Structure and thermal history dependent enthalpy relaxation at the glass transition of semicrystalline polyimides

Stephen Z. D. Cheng, Daniel P. Heberer, James J. Janimak, Shawn H.-S. Lien and Frank W. Harris
Institute and Department of Polymer Science, College of Polymer Science and Polymer Engineering, The University of Akron, Akron, Ohio 44325-3909, USA
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Quantitative differential scanning calorimetry (d.s.c.) measurements were conducted to assess the enthalpy relaxation behaviour of a series of semicrystalline polyimides with different chain flexibilities. The polymers consisted of a rigid group (the imide and aromatic rings, 4,4′-oxydiphthalic anhydride, (ODPA)) and a flexible linkage (ethylene glycol sequence). The polymers are designated as ODPA($n=x$) where x is the number of flexible ethylene glycol repeating units ($n=1$, 2 and 3). Non-isothermal experiments at different cooling and heating rates lead to hysteresis effects. Isothermal experiments in which the ODPAs were held for various times at three sub-T_g annealing temperatures (undercoolings) show physical ageing behaviour. The results are analysed based on the multi-order parameter model, which assumes thermorheological simplicity, a distribution of relaxation times, and structure and temperature dependent relaxation times. The apparent activation energies (Δh) of these ODPA polyimides were obtained through non-isothermal experiments, and they are assumed to be independent of thermal history. The parameter that characterizes the distribution of relaxation times (β) is, however, dependent on annealing temperature in the isothermal experiments. The parameter (x) used to fractionize the temperature and structure dependency of the relaxation time shows for each polymer only very minor changes with annealing temperature. The variation of these parameters with chain flexibility is also discussed.

(Keywords: amorphous glass; apparent activation energy; distribution of relaxation time; enthalpy relaxation; hysteresis effect; physical ageing behaviour; polyimide; structure and thermal history dependence; undercooling; sub-T_g annealing)

INTRODUCTION

The glass transition temperature is the main characteristic temperature of the amorphous solid and liquid states. In applications the glass transition temperature is one of the critical parameters determining the ultimate usage temperature of a material. The microscopic process involved during the glass transition is the freezing of large-scale molecular motion without a change in the overall chain conformation[1]. Since the heat capacity (and also the compressibility and thermal expansion coefficient) of a polymer glass is always lower than that of the liquid at the same temperature, and since there is no latent heat involved in stopping molecular motion, the glass transition superficially takes on the appearance of a thermodynamic second-order transition. The freezing of molecular motion is, however, time-dependent and, therefore, the glass transition must be called an irreversible process[1].

In non-isothermal experiments, different cooling and heating rates of non-crystalline materials cause hysteresis effects in the glass transition region (endotherms after the glass transition because of slow cooling and exotherms before the glass transition because of faster cooling than heating). The hysteresis effect has been observed in many polymers, such as polystyrene (PS)[2,3], poly(vinyl chloride) (PVC)[3], poly(methyl methacrylate) (PMMA)[3], and several thermoplastic engineering materials, such as poly(aryl ether ether ketone)[4], poly(thio-1,4-phenylene)[5], poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO)[6] and poly(ethylene-2,6-naphthalenedicarboxylate) (PEN)[7]. It has been reported that the enthalpy relaxation during reheating shows a linear relationship with the logarithm of the previous cooling rate[4–7] in the slow cooling rate region. In isothermal experiments, annealing of non-crystalline materials below the glass transition temperature before heating to above the transitions results in physical ageing behaviour. At a relatively short annealing time when the material is annealed at a temperature not too far below the glass transition, one finds an endothermic peak which generally appears before the main glass transition. With increased annealing time, the endothermic peak shifts to higher temperatures and increases its absolute value of enthalpy. Many polymers have been reported to show this behaviour, e.g. PS[8–12], PVC[13–15] and PMMA[16–18].

The observations in non-isothermal and isothermal experiments have been explained by relaxation phenomena. The hysteresis effect in glassy materials was first recognized by Tool[19,20]. Wunderlich *et al.*[2] proposed a hole theory, based on the Eyring[21] and Frenkel[22] models, to illustrate this effect. Later, Moynihan *et al.*[23,24] suggested a method to describe this effect by assuming an equilibrium isothermal relaxation function with non-exponential character. On the other hand, the physical ageing behaviour can be described by a phenomenological multi-order parameter model, which is based on ideas originally proposed by Davies and Jones[25]. Theories have been developed independently by Kovacs *et al.*[26] and Moynihan *et al.*[23,24], both groups following the earlier works of Narayanaswamy[27] and Tool[20]. The model as proposed by Kovacs *et al.*[26] implies a discrete

