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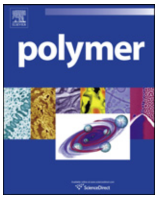

Effect of structure on enthalpy relaxation of polycarbonate: Experiments and modeling

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ABSTRACT

The enthalpy relaxation of bisphenol A (BPA) and copolycarbonates of BPA and trimethylcyclohexylidene bisphenol (TMC) is studied using low heating rate DSC measurements. The glass transition behavior of the polycarbonates shifts to higher temperatures with increasing TMC content. The relaxation behavior of BPA is characterized by large and narrow peaks whereas the copolycarbonates exhibit a broader relaxation. In this work, the ability of the TNM model to describe the enthalpy relaxation behavior of the polycarbonate systems is tested and the sensitivity of the model parameters to the changes in chemical composition is examined. The model parameters are found to vary with thermal history and a linear correlation is observed between the nonlinearity parameter (x) and the nonexponentiality parameter (β), although the nature of the parameter variation with thermal history is found to depend on the value of the activation energy parameter ($\Delta h/R$). The results in this work indicate the need for reformulating the treatment of nonlinearity and incorporating a temperature-dependent activation energy in the model.

1. Introduction

Enthalpy relaxation in glass-forming materials is often examined using differential scanning calorimetry (DSC) measurements on heating and several reviews have been written [1–4]. The measurements are characterized by the presence of enthalpy overshoots in the DSC heat flow measurements, which are representative of the structural relaxation undergone by the material during cooling from the equilibrium liquid state or during isothermal annealing at temperatures below the glass transition temperature (T_g). The slower the cooling rate from the equilibrium state or the longer the annealing time, the greater the magnitude of the enthalpy relaxation peak. Phenomenological models of the glass transition such as the Tool–Narayanaswamy–Moynihan (TNM) [5–7] and Kovacs–Aklonis–Hutchinson–Ramos (KAHR) [8] models have been found to provide a good description of enthalpy relaxation in a variety of glass formers [3,9–17].

According to the TNM model [5–7], the relaxation time is defined as shown below:

$$\ln\tau = \ln A + \frac{x\Delta h}{RT} + \frac{(1-x)\Delta h}{RT_{\mathrm{f}}} \tag{1}$$

where $\ln A$ is a constant, $\Delta h/R$ is the relative apparent activation energy, and x is the nonlinearity parameter which partitions the dependence of τ on temperature and structure, the latter of which is quantified by the fictive temperature T_{f} [1,9]. The fictive temperature is the temperature at which the enthalpy of a given state, if extrapolated along the glass line, would intersect the equilibrium liquid line. Hence, at equilibrium $T_{\mathrm{f}} = T$, deep in the glassy state T_{f} is a constant, and through the glass transition on heating or cooling, T_{f} evolves from one limiting case to another. This evolution of the fictive temperature can be calculated using the TNM model. For any arbitrary set of temperature scans starting initially in the equilibrium state at T_{o}, the fictive temperature can be calculated using the following equation [7]:

$$T_{\mathrm{f}}(t) = T_{\mathrm{o}} + \sum_{i=1}^{n} \Delta T_i \left\{ 1 - \exp\left[-\left(\sum_{j=i}^{n} \frac{\Delta T_j}{Q_j \tau_j} \right)^{\beta} \right] \right\} \tag{2}$$

where β is the nonexponentiality parameter, T_{o} is the initial temperature, ΔT_i is the temperature change corresponding to the ith step, and Q_j is the cooling rate or heating rate corresponding to the jth step.

In recent work, it was observed that the TNM model [5–7] could describe volumetric data on cooling and on heating for polystyrene

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with a single set of parameters [17]. Furthermore, the model was also found to provide an adequate description of DSC heating curves obtained after cooling at various rates [17]. However, several inadequacies of the model have been identified in the literature including the underestimation of the activation energy parameter [2], uncertainty over actual meaning of parameters [18], correlations between the parameters and variation of parameters with thermal history [2,19–22]. Some of the issues pertaining to the model have been suggested to be due to thermal lag in DSC measurements [23,24]; however, both O'Reilly and Hodge [22] and Simon [25] observed that the effect of thermal lag could not explain the discrepancies between model calculations and experiments in some cases. Furthermore, O'Reilly and Hodge [22], and later Simon and coworkers [26,27] also suggested that deviations from model predictions in a few cases might indicate some shortcomings of Eq. (1) in capturing the structure dependence of relaxation time, although as pointed out by Hodge [2,19], several alternate equations for the relaxation time have been employed in the literature, with little improvements. The TNM model, despite its shortcomings, is still the model of choice for modeling the glass transition and structural recovery due to its ability to capture all of the phenomenology associated with the glass transition kinetics.

An objective of this work is to test the ability of the TNM model [5–7] to characterize enthalpy relaxation behavior of copolycarbonates of bisphenol A (BPA) and trimethylcyclohexylidene bisphenol (TMC). Furthermore, since the physical aging behavior of copolycarbonates differs from that of pure BPA, the sensitivity of the model parameters to changes in the chemical composition of the polycarbonate systems will also be examined. The impact of thermal lag [28–30] on the measurements is minimized by performing the DSC measurements using low heating rates of 2 K/min and 5 K/min. These measurements facilitate a better test of the ability of Eq. (1) to capture the nonlinearity of enthalpy relaxation.

