Effects of thermo-mechanical glass-forming histories on enthalpy relaxation of amorphous poly(ethylene terephthalate)

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(Received 23 July 1993; revised 20 September 1993)

Enthalpy relaxations during physical ageing have been examined for two amorphous poly(ethylene terephthalate) (PET) samples with different thermo-mechanical glass-forming histories by differential scanning calorimetry. The relaxation behaviour of the PET glass formed by casting the drawn melts on a metal roller at 10°C can be explained from a molecular viewpoint, assuming that the glass consists of a network structure with strand chains and crosslinks. It is shown that the physical ageing of the glass gives rise to three different modes of structural rearrangement: (i) strand chain relaxation with relatively short relaxation times, associated with local segmental rearrangements within the strand chains; (ii) enthalpy redistribution, which forms the non-homogeneous dissipative structures of lower- and higher-enthalpy regions; and (iii) network rearrangements taking place slowly with long-distance, diffusive motions of the crosslinks. On the other hand, it is also shown that a single mode of structural rearrangement occurs for the ultraquenched PET glass formed by quenching directly into liquid nitrogen.

(Keywords: physical ageing; enthalpy relaxation; poly(ethylene terephthalate))

INTRODUCTION

When a polymer glass is aged below its glass transition temperature (T_g), the glassy structure is gradually reorganized towards an equilibrium state by eliminating some of the excess enthalpy. Such an enthalpy relaxation is combined with conformational transitions from one rotational isomeric state to another in the polymer backbone[1,2] and further requires large-scale conformational changes on the molecular level.

The relaxation gradually proceeds in the glassy state because the chain arrangements are strongly restricted by some intra- and inter-chain couplings of the neighbouring chain units (segments)[3]. The intra-chain coupling results from chemical bonding in a chain, while the inter-chain coupling results from inter-chain interactions between neighbouring segments. From the nature of cooperative couplings in the glassy state, the kinetics of thermodynamic quantities such as enthalpy and specific volume is strongly dependent on the instantaneous structure of glassy polymers.

The kinetics of physical ageing that occurs in glassy polymers has been extensively investigated experimentally[4–9] and theoretically[10–13] recently. Ngai *et al.*[14–18] have viewed the relaxation kinetics as the result of cooperative rearrangements of small parts of polymer chains. Further, some approaches using molecular models have been made for analysing the cooperative motions of amorphous glassy chains. Adachi[19] has developed a coupling model in which a segment of polymer chain rotates synchronously like gears together with the neighbouring segments. Takeuchi and Roe[20,21] have shown by means of molecular dynamics simulations that the configurational transitions in the polyethylene model are highly cooperative among the segments neighbouring the chain in the temperature region of T_g. Lindenmeyer[22–24] has analysed thermodynamically the relaxation process of glassy polymers and suggested that glass formation may occur by a dissipative process that results in inhomogeneous structures. However, the phenomena of relaxation in glassy polymers are not yet fully understood from the viewpoint of molecular kinetics.

The structure of amorphous glassy polymers is very delicate and sometimes complicated, and strongly dependent on the histories of glass forming. There have been several reports[25–31] on the formation of ordered structures in amorphous polymers during physical ageing, while other reports[32–35] have shown that the amorphous structure is homogeneous, rather than non-homogeneous.

If the relaxation kinetics leading to the formation of some ordered structures is operative during physical ageing, the thermodynamic quantities that are sensitive to such microstructures are expected to change characteristically with ageing period. Poly(ethylene terepthalate) (PET) is easy to obtain in different glassy states by selecting suitable preparation conditions. Therefore, PET appears to be a suitable material in which to study the effect of local chain organizations on the enthalpy relaxations of glassy polymers.

In this work the enthalpy relaxation of PET glasses with different glass-forming histories has been studied with a view to elucidating the molecular process occurring during physical ageing. The PET glasses have shown their own individual ageing behaviour reflected in the position, magnitude and shape of the endothermic recovery peak of heat capacity (C_p) in differential scanning calorimetry (d.s.c.). From the analysis of these

0032-3861/94/10/2117-06

ageing behaviours, some new information is derived on molecular kinetics occurring during physical ageing.

