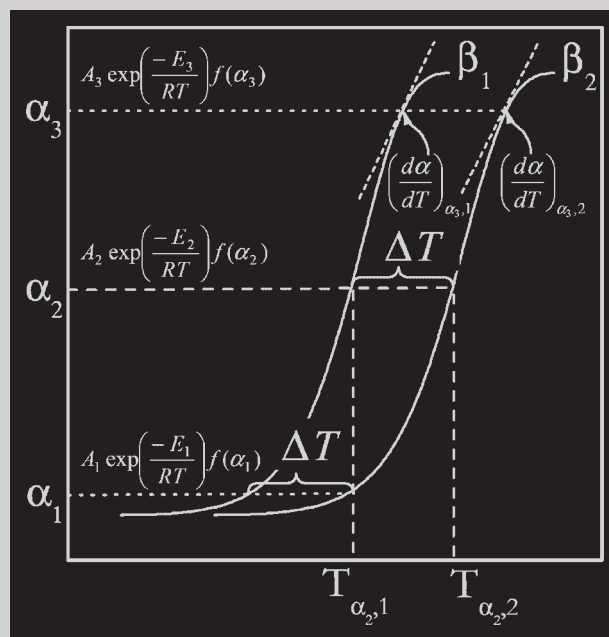


Summary: Isoconversional kinetic analysis involves evaluating a dependence of the effective activation energy on conversion or temperature and using this dependence for making kinetic predictions and for exploring the mechanisms of thermally stimulated processes. The paper discusses major results obtained by the authors in the area of the isoconversional analysis of polymer kinetics over the past decade. It provides a brief introduction to isoconversional methods and surveys the impact made by isoconversional analysis in several application areas that include kinetic predictions, thermal degradation, crosslinking (curing), glass transition, and glass and melt crystallization. It is concluded that isoconversional analysis has been used broadly and fruitfully because it presents a fortunate compromise between the single-step Arrhenius kinetic treatments and the prevalent occurrence of processes whose kinetics are multi-step and/or non-Arrhenius.



An isoconversional method applies the Arrhenius equation to a narrow temperature region, ΔT related to a given extent of conversion.

Isoconversional Kinetic Analysis of Thermally Stimulated Processes in Polymers

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Received: June 8, 2006; Accepted: June 30, 2006; DOI: 10.1002/marc.200600404

Keywords: crystallization; curing of polymers; degradation; glass transition; kinetics

Introduction

Temperature changes can stimulate a variety of chemical and physical processes in polymer systems. Important examples of these processes include thermal degradation, crosslinking, crystallization, glass transition, etc. The overall or macroscopic kinetics of these processes are conveniently measured by using thermal analysis methods such as thermogravimetry (TGA), differential scanning calorimetry (DSC), and other techniques.^[1,2] By its nature the macroscopic kinetics are

complex as they include information about simultaneously occurring multiple steps. Disentangling macroscopic kinetics presents a certain challenge that can only be met by the computational methods that allow for detecting and treating multi-step processes. According to the results of the ICTAC Kinetics Project,^[3] isoconversional methods are among a few methods that are up to this challenge.

The isoconversional methods may be best known through their most popular representatives, the methods of Friedman,^[4] Ozawa,^[5] and Flynn and Wall.^[6] Interestingly, all

three methods were conceived by the researchers working on the thermal degradation of polymers and since then they have been mostly used in polymer kinetics studies. The isoconversional methods require performing a series of experiments at different temperature programs and yield the values of effective activation energy as a function of conversion. More often than not, the activation energy is found to vary with the extent of conversion. Although it had been known since the work of Flynn and Wall^[6] that this variation was a sign of the process complexity, the E_α dependencies were not exploited but rather considered to be a major nuisance. The full potential of the isoconversional methods has been appreciated as Vyazovkin^[7] brought analysis of the E_α dependences to the forefront and demonstrated that they can be used for exploring the mechanisms of processes and for predicting kinetics. These two features make a foundation of the isoconversional kinetic analysis or so-called “model-free kinetics”.

The isoconversional analysis of polymer kinetics has been a topic of ongoing collaboration between the authors that has resulted in a number of joint papers, the first^[8] of which was published in 1996. Passing a decade seems like

an opportune occasion to revisit and refresh some of our past and more recent work in that area as well as to consider the impact of the isoconversional analysis on the way the macroscopic kinetics of polymers have been explored by other workers.

Isoconversional Methods

The methods take their origin in the single-step kinetic equation

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (1)$$

and make use of the isoconversional principle which states that at a constant extent of conversion, the reaction rate is a function only of the temperature so that

$$\left[\frac{d \ln(d\alpha/dt)}{dT^{-1}} \right]_\alpha = -\frac{E_\alpha}{R} \quad (2)$$

In Equation (1) and (2), A and E are Arrhenius parameters (the pre-exponential factor and the activation energy,



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respectively), $f(\alpha)$ is the reaction model, R is the gas constant, T is the temperature, t is the time, and α is the extent of conversion, which can be determined from TGA runs as a fractional mass loss or from DSC runs as a fractional heat release. Henceforth, the subscript α denotes values related to a constant extent of conversion.

The isoconversional methods employ multiple temperature programs (e.g., different heating rates and/or temperatures), because this is practically the only way to obtain data on varying rates at a constant extent of conversion [i.e., the left-hand side of Equation (2)]. Note that Equation (2) is derived from the single-step kinetic Equation (1). However, the fundamental assumption of the isoconversional methods is that a single-step Equation (1) is applicable only to a single extent of conversion and to the temperature region (ΔT) related to this conversion (Figure 1). In other words, isoconversional methods describe the kinetics of the process by using multiple single-step kinetic equations, each of which is associated with a certain extent of conversion (Figure 1). Thanks to this feature isoconversional methods allow complex (i.e., multi-step) processes to be detected via a variation of E_α with α . Conversely, independence of E_α on α is a sign of a single-step process.

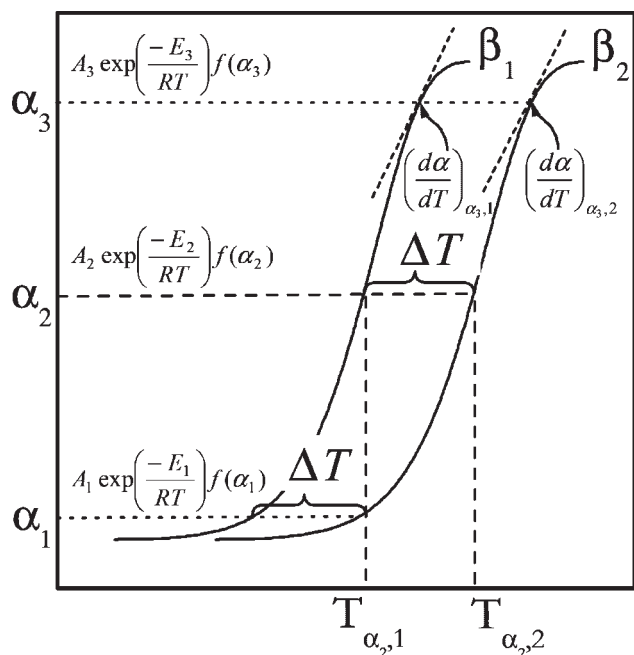


Figure 1. An isoconversional method applies the Arrhenius equation to a narrow temperature region, ΔT , related to a given extent of conversion. The temperature region changes with the extent of conversion that allows one to follow a variation in the value of E throughout the whole experimental temperature region. The use of different heating rates, β_1 and β_2 , allows for determining different rates ($\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \beta$) related to the same conversion, α_3 .

Simple rearrangement of Equation (1) leads to the following equation:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (3)$$

which forms the foundation of the differential isoconversional method of Friedman.^[4] The subscript i denotes different heating rates. The application of the Friedman method to the integral data (e.g., TGA) requires numerical differentiation of the experimental α versus T curves that typically results in quite noisy rate data and, thus, unstable E_α values.

The problems of numerical differentiation are avoided by using integral isoconversional methods. For isothermal conditions, integration of Equation (1) yields

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \exp\left(\frac{-E}{RT}\right) t \quad (4)$$

where $g(\alpha)$ is the integral form of the reaction model. Rearrangement of Equation (4) gives Equation (5)

$$-\ln t_{\alpha,i} = \ln\left[\frac{A_\alpha}{g(\alpha)}\right] - \frac{E_\alpha}{RT_i} \quad (5)$$

that can be readily used for determining the E_α dependence from isothermal runs performed at series of different temperatures, T_i . For nonisothermal conditions when the temperature is raised at a constant heating rate β , integration of Equation (1) involves solving the temperature integral $I(E, T)$

$$g(\alpha) \equiv \frac{A}{\beta} \int_0^{T_\alpha} \exp\left(\frac{-E}{RT}\right) dT = \frac{A}{\beta} I(E, T) \quad (6)$$

that does not have an analytical solution. It is solved by using either approximations or numerical integration. One of simplest approximations by Doyle^[9] gives rise to the following

$$\ln(\beta_i) = \text{Const.} - \frac{1.05E_\alpha}{RT_{\alpha,i}} \quad (7)$$

which is used in the most popular isoconversional methods of Flynn and Wall^[6] and Ozawa.^[5] The use of a more precise approximation by Coats and Redfern^[10] yields the equation

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{Const.} - \frac{E_\alpha}{RT_{\alpha,i}} \quad (8)$$

Further increase in precision of the integral methods [Equation (7) and (8)] can be accomplished by using numerical corrections^[11] or by directly performing numerical integration. An example of the latter is a method^[12] based on minimization of the following function:

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i}) \beta_j}{I(E_\alpha, T_{\alpha,j}) \beta_i} \quad (9)$$

For each given value of α in Equation (9), the E_α value is determined as a value that minimizes $\Phi(E_\alpha)$ and the temperature integral $I(E, T)$ is solved numerically.

