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Structural relaxation of glass-forming polymers based on an equation for configurational entropy: 3. On the states attained at infinite time in the structural relaxation process. Results on poly(ether imide)

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The aim of this paper is to discuss the limit state attained at infinite time in the structural relaxation process. This state usually is identified with the equilibrium state extrapolated from the experimental data obtained at temperatures above the glass transition. The analysis is conducted with the help of a phenomenological model with fitting parameters, based on an equation for the evolution of the configurational entropy during the process. The model avoids the use of the fictive temperature, which makes it easier to introduce a different hypothesis on the limit states of the process. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The knowledge about the glassy state of amorphous materials, as a non-equilibrium state, is closely connected with the knowledge of the kinetics of the structural relaxation, the process of approach to an hypothetic equilibrium state of the material. The glass transition itself is an effect of the exponential dependence of the structural relaxation times on temperature. In this sense the modelling of the structural relaxation is important and it has attracted the attention of many researchers in the past decades. Two main characteristics of the structural relaxation have been experimentally established since the pioneering studies: nonlinearity and nonexponentiality[1–5]. Several phenomenological models try to reproduce these two main features by means of three key tools[6–11]: (1) a distribution of relaxation times, (2) the dependence of the structural relaxation times on temperature and on a structure parameter, typically the fictive temperature, and (3) the hypothesis that linearity can be obtained when the equations of the model are expressed in terms of a reduced time[5,7]. The models thus developed contain a set of parameters that in most cases play the role of material constants in the deductions leading to the model equations. The model parameters are usually determined by fitting the experimental results with some least-squares routine, but other methods have been proposed[12] as well. In differential scanning calorimetry (d.s.c.) measurements the experimental results are curves of the specific heat capacity at constant pressure, $c_p(T)$, measured during heating scans from a temperature T_1 below the glass transition temperature T_g to a temperature T_0 above T_g. Previously, the samples have been subjected to a thermal treatment that may include or not an isothermal stage at an annealing temperature T_a for a certain annealing time t_a. The essential test for the validity of such models is to check whether or not the model parameters thus determined are in fact material parameters independent of the thermal history, i.e. whether the model equations with a single set of parameters can accurately reproduce the experimental $c_p(T)$ curves measured after different thermal histories. Several works have shown that this is not easy to accomplish in the case of the Scherer–Hodge or the Narayanaswamy–Moynihan models[13–16].

Most of the theories of the structural relaxation that have been developed employ the concept of the fictive temperature T_f introduced by Tool[1]. The fictive temperature equals the temperature T when the material is in equilibrium; in the glassy state, the value of T_f depends

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on the formation history of the glass starting from an equilibrium state, i.e. on the cooling rate and on temperature and time of the isothermal annealing periods[6]. The state of the polymer out of equilibrium (at a fixed pressure) is characterized both by the temperature and the fictive temperature, and the expressions for the structural relaxation times in processes at constant pressure contain T and T_f as arguments.

An important hypothesis of these phenomenological models is that the limit state attained at infinite time in the structural relaxation process at a constant temperature T_a is the equilibrium state in which $T_f = T_a$. This means that it is assumed that the structural relaxation process takes the material to a state which can be obtained from extrapolation of the equilibrium states measured at temperatures above the glass transition. However, some experimental evidence casts doubts on this assumption, as we will discuss below. Thus it is interesting to develop a phenomenological model for the structural relaxation which permits to introduce different hypothesis on the limit state at infinite time. This is easier to do if, instead of following the fictive temperature during the structural relaxation process, one determines the evolution of the configurational entropy S_c directly. We have recently proposed such a model[17,18]. It is a modification of the Scherer–Hodge one, in the sense that it uses the Adam–Gibbs equation for the dependence of the relaxation time on T and S_c, in addition to the usual linearization by means of the reduced time and the use of the Kohlrausch–Williams–Watts (KWW) relaxation function[19,20] employed in many phenomenological models. In the present paper, after recalling the model equations we compare the model predictions with d.s.c. experimental results on poly(ether imide).

