2$ will undergo volume expansion, while those having $V_i > V_2$ will undergo volume contraction. The cells of the former type, having shorter relaxation times, will predominate the overall response in the initial phases and, accordingly, the total volume will initially expand. As the time progresses, the contraction of cells having longer relaxation times will begin to be felt in the overall volume change, which eventually will exhibit a passage through a maximum.

The above model of a glassy sample consisting of cells undergoing independent structural relaxation is mathematically equivalent to the so-called multiparameter model of Kovacs et al.,[14,15] which assumes the overall structural relaxation to consist of a spectrum of independent relaxation modes. Although our model can undoubtedly be made more elaborate to achieve a quantitative fit, such an attempt would involve a number of adjustable parameters without necessarily enhancing our understanding of the underlying physical processes. Also, our model in its present form cannot account for the changes in both the volume and the density fluctuation at the same time without introducing additional assumptions.

In our previous paper[1] we reported that the polystyrene samples prepared under elevated pressure exhibited anomalously strong scattering of X-rays at extremely low angles ($s = (2 \sin \theta)/\lambda < 0.1$ nm^{-1}). We also ascribed this anomalous scattering to the presence of microcavities formed as a result of locally nonuniform expansion of volume at the time of pressure release. In the present work it is found that these microcavities undergo a process of "healing" on subsequent annealing. Figure 8 shows the slit-smeared intensity $\tilde{I}(s)$ of the sample prepared under 3-kbar pressure and annealed at 50 °C for various lengths of time. As has been shown earlier,[1,2] the intensity $\tilde{I}(s)$ (or $\log \tilde{I}$) scattered from polystyrene remains linear with s^2 for most of the angular range of measurement ($s < 0.7$ nm^{-1}). The anomalously intense scattering observable in the extremely low-angle region is clearly noticeable when the data obtained with the 3-kbar sample are compared with those obtained with an atmospheric sample. Figure 8 shows also that, as the annealing time is prolonged, the anomalous scattering is progressively reduced in intensity and in the angular range. This can be interpreted to mean that, with annealing, the number and the total volume of the microcavities become reduced and some of the very small ones collapse and disappear altogether. Such healing of microcavities, as well as the healing of quasi-static density fluctuation depicted in Figure 7, suggests that the structural reorganization occurring in these pressure-densified samples involves not only a local segmental motion but also a cooperative motion of regions extending into tens of nanometers.

The formation of microvoids in glassy polymers subjected to deformation has been noticed by other workers.[18] Both small-angle X-ray scattering[19] and electron microscopic[20] techniques were utilized to demonstrate the microvoids which were formed as a precursor to craze formation. To explain the creation of such spherical microvoids, Steger and Nielson[19] and Argon[21] postulated the presence of certain intrinsic inhomogeneities in glassy polymers, for example, as small regions of lower segment entanglement density[20] or some kind of microporosity.[21] We are inclined to identify these weak regions, which are prone to nucleation of microvoids, with the regions of particularly low density established as a result of the density fluctuation frozen in at T_g.

Above T_g the pattern of density fluctuation present changes very rapidly in comparison to the time scale of the deformation we apply to a polymeric material. Consequently the polymer behaves mechanically as a uniform, homogeneous material. Below T_g some of the density fluctuation (i.e., the quasi-static component) persists much longer than the duration necessary for the deformation. Because of the presence of such frozen-in fluctuation, a glassy polymer, in its response to mechanical deformation, behaves as it if contains a permanent, heterogeneous flaw structure. That some component of density fluctuation indeed changes only slowly in comparison to the observation time is vividly demonstrated by the persistence of speckle patterns[22] obtainable when laser light is scattered from polymers around and below T_g. The determination of density fluctuation and proper accounting of its relaxation behavior should therefore be important not only for the understanding of the structure of glassy polymers but also for the clarification of the mechanism of craze initiation and deformation of glassy polymers.

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Deuterium Isotope Effect on the Compatibility between Polystyrene and Polybutadiene

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ABSTRACT: We studied the effect of deuteration of polystyrene on the miscibility behavior of polystyrene–polybutadiene blend systems. We prepared a polystyrene having its aromatic hydrogens replaced by deuterium by starting from an ordinary polystyrene and treating it with deuterated benzene in the presence of an organometallic catalyst. We also prepared, as a control, a hydrogenated polystyrene of closely similar structure by repeating the same procedure except that this time ordinary, rather than deuterated, benzene was used. These matching pairs of hydrogenated and deuterated polystyrenes, when mixed with a polybutadiene or a styrene–butadiene random copolymer, were shown to give practically identical cloud point curves, thus indicating that the deuterium isotope effect is negligible.

Introduction

The availability of small-angle neutron scattering techniques in recent years has opened up many new avenues of research in the polymer field. In neutron scattering studies deuterated polymer molecules are often substituted for some of the usual, hydrogen-containing molecules as a means of selective labeling. Such substitution relies on the fact that the neutron scattering lengths of deuterium

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