

Isoconversion analysis of the glass transition

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Abstract

The activation energy of a kinetic process can be determined as a function of conversion using isoconversion methods. In the past, such isoconversion methods were used to examine the variation in apparent activation energy (E_x) through the glass transition using differential scanning calorimetry (DSC) heating data. In this work we apply a similar isoconversion analysis to data obtained by cooling polystyrene through the glass transition using both capillary dilatometry and differential scanning calorimetry (DSC), and we compare the results to an analysis of DSC heating data for the same material. Although the values of E_x obtained from the isoconversion analyses of cooling data are found to be in good agreement with values of average activation energy (E_{ave}), the values of E_x from analysis of heating data are considerably lower. Hence, we demonstrate that to obtain estimates of the activation energy, the isoconversion analysis should be performed on cooling rather than on heating. We also show that the conversion dependence of E_x can be directly related to the temperature dependence of the equilibrium relaxation time.

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1. Introduction

Upon cooling from the equilibrium liquid state, glass-forming materials deviate from equilibrium behavior after a certain point and start forming a glass [1,2]. The kinetic manifestations of the glass transition, such as the cooling rate dependence of the glass transition temperature (T_g) and structural relaxation, are well described by phenomenological models such as Tool–Narayanaswamy–Moynihan (TNM) [3–5] and Kovacs–Aklonis–Hutchinson–Ramos (KAHR) [6] models [7]. According to the TNM model [3–5], the relaxation time (τ) is defined as shown below

$$\ln \tau = \ln A + \frac{x E_{ave}}{RT} + \frac{(1-x) E_{ave}}{RT_f} \quad (1)$$

where T_f is the fictive temperature which defines the glassy structure, x is the nonlinearity parameter which accounts for the dependence of τ on both T and T_f , $\ln A$ is a constant, R is the universal gas constant, and E_{ave} is the average apparent activation energy (often represented as Δh), which can also be determined experimentally on cooling from the cooling rate (q) dependence

of T_g or, on heating, from the cooling rate dependence of the limiting fictive temperature (T_f') [8]

$$\frac{E_{ave}}{R} = -\frac{d \ln q}{d(1/T_g)} = -\frac{d \ln q}{d(1/T_f')} \quad (2)$$

Although some reports [8–10] support the use of constant activation energy in the TNM model [3–5], others [11–16] suggest that the activation energy increases significantly as the glassy state is approached. In fact, the relaxation time is known to follow a Williams–Landell–Ferry (WLF) [17] or Vogel temperature dependence [18–20] with the result that the activation energy increases as temperature decreases [21–24]. The apparent activation energy (E) for a WLF type dependence can be obtained from the following equation [25]:

$$E = \frac{2.303RC_1^0C_2^0T^2}{(C_2^0 + T - T_0)^2} \quad (3)$$

where C_1^0 and C_2^0 are constants and T_0 is a reference temperature. For temperatures in the vicinity of T_g and universal WLF parameters ($C_1^0 = 17.44$ and $C_2^0 = 51.6$ K), Eq. (3) suggests that the activation energy increases by approximately 26% for a 10 K decrease in temperature. However, although all glass-forming materials follow the WLF dependence [21–24] from approximately T_g to $T_g + 100$, not all seem to follow this dependence at

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temperatures below T_g , even at equilibrium density, and instead follow a more Arrhenius temperature dependence in the vicinity of T_g [26–31].

The variation of the apparent activation energy (E_x) through the glass transition can be determined as a function of the extent of conversion using isoconversion methods [15,16,32,33]. The value of E_x at each value of conversion is calculated as shown in the following equation:

$$\left(\frac{E_x}{R}\right)_x = -\left(\frac{d \ln q}{d(1/T)}\right)_x \quad (4)$$

where q is the cooling rate, R is the universal gas constant, and T is the temperature where the conversion x is attained. E_x can be easily measured upon cooling through the glass transition using Eq. (4) as thermodynamic properties such as C_p exhibit a monotonic decrease upon transformation from an equilibrium liquid to a glass; however, when measured on heating, C_p often shows an overshoot near the glass transition and the size of the enthalpic overshoot is influenced by thermal history and the heating rate [7]. Since the magnitude of the overshoot has an impact on the shape of the curves, researchers have tried to minimize this effect by analyzing heating curves as a function of the cooling rate while maintaining the ratio of cooling rate and heating rate constant.