EXPERIMENTAL

Poly(ether imide) (PEI) Ultem™ from General Electric was used in this study. The experiments were carried out in a Perkin–Elmer DSC4 differential scanning calorimeter on a single encapsulated sample. All the experiments started at 250°C with the sample in equilibrium. The sample was then cooled down to T_a at a rate of $40°\mathrm{C\,min^{-1}}$, kept at this temperature for a time t_a, and cooled down again at $40°\mathrm{C\,min^{-1}}$ until 150°C. Then the measuring scan was conducted heating at $10°\mathrm{C\,min^{-1}}$ till 250°C. The results of three such experiments with different T_a are presented together with two $c_p(T)$ curves measured after a cooling from 250°C to 150°C at $0.5°\mathrm{C\,min^{-1}}$ and $40°\mathrm{C\,min^{-1}}$ respectively. The last one will be called the reference scan.

MODEL FOR THE STRUCTURAL RELAXATION BASED ON THE EVOLUTION OF THE CONFIGURATIONAL ENTROPY

As is usual in phenomenological theories of the structural relaxation, the configurational entropy at a time t, $S_c(t)$, is regarded as a function of the whole thermal history experienced by the sample up to t, $T(\zeta)$, $-\infty < \zeta \leq t$ (we consider here only the dependence on temperature of S_c; other variables such as pressure are regarded as constant, as in fact happens in d.s.c.). This fact is sometimes expressed by saying that $S_c(t)$ is a function of the temperature history $T(\zeta)$. Both for simplicity and because it is adequate for the type of processes we have in mind, we consider only temperature histories which were constant up to time $\zeta = 0$. Moreover, as already mentioned in the Introduction, the functional relation between $S_c(t)$ and $T(\zeta)$ is a non-linear one. Whereas linear memory effects can all be represented in terms of a single model (Boltzmann's linear hereditary equation), such a universal representation does not exist for non-linear relationships. Some additional assumptions are thus necessary, which are fixed taking into account the existing experience with the phenomenology of the structural relaxation.

First of all, we rescale the elapsed time t by assigning to it a reduced time[5] ξ defined by a strictly increasing mapping $\hat{u}$

$$\xi = \hat{u}(t) = \int_0^t \frac{d\sigma}{\hat{\tau}(\sigma)} \tag{1}$$

where $\hat{\tau}$ is a positive function which takes into account the changing structure of the material: for each time argument σ it depends on the values of temperature and configurational entropy at that time instant, $\hat{\tau}(\sigma) = \tau[S_c(\sigma), T(\sigma)]$, and we assume that this last dependence has the same form as Adam and Gibbs' equation[21], i.e.

$$\tau(S_c, T) = A \exp\left(\frac{B}{S_c T}\right) \tag{2}$$

originally intended by its authors only for equilibrium. Indeed, when in equation (2) the configurational entropy S_c has the equilibrium value $S_c^{eq}(T)$ we have

$$\tau[S_c^{eq}(T), T] = A \exp\left(\frac{B}{S_c^{eq}(T)T}\right) = \tau^{eq}(T) \tag{3}$$

which defines Adam and Gibbs' curve $\tau^{eq}(T)$ of equilibrium relaxation times. A is a pre-exponential constant, and the parameter B in Adam and Gibbs' theory is related to the microscopic picture of the process through $B = s_c \Delta\mu / k$, where s_c means the configurational entropy of the smallest cooperatively rearranging region, $\Delta\mu$ is the free energy barrier hindering configurational rearrangement per mol of molecules or chain segments, and k is Boltzmann's constant.

Further we assume that, if the material is subjected to an arbitrary temperature history which reaches a temperature T and then stays at T for a time lapse Λ, the state attained by the material as Λ grows without limit is uniquely determined by the temperature value T, and is independent of further details of the temperature history. For this *limit state* we assume thus that a function $S_c^{lim}(T)$ exists, which depends only on temperature, which gives the limit value of the configurational entropy $S_c(t)$ in a process such as that just described when $t \to \infty$.

With these physical inputs in mind, we suppose that, after rescaling time in the way described, the non-linear function giving the dependence of $S_c(t)$ on $T(\zeta)$ is expressible in the form of a 'quasilinear' relationship between $S_c(t)$ and $\tilde{T}(u)$, the temperature history expressed in the new time scale [$\tilde{T}(u) = T(\zeta)$ when $u = \hat{u}(\zeta)$]:

$$S_c(t) = S_c^{lim}[T(t)] - \int_0^{\hat{u}(t)} \phi[\hat{u}(t) - u]\, dS_c^{lim}[\tilde{T}(u)] \tag{4}$$

In this equation ϕ is a relaxation function, and so it is guaranteed that, in processes of the type discussed above (which include those typical for the structural relaxation), $\lim_{t\to\infty} S_c(t) = S_c^{\lim}(T)$. Since the temperature history may include discontinuous jumps, the integral in equation (4) must be interpreted as a Riemann–Stieltjes integral, and, in general, it will not be possible to write $\mathrm{d}S_c^{\lim}[\tilde{T}(u)] = (\mathrm{d}S_c^{\lim}/\mathrm{d}\tilde{T})(\mathrm{d}\tilde{T}/\mathrm{d}u)\mathrm{d}u$. Equation (4) can be applied to any thermal history $T(\zeta)$ of the type considered at the beginning of this paragraph.