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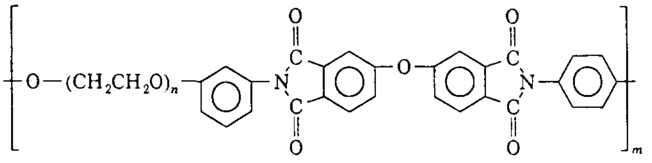
distribution of relaxation times, while Moynihan *et al.*[23,24] use a continuous relaxation function. The fundamental postulates of the model are that a wide distribution of relaxation times exists, and that the relaxation times are dependent upon the overall instantaneous structure as well as upon the temperature and pressure. If one considers that the multi-order parameter model is most easily visualized in the context of the physical ageing experiments, the non-isothermal experiments with continuous cooling and heating can be thought of as a series of infinitesimal physical ageing experiments.

The study of the structure and thermal history dependent enthalpy relaxation in the glass transition region has not, however, been extended to semicrystalline polyimides despite the fact that the synthesis of polyimides with high glass transition and melting temperatures and good thermal stabilities has been an active area of research in both academic and industrial research groups[28–30]. We have recently synthesized a series of polyimides consisting of a rigid group (the imide and aromatic rings, 4,4′-oxydiphthalic anhydride, (ODPA)), and a flexible linkage (the ethylene glycol sequence[31]). The polymers have been designated as ODPA ($n=x$) where x represents the number of ethylene glycol units. The repeating unit of the polymers is



and the molecular masses are as shown in *Table 1*.

In a recent paper[32] we reported on the thermodynamic properties of these polyimides, including the solid and liquid heat capacities, equilibrium melting temperatures and heats of fusion. A careful study of the glass transition and melting behaviour has led to a description of the interfacial region between the crystalline and amorphous states: the rigid amorphous fraction[32]. The thermodynamic properties of these ODPAs are summarized in *Table 2* along with the glass transition temperatures and the heat capacity increases at the glass transition. Our efforts now focus on the study of the structure formation kinetics in these polyimides. In the present paper, the structure and thermal history dependent enthalpy relaxation at the glass transition is discussed. The crystallization kinetics and crystal morphologies of these ODPAs will be published elsewhere[33].

Table 1 Molecular masses of OPDA($n=1$–3)

n	M_w (g mol^{-1})
1	518.5
2	562.6
3	606.6

Table 2 Thermodynamic properties of ODPA polyimides

ODPA	T_g (K)[a]	ΔC_p (J K^{-1} mol^{-1})[a]	T_m^0 (K)[b]	ΔH_f^0 (kJ mol^{-1})[b]
$n=1$	450	182	613	72.5
$n=2$	418	218	577	80.2
$n=3$	385	254	541	88.0

[a] Data determined for 100% amorphous polyimides; for details see Reference 32

[b] Data determined by extrapolating to 100% crystallinity of the polyimides; for details, see Reference 32

EXPERIMENTS AND ANALYSIS

Materials

The OPDAs were synthesized by following published procedures[31]. The diamines, 1-(3-aminophenoxy)-2(4-aminophenoxy)ethane (MPN1), 2-(3-aminophenoxy)-2′-(4-aminophenoxy)diethyl ether (MPN2), and 1-[2-(3-aminophenoxy)ethoxy]-2-[2-(4-aminophenoxy)ethoxy]-ethane (MPN3) were prepared by methods developed in our laboratory[34]. The 1-methyl-2-pyrrolidone (NMP) was obtained from GAF Chemical Co. and vacuum distilled at 353.2 K over phosphorous pentoxide.

The polyamic acids were prepared at 15% solids (w/v) by adding the diamine and NMP to a resin kettle flushed with nitrogen. An equimolar amount of dianhydride was then added to the dissolved diamine. After stirring for 10 h at room temperature, the resulting polyamic acid solution was chemically imidized with a 1:1 mixture of pyridine and acetic anhydride and then stirred overnight. The polyimides were precipitated in ethanol and collected by filtration. The polymers were dried under vacuum at 393.2 K for 24 h and then overnight under vacuum at 500 K to ensure complete imidization (>98%).

The polyamic acids exhibited inherent viscosities of 1.04, 1.06, and 0.68 dl g^{-1} for ODPA ($n=1$), ($n=2$) and ($n=3$), respectively, when measured in NMP with a concentration of 0.5 g dl^{-1} at 304.2 K.

