The origin of the β transition and its influence on physical ageing

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Volume dilatometry was used to explore the origin of the β transition (T_β) and its influence on physical ageing. The results show that volume recovery does occur even at temperatures below T_β, a phenomenon indicating the existence of molecular rearrangements and cooperative motions below this point. Lowering the ageing temperatures through T_β progressively retards short-term molecular rearrangements and cooperative motions. Nonetheless, the T_β quench does not incur any excess free-volume trapping, and its associated change in specific volume follows a linear relationship with respect to temperature. The existence of T_β is time-dependent, which leads to the conclusion that the formation of T_β has a kinetic origin.

(Keywords: β transition; physical ageing; atactic polystyrene)

INTRODUCTION

It is well known that cooling molten amorphous polymers through the glass transition temperature (T_g) to the glassy state will cause a rapid increase in viscosity and modulus because of the drastic decrease in molecular mobility. After this cooling process, macromolecules may not be in an equilibrium conformation; thus, molecular rearrangements and cooperative motions have to take place in order for a new equilibrium structure to be established. As a result, the physical properties of quenched polymers will vary with time[1–4], a phenomenon which is known as physical ageing.

In addition to T_g, the transition with the second highest transition temperature (i.e. T_β) also exerts some influence on the physical properties of glassy polymers. According to Illers and Jenckel[5] and Vol'kenshtein and coworkers[6,7], the β relaxation of polystyrene is a result of phenyl group rotation about the main chains. In accordance with this interpretation, Struik[2] has proposed a closed-loop scheme to explain the phenomenon of physical ageing. In the close-loop scheme, free-volume content determines segmental mobility while segmental mobility controls the rate of volume recovery. Furthermore, mobility below T_g should be small but not zero, because a decrease in segmental mobility requires a decrease in free-volume content. When the temperature is reduced through T_β, the polymer segments would (partially) lose their flexibility due to the freezing of the side-group motions[2]. Thus, Struik concluded that the ageing range should be limited to temperatures between T_β and T_g[2]. This argument, i.e. the freezing of the side-group rotations or motions, essentially implies that neither free-volume collapse nor relaxation behaviour would exist below T_β.

On the contrary, Odajima *et al.*[8] showed that the second moment narrowing of the n.m.r. spectrum in the β-relaxation region could be assigned to a backbone vibrational mode. Also, Tanaka *et al.*[9] detected line narrowing with poly(*p*-fluorostyrene), which however was not reported by Vol'kenshtein and coworkers[6,7]. The dielectric loss measurements of Yano and Wada[10] reflected a change of polarization and dielectric relaxation, a result favouring the interpretation of local mode relaxation in the backbone.

Nevertheless, convincing experimental evidence which can be used to assert the origin of T_β is still not available. Furthermore, whether T_β can either cause excess free-volume trapping or affect subsequent volume recovery remains unknown. For this reason, experiments were conducted using volume dilatometry.

EXPERIMENTAL

Atactic polystyrene with a molecular weight ($\bar{M}_w$) of 2.1×10^5 g mol^{-1} (supplied by Dow Chemical Company, in pellet form) was melt-moulded to form films with a thickness of ~ 250 µm, under a force of 5.17 MN m^{-2} at 220°C for 60 s.

A precision glass volume dilatometer was used to determine and to monitor the volume changes of polystyrene during quenching and ageing. The constructed dilatometer consisted of a reservoir, containing ~ 1.5 g of polystyrene film, joined to an accurately calibrated capillary with a known cross-sectional area. After being subjected to a vacuum of 1.33×10^{-4} Pa (10^{-6} torr) by a diffusion pump (DuoSeal Model 1392), the dilatometer was filled with mercury. The specimens were then subjected to different thermal histories by immersing the reservoir of the dilatometer in a glycerine bath to obtain volumetric equilibrium prior to being quenched to another glycerine bath and/or a

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water bath with lower temperatures. The temperature in the glycerine bath was thermostatically controlled to within ±0.05°C over the range 80–130°C. On the other hand, the temperature of the water bath was controlled to within ±0.001°C for the range 30–80°C by a specially constructed thermoregulator. Since the capillary had a volume of $0.15\,cm^3$ and a length of 100 cm, a volume change of $1\times10^{-5}\,cm^3$ was easily detected by a cathetometer which could be read to 50 μm. The absolute densities of the materials were determined using the hydrostatic weighing apparatus described in a previous paper[1].