Non-exponentiality, one of the most clearly recognized experimental features of structural relaxation[4,5,7], is accounted for by assuming a form of ϕ given by a Kohlrausch–Williams–Watts-type formula[19,20]: for $0 \leq u < \infty$

$$\phi(u) = \exp(-u^{\beta}) \tag{5}$$

If the limit state of the structural relaxation process would coincide with the extrapolation of the equilibrium values determined at temperatures above the glass transition one would have $S_c^{\lim}(T) = S_c^{\mathrm{eq}}(T)$ with

$$S_c^{\mathrm{eq}}(T) = \int_{T_2}^{T} \frac{\Delta c_p(\theta)}{\theta}\mathrm{d}\theta \tag{6}$$

where $\Delta c_p(T) = c_{pl}(T) - c_{pg}(T)$ is the configurational heat capacity, the difference between the heat capacity of the equilibrium liquid and the heat capacity of the glass at the same T, and T_2 is the Gibbs–DiMarzio transition temperature[22]. In general, we put

$$\Delta c_p^{\lim}(T) = T\frac{\mathrm{d}S_c^{\lim}(T)}{\mathrm{d}T} \tag{7}$$

and $\Delta c_p^{\lim}(T) = c_p^{\lim}(T) - c_{pg}(T)$. $S_c^{\lim}(T)$ is calculated as

$$S_c^{\lim}(T) = S_c^{\mathrm{eq}}(T^*) + \int_{T^*}^{T} \frac{\Delta c_p^{\lim}(\theta)}{\theta}\mathrm{d}\theta \tag{8}$$

where T^* is a temperature above T_g in the equilibrium liquid state, where the limit state coincides with the equilibrium state (below we take $T^* = T_g + 10°\mathrm{C}$).

The application of the above set of equations to a multiple-step thermal history, $T(t) = T_0 + \Sigma_{i=1}^{n}(T_i - T_{i-1})h(t - t_{i-1})$ (with $t_0 = 0$) leads to

$$\begin{aligned} S_c(t) &= S_c^{\lim}[T(t)] - \sum_{i=1}^{n}[S_c^{\lim}(T_i) \\ &\quad - S_c^{\lim}(T_{i-1})]\phi[\hat{u}(t) - \hat{u}(t_{i-1})] \\ &= S_c^{\lim}[T(t)] - \sum_{i=1}^{n}\left(\int_{T_{i-1}}^{T_i} \frac{\Delta c_p^{\lim}(T)}{T}\mathrm{d}T\right) \\ &\quad \exp\left(-\left(\int_{t_{t-1}}^{t} \frac{\mathrm{d}\sigma}{\hat{\tau}(\sigma)}\right)^{\beta}\right) \end{aligned} \tag{9}$$

when the form assumed for $\hat{\tau}(\sigma)$ is introduced in equation (9), an equation for configurational entropy out of equilibrium results which has, besides the function $\Delta c_p^{\lim}(T)$, four adjustable parameters: A, B, T_2 and β. Three of them, A, B, T_2, together with $\Delta c_p^{\lim}(T)$ define the dependence of the equilibrium relaxation times on temperature, equation (3), and β can be interpreted as a width parameter of a distribution of relaxation times.

Equation (9) must be solved numerically. In this work cooling and heating stages in the thermal histories were replaced by a series of 1-degree temperature jumps followed by isothermal stages with a duration calculated to result in the same overall rate of temperature change as in the actual experiments. The configurational entropy was calculated at time instants t_k with equation (9) and the relaxation time at those time instants is then calculated using equation (2). This value of the relaxation time is used to calculate the reduced time in the subsequent time instant t_{k+1}, according to equation (1). After each temperature jump the reduced time was evaluated at time instants $t_k = 0.001 \cdot 2^k$ s with integer k.