As mentioned earlier a common problem encountered upon using the model is the variation of parameters with history. By fitting DSC overshoots using the TNM model, some researchers [21,22] observed that the values of x and β increase with decreasing magnitude of cooling rate or increasing magnitude of enthalpy overshoots; however, Simon [25] observed that the magnitude of β decreases with decreasing cooling rate. Since different trends in model parameters lead to different interpretations of the results from model calculations, a second objective of this work is to examine the impact of the fitting procedure on the results obtained from the model. In general, the value of $\Delta h/R$ for DSC heating curves can be obtained experimentally from the cooling rate dependence of the limiting value of the fictive temperature (T_f') measured on heating, where the limiting fictive temperature is determined by the method described by Moynihan and coworkers [31]:

$$\int_{T_f'}^{T>T_g} \left(C_{pl} - C_{pg}\right) dT = \int_{T<T_g}^{T>T_g} (C_p - C_{pg}) dT \tag{3}$$

C_{pg} and C_{pl} represent the values of the glassy and liquid heat capacities, respectively. On the other hand, the value of $\Delta h/R$ can also be obtained from model calculations as the optimum value which results in the lowest chi squared upon fitting several thermal histories simultaneously [17,21] using the model. In this work both methods to obtain $\Delta h/R$ will be employed in order to observe the effect on the parameters obtained.

2. Methodology

2.1. Materials

The bisphenol A polycarbonate (BPA) was obtained from Bayer as Merlon resin. Three copolycarbonates of bisphenol A and trimethylcyclohexylidene bisphenol (TMC) were obtained from Miles (now, Bayer): 9330, 9350, and 9371. The copolymers are nominally 20 wt%, 35 wt%, and 55 wt% TMC, respectively [32], although TMC contents of 11.1 wt% and 64.2 wt% have been reported for 9330 and 9371 based on H NMR measurements [33]. Samples with thickness between 0.2 mm and 0.4 mm were prepared by compression molding.

2.2. DSC measurements

DSC measurements were performed using a Perkin Elmer DSC7. In order to minimize the impact of thermal gradients, DSC measurements were made at slow heating rates of 5 K/min and 2 K/min after cooling at various rates of 5 K/min, 2 K/min, 1 K/min, 0.5 K/min, 0.2 K/min, and 0.1 K/min. Temperature calibrations were performed at heating rates of 2 K/min and 5 K/min using indium and zinc. Heat flow calibrations were performed using sapphire.

2.3. Model calculations

The DSC heat capacity (C_p) data obtained on heating at 2 K/min and 5 K/min were fit using the TNM model, Eqs. (1) and (2). The model calculation yields the fictive temperature which was converted to absolute heat capacity in order to compare the model with the experimental data:

$$C_p(T) = C_{pg}(T) + \Delta C_p(T_f)\frac{dT_f}{dT}, \tag{4}$$

where $\Delta C_p(T_f)$ is the difference in heat capacity between the liquid and glassy states evaluated at T_f [24]. The glass and liquid heat capacities (C_{pg} and C_{pl}, respectively) were determined for each curve in the range from approximately T_g – 10 K to T_g – 20 K for the glassy state and from $T_g + 10$ to $T_g + 20$ in the liquid state.

The fitting procedure was performed by optimizing the values of x, β, and ln A while maintaining the value of $\Delta h/R$ as constant. The constant value of $\Delta h/R$ was obtained in two ways – experimentally and also from curve fitting. The experimental value of $\Delta h/R$, obtained from the cooling rate dependence of the limiting fictive temperature (T_f') for a given material, was used to individually fit each data set obtained at 5 K/min and 2 K/min heating rate for that material. In addition, the value of $\Delta h/R$ for each material was also evaluated as the optimum value which results in the lowest chi square for a simultaneous fit of all data obtained at 2 K/min heating rate for a given material. The optimum value of $\Delta h/R$ corresponding to each material was then used to individually fit the data obtained at 2 K/min for that material.

In this work, the T_f step size for all calculations on cooling or on heating was less than 0.1 K. In some early reports in the literature [18,31], the temperature step on cooling and heating while modeling sequential cooling and heating runs is typically taken to be 1 K. A temperature step size of 1 K on heating might lead to large changes in T_f between steps and result in significant errors especially while modeling large overshoots, as shown in Fig. 1a for a reasonable, but arbitrary, set of TNM parameters. This is generally understood in the literature, and consequently, the criteria that the fictive temperature must change less than 1 K between steps is often used. However, what is less well known is that the step size on cooling is also important if accurate estimates of the parameters are desired. The impact of the step size on cooling is demonstrated in Fig. 1b for a calculated cooling curve and the subsequent heating curve (for the same set of TNM parameters used in Fig. 1a). It should be noted that the results obtained upon employing 1 K temperature steps in the model calculations are also influenced by the nonlinearity parameter (x). For most values of x, the value of T_f in the glassy state decreases with increasing