By comparing the cooling rate dependence of various arbitrary temperatures in DSC heating curves with a constant ratio of cooling rate and heating rate, Moynihan [10] demonstrated that the apparent activation energy (E_x) does not vary through the glass transition for several inorganic glasses. However, by employing a similar analysis of DSC heating curves, other researchers [11–16] have reported a decrease in activation energy on heating through the glass transition region. In addition, Hancock et al. [11] determined the apparent activation energies using the onset, midpoint, and offset temperatures in DSC cooling curves and found the values to generally increase from the liquid state to the glass state for poly(vinylpyrrolidone) and small molecule glass formers. We note that the onset and offset temperatures may vary significantly depending on the temperature range of the tangents drawn to determine them.

Vyazovkin and coworkers applied an advanced isoconversion analysis [34,35] to study the relationship between E_x and conversion through the glass transition process using DSC heating curves in which the ratios of cooling rate to heating rate were kept constant. For polystyrene, the value of activation energy was found to decrease by more than 50% from the glassy state to the equilibrium liquid state, and this decrease was attributed to the increase in available free volume at higher temperatures [15]. However, the values of E_x reported in that work were found to be lower than most of the values reported in the literature for polystyrene [28,36–42], although we note that some lower values of E_x have also been reported [43,44]. One of the aims of this work is to examine whether the lower range of activation energies and the strong dependence of activation energy on conversion observed in the work of Vyazovkin et al. [15,16] is a consequence of performing the isoconversion analysis on heating.

The objective of this work is to perform isoconversion analyses to examine the relationship between E_x and conversion through the glass transition region for polystyrene using data obtained on cooling from capillary dilatometry and differential scanning calorimetry. Care is taken to ensure that cooling rates are low enough that negligible thermal gradients are present. Capillary dilatometry has been previously used to obtain the specific volume response on cooling [28,45–50]; however, DSC measurements have rarely been performed on cooling due to historical difficulties performing the calibration on cooling and difficulties controlling the cooling rate [1]. The values of E_x obtained from the isoconversion analysis of cooling measurements will be compared with the values of E_{ave} obtained from the cooling rate dependence of T_g and T_f' . As mentioned earlier, the determination of activation energy on cooling is straightforward; however, the analysis on heating is complicated by the presence of overshoots. Hence, in this work isoconversion methods will also be used to determine the apparent activation energy from DSC measurements on heating in order to illustrate the differences between performing the analysis on cooling and heating.

2. Experimental

2.1. Material

The experiments in this work were performed using a polystyrene (Dylene 8) obtained from Arco Polymers. Dylene 8 has a number average molecular weight of 92,800 g/mol and a polydispersity index of 2.38.

2.2. Dilatometric studies

The dilatometric studies were conducted using a capillary dilatometer following the design of Plazek [45] and Bekkedahl [46] in which mercury is used as the confining fluid. The 5.0 g polystyrene sample was molded under vacuum in to a cylinder of 1.27 cm diameter. A 0.3 cm hole was drilled along the axis of the cylinder to reduce the effect of thermal gradients by facilitating better contact with the mercury. The dilatometer was placed in an oil bath (Model 6025, Hart Scientific) filled with silicone oil. The bath temperatures were obtained to an accuracy of 0.1 K using a platinum resistance thermometer (Black Stack 1569, Hart Scientific). A linear variable differential transformer was used to track the change in the height of mercury with temperature [51]. A more detailed account of the experimental setup can be found elsewhere [31,47].