EXPERIMENTAL

Materials

A commercial PET with a number-average molecular weight of about 18 000 was used. The PET polymer was dried under vacuum at 20°C for more than 1 month. A 35 μm thick PET film placed between aluminium foils was moulded at 270°C for 2 min using a hydraulic press. PET samples cut directly from the moulded film were kept in a nitrogen-purged oven at 290°C for 5 min to erase the effect of the previous thermo-mechanical histories. The samples were then quenched directly in liquid nitrogen, and are designated as PET I glass.

The second PET sample (designated PET II glass) was prepared using a screw extruder with T die. The ca. 100 μm thick films were extruded at 290°C and then quenched by casting the drawn melts from the T die on a rotating roller plate with chromium, which was located under the T die and had a surface temperature of 10°C.

The PET I and II glasses were introduced into a thermostatic air oven maintained at the desired ageing temperature T_a, for an ageing time t_a between 0.1 and 800 h.

Measurements

The density of each unaged or aged sample was measured at 25°C using a density gradient tube with carbon tetrachloride and n-heptane. The crystallinity of all the samples was under 3.5%, estimated from density. Further, all the unaged and aged samples were amorphous by X-ray studies.

A Perkin–Elmer differential scanning calorimeter (DSC type II) was used for the thermal measurements at different heating rates, and C_p curves were obtained for each PET sample after isothermal ageing below T_g. The samples weighed 5 mg. The enthalpy lost by the ageing was determined by measurements of the peak area enclosed by C_p curves and the line obtained by extrapolating to the transition region the baseline established at temperatures above T_g.

RESULTS AND DISCUSSION

The C_p curves are shown in *Figure 1* for the PET II glass aged at 60 and 70°C for the indicated times. The glass aged at 60°C for 48 h indicates heat-capacity (C_p) composite peaks with a shoulder. The two peaks grow in magnitude and position with ageing time t_a, for ageing time above 48 h. Further, for the glasses aged at 70°C, a much broader two-peak curve appears at an early stage of physical ageing and changes its shape in somewhat irregular ways for ageing times between 2 and 166 h.

Figure 2 shows the ageing behaviours of the PET I glass aged at 60°C as a reference sample for the PET II glass. It can be seen that the single endothermic peak grows in magnitude and moves to higher temperatures with increasing t_a. These behaviours are well established features of physical ageing for glassy polymers, as observed by others[36–41].