Note that the simpler integral isoconversional equations [e.g., Equation (5), (7), and (8)] are arrived at by assuming that the value of E_α is constant in $I(E, T)$ throughout the whole interval of integration, i.e., $0-\alpha$. This assumption introduces a systematic error in the value of E_α if the actual value varies with α . In the case of strong variations, the error can reach 20–30%.^[13] This error does not appear in the differential method of Friedman and can be easily eliminated in the advanced isoconversional methods of Vyazovkin^[12–14] that use numerical integration as a part of E_α evaluation. For instance, in Equation (9) the error is eliminated by performing integration over small temperature segments as follows:

$$I(E, T) = \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha} \exp\left(\frac{-E}{RT}\right) dT \quad (10)$$

Then, the constancy of E_α is assumed for only a small interval of conversions, $\Delta\alpha$. The use of integration by segments yields the E_α that are similar to those obtained when using the Friedman method.^[13]

In addition to isothermal and constant heating rate temperature programs, other programs of practical interest include constant rate cooling that is widely used in crystallization of melts as well as distorted linear heating or cooling that frequently occurs in samples as a result of strong self-heating or self-cooling. The data obtained under such temperature programs cannot be treated by using typical integral isoconversional equations such as Equation (7) and (8) because they have been derived assuming β be constant (i.e., no deviation from linear heating) and positive (i.e., heating only). None of these assumptions is made in the differential method of Friedman that makes it applicable to the respective temperature programs. However, the integral isoconversional method represented by Equation (9) can be adjusted to an arbitrary temperature program $T(t)$ by replacing integration over the temperature with integration over the time. The resulting advanced isoconversional method of Vyazovkin^[13,14] allows one to handle a set of n experiments carried out under different arbitrary temperature programs, $T_i(t)$. The E_α value is determined as the value that minimizes the function

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (11)$$

where

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \quad (12)$$

In order to account for self-heating/-cooling, one needs to use the so-called “sample temperature” whose variation

with time represents the actual temperature program [i.e., $T(t)$] experienced by a sample.

A few comments should be made about the popular Kissinger method^[15] as it is sometimes erroneously grouped with the isoconversional methods. The confusion is likely due to the fact that the basic equation of the method

$$\ln\left(\frac{\beta_i}{T_{p,i}^2}\right) = \text{Const.} - \frac{E}{RT_{p,i}} \quad (13)$$

looks similar to the isoconversional Equation (8). However, in Equation (13), $T_{p,i}$ is the peak temperature at different heating rates, and the extent of conversion related to the peak is known to change with the heating rate.^[11] Also, compared to the isoconversional methods, the method has a limitation because it produces a single value of the activation energy for the whole process. As a result, the obtained value is sound only if there is no variation of E_α with α throughout the process. Unfortunately, such variations are quite typical, and the Kissinger method is not capable of detecting them. Therefore, the E values obtained by the Kissinger method should generally be treated with caution, unless an isoconversional method has demonstrated E_α be independent of α .

Kinetic Predictions

Predictions are among the most important practical features of kinetic analysis. They are widely used to evaluate the kinetic behavior of materials beyond the temperature regions of experimental measurements. For instance, thermal stability can be estimated as the time to reach a certain extent of conversion at a given temperature. Kinetic predictions of this type can be easily accomplished by using the E_α dependence evaluated by an isoconversional method. The respective predictive equation has been obtained by Vyazovkin^[7,16] in the following form:

$$t_\alpha = \frac{\frac{1}{\beta} \int_0^{T_\alpha} \exp\left(\frac{-E_\alpha}{RT}\right) dT}{\exp\left(\frac{-E_\alpha}{RT_0}\right)} \quad (14)$$

where t_α is the time to reach the extent of conversion α at a given temperature, T_0 , under isothermal conditions. Equation (14) is easily modified to employ data from arbitrary heating programs for predicting isothermal kinetics, as follows:

$$t_\alpha = \frac{J[E_\alpha, T(t_\alpha)]}{\exp\left(\frac{-E_\alpha}{RT_0}\right)} \quad (15)$$

The E_α dependence can also be used for making non-isothermal predictions related to a given heating rate.^[7]

The first experimental applications of the isoconversional predictive procedure have been performed by Vyazovkin^[7] and by Vyazovkin and Sbirrazzuoli^[8] and concerned with

using nonisothermal data to predict the epoxy curing kinetics under isothermal conditions. In both cases, the isoconversional predictions have agreed very well with the actual measurements and have been superior to predictions obtained by other methods. For epoxy–diisocyanate crosslinking kinetics, Privalko et al.^[17] have also found that the isoconversional predictions by far exceed the accuracy of the predictions made by using the ASTM E698 procedure, which makes use of the Kissinger method [Equation (13)]. Both isothermal and nonisothermal cure kinetics of an epoxy based photo-dielectric dry film (ViaLux™ 81) have been predicted [Equation (14)] by Dunne et al.,^[18] who reported excellent agreement with actual nonisothermal measurements. For isothermal conditions, the predictions have markedly deviated from the actual data. This is not entirely unexpected as the predictions have been made to the temperatures below the limiting glass transition temperature where the cure mechanism is likely to change, giving, in particular, rise to incomplete cure. Schawe^[19] has proposed some important extensions of the predictive methodology, making it applicable to incomplete cures that occur at temperature below the ultimate glass transition temperature.

Wang et al.^[20] have tested isothermal predictions for the curing of two commercial phenol-formaldehyde resins and reported good correspondence with the actual isothermal measurements. Good agreement of isothermal predictions with actual data has also been reported by He et al.^[21] for phenol-formaldehyde curing. Li et al.^[22] have provided several examples of successful kinetic predictions obtained by applying the isoconversional methodology to the curing process of polyurethane. Vazquez et al.^[23,24] have used the isoconversional predictions to demonstrate that the curing kinetics of the newly developed tannin–phenol–formaldehyde adhesive is faster than that of the presently used commercial systems. The predicted results have been confirmed in actual pilot plant runs.

He and Yan^[25] have employed isoconversional predictions to demonstrate the accelerating effect of moisture in wood on curing of polymeric diphenylmethane diisocyanate. Bulacovschi et al.^[26] have employed the isoconversional approach to predict the temperatures to reach 1 and 10% degradation of three crosslinked poly(ester-siloxane) urethanes in order to identify the most stable material. In order to circumvent the time-consuming isothermal analysis of the thermal endurance of Kapton HN® and Upilex S®, Heltzel and Semprimoschnig^[27] explored an alternative opportunity of using nonisothermal TGA tests in combination with kinetic simulations. By comparing actual isothermal data with simulations, it has been determined that simulations based on a model-free isoconversional approach are more reliable than those based on the ASTM E 1641 method. Polli et al.^[28] have applied the isoconversional analysis to predict the kinetics of thermal degradation of linear and branched polycarbonates in a wide temperature region. Vyazovkin et al.^[29] have reported that

the isoconversional predictions of polymer degradation to the flash ignition temperature can be very useful in assessing potential fire-resistance of polystyrene (PS) and PS–clay nanocomposite.

Thermal and Thermo-Oxidative Degradation

On heating, polymers degrade forming low molecular products. The process involves breaking of the bonds between individual atoms forming a polymer chain. For typical vinyl polymers [e.g., PS, polyethylene (PE), poly(propylene) (PP)] degradation involves breaking of C–C bonds whose bond energy is around $350 \text{ kJ} \cdot \text{mol}^{-1}$. Although this is a large energy, thermal degradation of vinyl polymers readily occurs above $200\text{--}300^\circ\text{C}$. Thermal degradation starts rather easily because of the weak link sites inherent with the polymer chain. Typical weak sites include head-to-head links, hydroperoxy, and peroxy structures. These sites serve as spots where thermal degradation is initiated. Once macro radicals are formed, further degradation occurs via various radical pathways whose activation energies are markedly smaller than the C–C bond energy. For this reason, the effective activation energy of thermal degradation of many polymers varies throughout the process. At earlier stages it tends to be lower representing the process of initiation at the weak links. Once the weak links have given way to initiation, the effective activation energy increases that typically occurs at the later stages of degradation. This tendency has been clearly demonstrated by Peterson et al.^[30] by applying an advanced isoconversional method [Equation (11)] to the TGA data on the thermal degradation of PS, PE, and PP. The application results in obtaining increasing E_α dependencies^[29,30] (Figure 2). However, a more complex E_α dependence that involves an increase ($60\text{--}190 \text{ kJ} \cdot \text{mol}^{-1}$) followed by quick falling off ($190\text{--}60 \text{ kJ} \cdot \text{mol}^{-1}$) and another increase ($60\text{--}230 \text{ kJ} \cdot \text{mol}^{-1}$) is detected by Peterson et al.^[31] for the thermal degradation of radically polymerized poly(methyl methacrylate). The behavior is explained by different mechanisms of initiation respectively occurring via the head-to-head linkages, the vinylidene end groups, and random scission. Bonnet and White^[32] have applied an isoconversional method to mass-spectral data obtained from TG-MS analyses of the thermal degradation of poly(vinyl butyral). Comparison of the E_α -dependencies related to individual degradation products with the E_α -dependence derived from the mass loss data allowed for mechanistic insights into the origin of the latter dependence.