Equipment and experiments

All experiments were conducted on a Perkin–Elmer DSC2. Both the temperature and heat flow scales of the differential scanning calorimeter (d.s.c.) at five different heating and cooling rates (0.31–10 K min^{-1}) were calibrated by using standard materials and following standard procedures in our laboratory. The heat capacity measurements of Al_2O_3 (sapphire) were reproducible to $\pm 0.1\%$ based on the data published by the National Bureau of Standards[35].

The polymer samples were enclosed in aluminium pans for the d.s.c. measurements. The weights of the empty pans, the reference pans and the sample pans were kept constant to a deviation of ± 0.002 mg. All sample weights were in the range 10–15 mg to ensure sufficient sensitivity for heat capacity measurements. Each sample was used only once to prevent sample degradation through cross-linking or decomposition.

The heat capacities of the polymers were determined in the glass transition regions to observe precisely the structure and thermal history dependence of enthalpy relaxation. The samples were heated to above their equilibrium melting temperature (*Table 2*), and held there for 2 min. They were then quenched to liquid nitrogen temperature to produce fully amorphous samples (the quench is fast enough to generate fully amorphous samples since the crystallization of these polyimides is relatively slow[33]). For non-isothermal experiments, the samples were heated to temperatures between the glass transition and onset crystallization temperatures and then cooled to 220 K at different cooling rates. Successive heat capacity measurements of the samples were conducted with a heating rate of 10 K min^{-1}. For isothermal experiments, the quenched samples were quickly brought to predetermined temperatures which were below the glass transition temperatures (*Table 2*) for sub-T_g annealing. The temperature difference between the glass transition temperature T_g and the annealing temperature T_a is called undercooling: $\Delta T = T_g - T_a$. After a certain annealing time, the samples were cooled to 220 K, and they were then ready for the heat capacity measurements which were conducted during heating at 10 K min^{-1}.

The enthalpy change in the non-isothermal experiments is denoted as $\Delta H(q)$, where q is the cooling rate. It is calculated by integrating the difference between the heat capacity of the samples at different cooling rates and that of the liquid heat capacity. The enthalpy changes on annealing after time t_a (h) at an isothermal temperature of T_a (K) are denoted as $\Delta H(t_a, T_a)$. The values of $\Delta H(t_a, T_a)$ were calculated by integrating the difference between the heat capacity of an annealed sample and that of an unannealed one.

Data analyses

For a cyclic process starting and ending at a point within the equilibrium supercooled melt region, the conservation of energy requires that[3]

$$\oint C_p \, dT = 0 \qquad (1)$$

This integral over any cyclic path has to be zero, independent of time dependent processes and their directions. Therefore, the glass transition temperature of the polymers can be determined during cooling. The apparent activation energy Δh can be estimated independently from the cooling rate dependence of the glass transition temperature as it is usually defined[24] as

$$\Delta h \approx -R[\mathrm{d} \ln q/\mathrm{d}(1/T_g)] \qquad (2)$$

where q is the cooling rate, R is the gas constant and T_g is the glass transition temperature at different cooling rates determined via equation (1).

For isothermal experiments exhibiting physical ageing behaviour, one may consider that the enthalpy relaxation can be expressed by

$$\Delta H(t_a) = \Delta H_\infty[1 - \phi(t_a)] \qquad (3)$$

at a constant annealing temperature. Here ΔH_∞ represents the equilibrium enthalpy relaxation at $t_a \rightarrow \infty$. The function $\phi(t_a)$ in equation (3) is the so-called relaxation function. The most widely used relaxation function is the empirical Williams–Watts function, generalized for the non-linear case[36]

$$\phi(t_a) = \exp[-(t_a/\tau)^\beta] \qquad (4)$$

where τ is the characteristic relaxation time and β $(0 < \beta \leqslant 1)$ is a parameter that characterizes the width of the distribution of relaxation time spectra. Substituting equation (4) into equation (3), and after taking double logarithms and rearranging, one has

$$\log[-\ln(1 - \Delta H/\Delta H_\infty)] = \beta \log t_a - \beta \log \tau \qquad (5)$$