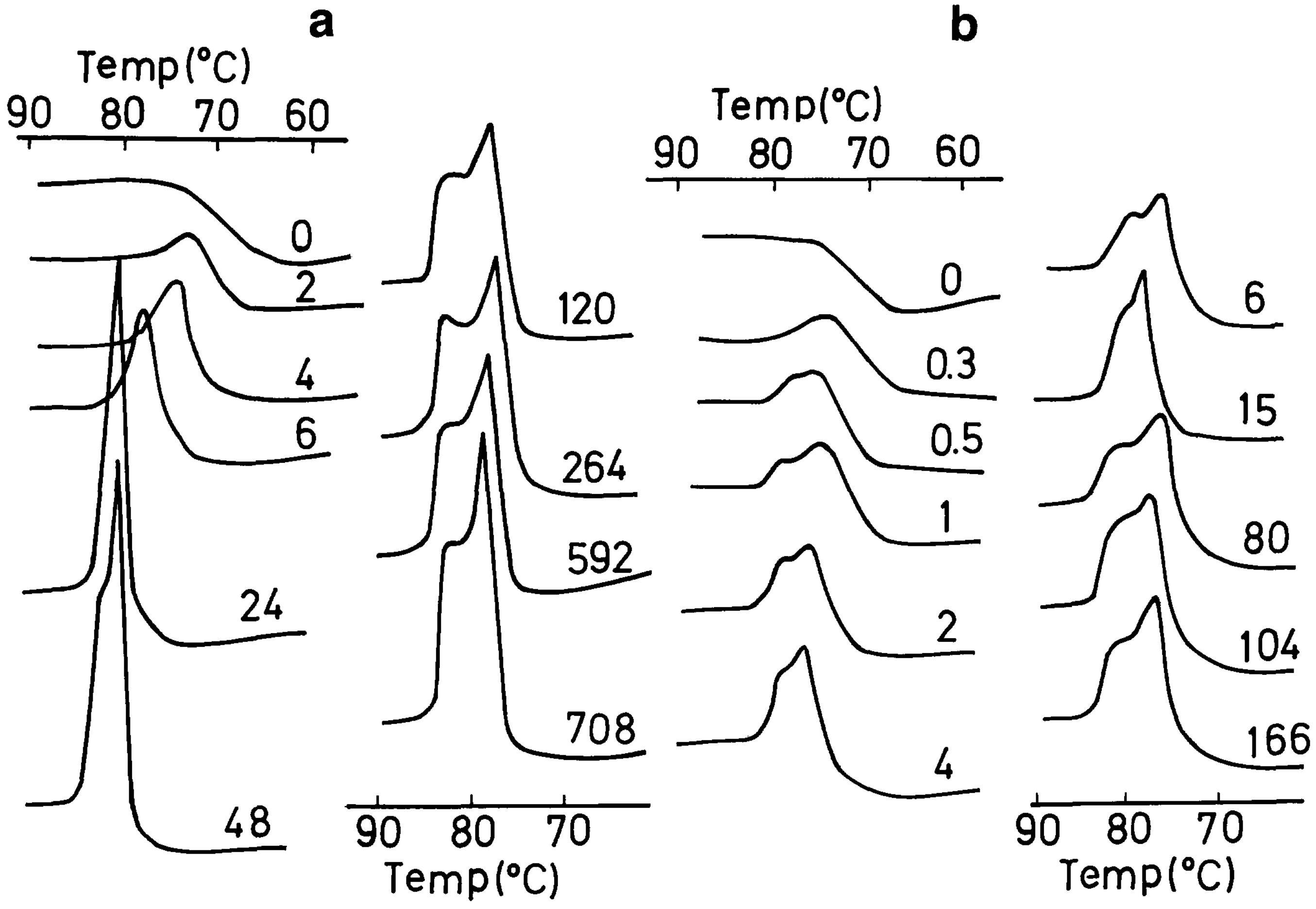

Figure 1 D.s.c. curves of the PET II glasses aged at $T_a = 60°C$ (a) and 70°C (b) for the indicated ageing times (h). Heating rate of 5°C min^{-1}

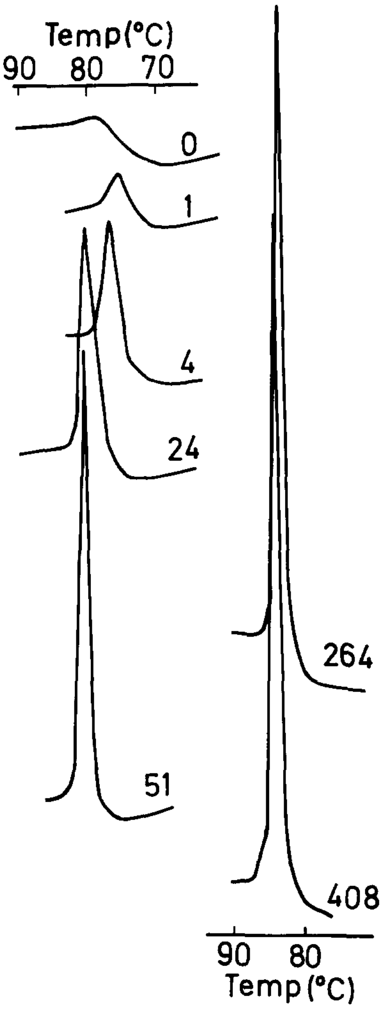

Figure 2 D.s.c. curves of the PET I glass aged at $T_a = 60°C$ for the indicated ageing times (h). D.s.c. measurements were made under the same conditions as *Figure 1*

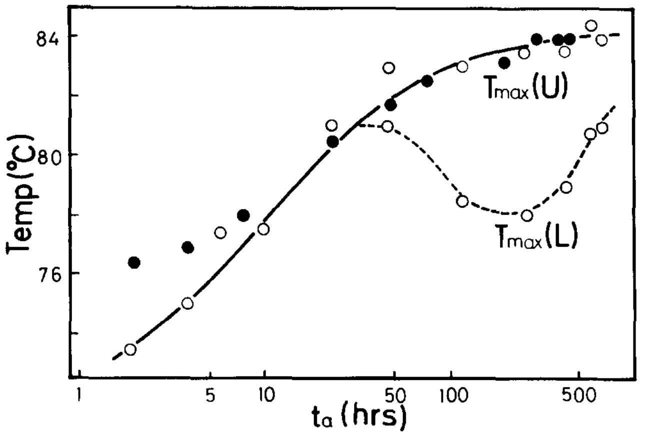

Figure 3 Peak temperature *versus* ageing time t_a for the PET I (●) and II (○) glasses aged at $T_a = 60°C$