In the presence of oxygen, polymers undergo thermo-oxidative degradation. Oxygen alters the pathways of thermal degradation by initiating reactions of lower activation energy. Thermo-oxidative degradation occurs at temperatures about 100°C lower than the regular thermal degradation under nitrogen. For vinyl polymers, thermo-oxidative degradation involves the hydroperoxide radical in

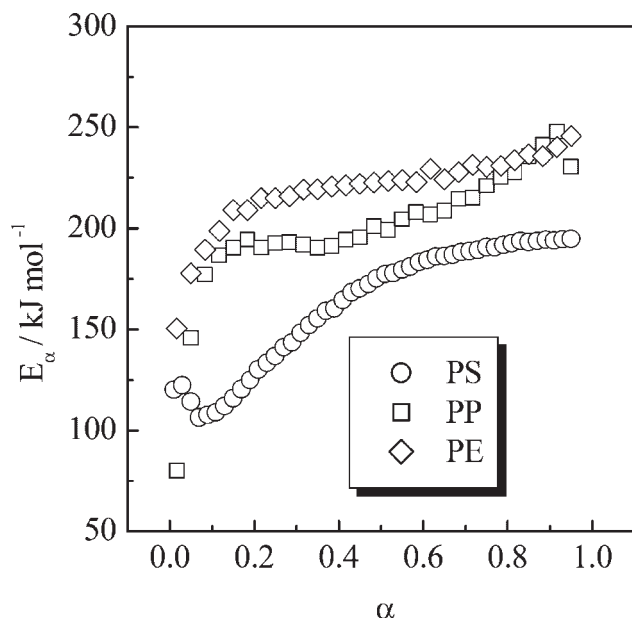


Figure 2. The E_{α} dependencies obtained for the thermal degradation of polystyrene (PS), poly(propylene) (PP), and polyethylene (PE) studied in TGA experiments under nitrogen.

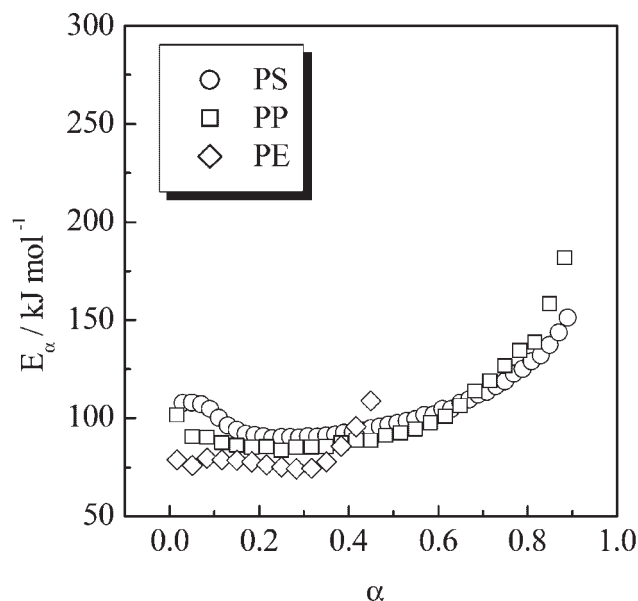


Figure 3. E_{α} dependencies obtained for the thermo-oxidative degradation of PS, PP, and PE studied in TGA experiments under air.

the propagation step of the degradation. Because of this, many oxygen-initiated degradations have activation energies in the range of 80–110 $\text{kJ} \cdot \text{mol}^{-1}$ that are typical for bimolecular decomposition of organic hydroperoxides. The respective activation energies are found (Figure 3) when an isoconversional method is applied to TGA data on the thermo-oxidative degradation of vinyl polymers.^[29,30]

On the other hand, in the presence of oxygen the degradation of poly(methyl methacrylate) slows down and gives rise^[31] to the E_{α} values around 200 $\text{kJ} \cdot \text{mol}^{-1}$ that is unusually big for thermo-oxidative degradation. Peterson et al.^[31] have provided a mechanistic explanation to this behavior that is associated with the formation of a thermally stable peroxy radical that inhibits unzipping of the poly(methyl methacrylate) chain. Zeng et al.^[33] stress the value of the obtained E_{α} dependencies^[31] for understanding poly(methyl methacrylate) combustion. Xi et al.^[34] have used isoconversional analysis to study a catalytic effect of sulfates on thermo-oxidative degradation of poly(methyl methacrylate). For virgin polymer they report the E_{α} values around 250 $\text{kJ} \cdot \text{mol}^{-1}$. Mixtures with metal sulfates do not demonstrate a significant variation in E_{α} with α , but show a considerable decrease in the E_{α} values [down to 140–150 $\text{kJ} \cdot \text{mol}^{-1}$ in the case of $\text{Fe}_2(\text{SO}_4)_3$] that is explained via acceleration of the β -scission due to coordination of the metal ion with the carbonyl group.

Determining for the thermo-oxidative degradation E_{α} values larger than those for thermal degradation does not appear to be a unique case of poly(methyl methacrylate). Similar phenomena have been reported^[35,36] as a result of

isoconversional analysis of the thermo-oxidative degradation of epoxy materials. For thermal degradation, Salla et al.^[36] report an increasing E_{α} -dependence (from ≈ 65 to $\approx 150 \text{ kJ} \cdot \text{mol}^{-1}$), whereas for thermo-oxidative degradation the E_{α} values reach over 200 $\text{kJ} \cdot \text{mol}^{-1}$ in the region $\alpha = 0.4$ – 0.6 . Regnier and Fontaine^[35] report a rather complex E_{α} -dependencies for both thermal and thermo-oxidative degradation. However, at $\alpha > 0.2$ the E_{α} values for the thermo-oxidative process remain at $\approx 140 \text{ kJ} \cdot \text{mol}^{-1}$ that is 10–40 $\text{kJ} \cdot \text{mol}^{-1}$ higher than the values for thermal degradation. The phenomenon is explained by invoking the mechanism proposed earlier by Peterson et al.^[31] Fernandes et al.^[37] have applied an isoconversional method to compare the kinetic of the thermal and thermo-oxidative degradation of poly(vinyl alcohol)/kraft lignin derivative blends. Although they have obtained rather complex E_{α} -dependencies, the E_{α} values for the thermo-oxidative degradation are $\approx 100 \text{ kJ} \cdot \text{mol}^{-1}$ larger than the respective values for the thermal degradation.

Analysis of the E_{α} -dependencies proves generally to be very helpful in exploring an effect of the structure or a composition of a polymer material on its degradation kinetics. In order to study the effect of the end groups on the thermal degradation of poly(methyl methacrylate), Hu and Chen^[38] have prepared a series of the polymer samples by using different initiators of polymerization. The E_{α} -dependencies obtained for the thermal degradation of these samples exhibit significant difference for the early degradation stages associated with initiation, whereas the later stages ($\alpha > 0.8$) demonstrate almost identical E_{α} values of around $\approx 220 \text{ kJ} \cdot \text{mol}^{-1}$. The effect of branching have been demonstrated by Polli et al.,^[28] who have synthesized linear

and branched poly(carbonate) samples and studied their thermal degradation kinetics by using an isoconversional method. Their results clearly show that branched poly(carbonate) degrades at higher temperatures and its degradation occurs with greater E_α than in linear poly(carbonate). In both systems, E_α increases with the extent of degradation. Chrissafis et al.^[39] have performed a comparative analysis of the thermal degradation of two aliphatic polyesters, poly(ethylene succinate) and poly(butylene succinate). Their study indicates that the use of a longer aliphatic segment (i.e., butylene) results in a less thermally stable structure as seen from lower temperatures of the glass transition and degradation as well as from lower values of E_α for the thermal degradation process. Both polymers have given rise to increasing E_α -dependencies: from ≈ 130 to ≈ 190 kJ·mol⁻¹ for poly(butylene succinate) and from ≈ 140 to ≈ 250 kJ·mol⁻¹ for poly(ethylene succinate). Further studies have shown that the E_α -dependencies for the thermal degradation of poly(ethylene succinate) are practically independent of its \bar{M}_w value varied from 9 820 to 53 700 g·mol⁻¹.

Tang et al.^[40] have compared the thermal degradation kinetics of chitin and chitosan, which is a partially deacetylated derivative of chitin. It has been shown that the presence of the acetylated side groups in chitin contributes to its higher thermal stability as indicated by larger decomposition temperature and greater E_α values (≈ 220 kJ·mol⁻¹). For chitosan, the E_α values increase with the extent of degradation from 160–280 kJ·mol⁻¹, but remain below the E_α values for chitin at $\alpha < 0.6$. However, for the thermal degradation of chitin, Stolarek and Ledakowicz^[41] have found that the E_α values increase from ≈ 20 to ≈ 170 kJ·mol⁻¹ where it plateaus at above $\alpha = 0.2$.