Therefore, a plot of $\log[-\ln(1 - \Delta H/\Delta H_\infty)]$ *versus* $\log t_a$ should demonstrate a linear relationship with a slope of β and an intercept of $\beta \log \tau$ at each constant annealing temperature. Several relations have been proposed for τ, but Kovacs *et al.*[37] have shown that they can all be written as originally proposed by Narayanaswamy[27]:

$$\tau(T_a, T_g) = A \exp[x \, \Delta h/RT_a + (1 - x) \, \Delta h/RT_g] \qquad (6)$$

where A is the relaxation time at some arbitrary reference temperature and Δh is an apparent activation energy which can be found through equation (2). The value of x is an empirical parameter introduced by Narayanaswamy[27] that fractionizes the temperature and structure dependence of the characteristic relaxation time τ. Finally, the value of A can be calculated by

$$\ln A \approx \ln \tau(T_g) - \Delta h/RT_g \qquad (7)$$

if one assumes that the value of the average relaxation time at T_g, $\tau(T_g)$, is nearly constant for each polymer. Equation (7) follows, in fact, from equation (6) if $T_a = T_g$. Estimates of ln A are thus obtained in this self-consistent way.

RESULTS

Hysteresis effects

Figure 1 shows the hysteresis effect of the heat capacity of amorphous ODPA($n = 2$) in the glass transition region. The samples were cooled at different rates from the supercooled liquid state to the glassy state before heating at 10 K min^{-1}. The biggest endothermic peak is $\Delta H = 0.96$ kJ mol^{-1} at a cooling rate of 0.31 K min^{-1}. The decrease in the endotherm with increased cooling rate can be clearly observed. Quantitative relationships between ΔH and the logarithmic of the cooling rate are illustrated in *Figure 2* for ODPA($n = 1$), ($n = 2$) and ($n = 3$). The data deviates from a straight line above cooling rates of 2.5 K min^{-1}, similar to the cases of PPO[6] and PEN[7]. The value of ΔH for a given cooling rate increases with increasing number of flexible linkages n. The ratio $\Delta H(n = 3)/\Delta H(n = 2)$ and $\Delta H(n = 2)/\Delta H(n = 1)$ are nearly equal and they are approximately between 1.3 and 1.4. The absolute value of the slope ($\mathrm{d}\Delta H/\mathrm{d} \ln q$) for ODPA($n = 1$) is smaller than for ODPA($n = 2$), which in turn is smaller than that for ODPA($n = 3$).

The integration of C_p from the glassy state to the equilibrium liquid establishes the relative enthalpy of the glass. This permits the evaluation of the glass transition

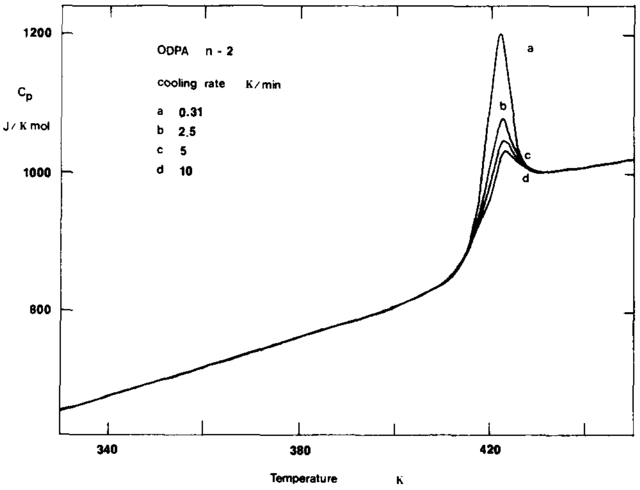


Figure 1 Hysteresis in the heat capacity of fully amorphous ODPA ($n = 2$) in the glass transition region at different cooling rates. Successive heating rate is 10 K min^{-1}

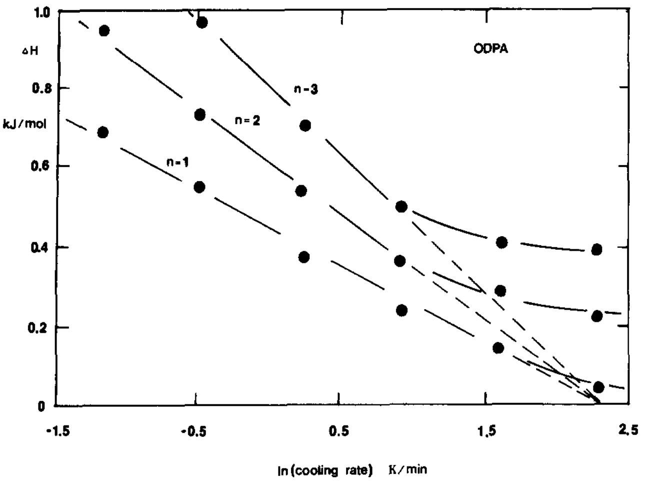


Figure 2 Relationships between enthalpy under hysteresis peak and logarithm of cooling rate for amorphous ODPA($n=1$), ($n=2$) and ($n=3$). Heating rate is 10 K min^{-1} (ln 10 = 2.303)