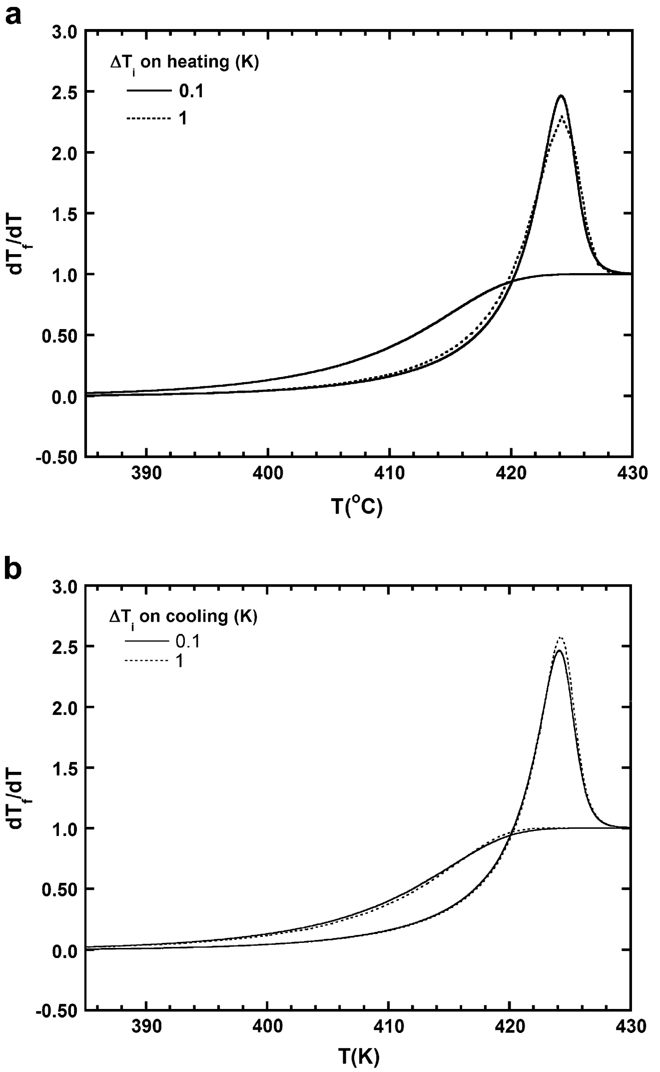

Fig. 1. (a) Effect of temperature step size (ΔT_i) on heating. The temperature step size on cooling was 0.1 K for both curves. (b) Effect of temperature step size (ΔT_i) on cooling on the subsequent heating scan. The temperature step size on heating was 0.02 K for both curves. The parameters used in all calculations were $\Delta h/R = 125\,000$, $x = 0.35$, $\beta = 0.40$, $\ln A = -294.28$.

temperature step size on cooling leading to larger overshoots on heating; however, as the values of x approach 1.0, the value of T_f in the glassy state increases with increasing temperature step size on cooling leading to smaller overshoots on heating. Hence, for calculations involving large step sizes, T_f (and thus, x and β) can either be under- or over-estimated depending on the value of x. The accuracy of the calculations in this work was confirmed by the negligible difference between the T_f values upon decreasing the calculation step size from 0.1 K to 0.01 K for various values of x between 0 and 1.

Although the DSC data and fits presented here have not been previously shown in the literature, limited results in the form of plots of x vs β have been shown from some earlier modeling work using the experimental values of $\Delta h/R$ on these polycarbonate materials [16]. As will be shown in the discussion section, the work presented here is consistent with that previous study but the model parameters reported differ due to our smaller step sizes and use of slightly different $\Delta h/R$ values (we use average values based on both the 2 K/min and 5 K/min data in this work rather than separate values for each heating rate).

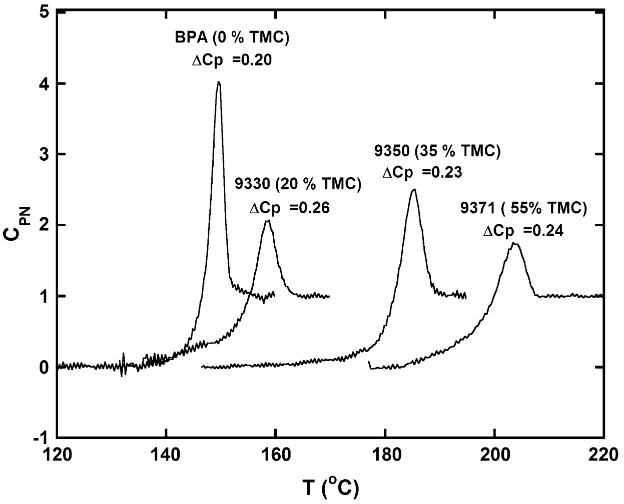

Fig. 2. The normalized heat capacity response on heating at 2 K/min after cooling at 0.1 K/min for BPA and the copolycarbonates.

3. Results

The glass transition behavior of the four polycarbonate materials shifts to higher temperatures with increasing content of the bulky trimethylcyclohexylidene bisphenol (TMC) groups, as shown in Fig. 2, where the normalized heat capacity response obtained on heating at 2 K/min after cooling at 0.1 K/min is compared. The value of the step change in heat capacity at T_g (ΔC_p) is also found to be lower for neat BPA compared to the copolycarbonates, and the magnitude of the enthalpy overshoot is higher for the BPA compared to the copolycarbonates.