Increasing E_α -dependencies have been reported by Morancho et al.^[42] for the thermal degradation of thermoset coatings that included polyester, epoxy, and hybrid systems. It is noteworthy that the hybrid (epoxy–polyester) material demonstrated an increase from ≈ 110 to ≈ 200 kJ·mol⁻¹ which is intermediate between that observed for epoxy (from ≈ 110 to ≈ 180 kJ·mol⁻¹) and polyester (from ≈ 110 to ≈ 220 kJ·mol⁻¹). However, the effect of additivity does not appear to be typical for degradation of polymer blends. Erceg et al.^[43] have explored an opportunity of increasing the thermal stability of poly(3-hydroxybutyrate) by blending it with more thermally stable aromatic/aliphatic copolyester produced from 1,4-butanediol, terephthalic acid, and adipic acid. The E_α -dependencies obtained for the thermal degradation of individual polymers have not shown a significant variation being around 140 kJ·mol⁻¹ for poly(3-hydroxybutyrate) and 180 kJ·mol⁻¹ for copolyester. The respective E_α values for the blends have been found lower than for the individual polymers showing the smallest values around 90 kJ·mol⁻¹ for a blend of 90:10 poly(3-hydroxybutyrate) to copolyester ratio. The opposite effect has been observed by Vrandecic et al.,^[44] who

studied the thermo-oxidative degradation of poly(vinyl chloride) and chlorinated PE blends of different compositions under nonisothermal conditions. For the interval $\alpha = 0.025$ –0.40, a significant increase in E_α has been found for chlorinated PE (from ≈ 107 to ≈ 150 kJ·mol⁻¹) and a minor increase for poly(vinyl chloride) (from ≈ 117 to ≈ 134 kJ·mol⁻¹). However, for a blend of 80:20 poly(vinyl chloride) to chlorinated PE ratio, an increasing E_α -dependence runs from ≈ 127 to 182 kJ·mol⁻¹. The effect has been reproduced by Vrandecic et al.^[45] by applying isoconversional analysis to the thermo-oxidative degradation of similar blends under nonisothermal conditions. According to Andricic et al.^[46] degradation of methacrylate-butadiene-styrene terpolymer gives rise to the E_α values that increase from ≈ 130 to ≈ 220 kJ·mol⁻¹ in the region $\alpha = 0.025$ –0.40. However, blending it into poly(vinyl chloride) does not increase the E_α -values for the thermo-oxidative degradation of poly(vinyl chloride). In contrast, addition of small amounts (5 or 10 phr) of the terpolymer lower the E_α -dependence by ≈ 20 kJ·mol⁻¹, whereas using greater amounts leads to obtaining the values similar to those observed for neat poly(vinyl chloride).

Vyazovkin et al.^[29] have applied isoconversional analysis to compare the degradation kinetics of a brush-type PS-clay nanocomposite and of virgin PS. For both thermal and thermo-oxidative degradation, the E_α values have been ≈ 50 kJ·mol⁻¹ or more larger than that for the degradation of neat PS that has been correlated with a decrease in the molecular mobility of the polymer chains as well as with potential alteration in the degradation mechanism. The later hypothesis has recently been confirmed spectroscopically for the thermal degradation by Chen et al.^[47] and for the thermo-oxidative degradation by Chen and Vyazovkin.^[48] Bourbigot et al.^[49] have studied the thermal and thermo-oxidative degradation of a PS-clay nanocomposite and observed a similar tendency of increasing the E_α values for the composites. Isoconversional analysis has been employed by Qiu et al.^[50] to examine the thermo-oxidative degradation of nanocomposites of linear low density PE with montmorillonite clay as well as with MgAl and ZnAl layered double hydroxides. For all nanocomposites, the E_α values have been reported to increase significantly compared to the value obtained for the thermo-oxidative degradation of the neat polymer. Kandare et al.^[51] have determined the E_α dependencies for the thermo-oxidative degradation of poly(methyl methacrylate)-layered copper hydroxy methacrylate composites. The reported E_α values are 30–50 kJ·mol⁻¹ larger than those for the thermo-oxidative degradation of virgin poly(methyl methacrylate). Avella et al.^[52] have investigated the effect of CaCO₃ nanoparticles on the thermal and thermo-oxidative degradation of Nylon 6 nanocomposites. They have discovered that for the thermal degradation of virgin Nylon the E_α values increase from ≈ 150 to ≈ 220 kJ·mol⁻¹ whereas for a nanocomposite with 5% of CaCO₃ the E_α values become

smaller while showing an increase from ≈ 110 to $\approx 150 \text{ kJ} \cdot \text{mol}^{-1}$. Nevertheless no effect has been observed for thermo-oxidative degradation whose E_α values increase from ≈ 110 to $\approx 280 \text{ kJ} \cdot \text{mol}^{-1}$ for virgin Nylon and its nanocomposites.

Thermal degradation of polymers plays an important role in the thermal response of many solid propellants and plastic bonded explosives. Sell et al.^[53] have applied isoconversional analysis to study thermal degradation of several propellants that include ammonium perchlorate as an oxidizer and polybutadiene-acrylic acid/acrylonitrile terpolymer, hydroxy terminated poly(butadiene), or bis-azidomethyloxetane/azidomethyl-methylazidocopolymer as polymer binders. They demonstrate that comparison of the E_α -dependencies for degradation of a neat polymer and of a propellant based on this polymer allows one to elucidate the role of the latter. For instance, it has been shown that the early stages of polybutadiene-acrylic acid-acrylonitrile terpolymer propellant are determined by decomposition of ammonium perchlorate, whereas the later stages ($\alpha > 0.25$) are determined by the thermal degradation of the polymer. All studied propellants have demonstrated increasing E_α -dependencies. An increasing E_α -dependence has also been reported by Rocco et al.^[54] for the thermal degradation of hydroxy terminated polybutadiene propellant. Their results and interpretation appear to agree with the earlier results by Sell et al.^[53] for the similar system. Felix et al.^[55] have studied an effect of addition of polymers, Kel F[®] and Viton[®] A, on the kinetics of the thermal degradation of a plastic bonded explosive. It is noteworthy that the standard model-fitting approach has not detected any effect, whereas isoconversional analysis revealed clearly that the addition of these polymers lowers the E_α values from 250 down to $180 \text{ kJ} \cdot \text{mol}^{-1}$ for the early stages of degradation. The result has inspired further mechanistic studies.

Crosslinking

Materials containing epoxy groups are widely used as precursors for producing highly crosslinked polymers. One of the most common epoxy materials is diglycidyl ether of bisphenol A (DGEBA). DGEBA can be copolymerized with a variety of substances such as amines. A reaction of DGEBA with a monoamine yields linear polymer chains. The use of diamines results in crosslinking (curing) of polymer chains. As any other polymerization, curing is a highly exothermic process whose kinetics can be readily measured by using DSC.

The mechanism of the curing process typically involves several steps that can give rise to complex kinetics. For instance, curing of DGEBA with a diamine involves two major steps associated with the two hydrogens of a primary amine. When the first hydrogen reacts with an epoxy group,

a secondary amine is formed as a part of the growing polymer chain. As a result, the second hydrogen becomes less accessible and reactive with respect to another epoxy group. For this reason, the early stages of curing occur predominantly via chain extension due to the primary amine reaction, whereas crosslinking associated with the secondary amine reaction tends to occur in somewhat later stages.

In addition, curing is accompanied by a dramatic physical change of the reaction medium. At the early stages, the reaction medium is a liquid composed of comonomers and just formed oligomers. As the reaction progresses, the molecular weight of the forming polymer increases, and so does viscosity and the glass transition temperature of the medium. The molecular mobility, in turn, decreases. The most dramatic decrease of the mobility is associated with crosslinking of polymer chains. The crosslinked chains lose their ability to move one past another, and the medium turns from flowing liquid to a solid that can be either rubbery or glassy. The formation of the glassy solid (i.e., vitrification) occurs when the glass transition temperature of the medium rises above the actual curing temperature. In either case, a dramatic decrease in the molecular mobility affects the curing kinetics that becomes controlled by diffusion of reactants.

The aforementioned complexity of the curing processes leads to a complex kinetic behavior that can be detected in the form of a variation of the effective activation energy with the cure progress. A comparison of an isoconversional method with other kinetic methods demonstrated^[56] that the former is much more sensitive in detecting curing kinetics complexity. Another important advantage is that isoconversional methods make it possible to obtain consistent values of the activation energy from isothermal and nonisothermal runs.^[56,57] However some care should be exercised^[58] not to introduce a systematic error in isoconversional calculations when isothermal runs are performed below the limiting glass transition temperature, i.e., when the system does not attain complete cure.

The original paper by Vyazovkin and Sbirrazzuoli^[8] on the application of isoconversional kinetics analysis to DSC data on epoxy curing has reported a characteristic decrease in the E_α values at the later stages of the process (from 60 to $40 \text{ kJ} \cdot \text{mol}^{-1}$ at $\alpha > 0.6$). The lower values of E_α are consistent with those for diffusion of small molecules in a liquid–solid medium, and the effect was explained by diffusion control that is associated with vitrification. A correlation of the effect with a decrease in molecular mobility was confirmed experimentally by Sbirrazzuoli and Vyazovkin^[59] by using temperature modulated DSC. Figure 4 provides a recent example of the E_α -dependencies obtained by Sbirrazzuoli et al.^[57] when applying an isoconversional method to curing DGEBA with 1,3-phenylene diamine (*m*-PDA). The two systems analyzed are: a stoichiometric one that has 2 mol of DGEBA per one mole of the amine and a nonstoichiometric one that has a five-fold excess of the

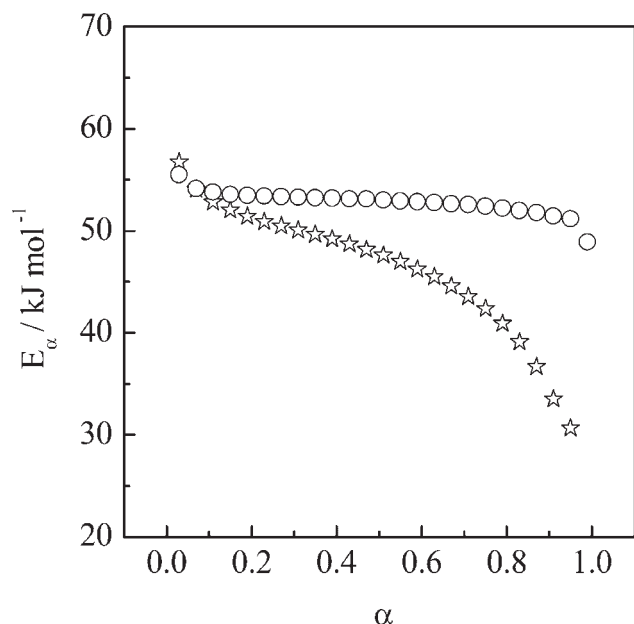


Figure 4. E_α -dependencies obtained for curing the stoichiometric (stars) and nonstoichiometric (circles) epoxy systems.