temperature which occurred on cooling from equation (1). Relationships linking the glass transition temperatures to the cooling rates can be identified. For ODPA($n=1$)

$$\ln q = 186.8 - 8.3033 \times 10^4/T_g \qquad (8)$$

with a root-mean-square deviation of ±0.8%; for ODPA ($n=2$)

$$\ln q = 153.1 - 6.265 \times 10^4/T_g \qquad (9)$$

with a root-mean-square deviation of ±0.8%; and for ODPA($n=3$)

$$\ln q = 139.8 - 5.291 \times 10^4/T_g \qquad (10)$$

with a root-mean-square deviation of ±0.7%.

From equation (2), one can calculate the apparent activation energies from the slopes of equations (8)–(10). They are 690.3 kJ mol^{-1}, 520.9 kJ mol^{-1} and 439.9 kJ mol^{-1} for ODPA($n=1$), ($n=2$) and ($n=3$), respectively. With increasing number of flexible linkages, the apparent activation energy and the ratio $\Delta h/T_g$ (see *Table 5*) decreases.

Physical ageing behaviour

Figure 3 shows d.s.c. heat capacity measurements for ODPA($n=1$) at an annealing temperature of 400 K and different annealing times. In this case, the undercooling ΔT was 50 K. At a short annealing time of 2.0 h, for example, a small endothermic peak located before the main glass transition temperature is observed at ≈432 K. With increased annealing time, the peak temperature shifts to higher temperatures and the enthalpy of the peak increases. At a prolonged annealing time of $t_a = 485.1$ h, the endothermic peak still appears in the upper-middle portion of the glass transition region.

After calculating the enthalpy relaxation $\Delta H(t_a, T_a)$, one can plot relationships between $\Delta H(t_a, T_a)$ and the logarithm of annealing time, as shown in *Figure 4* for a constant undercooling $\Delta T = 34$ K. Note that for the different ODPAs the annealing temperature is changed to keep the undercooling constant (see *Figure 4*). For these polymers $\Delta H(t_a, T_a)$ increases at a rate faster than a linear rate with $\log t_a$. ODPA($n=3$) has the highest values of enthalpy relaxation, and ODPA($n=1$), the lowest values. If ΔH is extrapolated to an infinite annealing time ($1/t_a \rightarrow 0$), the enthalpy relaxation at equilibrium ΔH_∞ can be obtained. The values of ΔH_∞ are 1.55, 2.05 and 2.64 kJ mol^{-1}, for ODPA($n=1$), ($n=2$) and ($n=3$), respectively. These values are inde-