The ageing-time dependences of the maximum position of endothermic C_p peak (taken as T_{max}) are shown in *Figure 3* for the ageing temperature of 60°C. The peaks appearing at lower and higher temperature for the PET II glass are designated $T_{max}(U)$ and $T_{max}(L)$, respectively. $T_{max}(U)$ increasees sigmoidally with $\log t_a$ in the same way as T_{max} for the PET I glass. On the contrary, $T_{max}(L)$ decreases at an early stage of ageing time in which the two peaks appear, and then increases through a minimum with t_a. For ageing times greater than about 500 h, T_{max} for the PET I glass and $T_{max}(U)$ for the PET II glass are close to 84°C.

From the appearance of two C_p peaks, it is suggested that different types of chain aggregates are formed in the amorphous matrix of the PET II glass at some degree of enthalpy relaxation. As previously mentioned, the PET II glass, prepared by gradually cooling the melt drawn mechanically from the T die in contact with the casting roller, experiences complicated thermomechanical histories, as compared with the ultraquenched PET II glass prepared by rapidly quenching from the isotropic static melt. Therefore, it is evident that the kinetics of enthalpy relaxations depends strongly on the glass-forming histories.

The time dependence of enthalpy is described by a relaxation function $\phi(t_a, T_a)$ defined as:

$$\phi(t_a, T_a) = [H(t_a, T_a) - H(\infty, T_a)]/[H(0, T_a) - H(\infty, T_a)] \quad (1)$$

where $H(t_a, T_a)$ is the enthalpy of the glasses aged at the temperature T_a for a period of time t_a; $H(0, T_a)$ is the enthalpy of the unaged glasses at T_a; and $H(\infty, T_a)$ is the equilibrium enthalpy at T_a. Experimental values of $[H(0, T_a) - \mathrm{H}(\infty, T_a)]$ were measured by determining the limiting value of d.s.c. energy absorption, obtained for a prolonged ageing time. The relaxation function ϕ is obtained by using the value of $H(t_a, T_a)$ determined from the C_p peak area, and also by approximating the value of $H(\infty, T_a)$ as the values obtained at 700 and 160 h for the ageing temperatures of 60 and 70°C, respectively.

The ageing-time dependences of ϕ are shown in *Figure 4* for the aged PET I and II glasses; ϕ decreases according to the following three modes for the PET II glass. Mode I appearing in the early stage of ageing is in a short-time regime where ϕ decreases linearly with $\log t_a$. In this regime the function ϕ of the PET II glass is linear in the same way as that of the PET I glass, although the slope of ϕ for the PET II glass is slightly larger. Mode II is in the middle-time regime where ϕ becomes almost independent of $\log t_a$. Finally, mode III is in the longer-time regime where a secondary decrease of ϕ occurs. It can be said that the chain rearrangements of glassy polymers occur in the second regime, accompanying enthalpy exchanges between chain segments, rather than with net enthalpy relaxations. The similar shape of ϕ curves is shown in *Figure 4* for the PET II glasses aged at 60 and 70°C, and one curve can be almost superimposed on the other by a horizontal shift along the $\log t_a$ axis.

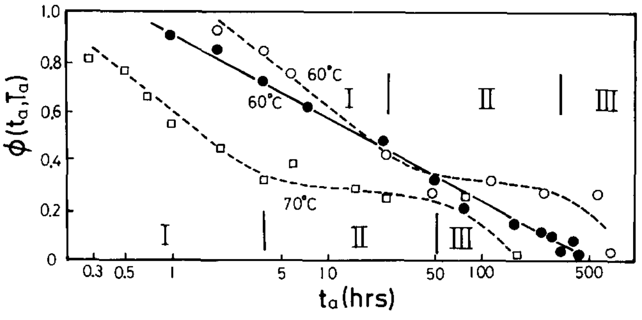

Figure 4 Relaxation function ϕ *versus* ageing time t_a for the PET I (●) and II (○, □) glasses. Ageing temperatures are indicated in the figure, and Roman numerals represent the types of enthalpy relaxation mode