The DSC heating curves obtained on heating at a constant rate after cooling at various rates for BPA are shown in Fig. 3. The magnitude of the enthalpy overshoot observed on heating increases with decreasing cooling rate, as expected. From the data, the value of the limiting fictive temperature (T_f') can be obtained, and these values decrease with decreasing cooling rate as shown in Fig. 4. This data can be used to determine the value of $\Delta h/R$ [31]:

$$\frac{\Delta h}{R} = -\frac{\mathrm{d}\ln q}{\mathrm{d}\left(1/T_{\mathrm{f}}'\right)} \qquad (5)$$

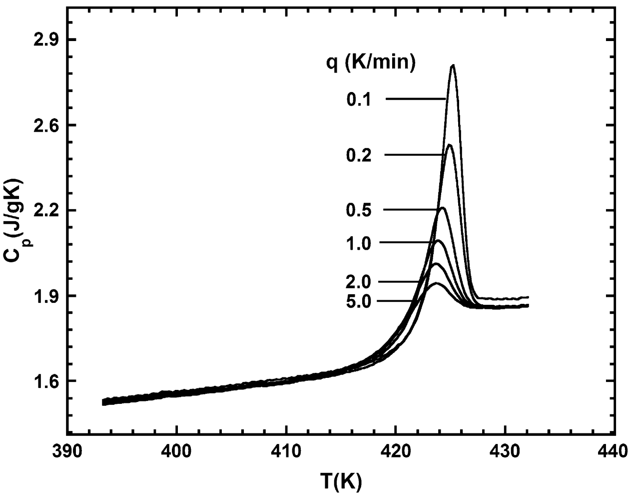

Fig. 3. Heat capacity response for BPA upon heating at 5 K/min after cooling at various rates q.

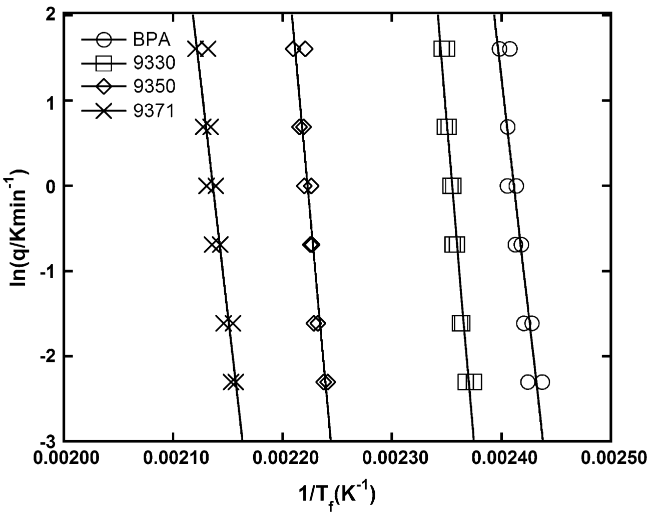

Fig. 4. Variation of T_f' with cooling rate for the four materials. The solid lines represent the best fits to the data.

The values of $\Delta h/R$ obtained from Eq. (5), as well as the average T_f' values corresponding to a cooling rate of 2 K/min for each material, are tabulated in Table 1. Only one average value of T_f' and $\Delta h/R$ is reported even though data were obtained at two heating rates because these values should depend only on the rate of cooling and not on the rate of heating [31]. It is acknowledged that due to the experimental errors in T_f', the uncertainties in the values of $\Delta h/R$ are expected to be between 10% and 15%. Hence, although the value of $\Delta h/R$ might be expected to increase with increasing TMC content and increasing T_g given the correlation between the $\Delta h/R$ and T_g [34], no particular trend can be ascertained from the experiments.

The fit of the TNM model [5–7] to the experimental data obtained using the value of $\Delta h/R$ from experiments is compared for BPA in Fig. 5a and b, for heating rates of 2 K/min and 5 K/min, respectively; in these figures where each heating scan is fit independently, the model is found to provide a reasonable description of the data over the range of cooling rates examined. Similar results are also observed for the copolycarbonates as shown in Fig. 6a and b through Fig. 8a and b for 9330, 9350, and 9371. However, some small deviations can be observed between the model calculations and the experimental results, for all materials. The possible reasons for the differences will be addressed in the discussion section.

The average parameters obtained by fitting the data are shown in Figs. 5–8 using the value of $\Delta h/R$ from experiments are tabulated in Table 1. The average values of the parameters appear to be similar, respectively, at 2 K/min and 5 K/min heating rates for a given polycarbonate. However, the model parameters vary with thermal history (i.e., with the size of the enthalpy overshoot), as evident from the relatively large standard deviations. In most cases, the parameters x and β decrease with decreasing cooling rate as discussed below, although there are exceptions.