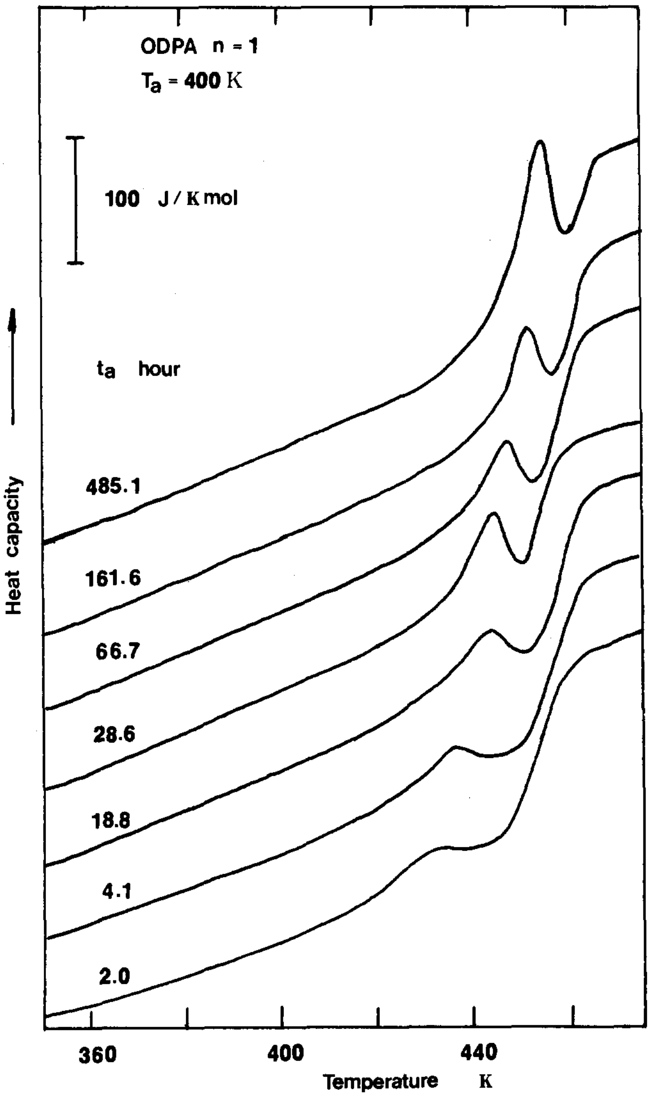


Figure 3 D.s.c. heat capacity curves measured during heating at 10 K min^{-1} for ODPA($n=1$) after the samples had been annealed at 400 K for various annealing times (2–485.1 h)

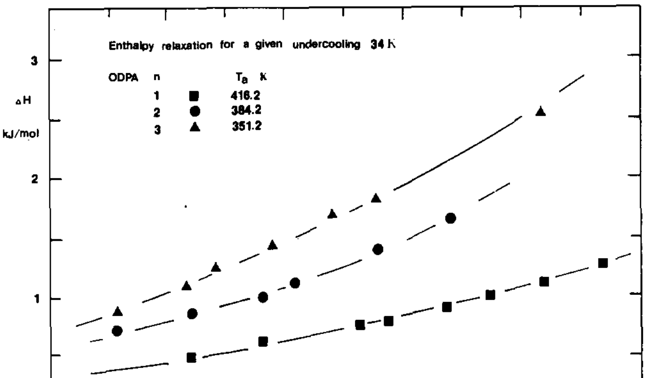


Figure 4 Relationships between enthalpy relaxation $\Delta H(t_a, T_a)$ and logarithm of annealing time at constant undercooling ($\Delta T = 34$ K) for ODPA($n=1$), ($n=2$) and ($n=3$), respectively

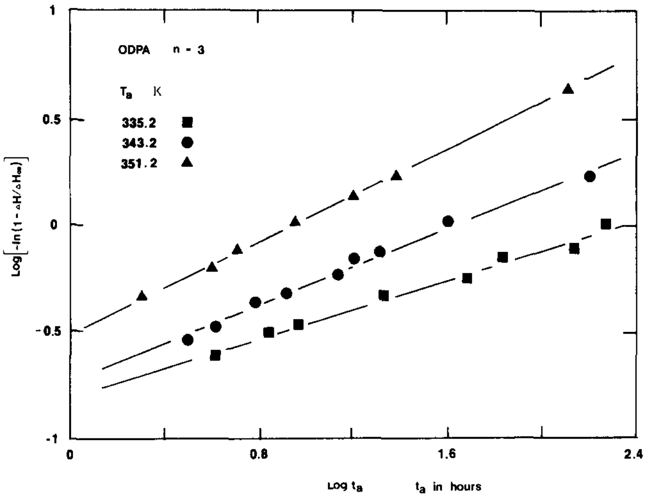


Figure 5 Relationships between $\log[-\ln(1-\Delta H/\Delta H_\infty)]$ and $\log t_a$ for ODPA($n=3$) at three different annealing temperatures (undercoolings)

Table 3 Enthalpy relation parameters in sub-T_g annealing experiments for ODPA polyimides

ΔT^a (K)	n^b	β ($\pm$0.02)	τ (h) ($\pm$0.1)
34	1	0.367	67.4
34	2	0.507	16.3
34	3	0.540	8.04
42	1	0.240	649
42	2	0.332	136
42	3	0.419	51.4
50	1	0.160	9.17×10^4
50	2	0.311	1.43×10^3
50	3	0.325	271

[a] Undercooling $\Delta T = T_g - T_a$
[b] ODPA($n=x$), $x=1, 2, 3$

pendent of annealing temperature. Following equation (5), a plot of $\log[-\ln(1-\Delta H/\Delta H_\infty)]$ *versus* $\log t_a$ should give linear relationships with a slope of β and an intercept of $\beta \log \tau$. *Figure 5* shows, for ODPA($n=3$) at three different annealing temperatures (or undercoolings), these linear relationships. *Table 3* lists the two parameters β and τ for these polymers at three different undercoolings. Evidently, at a constant undercooling, β increases and τ decreases with increasing number of flexible linkages. On the other hand, for each polymer, β decreases and τ increases with increasing undercooling.