amine. In the system with an excess of amine, the dominating pathway is chain-extension via the primary amine reaction. For this system, the E_α value remains constant throughout the entire process indicating that its rate determined by a single step. For the stoichiometric system, the initial stages demonstrate the E_α values similar to those found in the nonstoichiometric system. It suggests that in the stoichiometric systems the early stages of curing occur predominately via the primary amine reaction. As the process progresses further the E_α values start to drop quickly to low values characteristic of diffusion. The decrease in the effective activation energy was found to correlate with an increase in the shear modulus as measured by dynamic rheometry as well as with a decrease in the complex heat capacity as measured by temperature modulated DSC.^[57]

Following the original paper by Vyazovkin and Sbirrazzuoli,^[8] a decrease in E_α associated with the diffusion control has been reported in a number of papers. Leroy et al.^[60] have reported that for curing of dicyanate ester resin [polycyclotrimerization of 1,1-bis(4-cyanatophenyl)ethane], the values of E_α decrease quickly from ≈ 70 to ≈ 25 kJ \cdot mol⁻¹ at conversions above 0.8. The effect has been correlated with the onset of diffusion control caused by vitrification as detected by a decrease in the complex heat capacity measured by modulated DSC. Mercado et al.^[61] have studied curing of DGEBA with two phosphorus-containing diamines and with diamino diphenyl methane. In the case of using bis(3-aminophenyl)methyl phosphine oxide as well as with diamino diphenyl methane as a curing agent, the value of E_α showed a significant decrease to ≈ 30 kJ \cdot mol⁻¹ at $\alpha > 0.9$. The decrease has

been found to correlate with vitrification detected by modulated DSC and by dynamic mechanical analysis. He^[62] has also employed modulated DSC to detect vitrification that occurs on curing of epoxy based underfill material. The E_α values for this process are reported to decrease above $\alpha = 0.6$.

He et al.^[21] have studied the curing behavior of phenol-formaldehyde resins and have observed that E_α decreases from ≈ 65 down to 35 kJ \cdot mol⁻¹. A diffusion control kinetic model has been invoked to explain the effect. Castell et al.^[63] have observed E_α to decrease from 70 to 55 kJ \cdot mol⁻¹ at later stages of curing of diglycidyl trimellitimide esters with diaminodiphenylmethane due to diffusion control. Lu et al.^[64] have reported for curing of 4,4'-diglycidylbiphenyl with sulfanilamide that E_α decreases from 80 to 30 kJ \cdot mol⁻¹ at $\alpha > 0.7$. Dobre et al.^[65] have applied isoconversional method to the free radical emulsion polymerization of 3-O-methacryloyl-1,2:5,6-di-O-isopropylidene-D-glucofuranose and reported that in the initial range of conversions ($\alpha < 0.2$) E_α is increasing from ≈ 70 to ≈ 140 kJ \cdot mol⁻¹. The latter value remains practically constant up to $\alpha \approx 0.7$ after which it drops down to ≈ 100 kJ \cdot mol⁻¹. The three regions have been attributed to the respective processes of nucleation of polymer particles, their growth, and polymerization of monomer trapped within polymer particles. Note that the latter process is likely to be diffusion-controlled.

It is noteworthy that in a few papers a significant increase in E_α has been observed. This effect may indicate that in some incompletely cured systems the rate of crosslinking can be limited not by diffusion of small molecules, but by the mobility of longer polymer chains. In the latter case, diffusion encounters a larger energy barrier due to the cooperative nature of the motion. Alternatively, an increase in E_α values for the final stages of curing can be associated with chemical processes that are initiated at higher temperatures. This situation has recently been discussed by Sbirrazzuoli et al.^[66] for the curing process of stoichiometric and off-stoichiometric compositions of DGEBA and 1,3-phenylene diamine that demonstrate a significant increase in E_α at $\alpha > 0.8$. Similar results have been reported by Dimier et al.,^[67] who have studied the kinetics of the formation and curing of polyurethane in a three-component resin, consisting of a prepolymer which contains isocyanate functions, a butane-1,4-diol and poly(adipate glycol). Under nonisothermal conditions, the E_α values are practically constant (≈ 55 kJ \cdot mol⁻¹) below $\alpha \approx 0.7$, above which they increase to ≈ 85 kJ \cdot mol⁻¹. The increase is not observed for isothermal runs performed in the temperature range 40–100 °C. The increase is explained by the formation and reaction of allophanate, which is known to occur above 140 °C, i.e., in the temperature region that is accomplished only in nonisothermal runs.

Mondragon et al.^[68] have conducted kinetic analysis of polycyclotrimerization of bisphenol A dicyanate catalyzed by cobalt(II) acetylacetonate and nonylphenol in air and

argon atmospheres. They report that the value of E_α is practically constant ($\approx 85 \text{ kJ} \cdot \text{mol}^{-1}$ in air and $95 \text{ kJ} \cdot \text{mol}^{-1}$ in argon) but increases quickly to $\approx 200 \text{ kJ} \cdot \text{mol}^{-1}$ at $\alpha > 0.6$. It is suggested that the process becomes diffusion controlled in the respective region of conversions. Kessler and White^[69] have studied the cure kinetics of polydicyclopentadiene prepared by ring-opening metathesis polymerization with three different concentrations of Grubbs' catalyst. By applying an isoconversional method they have found that the E_α values undergo a significant increase (from ≈ 70 to $\approx 150 \text{ kJ} \cdot \text{mol}^{-1}$) at $\alpha > 0.6$. The effect has been explained by a decrease in molecular mobility after the reaction system gels. Ruiz et al.^[70] have synthesized glycidyl derivatives of poly(vinyl alcohol) and studied their curing kinetics with 4-dimethylaminopyridine as a catalyst. The use of an isoconversional method has resulted in obtaining a large initial value of $E_\alpha \approx 110 \text{ kJ} \cdot \text{mol}^{-1}$ that has been assigned to the process of initiation, involving the oxirane ring and the catalyst. Propagation has been predominant at higher extents of conversion and has been characterized by $E_\alpha \approx 60 \text{ kJ} \cdot \text{mol}^{-1}$. At $\alpha > 0.6$, E_α has demonstrated a steady increase explained by the onset of a diffusion control due to an increase in viscosity. Zvetkov^[71] have reported the values of E_α , for curing of DGEBA with *m*-phenylene diamine, demonstrate an increase at $\alpha > 0.8$ that has been assigned to some unidentified side reactions.

The application of isoconversional methods to the curing reactions frequently results in large E_α values at the early stages of the process ($\alpha \rightarrow 0$) that decrease quickly to more typical values of the activation energy. An explanation of this phenomenon has been proposed by Vyazovkin and Sbirrazzuoli,^[72] who demonstrated that in the systems of high viscosity the initial curing stages may be controlled by the temperature dependence of viscosity. The hypothesis has been confirmed by demonstrating that for $\alpha \rightarrow 0$ the E_α values derived from DSC data are similar to the activation energy of viscous flow determined from rheological measurements. Alternatively, the fast decrease in E_α at the early stages is frequently explained by changing the curing process from a noncatalyzed to an autocatalytic mode. Although it makes sense that the activation energy of the noncatalyzed reaction is larger than that of the autocatalytic one, special attention should be paid to the actual values of E_α at $\alpha \rightarrow 0$ as the activation energy of the noncatalyzed reaction should not be unreasonably large. For instance, by using a model reaction of DGEBA with aniline, Swier et al.^[73] have demonstrated that the cure is initiated by the reaction of the primary amine with epoxy-aniline complex that has activation energy of $80 \text{ kJ} \cdot \text{mol}^{-1}$, whereas for above $\approx 2\%$ of epoxy conversion the cure rate is determined by the reaction of the primary and/or secondary amine with the epoxy-hydroxyl complex that has activation energy of $48 \text{ kJ} \cdot \text{mol}^{-1}$.

Vazquez et al.^[23] have observed a decrease in E_α from ≈ 200 to $\approx 90 \text{ kJ} \cdot \text{mol}^{-1}$ for curing of tannin-phenol-

formaldehyde adhesives and explained it by the viscosity control. Zhou et al.^[74,75] have applied isoconversional analysis to curing kinetics of DGEBA with 2-ethyl-4-methylimidazole in the presence of SiC nanoparticles and found that E_α decreases quickly from 90 to $20 \text{ kJ} \cdot \text{mol}^{-1}$ in the α region 0–0.5. The effect is discussed in terms of an autocatalytic mechanism as well as the mechanism of viscosity related diffusion that is supported by rheological measurements.