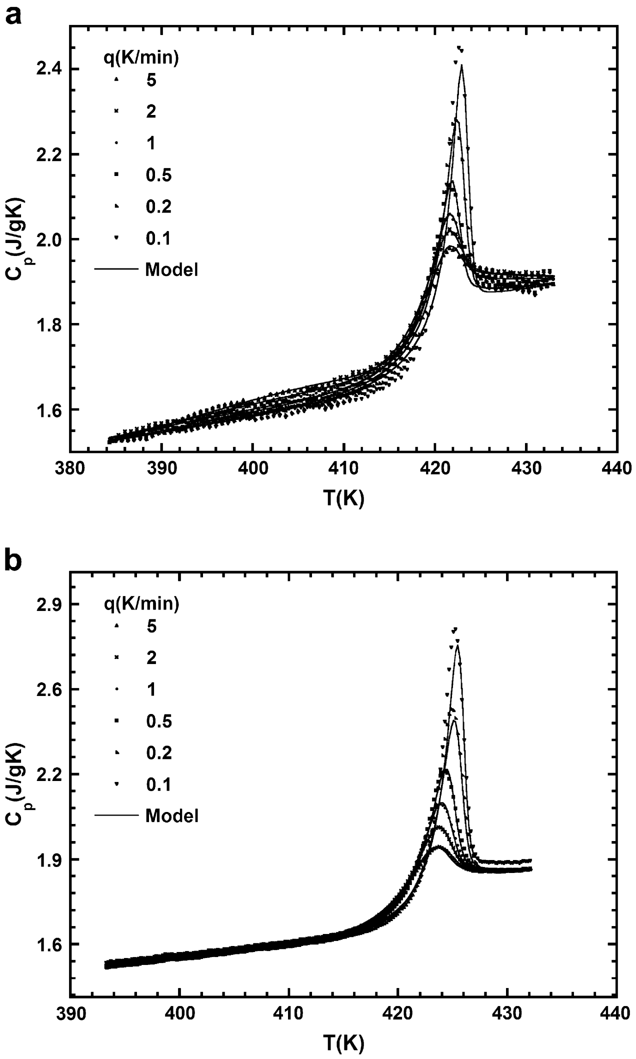

Fig. 5. (a) TNM model fits of 2 K/min heating rate data for BPA using a constant value of $\Delta h/R$ from experiments (=111 kK). (b) TNM model fits of 5 K/min heating rate data for BPA using a constant value of $\Delta h/R$ from experiments (=111 kK).

For BPA, the values of x and β decrease by 32% and 16%, respectively, with decreasing cooling rate (or with increasing enthalpy overshoot) at 2 K/min heating rate; however, at 5 K/min heating rate, the values of x and β are found to increase by 21% and 32% with increasing magnitude of overshoots. For 9330, the average decrease in the values of x and β from the lowest to the highest

Table 1

Parameters for the polycarbonate materials at 2 K/min and 5 K/min heating rate. The parameters x, β, and ln A are obtained by averaging the values obtained upon fitting data for a given heating rate following cooling at six different rates

Material	T_f' average (°C)	$\Delta h/R$ (kK)	Heating rate (K/min)	x	β	ln A
BPA	142.7	111 ± 16	2	0.46 ± 0.08	0.67 ± 0.04	−261.6 ± 0.1
			5	0.53 ± 0.04	0.74 ± 0.07	−261.0 ± 0.1
9330[a] (20% TMC)	152.6	152 ± 17	2	0.32 ± 0.20	0.43 ± 0.08	−351.8 ± 0.2
			5	0.23 ± 0.05	0.46 ± 0.05	−350.8 ± 0.2
9350 (35% TMC)	178.0	141 ± 19	2	0.48 ± 0.09	0.53 ± 0.09	−306.6 ± 0.3
			5	0.33 ± 0.09	0.49 ± 0.04	−306.4 ± 0.2
9371[a] (55% TMC)	196.3	110 ± 15	2	0.59 ± 0.05	0.48 ± 0.04	−229.1 ± 0.5
			5	0.52 ± 0.02	0.48 ± 0.02	−228.6 ± 0.3

[a] Discrepancies for the reported compositions exist; see text.

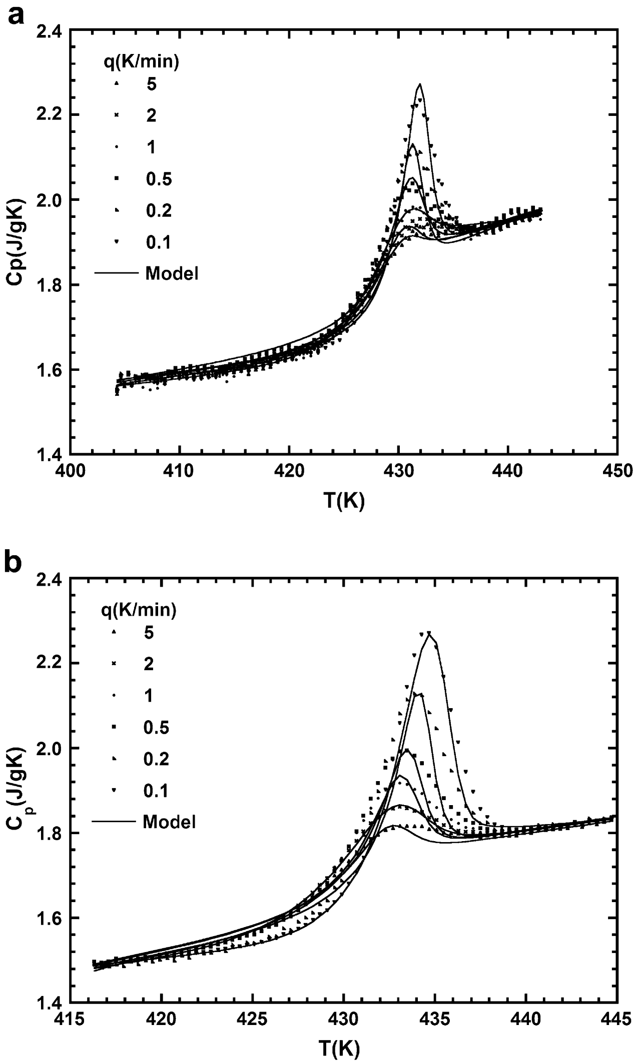

Fig. 6. (a) TNM model fits of 2 K/min heating rate data for 9330 using a constant value of $\Delta h/R$ from experiments (=152 kK). (b) TNM model fits of 5 K/min heating rate data for 9330 using a constant value of $\Delta h/R$ from experiments (=152 kK).