The cooling experiments were performed from 105 to 60 °C using cooling rates from 0.1 to 0.003 K/min. The 0.003 K/min cooling run was performed from 97.5 °C, still above T_g to reduce run time. Note that the sample was at equilibrium prior to starting the 0.003 K/min cooling run. To obtain an accurate estimate of the liquid slope, cooling and heating runs were also performed in the temperature range between 120 and 105 °C using various rates from 0.2 to 0.03 K/min. The average liquid slope was estimated from thirteen runs. The absolute specific volumes were obtained by shifting the measured specific volumes to the value

obtained at 105 °C in previous work [28] in our laboratory. The thermal lag in the sample was found to be less than 0.1 K for the cooling rates employed. Hence, no corrections were performed to the experimental data. The standard deviation of dilatometric T_g values is ± 0.2 °C based on repeat measurements performed at cooling rates of 0.1 and 0.03 K/min.

2.3. DSC studies

The DSC studies were conducted using a PerkinElmer Pyris 1 DSC equipped with an ethylene glycol cooling system maintained at 5 °C. The measurements on cooling were performed at various rates from 30 to 2 K/min. A thin sample with a thickness of 0.27 mm was used to minimize the effect of thermal gradients. All experiments were performed under a nitrogen atmosphere. The fast cooling runs at 30 K/min were performed from 170 to 60 °C in order to ensure that the instrumental cooling rate was well controlled at T_g , whereas the other runs were performed from 130 to 60 °C. The thermal gradients were calculated to be less than 0.1 K for a cooling rate of 30 K/min and lower for slower cooling rates. Hence, no corrections were made to the experimental data. The standard deviation of calorimetric T_g values is ± 0.3 °C based on two or three measurements performed at each cooling rate.

In order to demonstrate the difference between performing the isoconversion analysis on cooling and heating, DSC measurements were performed on heating at various rates from 30 to 2 K/min following the cooling runs at the same rates using a thin 0.35 mm thick sample. From these heating runs, the limiting fictive temperature (T_f') is obtained based on the method of Moynihan [8]:

$$\int_{T_f'}^{T > T_g} (C_{pl} - C_{pg}) dT = \int_{T < T_g} (C_p - C_{pg}) dT \quad (5)$$

where C_{pg} and C_{pl} represent the values of the glassy and liquid heat capacities, respectively. The standard deviation of T_f' is ± 0.3 °C based on repeat measurements at each heating rate.

The temperature calibrations on cooling were performed using two liquid crystal standards, (+)-4-nhexylophenyl-4'-(2'-methylbutyl)-biphenyl-4-carboxylate (CE-3 from Leslie [52], University of Alabama; smectic to cholesteric transition at 78.8 °C) and 4,4-azoxyanisole (Sigma–Aldrich Co. Ltd.; liquid crystal to isotropic liquid transition at 134.5 °C). Heat flow calibrations on cooling were performed using indium. The temperature and heat flow calibrations on heating were performed using (+)-4-nhexylophenyl-4'-(2'-methylbutyl)-biphenyl-4-carboxylate and indium, respectively.

3. Results

The specific volume (v) curves obtained on cooling from the equilibrium liquid state to the glassy state at various rates of cooling are shown in Fig. 1. As expected, the specific volume response deviates from the equilibrium liquid line at lower temperatures on for slower cooling rates [1]. This trend is qualitatively similar with the dilatometric results obtained by Greiner

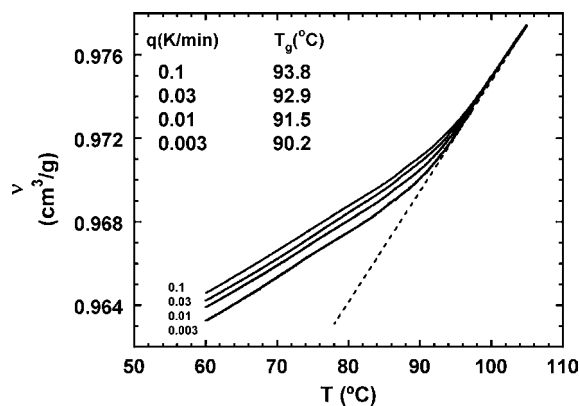


Fig. 1. Specific volume (v) vs. temperature (T) obtained on cooling at various cooling rates q . The dashed line represents the equilibrium liquid line.