Castell et al.^[63] have found that E_α decreases from 180 to $80 \text{ kJ} \cdot \text{mol}^{-1}$ for diglycidyl trimellitimide esters with 4-dimethylaminopyridine. The initial high value of E_α was attributed to the attack of the tertiary amine on the oxirane ring. The hydroxyl groups formed during the cure facilitate ring opening, leading to a lower activation energy than that for the nonautocatalyzed reaction at the beginning of the process. For curing of 4,4'-diglycidylbiphenyl with sulfanilamide Lu et al.^[64] have found E_α to decrease from 130 to $80 \text{ kJ} \cdot \text{mol}^{-1}$ at $\alpha < 0.5$ and explained this as the change due to autocatalytic mechanism associated with the formation of hydroxyl groups. For the curing reaction of biphenyl epoxy with a polyphenol compound obtained from phenol and *p*-hydroxybenzaldehyde, Kim et al.^[76] have reported a decreasing E_α -dependence that starts just above $95 \text{ kJ} \cdot \text{mol}^{-1}$ and levels off at just below $80 \text{ kJ} \cdot \text{mol}^{-1}$ when α reaches 0.4. The higher activation energy process has been attributed to the reaction between the phenol hydroxyl and epoxy group. As the ring opening process advances, new hydroxyls are formed that turns the curing process in the autocatalytic regime having smaller activation energy. Gimenez et al.^[77,78] have prepared esterified poly(vinyl alcohol) and two esterified ethylene-vinyl alcohol copolymers in order to study their crosslinking that occurs through double bonds in the presence of dicumyl peroxide. All systems demonstrated very high values ($200\text{--}300 \text{ kJ} \cdot \text{mol}^{-1}$) of E_α at $\alpha \rightarrow 0$ that decreased quickly and tended to level off at $E_\alpha \approx 100\text{--}140 \text{ kJ} \cdot \text{mol}^{-1}$. The high initial values have been assigned to the process of initiation that at greater conversions gives way to propagation characterized by markedly lower values. The latter have been found to be smaller for the esterified alcohols, having greater content of double bonds as measured by NMR.

Mercado et al.^[61] report a decrease in E_α from ≈ 140 to $\approx 80 \text{ kJ} \cdot \text{mol}^{-1}$ for curing of DGEBA with bis(3-amino-phenyl)methyl phosphine oxide. Ramis et al.^[79] have studied the curing of a thermosetting powder coating that consists of branched carboxyl-terminated polyester and triglycidylisocyanurate and reported that in the α region 0–0.5, E_α decreases from ≈ 170 down to $\approx 90 \text{ kJ} \cdot \text{mol}^{-1}$. No detailed discussion of the effect has been provided in either paper.

Of special interest is the effect of the liquid crystalline structures on the kinetics of curing. Vyazovkin et al.^[80] have applied an isoconversional method to probe the kinetics diglycidyl ether of 4,4'-bisphenol with 2,6-diaminopyridine

and found that the initial stages of curing ($\alpha < 0.2$) are accompanied by a sharp decrease in E_α from 60 to 10 $\text{kJ} \cdot \text{mol}^{-1}$ that does not occur in curing of DGEBA with the same amine. By using polarized light microscopy, the decrease in E_α has been correlated with the formation of a liquid crystalline structure. Apparently the low value of E_α is associated with concerted motion of oligomers toward alignment. The effect of a liquid crystalline phase on the curing kinetics has been examined by Ren et al.,^[81] who respectively compared the reaction of phenol novolac with liquid crystalline (diglycidyl ether of 4,4'-dihydroxybiphenol) and with regular (diglycidyl ether of 3,3',5,5'-tetramethyl-4,4'-biphenyl) epoxy. Both systems have demonstrated a slight decrease in E_α below $\alpha \approx 0.6$, above which the E_α value has remained practically constant ($\approx 80 \text{ kJ} \cdot \text{mol}^{-1}$) in the liquid crystalline system, but has decreased markedly in the regular system. The absence of the expected decrease in E_α due to diffusion control has been explained by the formation of the liquid crystalline structure that is capable of decreasing the overall viscosity. Jannesari et al.^[82] have synthesized liquid crystalline oligoester, poly(4,4'-biphenyl sebacate) and studied its kinetics of curing with a mixture (75:25) of diglycidyl terephthalate and triglycidyl trimellitic acid ester. The E_α has been reported to be almost constant ($\approx 95 \text{ kJ} \cdot \text{mol}^{-1}$) in the range of conversions 0.2–0.7. However, below $\alpha = 0.2$ the E_α value is decreasing from ≈ 220 to $\approx 95 \text{ kJ} \cdot \text{mol}^{-1}$, and above $\alpha = 0.7$ it is increasing back to $\approx 220 \text{ kJ} \cdot \text{mol}^{-1}$ with increasing α . Depolarizing transmittance measurements and optical microscopy have been used to correlate the E_α changes with the changes in mesophases. In their study of crosslinking in vinyl-terminated biphenyl and naphthalene side-chain liquid-crystalline polyethers, Callau et al.^[83] have demonstrated that the form of the E_α -dependence changes depending on the state of the reaction medium. For instance curing of the same system below the temperature of isotropization, i.e., in the mesomorphous state, has given rise to practically constant $E_\alpha \approx 130 \text{ kJ} \cdot \text{mol}^{-1}$, whereas in the isotropic state E_α has been increasing from 70 to 160 $\text{kJ} \cdot \text{mol}^{-1}$.

Analysis of the E_α dependence also gives helpful clues about the chemical mechanisms. For an epoxy-anhydride curing reaction catalyzed by tertiary amine, Vyazovkin and Sbirrazzuoli^[84] have found that E_α increases from 20 to 70 $\text{kJ} \cdot \text{mol}^{-1}$ throughout the process. Applying an isoconversional method to the same reaction without anhydride has resulted in obtaining a practically constant value of $E_\alpha \approx 20 \text{ kJ} \cdot \text{mol}^{-1}$ that gives an estimate of an activation energy of initiation (self-curing) so that 70 $\text{kJ} \cdot \text{mol}^{-1}$ provides an estimate of an activation energy for the propagation process. The application of the method to the curing reaction of diglycidyl ether of 4,4'-biphenol with nitro-substituted phenylenediamine has helped Zhang and Vyazovkin^[85,86] to detect a strong effect of the nitro-group position on the amine reactivity that has been observed as a change in the activation energies from 50 to over 100 $\text{kJ} \cdot \text{mol}^{-1}$. Ramis and Salla^[87] have performed a study of

curing orthophthalic-type unsaturated polyester resin with styrene as a crosslinking agent and benzoyl peroxide as an initiator and reported a small decrease in E_α from 120 to 110 $\text{kJ} \cdot \text{mol}^{-1}$ in the α range of 0.05–0.8. Curing of the same resin in the presence of methyl ethyl ketone peroxide as an initiator resulted in obtaining lower average E_α values ($\approx 85 \text{ kJ} \cdot \text{mol}^{-1}$).^[88] The effect of cobalt octoate as a promoter on the kinetics of this reaction system has been examined by Salla et al.^[88] They have found that the E_α values vary little with α , but the average E_α value decreases notably with increasing the concentration of the promoter. Castell et al.^[89] have explored the effect of cationic initiators, lanthanide triflates, on the curing kinetics of DGEBA. Although below $\alpha \approx 0.2$ the systems with different initiators have shown completely different E_α dependencies, in the range of $\alpha = 0.2$ –0.8 the E_α values have been practically invariable. However the average E_α values for this region have decreased from ≈ 90 to $\approx 20 \text{ kJ} \cdot \text{mol}^{-1}$ when changing triflates cations in the following order: Ce, Yb, La, Sm, Dy, Er. Xu et al.^[90] have synthesized naphthalene based epoxies and studied the kinetics of their curing with different curing agents that included dicyandiamide and 4,4'-methylenedianiline. They have found that the E_α dependencies for all systems have rather similar shape with a minor variation in E_α . However, for each of the epoxides a change of the curing agent from dicyandiamide to 4,4'-methylenedianiline have resulted in a decrease in the average E_α values of about 60 $\text{kJ} \cdot \text{mol}^{-1}$. Pielichowski et al.^[91,92] have compared the respective kinetics of curing hexahydrophthalic anhydride with a series of similarly substituted (1,3-oxathiolane-2-thione)s and epoxides. The observed E_α -dependencies for (1,3-oxathiolane-2-thione)s systems have showed a very complex behavior that changed significantly between differently substituted systems. However all these systems have consistently had greater activation energies than similarly substituted epoxy systems.

He and Yan^[25] have examined the effect of moisture on the curing process of polymeric diphenylmethane diisocyanate with wood. They have found that a reaction with oven-dried wood demonstrates a slight increase in E_α -dependence (≈ 60 to 75 $\text{kJ} \cdot \text{mol}^{-1}$), whereas with wet wood the values of E_α remain practically constant. The average E_α value has decreased from 70 to 65%, and to 60% with increasing moisture content from 6 to 12 $\text{kJ} \cdot \text{mol}^{-1}$, and to 50 $\text{kJ} \cdot \text{mol}^{-1}$. The effect has been explained by competition of water molecules with the hydroxyl groups in wood for isocyanate groups of the resin. For a series of water-based phenol-formaldehyde coatings of different solid content, He et al.^[93] have observed E_α dependencies passing through a maximum at $\approx 60 \text{ kJ} \cdot \text{mol}^{-1}$. Although the initial E_α values at $\alpha \rightarrow 0$ have been lower for systems with lower solid content, all systems demonstrated an increase in E_α that has been explained by a competition of the reactions of addition and condensation. This has been followed by a decrease in E_α that is similar in all systems and has been

interpreted as a change to diffusion controlled kinetics. A similar type of the E_α dependencies have been reported by He and Riedl^[94] for curing of several phenol–urea–formaldehyde cocondensed resol resins synthesized by different procedures as well as for curing of phenol–formaldehyde resin and in the presence of different wood substrates.^[95] The similarity of the dependences appears to hint at a similarity of the curing mechanisms that include parallel reactions kinetics turning into diffusion mode at higher conversions ($\alpha > 0.4$). It has been, however, noted that wood may accelerate the addition reactions and retard the reactions of condensation.