RESULTS AND DISCUSSION

The origin of the β-transition

It has been reported that polystyrene possesses a β transition near 50°C[11,12]. To pinpoint this transition through the study of volume–temperature (V–T) relationships is rather difficult, due to the fact that the deflection in the V–T plot, above and below T_β, is quite limited. The difficulty, however, can be overcome if a dilatometer with a high enough resolution and accuracy is used to conduct a 'rate-independent' experiment. For this purpose, in this study, a precision dilatometer containing a polystyrene thin-film specimen was repeatedly quenched from a liquid-like equilibrium structure to various selected lower temperatures. Then, the specific volume of the specimen was measured at two isochronal times, i.e. $t = 1$ min and 50 h, representing short and long ageing intervals, respectively. The results of this isochronal experiment are shown in *Figure 1*, in which three fictive temperatures, $T_\beta^{50\,h} = 52.8°C$, $T_g^{1\,min} = 96.8°C$, and $T_g^{50\,h} = 88.7°C$, are labelled. It should be noted that the associated, fictive temperature, $T_\beta^{1\,min}$, is not labelled because of its insignificant deflection. The most important feature of this figure is that the deflection of the β transition is far less distinct than that of the α transition. Furthermore, ageing shifts the fictive temperature of the β transition to a higher temperature, which is opposite to that observed for the α transition (i.e. T_g).

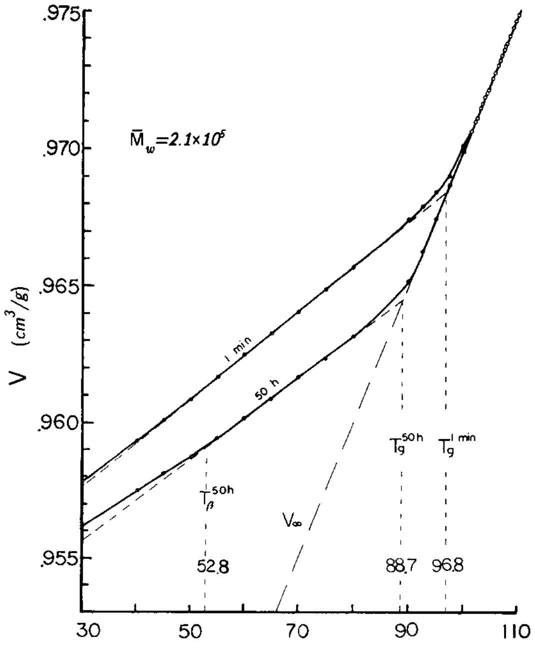

Figure 1 Isochronal specific volume *versus* temperature curves of polystyrene, showing the time dependence of T_g and T_β

Table 1 Thermal expansion coefficients of atactic polystyrene shown for various temperature ranges and ageing times

	Thermal expansion coefficients ($\times10^{-4}$) ($cm^3\,°C^{-1}$) and associated temperature ranges (°C)		
Ageing time	α_l (118–100)	α_g (80–50)	α_β (50–30)
1 min	4.865	1.569	1.511
50 h	4.865	1.475	1.286

Kinetic theories[13–18] of glass transitions are based on the assumption that the observed T_g is an artifact due to the experimental interval being too short for relaxational processes to be completed. If an infinite time or cooling rate is given for molecules to proceed with rearrangements toward equilibrium, the extrapolated equilibrium volume (or state) would eventually be reached; thus, there would exist no transition point (or temperature). If this argument were true, the difference in isochronal thermal expansion coefficients above and below the so-called T_g (i.e. $\Delta\alpha_{lg} = \alpha_l - \alpha_g$) should eventually become zero or at least show evidence of diminishing with the ageing time. In other words, ageing must be able at least to increase the isochronal thermal expansion coefficient of the glassy state (α_g). To examine further this deduction (derived from the fundamental basis of kinetic theories), the data of *Figure 1* were used to obtain isochronal thermal expansion coefficients for various temperature regions.