and Schwarzl [48] for a different polystyrene sample. Analogous to the dilatometric data, the normalized heat capacity (C_{PN}) versus temperature curves obtained on cooling at various rates using DSC are shown in Fig. 2. The normalized heat capacity is defined as

$$C_{PN} = \frac{C_p(T) - C_{pg}(T)}{C_{pl}(T) - C_{pg}(T)} \quad (6)$$

where $C_{pg}(T)$ and $C_{pl}(T)$ refer to the glassy and liquid heat capacities, respectively, and are functions of temperature. For dilatometry, T_g is obtained as the temperature at which the extrapolated glass and liquid equilibrium lines cross. For DSC, T_g is calculated as the temperature where the step change in C_{PN} attains half the value of the total change. The values of T_g are indicated as function of cooling rate for capillary dilatometry and DSC in Figs. 1 and 2, respectively. The DSC curves obtained on heating at the same rate following cooling at a given rate are shown in the inset of Fig. 2. The value of E_{ave} calculated from the cooling rate dependence of dilatometric T_g s is compared with the values obtained using the cooling rate dependence of T_g and T_f' from DSC measurements, as shown in Fig. 3; the errors reported were calculated from a t -test at 90% confidence. The values of E_{ave} from cooling rate dependence of T_g and T_f' in

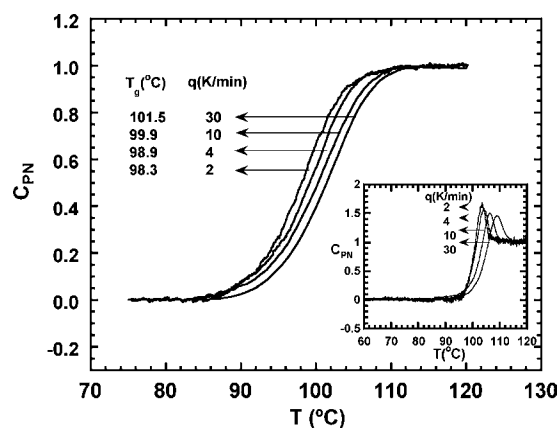


Fig. 2. Normalized heat capacity (C_{PN}) vs. temperature (T) obtained on cooling at various rates q from 30 to 2 K/min. The subsequent heating response obtained on heating at the same rate as the previous cooling run is shown in the inset.

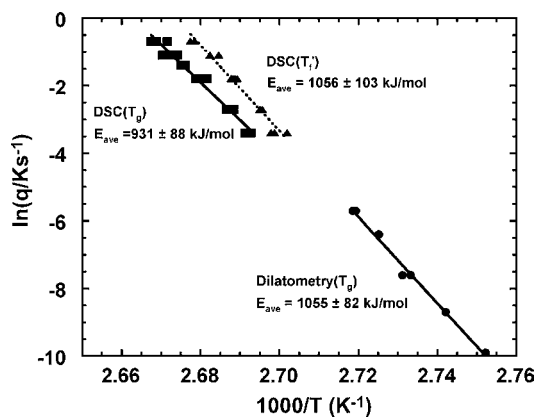


Fig. 3. Relationship between the natural logarithm of the cooling rate (q) and the reciprocal absolute transition temperature, T_g measured on cooling or T_f' measured on heating. The slope of the relationship yields the average activation energy, as shown. The squares and triangles represent values of T_g and T_f' from DSC measurements. The circles represent T_g values from capillary dilatometry.

the DSC measurements are statistically similar within the errors from the t -test. Furthermore, the E_{ave} value from dilatometry is statistically similar to the values of E_{ave} from DSC measurements within the errors, in agreement with our previous work [53].

In order to obtain the apparent activation energy through the glass transition region using the isoconversion analysis, we first need to define the conversion (x). Since the glass transition temperature is correctly measured on cooling [1], we take the conversion to be 0.0 in the liquid state and 1.0 in the glass. Hence, for the volumetric data, we have

$$x = \frac{\alpha_l(T) - \alpha(T)}{\alpha_l(T) - \alpha_g(T)} \quad (7)$$

where $\alpha(T) = dv/dT$ is the temperature derivative of the volumetric data and $\alpha_l(T)$ and $\alpha_g(T)$ represent the liquid and glassy values of the temperature derivatives of the volumetric curves. (Note that this definition is the opposite of that used in the literatures [15,16] for evaluating heating curves where $x=0.0$ is taken to be the glass and $x=1.0$ is taken to be the liquid.) For the calorimetric measurements, the conversion is obtained as shown in the following equation:

$$x = \frac{C_{pl}(T) - C_p(T)}{C_{pl}(T) - C_{pg}(T)} = 1 - C_{PN} \quad (8)$$

The relationship between the activation energy and conversion through the glass transition for capillary dilatometry is shown in Fig. 4 with the error bars representing the standard errors of the values. The solid symbols represent E_x values when the temperature corresponding to a desired value of conversion was obtained through linear interpolation of the smoothed data (approximately 1 data point/K). On the other hand, the open symbols represent the E_x values when the temperature corresponding to a certain value of conversion was obtained using a piecewise sigmoidal fit of less smoothed data (approximately 10 data points/K). The average error in the value of E_x from both procedures is calculated to be 13% based on the error in the linear fit of $\ln q$ versus $1/T$. The errors are expected to be higher at the

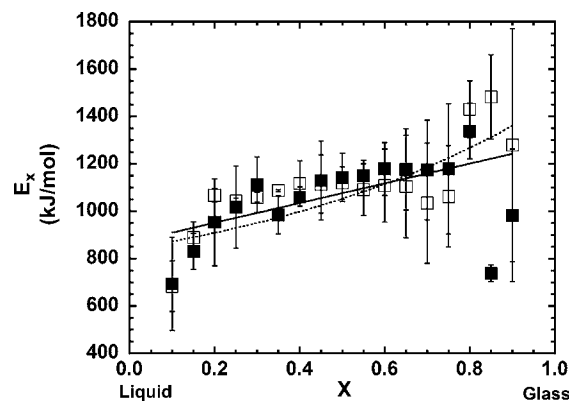


Fig. 4. Relationship between activation energy (E) and conversion through the transition (x) for capillary dilatometry. The solid symbols represent E_x values when the temperature corresponding to a desired value of conversion was obtained through linear interpolation of smoothed data (1 data point/K). On the other hand, the open symbols represent the E_x values when the temperature corresponding to a certain value of conversion was obtained using a piecewise sigmoidal fit of less smoothed data (10 data points/K). The error bars represent the standard errors of the values. The solid line represents the best linear fit through all of the data; the dashed line is the best fit assuming a "universal" WLF temperature dependence.

highest or lowest extents of conversion since the conversion is invariant with temperature at the extremes; this can be observed by the increase in difference between E_x obtained in the two methods particularly at high conversions. The values of E_x are in good agreement with the value of E_{ave} ($=1055 \pm 82$ kJ/mol) obtained from the cooling rate dependence of T_g , as expected. In addition, the variation of E_x with x is statistically significant based on the value of the Spearman's correlation coefficient ($\rho=0.59$) for the data. Hence, the activation energy increases with increasing conversion towards the glassy state. To further ascertain the origin of the increase in E_x with conversion, the following equation was used to fit the data as a function of x :

$$E_x = a + \frac{dT}{dx} \frac{dE}{dT} x \quad (9)$$

where a is a fitting parameter, dT/dx is obtained as the average slope of the linear region in conversion–temperature plot, dE/dT represents the temperature dependence of E . The solid line represents the best fit assuming that E follows linear temperature dependence and the dashed line represents the best fit upon assuming WLF type dependence for E . Although within the errors, both fits appear to provide a reasonable description of the data, the linear fit is more appropriate based on a sum of squares F -test; this is consistent with the observation that the temperature dependence of polystyrene deviates from WLF dependence at temperatures below T_g and instead follows an Arrhenius or linear temperature dependence [26–31].