The rate of isothermal change of the function ϕ is given approximately in terms of an effective relaxation time τ_{eff} by directly applying the phenomenological equation proposed by Kovacs[42]:

$$\mathrm{d}\phi/\mathrm{d}t_a = -\phi/\tau_{\mathrm{eff}} \qquad (2)$$

The value of τ_{eff} can be calculated from the values of ϕ and t_a by using the equation:

$$\tau_{\mathrm{eff}} = -t_a\phi/[0.4343\,\mathrm{d}\phi/\mathrm{d}(\log t_a)] \qquad (3)$$

From the thermo-rheological assumption that the distribution of relaxation times is independent of temperature, confirmed above by the time–temperature superposition of ϕ, the effective relaxation time τ_{eff} is given[43] by:

$$\tau_{\mathrm{eff}} = A\exp(E_h/RT)\exp(-C\phi) \qquad (4)$$

where E_h is the apparent activation energy and A and C are constants.

The calculated values of $\log\tau_{\mathrm{eff}}$ are shown *versus* ϕ in *Figure 5*. It is found that the value of $\log\tau_{\mathrm{eff}}$ decreases linearly with ϕ for the PET I glass, while the PET II glass shows a discontinuous jump of $\log\tau_{\mathrm{eff}}$ at nearly the same value of ϕ for the different ageing temperatures. This discontinuous point for $\log\tau_{\mathrm{eff}}$ corresponds to the transition of ϕ from mode II to mode I. From the data of τ_{eff} for the ageing temperatures of 60 and 70°C, the following values are obtained in the range of $\phi = 0.35$–1.0 for the PET II glass using equation (4):

$$A = 10^{-30} \qquad E_h = 55\,\mathrm{kcal\,mol^{-1}} \qquad C = 3.3 \qquad (5)$$

This value of E_h is in reasonable agreement with that reported by others[37,43]. Another method of obtaining the apparent activation energy was proposed by Moynihan *et al.*[44]. They showed that the dependence of the maximum position of endothermic C_p peak, $T_{\max}$, on heating rate q is given to a high degree of approximation by:

$$\mathrm{d}\ln|q|/\mathrm{d}T_{\max} = E_h/RT_{\max}^2 \qquad (6)$$

where $T_{\max}$ is the temperature in the middle of the transition range.

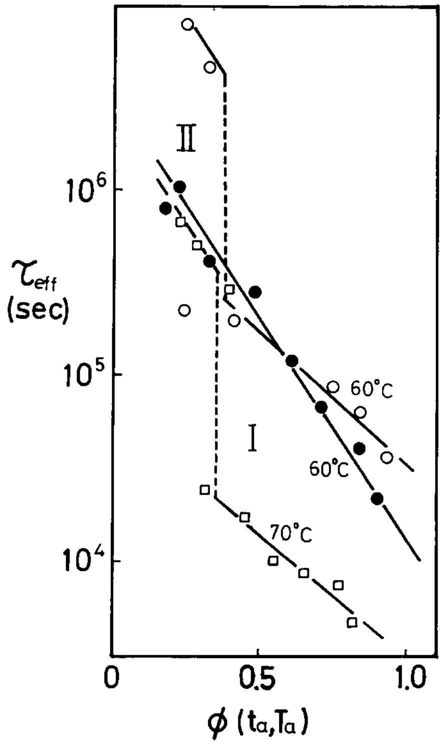

Figure 5 Effective relaxation time τ_{eff} *versus* relaxation function ϕ for the PET I (●) and II (○, □) glasses aged at the indicated temperatures for various ageing times. Roman numerals represent the types of enthalpy relaxation mode