In equation (7), to calculate $\ln A$, where A is the coefficient in equation (6), one needs values of $\tau(T_g)$, the characteristic relaxation time at the glass transition temperature. This can be obtained by plotting the relationship between $\ln \tau$ and undercooling ΔT, and extrapolating to $\Delta T=0$. We have found that the intersections $[\ln \tau(T_g)]$ of these relationships at $\Delta T=0$ are -11.6, -6.75 and -5.36 for ODPA($n=1$), ($n=2$) and ($n=3$), respectively. Therefore, based on equation (7), one can calculate the values of $\ln A$ to be -196.1, -156.6 and -142.6 for the three polyimides, correspondingly. Finally, since $\ln A$ and Δh are now known, values of x, which fractionizes the temperature and structure dependence of the characteristic relaxation time τ, can be obtained through equation (6). They are listed in *Table 4*. It is clear that at a constant undercooling, increasing the number of flexible linkages decreases the temperature dependent fraction. In other words, the relaxation time is more dependent upon the structure changes. When the undercooling is decreased, for each ODPA one can find a slight decrease of x. However, these decreases are marginal.

DISCUSSION

From our experimental observations we can focus on two different aspects in our discussion. First, we have applied the phenomenological multi-order parameter model to treat the experimental data and generate the parameters x, β and Δh for this series of ODPA polyimides. In turn, we can ask whether these parameters reflect what is predicted from theory. Secondly, this series of ODPA polyimides has provided a unique opportunity to investigate how the structure and thermal history dependent enthalpy relaxation is influenced by a change in the chain flexibility.

The fractionizing parameter x is empirically defined as the fraction of the relaxation time τ that is due solely to the absolute temperature of the system; its complement, $1-x$, defines the part of the relaxation time that is determined by the instantaneous state of the system as reflected in the glass transition temperature (or fictive temperature). In the original development of the theory, x is not considered to be explicitly dependent upon the annealing conditions. From *Table 4*, for each ODPA polyimide, in a 16 K undercooling range ($34 \leqslant \Delta T \leqslant 50$ K), the change of x is within 2–4%. Since the root-mean-square deviations of these values are about $\pm2\%$, the present results show a good fit to the theory. However, we note that a tendency of slightly decreasing x with annealing temperature (or increasing undercooling) can still be identified. Before a further study of experiments in a wider undercooling range is conducted, it is not appropriate to draw detailed conclusions about changes in x with annealing temperature. Our observations here seem to differ from the enthalpy relaxation in PMMA reported by Tribone *et al.*[18], who found that the parameter x is required to be a function of annealing temperature.

The parameter β is an empirical measure of the width of the relaxation time spectrum. There is a single relaxation time when $\beta=1$. The model makes an explicit assumption that β is independent of temperature by assuming thermorheological simplicity. Based on our results listed in *Table 3* for each ODPA polyimide, the value of β decreases with annealing temperature (or with increasing undercooling), in contrast to the theoretical prediction. Since our root-mean-square deviation is $\pm2\%$, the changes in β listed in *Table 3* are experimentally sound. This indicates that the relaxation time

Table 4 Fraction parameters of the temperature (x) and structure ($1-x$) dependence at different undercoolings for ODPA polyimides

ODPA($n=x$)	ΔT (K)	x ($\pm$0.02)	$1-x$ ($\pm$0.02)
1	34	≈1.00	≈0.00
1	42	0.99	0.01
1	50	0.98	0.02
2	34	0.72	0.28
2	42	0.69	0.31
2	50	0.68	0.32
3	34	0.55	0.45
3	42	0.54	0.46
3	50	0.53	0.47

spectrum narrows with increasing annealing temperature. It may be associated with two different relaxing components in these polymers, namely the rigid group and the flexible linkage, both having a different relaxation time spectrum. Indeed, we have found that abnormally wide glass transition regions exist in these ODPA polyimides. The pre-glass transition portions are mainly contributed by the flexible linkage[32]. On the other hand, Plazek *et al.*[38] and McCrum[39] could show that the assumption of constant β may break down in their experiments. Prest *et al.*[40] also saw much larger changes in β when a four-parameter optimization was used. They suggested that the Williams–Watts function may be an inadequate representation of the relaxation time spectrum. Furthermore, Ngai[41] suggested a model in which the parameter of the relaxation time spectrum is considered to be an explicit function of both temperature and annealing time. However, it is still not clear whether changes in the parameters, such as β, with annealing conditions might be eliminated by the proper choice of the structure dependence and/or the function of the relaxation time spectrum. This is particularly true for our case where two different relaxation time spectra apparently exist.