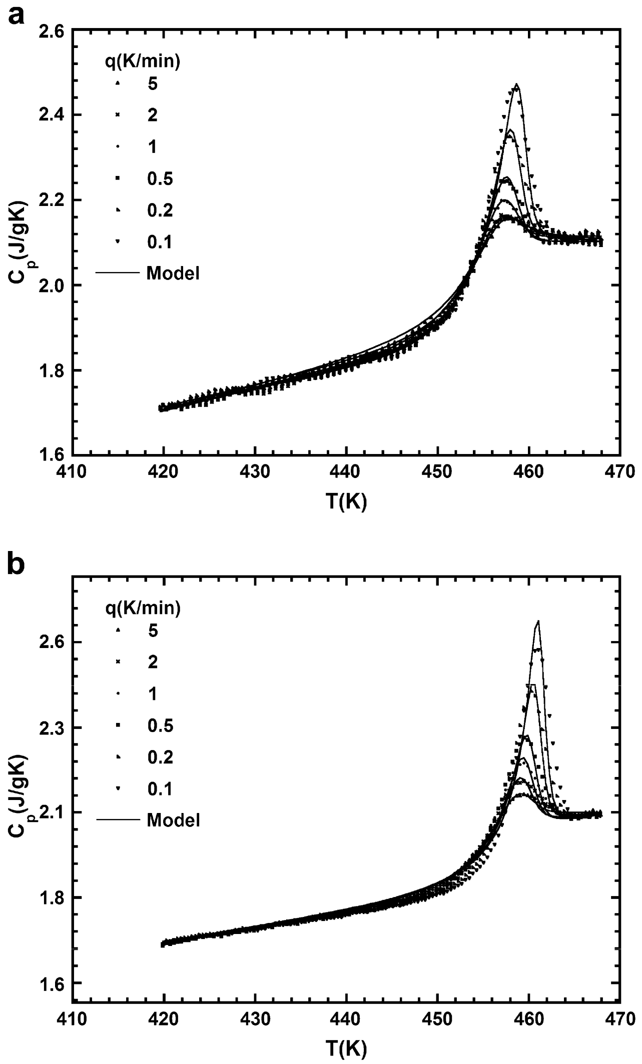

Fig. 7. (a) TNM model fits of 2 K/min heating rate data for 9350 using a constant value of $\Delta h/R$ from experiments (=141 kK). (b) TNM model fits of 5 K/min heating rate data for 9350 using a constant value of $\Delta h/R$ from experiments (=141 kK).

overshoot is found to be 56% and 35%, respectively, at 2 K/min and 5 K/min heating rate. For 9350, the average decrease in the values of x from the lowest to the highest enthalpy overshoot is found to be 27% at 2 K/min heating rate; however, although the values of β decrease by 15% at 5 K/min heating rate, there is no systematic trend in β at 2 K/min heating rate. Among the four materials the results obtained for 9371 appear to be unique in the sense that there is no systematic variation in x or β as a function of cooling rate at either 2 K/min heating rate or 5 K/min heating rate. The lack of variation in the model parameters might be to be due to the relatively low magnitude of the enthalpy overshoots for this material. Hence, the TNM model provides a better description of the heating scans for 9371 in the sense that the model parameters are not found to be thermal history dependent.

Comparing the average values of parameters reported in Table 1, it can be observed that the range of values of β is significantly higher for BPA compared to the copolycarbonates; this result is expected since the distribution of relaxation times is narrower for BPA [1,22,35], whereas the copolycarbonates exhibit broad relaxation peaks and are characterized by lower values of β. However, such a distinctive trend cannot be established for the nonlinearity parameter (x) or the value of the activation energy parameter from experiments. In addition, ln A which depends strongly on the value of $\Delta h/R$ also does not show any trend with chemical composition. The parameters $\Delta h/R$ and ln A can be used to evaluate the relaxation time at the glass transition temperature (T_g), as shown below:

$$\ln \tau_{T_g} = \ln A + \frac{\Delta h}{RT_g} \qquad (6)$$

The values of $\ln \tau_{T_g}$ were found to range between 5.4 ± 0.3 and 6.0 ± 0.1 with no particular trend upon taking T_g to be equal to the average T_f' value reported in Table 1.