Comparison of the experimental results with the model calculations requires to express these in terms of $c_p(T)$ curves. Owing to the inherent irreversibility of the structural relaxation process, there is no straightforward relationship between the configurational entropy and $c_p(T)$. However, it is true that

$$c_p(T) - c_{pg}(T) = \frac{\partial H_c}{\partial T}$$

where H_c is the specific configurational enthalpy. For the dependence of H_c upon the thermal history an analogous derivation to that of S_c is assumed, which leads to the equation, analogous to equation (9),

$$\begin{aligned} H_c(T) &= H_c^{\lim}[T(t)] - \sum_{i=1}^{n}[H_c^{\lim}(T_i) - H_c^{\lim}(T_{i-1})] \\ &\quad \phi[\hat{u}(t) - \hat{u}(t_{i-1})] = H_c^{\lim}[T(t)] \\ &\quad - \sum_{i=1}^{n}\left(\int_{T_{i-1}}^{T_i} \Delta c_p^{\lim}(T)\mathrm{d}T\right) \\ &\quad \times \exp\left(-\left(\int_{t_{i-1}}^{t} \frac{\mathrm{d}\sigma}{\hat{\tau}(\sigma)}\right)^{\beta}\right) \end{aligned} \tag{10}$$

for a stepped temperature history. The assumption made here in order to determine H_c is that enthalpy and entropy have the same relaxation function ϕ, i.e. it is assumed that the relaxation times for enthalpy and entropy are the same, and consequently they are also the same for the Gibbs free energy.

RESULTS

The five experimental $c_p(T)$ curves measured are shown on *Figure 1*. The glass transition in this polymer is quite narrow, as shown by the small differences between the onset of the glass transition $T_{g\,\mathrm{onset}} = 209°\mathrm{C}$, the midpoint glass transition temperature, $T_{g\,\mathrm{midpoint}} = 213°\mathrm{C}$ (determined from the midpoint of the c_p increment in the transition), and the fictive temperature in the glassy state, $T_{f'} = 210°\mathrm{C}$, determined by the intersection of the enthalpy lines corresponding to the glass and the equilibrium liquid[23]. All three of them were determined from the $c_p(T)$ curve measured after cooling at $40°\mathrm{C\,min}^{-1}$ (reference scan). In this work we take the value $T_{f'} = 210°\mathrm{C}$ measured in the reference scan as the glass transition temperature T_g of the sample.

Three annealing temperatures were selected: 210°C, 200°C and 170°C, i.e. $T_a = T_g$, $T_a = T_g - 10°\mathrm{C}$ and $T_a = T_g - 40°\mathrm{C}$. The peak showing up in the $c_p(T)$ curve measured after thermal treatments including isothermal annealings depends only weakly on the value of T_a, maybe because of the narrow temperature interval of the glass transition.

In none of the $c_p(T)$ curves measured does a peak appear at a temperature below T_g (a sub-T_g peak), as happens in other polymers for high cooling rates and low annealing temperatures[9,15,16,24–29]. Probably this is also