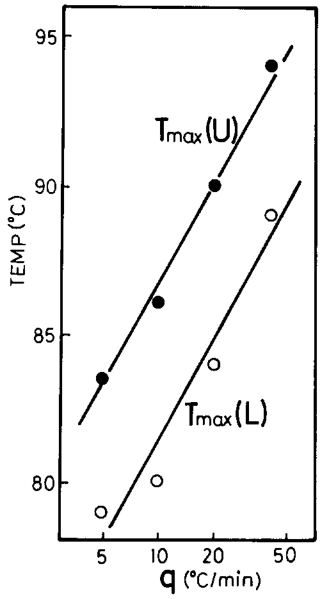

Figure 6 Peak temperature *versus* q for the PET II glass aged at 60°C for 450 h

Figure 6 shows the values of $T_{\max}$(U) and $T_{\max}$(L) as a function of $\log q$ for the PET II glass aged at 60°C for 450 h. As expected from equation (6), the two plots of $T_{\max}$(U) and $T_{\max}$(L) are linear, and the value of E_h, determined from the slope, is 49 kcal mol^{-1} and agrees well with the above value of 55 kcal mol^{-1} from the temperature dependence of τ_{eff}.

A MODEL FOR RELAXATION

Now, a model of chain networks is proposed to account for the above-mentioned relaxation phenomena of the PET II glass from molecular points of view. An essential structural feature of the model is the existence of a chain aggregate structure within the amorphous matrix of the unaged PET II glass. The existence of such a structure has been confirmed by Lee *et al.*[45], who have shown that aggregate nuclei consisting of a local alignment of neighbouring chains exist in the PET glass quenched at a relatively high temperature below T_g, while the ultraquenched PET glass quenched directly in liquid isopentane has no structure and no local order.

In the chain-network model for the PET II glass, it is assumed that the local order aggregate existing uniformly in the amorphous matrix of polymer chains acts as crosslinks of the chain network. In *Figure 7a*, the strand chains and crosslinks are shown schematically as a structural element of the network. In this model, a strand (tie) chain between two crosslinks is loose just as a random coil chain in amorphous isotropic polymers, since the amorphous chains of the PET II glass are possibly in relaxed states though the glass is formed by quenching of the drawn melt. Therefore, the configurations and local environments of the strand chain are the same as those of free chain segments. Further, it is also

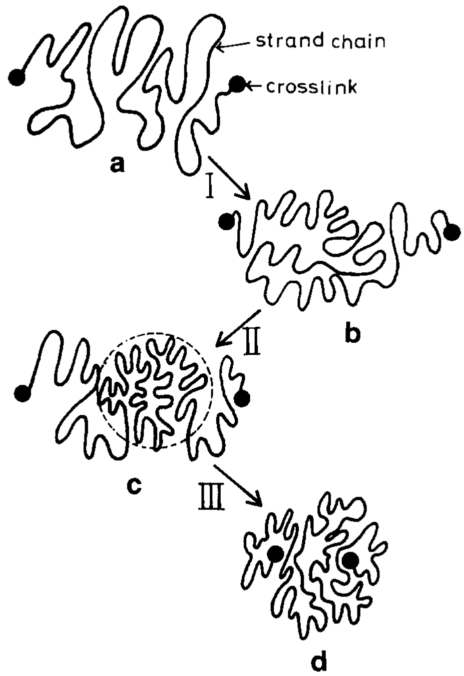

Figure 7 Microstructure models formed during isothermal ageing. Unaged glassy (a), homogeneous relaxed (b), two-phase dissipative (c) and equilibrium liquid-like (d) structures. Roman numerals represent the types of enthalpy relaxation mode

assumed that the presence of free chains and chain ends (cilia) is negligible.

In the isothermal ageing, the following three modes are proposed for the decay of the excess enthalpy stored by the segments of strand chains. The excess enthalpy of the chain segments is either (a) transformed into enthalpy, which flows to the inter-chain local environments of the neighbouring chains (designated by process I), or (b) stored by increasing the enthalpy of other neighbouring local segments along the strand chain (designated by process II). Further, the excess enthalpy stored as inter-chain potential energy is (c) converted into heat flowing to the environments of polymer samples, followed by inter-chain packing accompanying the arrangements of the centre of gravity of polymer chains within the matrix of polymer chains. In the polymer-chain systems, the enthalpy transfer along a polymer chain is more predominant than that between two separate chains because of weak inter-chain interactions, compared with the relatively strong intra-chain interaction of segment connectivity. Consequently, it is possible that the chain molecule is maintained at different energy levels from its neighbouring chains.