The values of activation energy calculated from calorimetric data obtained on cooling and heating are plotted as a function of conversion in Fig. 5. The solid and open symbols represent the values of E_x obtained on cooling and heating, respectively, with the error bars representing the standard errors of the values obtained from the fit of $\ln q$ versus $1/T$. Similar to the results from dilatometry, the Spearman's correlation coefficient was

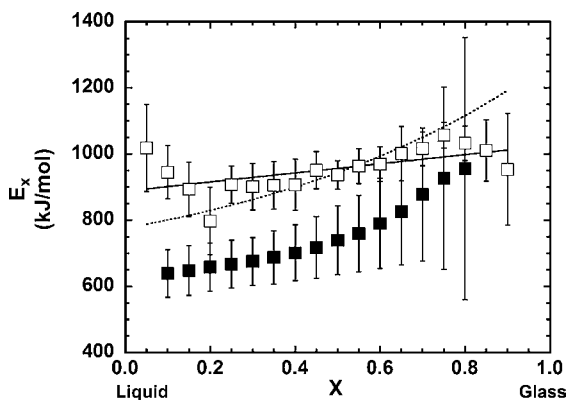


Fig. 5. Relationship between activation energy (E_x) and conversion (x) through the transition for DSC. The solid squares and triangles represent E_x obtained on cooling and heating, respectively. The error bars represent the standard errors of the values. The solid line represents the best linear fit through all of the data; the dashed line is the best fit assuming a “universal” WLF temperature dependence.

found to be statistically significant for E_x determined on cooling ($\rho = 0.59$) and heating ($\rho = 1.0$) suggesting an increasing trend in E_x with conversion as the glassy state is approached. Furthermore, the value of ρ for the conversion dependence of E_x for cooling data was found to be exactly same as the value obtained from the dilatometry data, indicating a similarity in the correlation between activation energy and conversion for both cases. The larger value of ρ from heating data implies that the variation in E_x with conversion is greater on heating than on cooling; this issue will be addressed subsequently. The solid lines and the dashed lines in Fig. 5 represent the best fits to the data obtained on cooling assuming a linear temperature dependence and WLF temperature dependence, respectively. As in the case of the dilatometry data, a reasonable description is observed for both linear and WLF dependence; however, the quality of fit assuming a linear temperature dependence for E is found to be better. The values of E_x determined from the DSC cooling measurements are in good agreement with the values of E_{ave} (≈ 1000 kJ/mol) determined from the cooling rate dependence of T_g and T_f' , as expected. On the other hand, the values of E_x determined from the DSC heating curves are found to be significantly lower than the values of E_{ave} and lower than the values of E_x from cooling; the reasons for this discrepancy will be discussed in the next section.

4. Discussion

In the work of Vyazovkin et al. [15], the activation energy of polystyrene evaluated from DSC heating scans decreased from 280 to 120 kJ/mol from the glassy state to the liquid state. These values are in the lower range of the activation energies reported in the literature, which range from 160 to 1215 kJ/mol [28,36–44]. Similarly, the values of E_x from heating measurements in this work are also found to be significantly lower than the values of E_x on cooling and the values of E_{ave} ; we suggest that the lower values of E_x are simply a consequence of performing the analysis on heating, where complications due to overshoot kinetics are encountered. For the heating curves, con-

version as defined by Eq. (8) is negative in the overshoot regime. Hence, the calculations cannot be performed from the glass all the way through the transition, and therefore, a significant amount of enthalpy relaxation is ignored resulting in significant error in the calculations. Consequently, for the heating curves, a conversion of $x = 0$ (or $x = 1$ in the work of Vyazovkin and coworkers) does not correspond to the equilibrium liquid state but rather to some point in the glass transition. The error is accentuated for larger overshoots, such as those observed at high heating rates. We note that even if one takes the point at the maximum in the overshoot to be a conversion of 0.0 (or 1.0, depending on convention), still the calculations cannot be performed through the entire transition. However, in spite of the errors involved in performing the isoconversion analysis on heating, Moynihan et al. [10] observed good agreement between the values of activation energies obtained from the cooling rate dependence of the onset temperature, inflection temperature, the maximum in the peak temperature, and the limiting fictive temperature from DSC heating curves for B_2O_3 . In that work [10], it appears that the DSC enthalpic overshoots do not depend strongly on cooling rate (or heating rate since the ratio is maintained constant). Although the expectation of the TNM model is that the enthalpy overshoot should be invariant if the ratio of the heating rate to cooling rate is constant, this differs from the results for polystyrene in this work (see the inset in Fig. 2) and the results of Vyazovkin et al. [16]—and this difference may be why Moynihan et al. [10] obtained the same value of activation energy for various analyses of their heating data for B_2O_3 , whereas the isoconversion analysis on heating and cooling do not yield the same result for polystyrene.