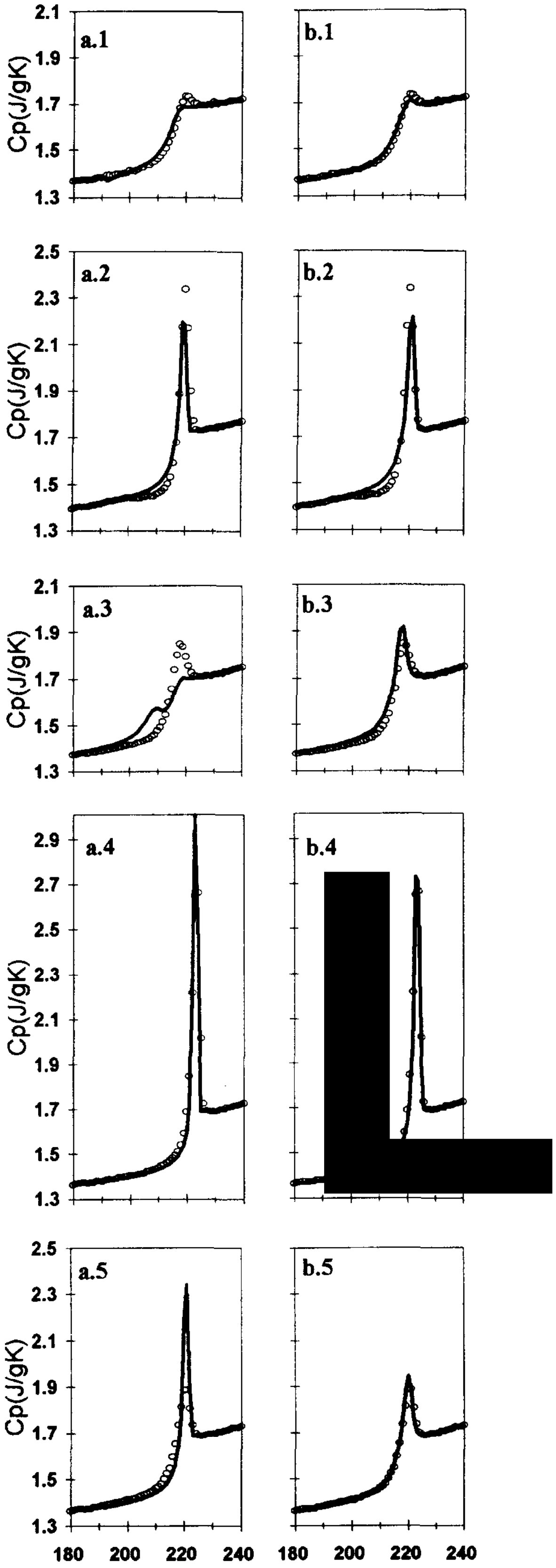

Figure 1 Experimental $c_p(T)$ curves (open circles) measured after cooling at 40°C min^{-1} (a1,b1), and 0.5°C min^{-1} (a2,b2) and after thermal histories that include an isothermal annealing at 170°C for 1550 min (a3,b3), 200°C for 1200 min (a4,b4) and 210°C for 1000 min (a5,b5). The solid line in a1 to a5 represents the prediction of the model with the assumption $S_c^{\mathrm{lim}}(T) = S_c^{\mathrm{eq}}(T)$, $B = 1500\,\mathrm{J\,g^{-1}}$ and the remaining parameters shown in *Table 1*. The solid line in b1 to b5 represents the calculations with a $S_c^{\mathrm{lim}}(T)$ curve according to *Figure 3*, $B = 1500\,\mathrm{J\,g^{-1}}$ and the remaining parameters as shown in *Table 2*

due to the narrow temperature interval of the glass transition.

DISCUSSION

Application of the model with $S_c^{lim}(T) = S_c^{eq}(T)$

With the assumption $S_c^{\mathrm{eq}}(T) = S_c^{\mathrm{lim}}(T)$ the model contains four adjustable parameters, A, B, T_2 and β. The configurational heat capacity $\Delta c_p(T)$ measured in this polymer is nearly independent from temperature. In the model calculation it was considered temperature-independent with a value of 0.251 J g K^{-1}, the average of the values determined for the $c_p(T)$ curves measured after the different thermal treatments.

The set of four parameters of the model was determined via a simultaneous least-squares fit of a set of five experimental $c_p(T)$ curves, shown on *Figure 1(a1–a5)*. The correlation between the four parameters has been amply reported for phenomenological models such as those of Narayanaswamy–Moynihan or Scherer–Hodge[9,13,15,16,25,30–32], and it is also found in the one proposed in the present work. Basically, a correlation is found between B and T_2 (see below). To handle this problem, the parameter B was kept fixed while the other three were adjusted, and the fitting procedure was then conducted for different values of B. The Nedler and Mead[33] search routine was employed here. The fitting procedure thus leads to a set of three parameters, β, T_2 and A, for each fixed value of the parameter B.

Figure 1a shows the fit obtained keeping $B = 1500\,\mathrm{J\,g^{-1}}$ constant. The values of A, T_2 and β obtained with the search routine are shown in *Table 1*. The model is unable to reproduce accurately the five $c_p(T)$ curves considered, and this happens for all the selected values of the parameter B. It must be remarked that the peak in the $c_p(T)$ curve predicted by the model for a thermal treatment including an annealing at 210°C is much higher than the one appearing in the experiment. The $c_p(T)$ curves predicted for the thermal treatment including no annealing and for the corresponding to an annealing at 200°C are close to the experimental ones. For the four thermal treatments mentioned above, the fitting routine leads to calculated $c_p(T)$ curves coincident for all the values of B. The height of the peak in the calculated $c_p(T)$ curve for the annealing at 170°C depends on the value of B fixed in the search routine as shown in *Figure 2*, but the peak shows up always at a temperature lower than the experimental one. This behaviour is quite similar to that found in polycarbonate[17], a polymer that shows also a narrow glass transition temperature interval. In polymethacrylate polymers[18] the $c_p(T)$ measured after thermal treatments including an annealing at low temperature shows a sub-T_g peak that is correctly reproduced by the model with the assumption $S_c^{\mathrm{lim}}(T) = S_c^{\mathrm{eq}}(T)$, but the behaviour of the model predictions in thermal treatments including annealing at temperatures near T_g was in these polymers the same as described here for PEI.