The apparent activation energy Δh is the third parameter for enthalpy relaxation. The model assumes that the activation enthalpy is constant and hence that the temperature dependence is Arrhenius, as applied in our ODPA cases. Since the microscopic description of glass transition is related to conformational energies of the rotational isomers[42–44], the measured Δh values with the change of T_g [equations (8)–(10)] directly suggest that Δh is related to the conformational energy barrier. However, its magnitude reflects the cooperative nature of the relaxation process. Our Δh values are of the same order of magnitude as for other polymers reported by many laboratories, as shown in *Table 5*, where $\Delta h/T_g$ values are also shown. Certainly, one also has to consider the non-Arrhenius behaviour of amorphous materials in the glass transition region. The functions of non-Arrhenius relaxation times can sometimes be described by Adam–Gibbs theory[45] where a conformational entropy-controlled process was taken into account, or by the WLF equation[46] where a free volume-controlled process was proposed. Nevertheless, neither kind of description has been tested adequately in the enthalpy relaxation processes.

Of special interest in this enthalpy relaxation study is the chain flexibility dependence for these parameters. It is clear that ODPA($n=1$) is the most rigid among these three polyimides and ODPA($n=3$) is the most flexible one. The rotational energy barriers of these ODPA polyimides are thus also different. The decrease in the apparent activation energy Δh with increasing size of the flexible linkage (see *Table 5*) is a strong indication if one considers that the degree of cooperativity of chain motion during the glass transition is not changed very much. This can also be reflected by a shortened relaxation time τ (see *Table 3*). The relaxation times of ODPA($n=3$) are always the shortest and those of ODPA($n=1$) are always the longest at the same undercooling despite the fact that the absolute annealing temperature of ODPA($n=3$) is always the lowest.

The changes in both β and x with chain flexibility in the ODPA polyimides are striking. The values of β for ODPA($n=1$) are always smaller than those for ODPA($n=2$), which are always smaller than those for ODPA($n=3$). What this means is that, at constant undercooling, ODPA($n=1$) has the broadest relaxation time spectrum and ODPA($n=3$) the narrowest one. We ask whether, on a molecular scale, the chain rotational mobility gradually moves towards uniformity with increasing chain flexibility? Even more surprising is that the relaxation time of ODPA($n=1$) is shown to be almost solely dependent upon temperature. With increasing number of flexible linkages, the structure dependent part increases, with a corresponding decrease in the temperature dependent part (see *Table 4*). Does this mean that rigid chains have a greater temperature dependence in this enthalpy relaxation process? From literature data we find that for PS the parameter β ranges from 0.39 to 0.68, while the parameter x is between 0.12 and 0.48 (References 10, 11, 47 and 48). For PVC β is near 0.25, and the parameter x varies in the range 0.12–0.3 (References 10 and 49). For PMMA $0.3 \leqslant \beta \leqslant 0.45$ and x varies between 0.1 and 0.3. The x values are also annealing time dependent[18]. These values are further obscured by molecular mass and molecular mass distribution effects. However, a qualitative comparison can still be made since the PS chain is relatively rigid among these three polymers. Therefore, the value of x in PS is the highest. We have found that for OPDA polyimides x values are all higher than 0.5 (*Table 4*), even for ODPA($n=3$). This reveals that, indeed, rigid chain polymers should have higher x values. The values of β are more thermal history, molecular mass and molecular mass distribution dependent. No qualitative comparison can currently be made with the other three polymers.

Table 5 Apparent activation energies estimated from the heating rate dependence of T_g for various polymers

Polymer	Δh (kJ mol^{-1})	$\Delta h/T_g$ (kJ K^{-1} mol^{-1})	Reference
PS	648.5	1.74	2
	685.9	1.84	10
	632.7–914.5	1.70–2.45	11
PVC	1871	5.28	50
PMMA			
Isotactic	669.4	2.05	18
Atactic	878.6	2.34	18
Syndiotactic	962.3	2.43	18
ODPA			
($n=1$)	690.3	1.53	This work
($n=2$)	520.9	1.25	This work
($n=3$)	439.9	1.14	This work

CONCLUSIONS

The results of the above analysis for a series of ODPA semicrystalline polyimides illustrate the applicability of the multi-order parameter model to a semi-quantitative description of the structure and thermal history dependent enthalpy relaxation at the glass transitions. However, in contrast to the theory, the parameter β changes with annealing temperature. Of special interest is that all the parameters used in this theory (Δh, β and x) are chain flexibility dependent. Both Δh and x decrease and β increases with increasing number of flexible linkages.

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