In order to investigate the possibility that the lack of sensitivity in model parameters other than β to chemical composition might be due to a lack of any systematic trend in $\Delta h/R$ from experiments with % TMC content, the 2 K/min heating data were also fitting using the optimum value of $\Delta h/R$ for each material obtained from a simultaneous fit of several thermal histories for a given material, as discussed earlier. The average values of the parameters obtained upon using the optimum $\Delta h/R$ in the model fits are shown in Table 2. Similar to the results using the experimental $\Delta h/R$ values, the optimum values of $\Delta h/R$ obtained by minimizing chi square do not vary systematically with chemical composition and the range of values of β is found to be higher for BPA compared to most of the copolycarbonates, except 9350. Also similar to the results obtained

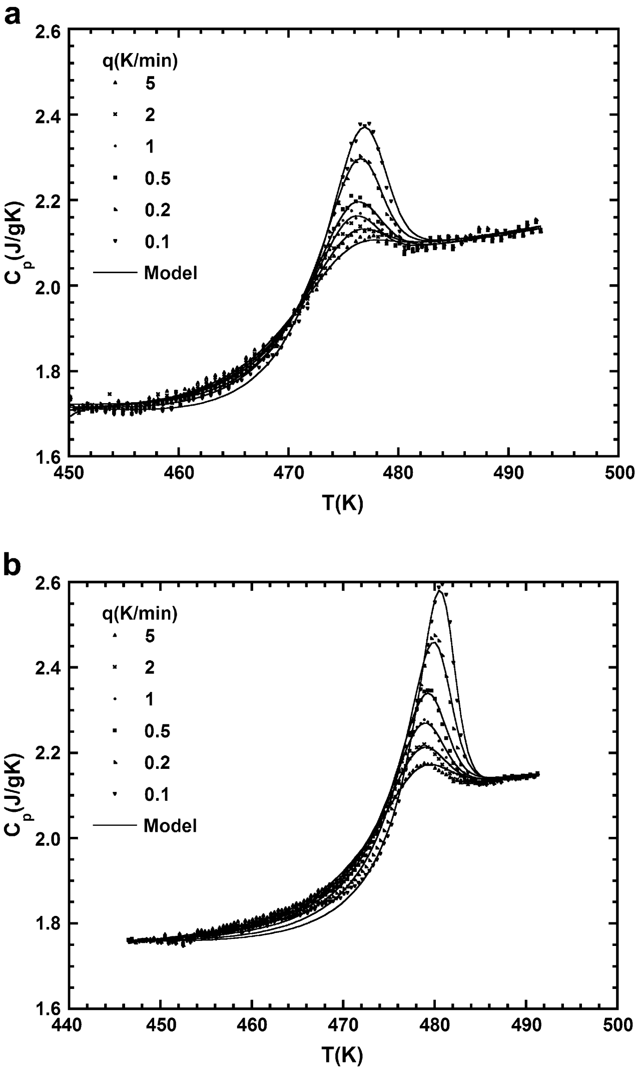

Fig. 8. (a) TNM model fits of 2 K/min heating rate data for 9371 using a constant value of $\Delta h/R$ from experiments (=110 kK). (b) TNM model fits of 5 K/min heating rate data for 9371 using a constant value of $\Delta h/R$ from experiments (=110 kK).

using the experimental $\Delta h/R$, the value of x is not found to be sensitive to the chemical composition. For two of the copolycarbonates (9330 and 9371), the parameters x and β exhibit no systematic trend as a function of cooling rate although the parameters are still found to depend on thermal history for the other two materials. For BPA, x and β increase by 57% and 45% with decreasing cooling rate, from the lowest to the highest overshoot. Similarly, for 9350, x and β increase by 62% and 17% from the lowest to the highest overshoot. Hence, although, the parameters are generally found to vary with thermal history irrespective of whether the value of $\Delta h/R$ is determined from experiments or from curve fits, the nature of variation of the parameters with the cooling rate appears to be sensitive to the value of $\Delta h/R$. While a decrease in the value of x accompanied by an increase in the value of β with increasing magnitude of overshoot might be rationalized in terms of increasing nonlinearity or nonexponentiality, the origins for the increase in x and β with increasing overshoot are not clear. Prest and coworkers [21] suggested that such a result is indicative of the need to readdress the description of nonlinearity and nonexponentiality in the model.

Table 2

Average parameters obtained from an individual fit of 2 K/min heating data using the optimum $\Delta h/R$ determined from curve fitting. The error in $\Delta h/R$ is ±1 kK

Material	$\Delta h/R$ (kK)	x	β	$\ln A$
BPA	125	0.46 ± 0.10	0.69 ± 0.10	-294.2 ± 0.3
9330	107	0.31 ± 0.05	0.43 ± 0.02	-246.4 ± 0.2
9350	95	0.53 ± 0.10	0.68 ± 0.04	-204.9 ± 0.2
9371	141	0.39 ± 0.05	0.41 ± 0.02	-294.7 ± 0.6

4. Discussion

Although some of the problems associated with the TNM model are not resolved by using the optimum value of $\Delta h/R$ in the model calculations, the quality of the fits is significantly improved. The improvement in the fits for 9330 upon using the optimum value of $\Delta h/R$ to fit data obtained at 2 K/min heating rate is demonstrated in Fig. 9. The probable cause for deviations between model and experiment upon using the value of $\Delta h/R$ from experiments needs to be examined. The differences may be due to an erroneous equation for the relaxation time [21,22] indicating problems in the description of nonlinearity in the model. We note that at 5 K/min heating rate, instrument thermal lag [1,23,24,28] in the DSC measurements might also play a small role in the differences between model calculations and experiments; however, the effect of thermal lag is expected to be negligible at 2 K/min heating rate.