At a temperature above 100°C, the polymer almost instantaneously reaches equilibrium upon a sudden temperature jump, implying that main chains are able to perform liquid-like motions to respond to sudden temperature changes. As listed in *Table 1*, the thermal expansion coefficient (α_l) of the rubber state is $4.865\times10^{-4}\,cm^3\,°C^{-1}$ in the temperature region 118–100°C. The 50-h ageing interval extends the equilibrium range to 92.5°C; however, its thermal expansion coefficient remains unchanged. Therefore, α_l will be constant, regardless of the time intervals required for the molecules to reach equilibrium. In the vicinity of T_g (i.e. 100–85°C), a sharp reduction in isochronal thermal expansion coefficient occurs, as embodied in *Figure 1*. This reduction can reach a value as high as two-thirds of the value of α_l (see *Table 1*). Such a sudden reduction must be directly associated with the disability of liquid-like molecular motions. As ageing proceeds, the discontinuity shifts to a lower temperature region. Even so, the magnitude of the discontinuity (i.e. $\Delta\alpha_{lg}$, or the difference in isochronal thermal expansion coefficients above and below T_g) shows no sign of diminishing. Instead, as suggested in *Table 1*, $\Delta\alpha_{lg}$ increases slightly due to a minor reduction in the thermal expansion coefficient (α_g) of the glassy state, an experimental observation in contradiction with the deduction derived from the basic assumption of the kinetic theories mentioned earlier. Thus, the discontinuity which represents the observed glass transition will always exist regardless of the length of ageing time. This conclusion virtually does *not* support the fundamental basis of the kinetic theories that the observed T_g is an artifact due to the experimental interval being too short for relaxational processes to be completed.

With regard to the β transition, $\Delta\alpha_{g\beta}$, which denotes the difference between the isochronal thermal expansion coefficients above and below T_β, is hardly seen at the ageing interval of 1 min. After a certain period of ageing, $\Delta\alpha_{g\beta}$ just becomes noticeable, leading to the formation of T_β. However, this difference can almost be ignored when compared to $\Delta\alpha_{lg}$; thus, the modes of molecular motions proceeding at temperatures above and below T_β should remain similar.

In conclusion, the existence of T_β is intrinsically time dependent; and the origin of T_β can be ascribed to a kinetic process, a phenomenon that is totally different from the formation of T_g[19,20].

Isothermal volume recovery

Between sub-T_g *and* T_β. To understand how volume recovery would proceed differently at temperatures above T_β, but below T_g, quenching was performed from the equilibrium state of 110°C to various ageing temperatures of 80.0, 75.0, 65.0, and 60.0°C. The isotherms are plotted in *Figure 2* as a function of $(V - V_\infty)/V_\infty$ (i.e. δ) *versus* the logarithm of the ageing time. According to Kovacs[13], δ represents a dimensionless departure from the postulated underlying equilibrium volume (V_∞) which is extrapolated from the equilibrium, liquid-like state.

The most important feature of *Figure 2* is that the volume contraction of these isotherms has a great deal of resemblance in linearity and recovery rates, in spite of being far away from reaching the postulated equilibrium line (V_∞). This implies that in the temperature range between sub-T_g and T_β a large difference in ageing temperature does not correspondingly change the volume recovery rates of the isotherms.

Another important feature of *Figure 2* is that the isotherms are nearly parallel to one another. Because of this parallelism, the relative isochronal δ-difference in any two of the isotherms is simply proportional to the relative temperature difference. This observation further holds irrespective of the length of the ageing interval studied here. If these results are plotted in a curve of isochronal volume *versus* temperature, a linear relationship will be seen over this temperature range, which suggests that under an isochronal condition the α value is constant. In essence, this atactic polystyrene possesses no transition in the temperature range of 80.0–60.0°C.