The values obtained for the model parameters are significantly different for the different values of B chosen, as shown in *Table 1*. Obviously there is a great uncertainty in the values of the parameters due to the considerable error in the curve fitting. The correlation between the parameters in the model appears quite clearly. It will be discussed in some detail in the next section.

Application of the model with an additional assumption for Δc_p^{lim}

The impossibility of modelling the $c_p(T)$ experimental curves after annealings at temperatures close to T_g simultaneously with the $c_p(T)$ curves measured after the rest of thermal treatments has been found with our model in different polymers, and this difficulty also appears with other four-parameter models, which usually predict narrower and higher peaks than the experimental ones after annealings close to T_g[9,16]. Studies of enthalpy relaxation in amorphous polymers have reported that the extrapolation of the experimental values of $\Delta h(T, t)$ to long times leads to limit values considerably lower than the theoretically predicted ones[29,34–37] (a significant exception to this is represented by ref. 38; in it, heat capacity increments in the glass transition of polycarbonate seem to be compatible with the limiting values of the enthalpy loss during the isothermal annealing at temperatures very close to T_g). This raises doubts on the identification of S_c^{lim} with S_c^{eq}. This argument would support the hypothesis of a metastable state, intermediate between those of equilibrium liquid and glass, as the limit condition of the material in the structural relaxation process, which accordingly would be unable to reach the equilibrium state. The reason for this could lie in a collapse of the configurational rearrangements when the number of conformations available for the molecules or polymer segments would attain a certain limit value higher than the one corresponding to equilibrium. Topological constraints such as entanglements, present in polymers but not in inorganic glasses, could explain why structural relaxation in polymers would exhibit this distinctive feature[37].

Our model equations can be used to check whether the predicted curves under such a hypothesis are closer to experiment than those previously analysed. The sketch of *Figure 3a* shows the assumed shape for the curve of configurational entropy in these metastable states, $S_c^{lim}(T)$, in the temperature interval of the glass transition: a shape similar to that of an experimental cooling at a finite rate, but with a different change of Δc_p. *Figure 3b* represents the assumption here made regarding the $c_{pl}(T)$ behaviour of the limit states, to be introduced in the model equations. Simply, we assume that the behaviour of the transition from liquid to the hypothesized metastable limit states is analogous to that from the liquid to the glassy states. Further, for temperatures above $T^* = T_g + 10°C$ we take $c_p^{lim}(T) = c_{pl}(T)$.

The definition of the shape of the curve $S_c^{lim}(T)$ introduces a new parameter δ in the model (see *Figure 3*). The fitting routine was the same described above. The value of B was fixed and the least-squares routine sought the set of four parameters δ, β, T_2 and $\ln A$ that best reproduced the five experimental $c_p(T)$ curves shown on *Figure 1*. *Table 2* shows the set of parameters found for each value of B. The curves predicted by the model are nearly identical for values of B ranging between 1000 and 3500 J g^{-1}. The model curves predicted are represented in *Figure 1(b1–b5)* for the parameters corresponding to $B = 1500$ J g^{-1}. The improvement of the theoretical prediction with the modified hypothesis on S_c^{lim} is very apparent. Not only is the height of the peak in the $c_p(T)$ curve measured after annealing at 210°C (*Figure 1(b5)*) correctly reproduced, but also the $c_p(T)$ curve calculated for an annealing at 170°C perfectly matches the

Table 1 Model parameters found with the assumption $S_c^{lim}(T) = S_c^{eq}(T)$ for each value of B

B (J g^{-1})	β	T_2 (°C)	ln A (s)
500	0.36	170	−38.5
1000	0.39	150.7	−55.0
1500	0.42	138	−68.5