It is suggested from the above results of *Figures 2–4* that the aged PET I glass is composed mainly of a single amorphous phase of free chains with no microstructure. Then, during the isothermal ageing, progressive relaxations of the glassy structures occur towards its equilibrium chain conformation as defined by a given ageing temperature. Further, a homogeneous high packing of polymer chains is formed by a simultaneous operation of the processes I, II and III. That is to say, there is no necessity to assume some formations of order structures to account for the enthalpy relaxation phenomena.

In the case of the PET II glass, the initial enthalpy relaxation of mode I, occurring for relatively short times of ageing, is governed by the local conformational rearrangements of strand chains, characterized by the local environment of neighbouring chains. According to the above model, there are no substantial differences in the local chain environments between the PET I and II glasses. The chain aggregate formed in the aged PET II glass by mode I relaxations is shown schematically in *Figure 7b*. From the above-mentioned similarities of the local environments and configurations of strand chains, the relaxation function ϕ and the effective relaxation time τ_{eff} of the PET II glass are nearly the same as those of the PET I glass in the early stage of ageing (*Figures 3* and *4*).

In the second stage of ageing, the relaxation mode II in which the excess enthalpy is redistributed in the network chains is governed mainly by process II. The long-distance configurational changes of strand chains are disturbed, and then hindered appreciably by the existence of crosslinks owing to the large differences in relaxation times between the strand chains and crosslinks of networks. Therefore, the chain arrangements proceed mainly within the strand chains with a constant distance between two crosslinks. As shown in *Figure 7c*, the structure (b) formed by the mode I process is transformed into the two-phase structure (c) by the mode II process, in which the lower-density regions of chain packing are produced by simultaneously forming higher-density regions in the strand chain. In other words, the excess enthalpy of strand chains can be more efficiently redistributed by the formation of non-homogeneous structures, in which enthalpy liberated in one region of the strand chains is dissipated by the process of concentrating high-enthalpy (lower-density) structures in adjacent regions along the strand chains. Lindenmeyer[22–24] discussed the formation of the same non-homogeneous dissipative structures during the glass-forming process of amorphous polymers. Further, it is quite obvious that the two C_p peaks appearing at lower and higher temperatures correspond to the higher-enthalpy (lower-density) and lower-enthalpy (higher-density) regions, respectively. At the early stage of enthalpy redistributions, the excess enthalpy of the lower-enthalpy regions decreases with ageing time, following an increase in the excess enthalpy of the higher-enthalpy regions. However, as the physical ageing proceeds, the enthalpy supplied from the lower-enthalpy regions decreases owing to an increase in the relaxation times of chain arrangements in the regions. Therefore, the excess enthalpy of the higher-enthalpy regions is released appreciably by the inter-chain enthalpy transfers of the processes I and III, rather than stored by the process II. Consequently, $T_{\mathrm{max}}(\mathrm{L})$ decreases and then increases through a minimum with ageing time (*Figure 3*), since T_{max} increases with amount of excess-enthalpy relaxation. On the other hand, from the monotonic increases of $T_{\mathrm{max}}(\mathrm{U})$ in the same way as T_{max} of the PET I glass (*Figure 3*), the chain conformations seem to be rearranged in the lower-enthalpy regions, irrespective of the existence of the crosslinks.

In the final stage of ageing, the large-distance rearrangements of the networks to form their homogeneous equilibrium conformations (the mode III of relaxation) are induced by accompanying the displacement and rearrangement of the crosslinks. A structural model is shown in *Figure 7d* for the formed chain packing of the equilibrium PET II glass.

In *Figure 1*, the two C_p peaks appear for the PET II glass aged at 60°C even for an ageing time of ca. 700 h. Therefore, it can be said that the equilibrium structure is not established for the aged glass, although the glass possesses nearly its equilibrium enthalpy.