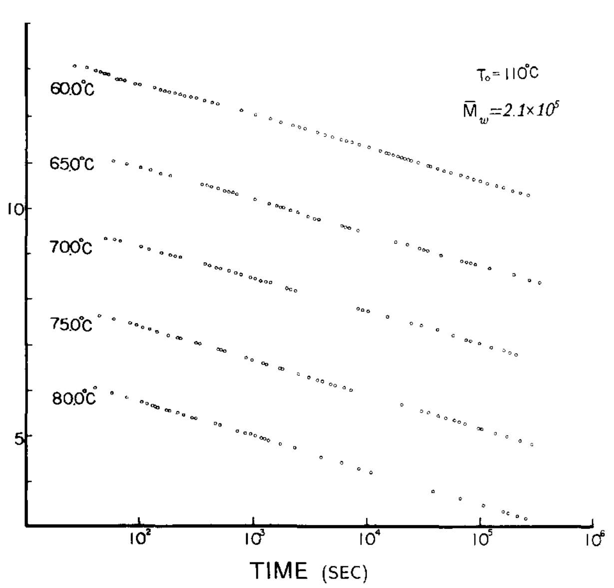

Figure 2 Isothermal volume contractions of polystyrene, quenched from the equilibrium temperature of 110°C to various ageing temperatures between sub-T_g and T_β

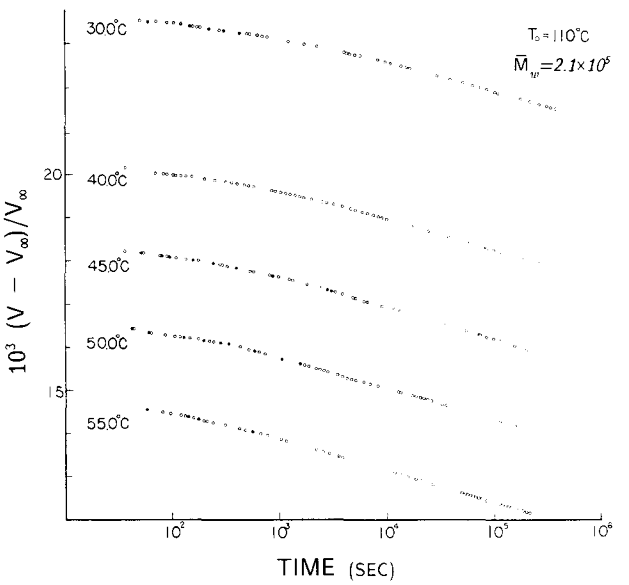

Figure 3 Isothermal volume contractions of polystyrene, quenched from the equilibrium temperature of 110°C to various ageing temperatures near or below T_β

If one believes that the behaviour of the isotherm is a combined consequence of molecular motions toward equilibrium, a consistency in α substantiates the conclusion mentioned earlier that the modes of molecular motions involved here must be similar. Furthermore, the resemblance of the isotherms in contraction rate and linearity implies that molecular motions which induce structural rearrangements toward equilibrium are independent of ageing temperature in the region of sub-T_g to T_β.

Below T_β*: ageing persists.* As mentioned in the introduction, phenyl group rotation and local mode relaxation have been proposed to explain the mechanism of T_β. Even if the β transition of polystyrene were due to local mode relaxation, in no case would collapse of free volume occur below T_β. This is because at temperatures below T_β the local mode relaxation (or segmental motion of the backbone) will be frozen, not to mention the absence of molecular rearrangements and cooperative motions which are necessary for structural recovery to occur.

In an attempt to clarify this argument, the polystyrene was iteratively quenched from the equilibrium state of 110°C to the ageing temperatures of 55.0, 50.0, 45.0, 40.0, and 30.0°C. The results are depicted in *Figure 3*. Note that there are two identical isotherms at each of the following temperatures, i.e. 55.0, 50.0, 45.0, and 30.0°C, confirming measurement reliability as well as experimental reproducibility. Evidently, isothermal volume contraction persists even if the ageing temperature is below T_β. Therefore, segmental motions, as well as cooperative motions, must exist even at temperatures well below T_β.