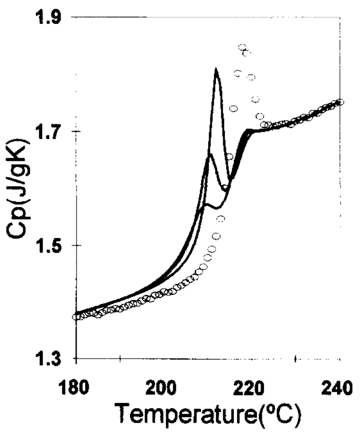

Figure 2 $c_p(T)$ measured after a thermal history that includes an isothermal annealing at 170°C for 1500 min. Model calculations with $B = 500$, 1000 and 1500 J g^{-1} (and the remaining parameters according to *Table 1*) are shown as solid lines. The peak appearing in c_p at approximately 210°C decreases for increasing values of B; this identifies the different curves. The experimental results are represented by open circles

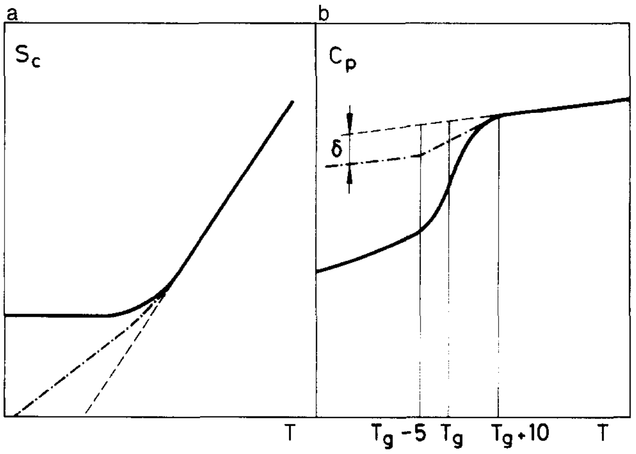

Figure 3 (a) Sketch of the configurational entropy corresponding to the liquid state (dashed line), to an experimental cooling scan at a finite cooling rate (solid line) and to the metastable state line, hypothetical limit of the structural relaxation process (dashed–dotted line). (b) $c_p(T)$ lines corresponding to the three cases described in (a)

Table 2 Model parameters found with $S_c^{lim}(T)$ as in *Figure 3* for each value of B

B (J g^{-1})	δ J (g K)$^{-1}$	β	T_2 (°C)	ln A (s)
500	0.134	0.40	167.2	−36.6
1000	0.115	0.44	138.7	−45.0
1500	0.116	0.48	120.0	−53.6
2000	0.115	0.52	103.9	−60.3
2500	0.114	0.55	87.3	−64.3
3000	0.113	0.58	71.2	−67.1
3500	0.115	0.60	63.6	−73.9

experimental one. Thus a single set of five parameters is able to reproduce the structural relaxation process of this polymer. The problem, as in the case of polycarbonate[17] and polymethacrylate polymer[18], is that there exist several sets of five parameters that predict the same $c_p(T)$ curves. It is thus necessary to find some complementary information to decide between the different sets of parameters.

Before that, nevertheless, some conclusions can be reached from the d.s.c. experiments and the model calculations alone. The value of δ that characterizes the difference between the curves of $S_c^{\lim}(T)$ and $S_c^{eq}(T)$ is independent of B with a value of 0.115, which is a 46% of $\Delta c_p(T)$. This seems to imply that the structural relaxation process would take the material to a limit state quite far from the extrapolated equilibrium line.

The correlation between the model parameters appears quite clearly. When B increases, lower values of T_2 and of $\ln A$ are found. These three parameters determine the curve of equilibrium relaxation times. *Figure 4* shows the $\tau^{eq}(T)$ and $\tau^{\lim}(T)$ curves determined from the different sets of parameters of *Table 2*, where

$$\tau^{\lim}(T) = A\exp\left(\frac{B}{TS_c^{\lim}(T)}\right) \qquad (11)$$

and $\tau^{eq}(T)$ is given by equation (3) (of course, $\tau^{\lim}(T) = \tau^{eq}(T)$ for $T > T_g + 10°\mathrm{C}$). The $\tau^{\lim}(T)$ curves show a change of slope around T_g that corresponds to the change of slope of $S_c^{\lim}(T)$. There is an outstanding coincidence between the curves corresponding to the different values of B, at least in the time interval comprised between 10^{-5} and 10^3 s. The relaxation time in the limit state is 200 s when the temperature is equal to T_g for all the sets of parameters. It can be concluded that the curve of 'calorimetric' relaxation times in equilibrium or in the limit state of the structural relaxation is a material 'parameter' which can be determined uniquely from the d.s.c. experiments. The numerical determination of the parameters B, T_2 and $\ln A$ requires additional information.