The errors arising from the overshoot kinetics might be avoided if the isoconversion analysis is performed on cooling. However, it is acknowledged that performing the analysis on cooling also involves some assumptions particularly since different glassy states are attained at different cooling rates and the use of the isoconversion analysis involves assigning these different glassy states the same value of conversion (i.e., $x = 1$). Furthermore, the glassy structure continues to evolve towards equilibrium due to the kinetic nature of the glass transition, even though a conversion of $x = 1$ is assumed to represent a single state; these problems might be alleviated if the isoconversion methods are applied to evaluate activation energies from linear heat spectroscopy (e.g., 3- ω ac calorimetry) measurements (performed on cooling at various frequencies or isothermally as function of frequency) [54,55] since in such experiments the sample can be maintained at equilibrium density through the entire temperature range with vitrification occurring due to the applied frequency rather than due to the temperature changes. In such experiments, issues arising from structural relaxation of the glass are avoided. We note that an analysis of heat spectroscopy data obtained by Birge and Nagel [55] suggests that the activation energy decreases by at least 12% from the glassy state to the equilibrium liquid state consistent with the effect arising from the temperature-dependent activation energy in this work. The use of temperature modulated DSC with very slow cooling rates, such that, again, vitrification occurs at equilibrium density

as a result of the applied modulation [56], to obtain activation energies as a function of conversion through the glass transition may also be feasible, although the current range of modulation frequencies is perhaps too small to obtain accurate apparent activation energies.

In the work of Vyazovkin et al. [15,16], a pronounced variation in E_x is observed as a function of conversion for data obtained on heating. In this work, the large variation of E_x with x is shown to be a consequence of performing the analysis on heating; however, E_x is found to vary with x , although less significantly when the analysis is correctly performed on cooling. The implications of the results obtained in this work—particularly the observation that E_x varies as a function of conversion on the TNM model [3–5] framework needs to be further examined. Due to the widely reported deficiencies [57–59] of the model, various attempts [9,58–61] have been made to modify the TNM model framework, including the incorporation of a WLF temperature dependence [60] and incorporation of a temperature-dependent β [9]; these modifications have not enhanced the capabilities of the model. In more recent work Hodge [62] has attempted to incorporate thermorheological complexity in the TNM model framework by using a truncated Gaussian distribution of activation energies. However, the efficacy of such an approach in describing a wide range of thermal histories is yet to be tested. The analyses performed in this work indicate that a temperature-dependent activation energy is warranted but that, at least in the vicinity and below T_g , this dependence should be weaker than the prediction from the WLF equation, in agreement with other findings in the literatures [26–31].

5. Conclusions

In this work, an isoconversion analysis was applied to the data in the glass transition region obtained on cooling from capillary dilatometry and DSC studies. From the analysis, the apparent activation energy on cooling was found to be in good agreement with the values of E_{ave} , for both capillary dilatometry and DSC. The values of E_x and E_{ave} from capillary dilatometry and DSC were found to be similar, in agreement with the results from our previous work [53]. Furthermore, the variation in E_x with conversion was also found to be similar for the values determined on cooling for dilatometry and DSC; however, the values of E_x on heating from DSC measurements appear to have a stronger dependence on x when compared to the values on cooling. The variation of E_x with x during cooling is suggested to be due to the temperature dependence of the activation energy for the equilibrium liquid.

The values of E_x on heating were found to be significantly lower than the values of E_x on cooling and E_{ave} . The lower values of E_x on heating is suggested to be due to the fact that the overlap of step change in heat capacity and the enthalpy relaxation peak cannot be separated in the isoconversion analysis of the DSC heating curves. Hence, isoconversion analysis of the glass transition should be performed on cooling rather than on heating in order to avoid complications associated with the enthalpy or volume overshoots on heating. In addition, we suggest that the isoconversion methods might be best applied to linear measure-

ments where the sample is maintained at equilibrium density in order to determine the conversion dependence of the activation energy through the glass transition.

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