When the ageing time is short enough ($t < 60$ s, in particular), the δ-difference between the isotherms is proportional to the relative temperature difference. In other words, the instantaneous volume reduction is

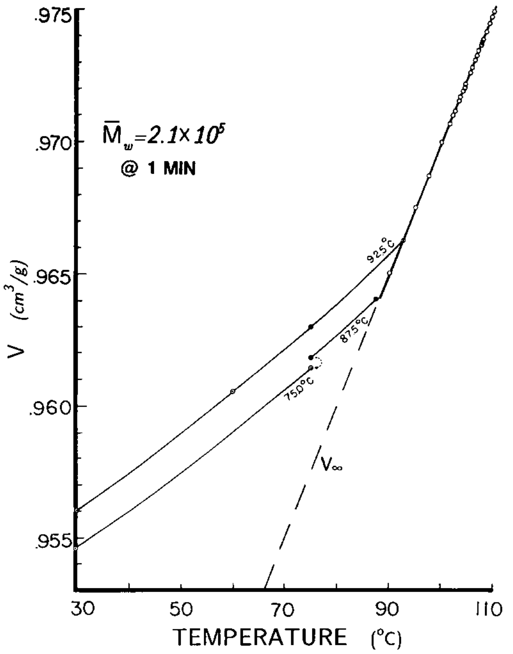

Figure 4 Isochronal specific volume *versus* temperature curves of polystyrene, demonstrating that the T_β-quench does not induce any excess free-volume trapping

directly proportional to the corresponding temperature decrease. This phenomenon is similar to that discussed earlier for the isotherms obtained in the temperature region of sub-T_g to T_β (shown in *Figure 2*). Thus, the fact that T_β does not exist immediately after quenching is further substantiated.

As ageing proceeds, however, non-linearity appears at the beginning of the isotherms. The non-linear portion of the isotherm increases as the ageing temperature decreases. After a certain time, the non-linear relaxation is eventually displaced by a linear contraction. Furthermore, the slopes of the linear portions are close to that of the isotherms show in *Figure 2* for higher ageing temperatures (i.e. between sub-T_g and T_β). Both observations indicate that the long-term α value will be constant. In other words, once the polystyrene has relaxed for a certain period of time, the long-term volume contraction towards equilibrium will proceed in a similar type of cooperative motion, irrespective of the ageing temperatures being either above or below T_β.

Influence of the T$_\beta$ *quench on molecular motions and excess free volume*

To determine whether the T_β quench could, like the T_g quench, exert some influence on changing the modes of molecular motions, the behaviours of two isochronal *V–T* curves at $t = 1$ min (as shown in *Figure 4*) were studied. The first curve was obtained by quenching the polystyrene, which had been aged at $T_0 = 87.5$°C for 600 h and then at 75.0°C for 1100 h, to 30.0°C. Both ageing conditions did not lead to the polymer acquiring an equilibrium structure. The second curve originated from 92.5°C where the equilibrium state was reached prior to quenching. Note that the thermal histories of both isochronal curves were intended to minimize any potential influence resulting from T_g. Both T_β-quenched curves show a good consistency in slope, i.e. thermal expansion coefficient. The consistency in thermal expansion coefficient implies that, unlike the T_g quench, the T_β quench cannot alter the modes of molecular motions.

To further understand whether this T_β quench could incur any excess free-volume trapping, the corresponding volume change due to the quench from 75.0 to 30.0°C, which is the first curve mentioned above, was considered. For this purpose, the isochronal thermal expansion coefficients above and below T_β (represented by α_g and α_β, respectively) need to be determined first. This requires a proper selection of t since both α_g and α_β vary slightly with time. Two cases are discussed here.