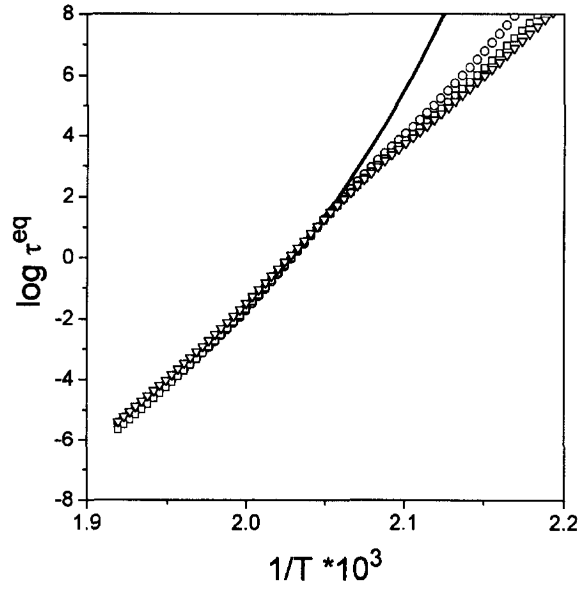

Figure 4 Limit relaxation times $\tau^{\lim}(T)$ determined by the model with $S_c^{\lim}(T)$ as in *Figure 3*, for different values of B (see text): (○) $B = 1000\,\mathrm{J\,g^{-1}}$; (□) $B = 2000\,\mathrm{J\,g^{-1}}$; (▽) $B = 3000\,\mathrm{J\,g^{-1}}$. The values of the remaining parameters are shown in *Table 2*. The full line represents the equilibrium relaxation time $\tau^{eq}(T)$ with $B = 1000\,\mathrm{J\,g^{-1}}$ and the remaining parameters as in *Table 2*

As happened in polycarbonate[17] and polymethacrylate polymers[18], as the value of B increases the value of T_2 decreases and thus the difference $T_g - T_2$ increases. In PEI, $T_g - T_2$ varies between 71°C for $B = 1000\,\mathrm{J\,g^{-1}}$ and 146.4°C when $B = 3500\,\mathrm{J\,g^{-1}}$. Reported values for this difference obtained from viscoelastic measurements[39] agree better with the lower values of B. The absolute value of the pre-exponential factor $\ln A$ also increases with the value of B, and the more reasonable ones are those corresponding to the lowest values of B.

There is also a correlation between the value of B and the one found for β, which varies from 0.44 to 0.60 when B ranges from 1000 to $3500\,\mathrm{J\,g^{-1}}$. The uncertainty in the determination of this parameter is very high when such a broad range of B values is considered but, taking into account the arguments of the above paragraph, the more reasonable values are around 0.45, the ones corresponding to the lowest values of B.

The present study and the previous ones[17,18], show that the phenomenological model is significantly improved in its agreement with experiment if the additional hypothesis is made, that the limit behaviour of the structural relaxation process departs from the usually accepted extrapolation from super-T_g equilibrium. This encourages further thoughts about the meaning of this situation. In this regard, it must be remarked that, from the point of view of the structural relaxation kinetics, the hypothesis of metastable limit states defined by $S_c^{\lim}(T)$ different from the *extrapolated* equilibrium states is indistinguishable from the hypothesis that the very same equilibrium line is 'bended' through the glass transition region (and thus departs, for temperatures in this interval and lower, from the extrapolation defined by the super-T_g portion of the line). In this last case, the usual extrapolation based on an analytical expression for the super-T_g $c_p(T)$-curve would have to be replaced by something similar to the sketch of *Figure 3b*, i.e. $c_p^{\lim}(T)$ would be, in fact, the true course of $c_{pl}(T)$ (the concrete form of this curve probably can vary to a certain extent without influencing appreciably the model fit, and our choice for it in the present work was determined solely by the want of introducing not more than one additional parameter into the model). The important consequence of this line of reasoning would be that the configurational entropy in the limit states of the structural relaxation process would not be zero at T_2 and, moreover, this parameter would thus lose much of its physical meaning. In any case, to keep a distinction between $S_c^{\lim}$ and S_c^{eq} would be justified if the latter were the outcome of some theoretical consideration based, for example, on statistical mechanics, and the former could be influenced by kinetic parameters of the process.

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