The relationship between x and β for all the materials upon using both calculation methods is shown in Fig. 10. The values of x and β for BPA and 9371 reported in a previous study by one of us [16] which employed larger step sizes and slightly different values of $\Delta h/R$ are also included for comparison; although the absolute values of x and β are found to differ from those reported in this work, the trends are found to be similar. Spearman's correlation coefficient [36] for the data is found to be statistically significant which implies that x and β are correlated parameters, in agreement with the results in the literature [1,2]. Hence, although x and β are not independent parameters, as expected in the formulation of the TNM model framework, introduction of more parameters or using alternate equations for τ has not resolved the problems associated with the model [1,37].

The fact that the data can be described using two different values of $\Delta h/R$ indicates that the assumption of constant activation energy in the model framework might be a possible cause for some of the observed discrepancies, although we note that enthalpy

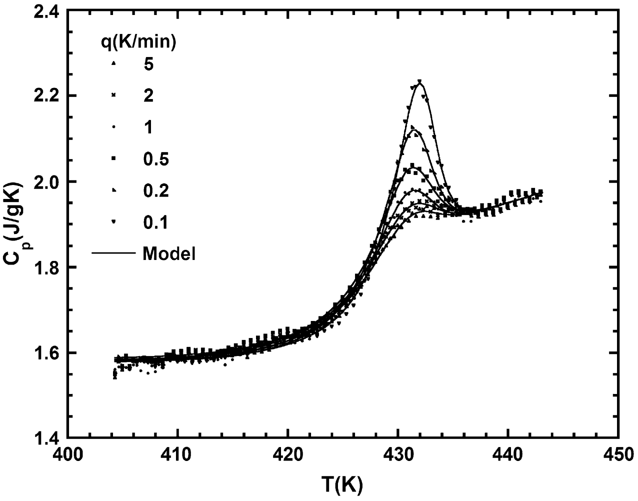

Fig. 9. Individual fits of 2 K/min heating data for 9330 using a constant $\Delta h/R$ of 107 kK obtained upon optimizing $\Delta h/R$ in the curve fitting.

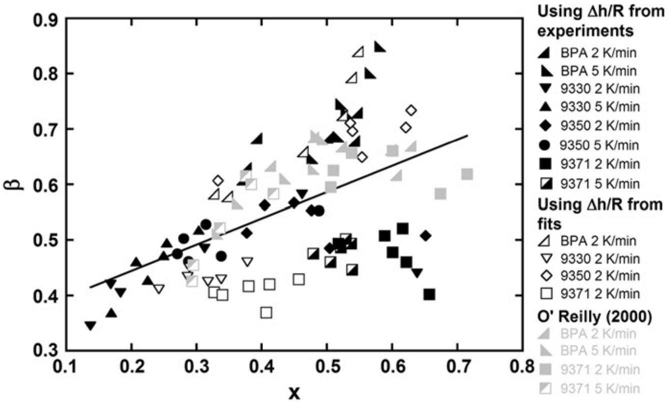

Fig. 10. Relationship between β and x for all materials at various thermal histories. The filled symbols represent the values of x and β obtained when the value of $\Delta h/R$ from experiments was used in the fits. The open symbols represent the values of x and β obtained when the optimum value of $\Delta h/R$ from curve fitting was used in the fits. The grey symbols represent the values reported in previous work [16] for 9371 and BPA.

recovery only occurs over a narrow temperature range of between 10 K and 20 K for the materials examined in this work. In recent work [38], we observed that the activation energy decreases throughout the glass transition from the glassy state to the equilibrium liquid state for polystyrene in agreement with other results in the literature [39–44], although for DSC data, the change was less than 15% – on the order of what we expect for the error in our experimental activation energies. Furthermore, in a previous modeling work [25], Scherer's equation [45] was used which implicitly accounts for a temperature-dependent activation energy; in that work, model parameters still varied with thermal history. Hodge [37] has recently modified the model by incorporating a distribution of activation energies although the ability of the modified model in describing a wide range of thermal histories with a single set of parameters is yet to be tested.

5. Conclusions

In this work, the effect of chemical composition on the glass transition behavior of polycarbonates was examined by low heating rate DSC measurements and the TNM model. The enthalpy relaxation of BPA is characterized by large narrow peaks, whereas the copolycarbonates exhibit a broader relaxation. The values of the limiting fictive temperatures were found to shift to higher temperatures upon the addition of trimethylcyclohexylidene bisphenol (TMC); however, the value of $\Delta h/R$ from experiments is not found to vary systematically with chemical composition. The TNM model is found to provide an adequate description of the enthalpy relaxation for all materials examined in this work, although some deviations can be observed. The values of β are found to larger for BPA compared to the copolycarbonates, as expected, although a systematic trend could not be established for the nonlinearity parameter. A better fit of the 2 K/min DSC heating curves was obtained upon using the optimum value of $\Delta h/R$ from curve fitting but in this case, no trend in the parameters x and β could be observed as a function of chemical composition. For both methods of estimating $\Delta h/R$, the parameters are found to be dependent on thermal history although the trends in the parameters are sensitive to the value of $\Delta h/R$. Even though the trends in x and β are different for different values of $\Delta h/R$, the parameters are found to be strongly correlated, demonstrating the interdependence of the parameters and consistent with prior results in the literature. The results in this work suggest, also consistent with other works in the literature, that implementation of thermorheological complexity and reformulation of the nonlinearity in the model may be necessary.

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