Although variations in E_α appear to be most common, some curing processes demonstrate practically constant E_α values in a wide range of conversions. For instance, this occurs in epoxy amine curing with a significant excess of amine. An example of such effect has been given by Sbirrazzuoli et al.^[57] for curing of DGEBA with an excess of 1,3-phenylene diamine and by Zhang and Vyazovkin^[85] for curing of diglycidyl ether of 4,4'-biphenol with an excess of nitro-substituted phenylenediamine. Catalani and Bonicelli^[96] have reported that E_α remains almost invariable ($\approx 60 \text{ kJ} \cdot \text{mol}^{-1}$) in the whole range of conversions for curing of DGEBA with a polyaminophenolic compound derived tetraethylenepentamine. Yao et al.^[97] have reported comparative curing kinetics of DGEBA with hyperbranched poly(3-hydroxyphenyl) phosphate and with 1,3-dihydroxy-benzene. In the region $\alpha = 0.3\text{--}0.7$, both systems demonstrate invariable E_α values that are 67 and $76 \text{ kJ} \cdot \text{mol}^{-1}$ for hyperbranched poly(3-hydroxyphenyl) phosphate and 1,3-dihydroxy-benzene, respectively. The lower values of E_α are linked to strong electron withdrawing properties of the phosphate group. Li and Jarvela^[98] have applied several methods to determine the kinetics of curing of phenolic resole under isothermal conditions. An isoconversional method has yielded an almost constant value of E_α around $40 \text{ kJ} \cdot \text{mol}^{-1}$ that agrees well with the activation energy derived from the temperature dependence of the gel time. On the other hand, fitting the data to the kinetic model of reaction order has not resulted in obtaining a consistent value.

Ramis et al.^[99] have applied an isoconversional method to DSC, FTIR spectroscopy, and thermomechanical analysis data on curing of DGEBA with γ -butyrolactone catalyzed by ytterbium triflate. The E_α data derived from DSC have shown little systematic variation within the range of $65\text{--}75 \text{ kJ} \cdot \text{mol}^{-1}$ that have been consistent with the E_α values obtained from the absorption bands for epoxy ring (915 cm^{-1}), γ -Butyrolactone (1773 cm^{-1}), and spiroorthoester (1736 cm^{-1}). This has confirmed that the DSC measured kinetics represents the assumed chemical reaction. By using an isoconversional method Ramis et al.^[100] have compared the curing kinetics of thermosetting powder coating made of carboxyl-terminated polyester and triglycidylisocyanurate that have been measured by means of

dynamic mechanical thermal analysis, thermal mechanical analysis, and DSC. It has been established that the E_α values derived from the two mechanical methods are generally consistent with each other spanning the range $60\text{--}80 \text{ kJ} \cdot \text{mol}^{-1}$. However, the values have been markedly smaller than those derived from DSC data that give rise to the E_α values above $100 \text{ kJ} \cdot \text{mol}^{-1}$. Similar difference between the E_α values obtained from mechanical and DSC data have been reported by Ramis et al.^[99] for curing of DGEBA with γ -butyrolactone. This apparently suggests that the kinetics of the development of mechanical properties can be significantly different from the heat release kinetics that reflects the progress of the chemical reaction.

Madbouly and Otaigbe^[101] have employed dynamic rheometry to measure the kinetics of the gel formation in waterborne polyurethane dispersions. The application of an isoconversional method to the storage modulus data have resulted in determining the E_α values that remain practically constant ($\approx 120 \text{ kJ} \cdot \text{mol}^{-1}$) throughout the gelation process. The standard procedure of plotting the logarithm of the gel time against the reciprocal temperature has yielded a similar value of the activation energy ($125 \text{ kJ} \cdot \text{mol}^{-1}$).

Glass Transition

Most polymers are either entirely or at least partially amorphous glassy materials. Because the glassy state is a nonequilibrium state it tends to relax toward the equilibrium liquid state. The process is associated with a dramatic intensification of the molecular motion and can be easily detected and measured by a variety of thermal techniques. The rate of the process is characterized by the relaxation time, τ whose temperature dependence can be represented, in the simplest case, by the Arrhenius equation,

$$\tau = A \exp\left(\frac{E}{RT}\right) \quad (16)$$

More generally, the temperature dependence is described by the Williams–Landel–Ferry (WLF) equation

$$\log \frac{\tau}{\tau_0} = \frac{-C_1(T - T_0)}{(C_2 + T - T_0)} \quad (17)$$

where T_0 is a reference temperature, τ_0 is the relaxation time at T_0 , and C_1 and C_2 are constants. The WLF equation is typically applied for relaxation processes above T_g . The Arrhenius equation works well below T_g , but may also serve as a reasonable approximation above T_g if relaxation is measured over a narrow temperature region.

DSC is one of the most common techniques for measuring the glass transition. The process reveals itself as a heat capacity step that shifts to higher temperatures with increasing heating rate. This effect was used by Moynihan et al.^[102] to propose estimating the activation energy of the process as follows

$$E = -R \frac{d \ln |\beta|}{dT^{-1}} \quad (18)$$

Note that there is no single accepted definition of T_g . For instance, Moynihan et al.^[102] used three different definitions that included the extrapolated onset, the inflection point, and the position of a DSC peak obtained on heating.

Obviously, the differently defined values of T_g correspond to different stages of the glass transition process. It has been later reported by Lacey et al.^[103] that the value of E derived from Equation (18), decreases with increasing T_g value. That is, it is larger when T_g is defined as an onset temperature and smaller when it is defined as the midpoint and/or peak temperature. In order to explore this phenomenon in greater detail, Vyazovkin et al.^[104] have proposed to employ an isoconversional method that allows one to follow a variation in E throughout the glass transition. The conversion, α , can be evaluated from DSC data as the normalized heat capacity^[105]

$$C_p^N = \frac{(C_p - C_{p,g})|_T}{(C_{p,l} - C_{p,g})|_T} \equiv \alpha \quad (19)$$

where C_p is the observed heat capacity, and $C_{p,g}$ and $C_{p,l}$ are, respectively, the glassy and liquid heat capacities. Because the values of $C_{p,g}$ and $C_{p,l}$ depend on temperature, they must be extrapolated into the glass transition region. Figure 5 displays the normalized heat capacities obtained from Equation (19) for the glass transition in PS measured at different heating rates. The application of an isoconversional method to the resulting data yields a decreasing dependence of E_α on α (Figure 6).

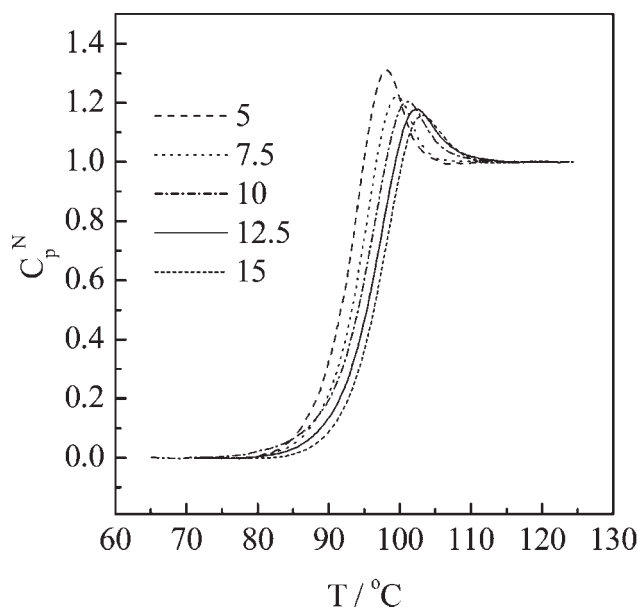


Figure 5. Normalized heat capacities for the glass transition in PS evaluated from DSC runs by Equation (19). The numbers by the lines represent the heating rates ($^{\circ}\text{C} \cdot \text{min}^{-1}$) used in DSC runs.

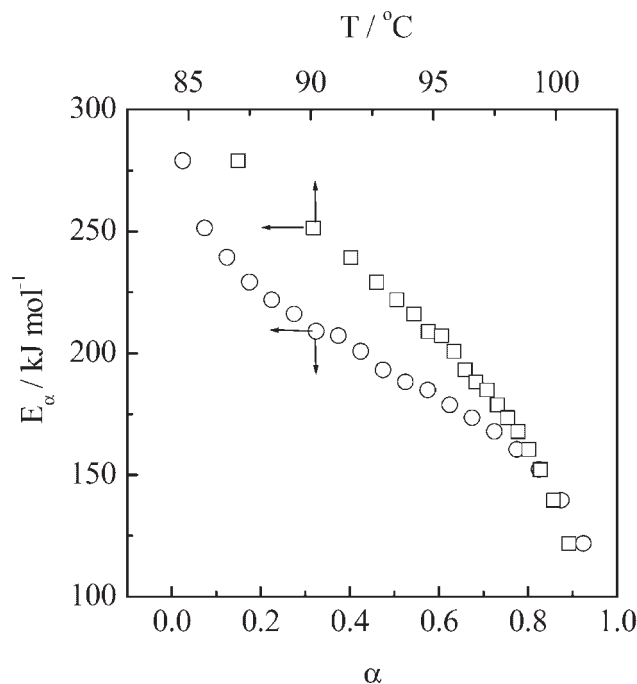


Figure 6. Variation of the effective activation energy with conversion (circles) and temperature (squares). E_α -dependencies derived by applying the advanced isoconversional method [Equation (11)] to the data shown in Figure 5.