In the first case, the α_g at $t = 50$ h and the α_β at $t = 1$ min are used because this test involves a long ageing time of 1100 h at 75.0°C and a short ageing time of 1 min at 30.0°C. According to *Table 1*, the values of $\alpha_g^{50\,\mathrm{h}}$ and $\alpha_\beta^{1\,\mathrm{min}}$ are 1.475 and 1.511, $\times 10^{-4}$ cm^3 °C^{-1}, respectively. Since the T_β is located at 52.8°C and the measured specific volume at 75.0°C is 0.96139 cm^3 g^{-1}, the specific volume at 30.0°C can thus be calculated. The resulting value of 0.95467 cm^3 g^{-1} is in good agreement with the measured value of 0.95478 cm^3 g^{-1}, with a 0.01% deviation.

In the second case, it is assumed that the T_β quench cannot incur any excess free-volume trapping, i.e. the isochronal thermal expansion coefficients, both above and below T_β, would be identical. Thus, the instantaneous volume change induced by a temperature jump will be controlled by a fixed α, which is close to the $\alpha_g^{50\,\mathrm{h}}$. This assumption results in a value of 0.95475 cm^3 g^{-1} for the calculated specific volume at 30.0°C and 1 min, i.e. a 0.003% deviation from the measured value. This leads to a far better prediction than the first case.

Accordingly, the T_β quench cannot incur any excess free-volume trapping, and the instantaneous change in specific volume associated with this quench is the direct consequence of the contraction of molecular structures (including molecules as well as unoccupied volume). This finding further substantiates the conclusion mentioned above that unlike the T_g quench, the T_β quench does not alter the modes of molecular motions.

Influence of T$_\beta$ *on structural recovery*

Down-quench. What remains to be explored further is how T_β affects structural recovery. To understand this question, the polymer, which had been annealed first at 87.5°C for 600 h and then at 75.0°C for 1100 h, was quenched to 30.0°C, during which the volume recovery was monitored. As shown in *Figure 5*, the volume

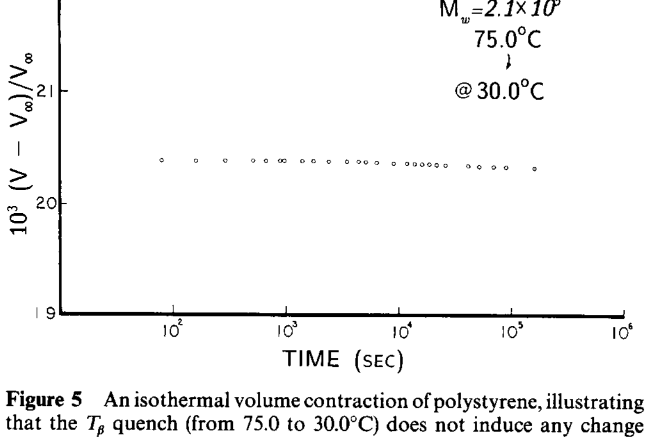

Figure 5 An isothermal volume contraction of polystyrene, illustrating that the T_β quench (from 75.0 to 30.0°C) does not induce any change in structural recovery

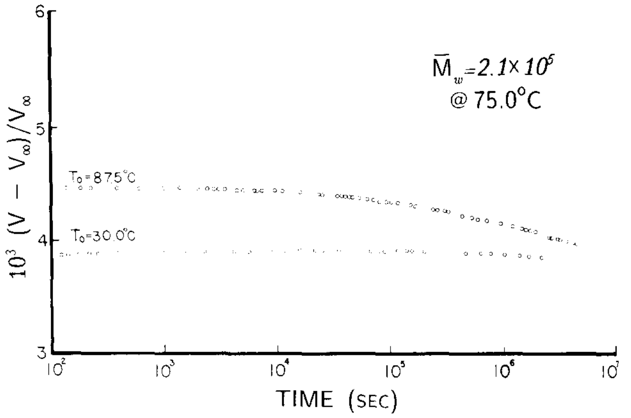

Figure 6 Down-quenched and up-quenched isotherms of polystyrene, demonstrating the effect of the T_β quench on volume recovery

recovery is hardly seen at all because the total contraction of the isotherm is only 6×10^{-5} for a period of 45 h at 30.0°C. This phenomenon is totally different from that obtained for the T_g quench shown in *Figures 2* and *3*. The nearly horizontal slope of the isotherm is additional evidence in confirming the fact that the T_β quench virtually does not freeze any excess free volume into the glassy matrix.