REFERENCES

1 Robertson, R. E. *J. Polym. Sci., Polym. Symp.* 1978, **63**, 173
2 Robertson, R. E. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 597
3 Adam, A. and Gibbs, J. H. *J. Chem. Phys.* 1965, **43**(1), 139
4 Hodge, I. M. *Macromolecules* 1983, **16**, 898
5 Bauwens-Crowet, C. and Bauwens, J.-C. *Polymer* 1986, **27**, 709
6 Privalks, V. P., Demehenko, S. and Lipatov, Y. S. *Macromolecules* 1986, **19**, 901
7 Chen, H. S. and Wang, T. T. *J. Appl. Phys.* 1981, **52**, 5898
8 Chow, T. S. and Prest, W. M., Jr *J. Appl. Phys.* 1982, **53**, 6568
9 Debolt, M. A., Easteal, A. J., Macedo, P. B. and Moynihan, C. T. *J. Am. Ceram. Soc.* 1976, **59**, 16
10 Chow, T. S. *J. Chem. Phys.* 1983, **79**(9), 4602
11 Kovacs, A. J., Aklonis, J. J., Hutchinson, J. M. and Ramos, A. R. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 1097
12 Hutchinson, J. M. and Kovacs, A. J. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1575
13 Matsuoka, S. and Quan, X. *Macromolecules* 1991, **24**, 2770
14 Ngai, K. L. and Plazek, D. J. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 619
15 Ngai, K. L. *J. Chem. Phys.* 1993, **98**(9), 7588
16 Ngai, K. L. *Comments Solid State Phys.* 1979, **9**, 121
17 Ngai, K. L., Rendell, R. W., Rajagopal, A. K. and Teiler, S. *Ann. NY Acad. Sci.* 1986, **484**, 150
18 Nagi, K. L., Mashimo, S. and Fytas, G. *Macromolecules* 1988, **21**, 3030
19 Adachi, K. *Macromolecules* 1990, **23**, 1816
20 Takeuchi, H. and Roe, R.-J. *J. Chem. Phys.* 1991, **94**(11), 7446
21 Takeuchi, H. and Roe, R.-J. *J. Chem. Phys.* 1991, **94**(11), 7458
22 Lindenmeyer, P. H. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 1965
23 Lindenmeyer, P. H. *Polym. J.* 1979, **11**, 677
24 Lindenmeyer, P. H. *Polym. Eng. Sci.* 1981, **21**, 958
25 Yeh, G. S. Y. and Geil, P. H. *J. Macromol. Sci.–Phys. (B)* 1967, **1**, 235
26 Car, S. H., Geil, P. H. and Baer, E. J. *J. Macromol. Sci.–Phys. (B)* 1968, **2**, 13
27 Siegmann, A. and Geil, P. H. *J. Macromol. Sci.–Phys. (B)* 1970, **4**, 239
28 Siegmann, A. and Geil, P. H. *J. Macromol. Sci.–Phys. (B)* 1970, **4**, 273
29 Yeh, G. S. Y. and Lambert, S. L. *J. Macromol. Sci.–Phys. (B)* 1972, **6**, 599
30 Yeh, G. S. Y. *Crit. Rev. Macromol. Sci.* 1972, **1**, 173
31 Geil, P. H. *Polym. Prepr.* 1974, **15**, 35
32 Renninger, A. L., Wicks, G. G. and Uhmann, D. R. *J. Polym. Sci.* 1975, **13**, 1247
33 Benoit, H. J. *J. Macromol. Sci.–Phys. (B)* 1976, **12**, 27
34 Meyer, M., Sande, J. V. and Uhlmann, D. R. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 2005
35 Aharoni, S. M. *J. Macromol. Sci.–Phys (B)* 1973, **7**, 73
36 Aref-Azar, A., Biddlestone, F., Hay, J. N. and Haward, R. N. *Polymer* 1983, **24**, 1245
37 Montserrat, S. and Cortes, P. *Makromol. Chem., Macromol. Symp.* 1988, **20/21**, 389
38 Tant, M. R. and Wilkes, G. L. *Polym. Eng. Sci.* 1981, **21**, 874
39 Aref-Azar, A. and Hay, J. N. *Polymer* 1982, **23**, 1129
40 Bosma, M., Brinke, G. T. and Ellis, T. S. *Macromolecules* 1988, **21**, 1465
41 Petrie, S. E. B. *J. Macromol. Sci.–Phys (B)* 1976, **12**, 225
42 Kovacs, A. J. *Fortsch. Hochpolym. Forsch.* 1963, **3**, 394
43 Petrie, S. E. B. *J. Polym. Sci. (A-2)* 1972, **10**, 1255
44 Moynihan, C. T., Easteal, A. J., Wilder, J. and Tucker, J. *J. Phys. Chem.* 1973, **78**, 2673
45 Lee, S., Miyaji, H. and Geil, P. H. *J. Macromol. Sci.–Phys. (B)* 1983, **23**, 489