Down-quench and up-quench. To gain further insight into the influence of the T_β quench on volume recovery, the behaviour of a down-quenched isotherm and an up-quenched isotherm was studied at the same ageing temperature. The down-quenched isotherm was obtained by quenching the polystyrene that had been annealed at $T_0=87.5$°C for 600 h down to a temperature of 75.0°C, during which the volume recovery was monitored. Then, the specimen was down-quenched to 30.0°C where a period of 45 h was allowed for molecular structures to proceed to relaxation. Finally, after this intermediate stage, the specimen was up-quenched to 75.0°C to study the volume recovery; this curve is designated as the up-quenched isotherm. Both isotherms are depicted in *Figure 6* for use in the following discussion.

The beginning of the down-quenched isotherm is characterized by a fairly languid molecular relaxation. As ageing proceeds further, volume recovery becomes noticeable. At the ageing time of $t=1100$ h, the fractional free volume is 0.00396.

The up-quenched isotherm is even far more languid than the down-quenched isotherm. This observation signifies the fact that molecular rearrangements and cooperative motions are severely restricted due to the lack of excess free volume. In this isotherm, there is a volume dilation with a magnitude of 6×10^{-5} from 1 min to 1 h. Whether the observed dilation is due to the memory effect[13] needs further consideration, because of its negligible magnitude. After this dilation, the apparent volume remains at its maximum (i.e. $\delta=0.00390$) for a period of time. Subsequently, volume contraction follows, but the amount of fractional free volume (from the maximum) contracted at 75.0°C for the ageing time of 630 h is just 6×10^{-5}.

The difference between the final δ of the down-quenched isotherm and the maximum δ of the up-quenched isotherm is 6×10^{-5} which is exactly equal to the amount of the volume contraction undergone in the intermediate stage, i.e. at 30.0°C for 45 h. This further substantiates the fact that quenching performed at temperatures below T_g neither induces excess free-volume trapping nor affects subsequent volume recovery. In other words, the T_β quench does not alter the modes of molecular motions.

CONCLUSIONS

As is known, the quench of atactic polystyrene from the rubbery state to the glassy state forms a region of glass–rubber transition or a discontinuity in the curve of the isochronal thermal expansion coefficient *versus* temperature. Ageing shifts the discontinuity to a lower temperature region. However, the magnitude of the discontinuity ($\Delta\alpha_{lg}$) increases slightly with ageing time. This phenomenon indicates that the discontinuity will always exist, as does the glass–rubber transition. This conclusion does not support the fundamental basis of kinetic theories for explaining the mechanism of T_g, in which the observed T_g is considered as an artifact, due to the experimental interval being too short for relaxational processes to reach completion.

The β transition is seen at 52.8°C for this polystyrene when t is 50 h. However, unlike T_g, the existence of T_β is obscure if the ageing time is not longer than 1 min. This phenomenon can be ascribed to the fact that at the very beginning of ageing the isochronal thermal expansion coefficients of the glassy states at temperatures above and below T_β are identical. Thus, quenching the polymer from sub-T_g to below T_β does not incur any excess free-volume trapping. In other words, the 'instantaneous' change in specific volume due to the T_β quench follows a linear relationship with respect to temperature.

Volume recovery does occur at temperatures below T_β, which strongly suggests the existence of molecular rearrangements and cooperative motions below T_β. Lowering the ageing temperature through T_β progressively increases the initial contraction non-linearity of the isotherms, indicating the retardation of short-term cooperative molecular motions. However, after a certain period of ageing, the slopes of the isotherms resemble one another despite the ageing-temperature difference, a fact that reflects the similarity in the modes of molecular motions above and below T_β. Therefore, the T_β quench does not alter the modes of molecular motions, except for the retardation of molecular motions, at the earlier stage of ageing due to the temperature decrease. None of the phenomena support any of the current interpretations regarding the mechanism of T_β.

In essence, this study ascribes the origin of T_β to a kinetic process, a phenomenon that is totally different from the origin of T_g.

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