Recall that each value of E_α is related to a given α , which, in turn, is associated with a narrow temperature region, ΔT (see Figure 1). This allows one to correlate the E_α values with the temperature by replacing α with an average of the temperatures corresponding to this α at different heating rates. Figure 6 shows the E_α versus T plot obtained after replacing α with the average T_α . A decrease in the effective activation energy with temperature is typical of the glass transition.^[104] The trend is consistent with that predicted by the WLF equation that allows deriving a temperature dependent activation energy as

$$E = R \frac{d \ln \tau}{dT^{-1}} = 2.303R \frac{C_1 C_2 T^2}{(C_2 + T - T_0)^2} \quad (20)$$

Physically, the decrease in E is rationalized in terms of cooperative molecular motion. At early stages of the glass transition, the available free volume is insufficient for individual molecules to move independently so that they engage in a correlated cooperative motion, which is associated with a large energy barrier. The free volume increases with increasing temperature that allows the molecules to relax more independently. As a result, the E value decreases, reflecting a relief in the energetic constraints. A link between the magnitude of E and co-operativity of the molecular motion has been demonstrated by Vyazovkin and Dranca^[106] by comparing the glass transition kinetics of PS and PS-clay nanocomposite. Because the latter has a brush

structure,^[47] the PS chains move in a correlated fashion that results in marked increase in the size of co-operatively rearranging region and, therefore, the activation energy.

It has been demonstrated by Vyazovkin et al.^[104,107] that the variability in E correlates with the so-called dynamic fragility of the glass forming systems. The variability has been the largest for polymers of the largest fragility such as poly(vinyl chloride) and poly(ethylene terephthalate) and the lowest for low fragility systems as poly(butyl methacrylate) and boron oxide.^[107] This result indicates that the kinetic models of the glass transition that assume the activation energy to be constant may have a very limited applicability to polymeric systems as they tend to be the most fragile glassformers.

Melt and Glass Crystallization

Crystallization of polymers can be initiated by cooling of the polymer melt. The process of crystallization is relatively slow and typically results in semi-crystalline materials that contain a substantial fraction of the amorphous (glassy) phase. This fraction can be increased by increasing the rate of cooling. Ultimately, fast cooling results in the formation of an entirely amorphous polymer, i.e., a polymer glass. Polymer glasses can be crystallized by heating above their glass transition temperature. The process is frequently called “cold crystallization”.

Crystallization of polymers releases a significant amount of heat that makes DSC a preferred method for measuring the overall crystallization kinetics. The kinetics are quite commonly parameterized by using the Avrami equation that tends to yield kinetic parameters whose intrinsic value is rather marginal.^[108] A similar problem arises when one employs the popular Kissinger method. Its application to the glass crystallization yields the so-called “activation energy of crystallization”, the meaning of which is very obscure^[109] because the crystallization rate does not obey the simple Arrhenius law. The situation is even worse when the method is applied to the melt crystallization, because, as shown by Vyazovkin,^[110] the Kissinger method is inapplicable to the processes occurring on cooling. As an alternative, the use of an advanced isoconversional method [Equation (11)] and the method of Friedman [Equation (3)] has been recommended.^[110] Vyazovkin and Sbirrazzuoli^[111] have also explained that the resulting values of E have a meaning of the temperature coefficient and have to be negative and increase with the extent of the melt crystallization as shown for poly(ethylene terephthalate) (Figure 7),^[111] poly(ethylene oxide),^[112] and poly(ethylene 2,6-naphthalate).^[109] The recommendation has been followed and tested by a number of workers who discovered the negative and increasing E_{α} -dependencies for poly(ethylene terephthalate), poly(trimethylene terephthalate), and poly(butylene terephthalate),^[113] poly(propylene terephthalate) of different molecular weights,^[114] different

samples of ethylene–acrylic acid copolymers and ethylene–methyl acrylate–acrylic acid terpolymers,^[115] nylon 1212,^[116] poly(trimethylene terephthalate) and poly(butylene terephthalate) and their blends,^[117] PP and its blends with hyperbranched polyurethane acrylate,^[118] poly(propylene terephthalate) and poly(butylene naphthalate),^[119] atactic^[120] and syndiotactic^[121,122] 1,2-polybutadiene, the blends of metallocene PE, low-density PE and linear low-density PE,^[123] PP and its surface-treated SiO₂ nanocomposites,^[124] low-density PE and its copper nanocomposites,^[125] poly[(butylene succinate)-*co*-adipate],^[126] poly[(glycolic acid)-*alt*-(6-aminohexanoic acid)],^[127] poly(trimethylene terephthalate)/poly(ethylene 2,6-naphthalate) blends^[128] as well as for crystallization of a model fat, 1,3-dipalmitoyl-2-oleoylglycerol.^[129] The isoconversional methods appear quite sensitive in detecting various changes in the melt crystallization mechanisms that are detected as irregularities in the E_{α} -dependencies (cf., Figure 7) for poly(ethylene 2,6-naphthalate),^[109] poly(ethylene terephthalate),^[111] poly(ethylene oxide),^[112] syndiotactic 1,2-polybutadiene,^[121] and copper nanocomposites of low-density PE.^[125]

However, the most attractive feature in applying the isoconversional methods to DSC data is that the resulting E_{α} -dependencies can be utilized^[130] for estimating the parameters of the Hoffman–Lauritzen theory.^[131] The theory suggests that the linear growth rate of a polymer crystal, G depends on temperature, T as follows:

$$G = G_0 \exp\left(\frac{-U^*}{R(T - T_{\infty})}\right) \exp\left(\frac{-K_g}{T\Delta T f}\right) \quad (21)$$

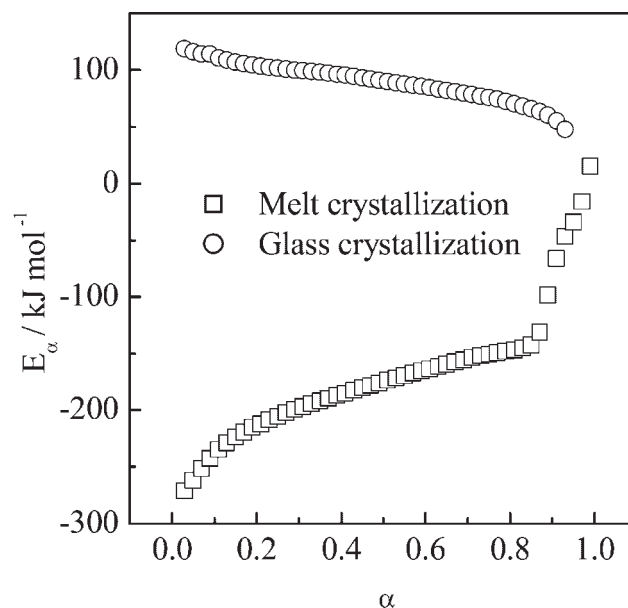


Figure 7. E_{α} -dependencies for the melt and glass crystallization of PET. The melt crystallization dependence has been derived by applying the advanced isoconversional method [Equation (11)] to DSC data obtained on cooling the PET melt. The glass crystallization dependence has been evaluated by applying the same method to DSC data produced on heating the PET glass.

where G_0 is the pre-exponential factor, U^* is the activation energy of the segmental jump, $\Delta T = T_m - T$ is the under-cooling, $f = 2T/(T_m + T)$ is the correction factor, T_∞ is a hypothetical temperature at which viscous flow ceases (usually taken 30 K below the glass transition temperature, T_g). The kinetic parameter K_g has the following form:

$$K_g = \frac{2nb\sigma\sigma_e T_m}{\Delta h_f k_B} \quad (22)$$

where b is the surface nucleus thickness, σ is the lateral surface free energy, σ_e is the fold surface free energy, T_m is the equilibrium melting temperature, Δh_f is the heat of fusion per unit volume of crystal, k_B is the Boltzmann constant, and n takes the value 2 for crystallization regime I and III, and 1 for regime II. The parameter U^* is usually taken as the universal value $1.5 \text{ kcal} \cdot \text{mol}^{-1}$.

Equation (21) has been used by Vyazovkin and Sbirrazzuoli^[130] to derive the temperature dependence of the effective activation energy of the growth rate as follows:

$$E = -R \frac{d \ln G}{dT^{-1}} = U^* \frac{T^2}{(T - T_\infty)^2} + K_g R \frac{T_m^2 - T^2 - T_m T}{(T_m - T)^2 T} \quad (23)$$

Extensive experimental measurements by Toda et al.^[132,133] demonstrate that the logarithmic derivative of the microscopic growth rate (measured under microscope) is equivalent to the logarithmic derivative of the overall crystallization rate (measured by DSC). Therefore, the temperature dependence of the effective activation energy derived from DSC data can be fit to Equation (23) to evaluate the U^* and K_g parameters. As shown in the previous section, the temperature dependence of E is readily determined from the isoconversional dependence of E_α on α .

It should be stressed that according to Equation (23) the effective activation energy should decrease upon increasing the temperature of crystallization throughout both glass and melt crystallization regions.^[109] The regions are separated by the maximum crystallization rate so that the value of E changes its sign from positive to negative on passing from the glass to melt crystallization region (Figure 7). In other words, by performing crystallization in different temperature regions one can obtain practically any value of E that clearly suggests that it does not represent an "energy barrier" to crystallization, although sometimes it is interpreted this way. This value should be referred to as the *effective* activation energy in order to emphasize its difference from the true activation energy, which represents the energy barrier.

Figure 7 displays the E_α dependencies for the melt and glass crystallization of poly(ethylene terephthalate). As discussed above, the glass crystallization data yield positive E_α values that decrease with increasing α (i.e., increasing T). A similar dependence has also been observed by Supaphol and Apiwanthanakorn^[134] for the glass crystallization of

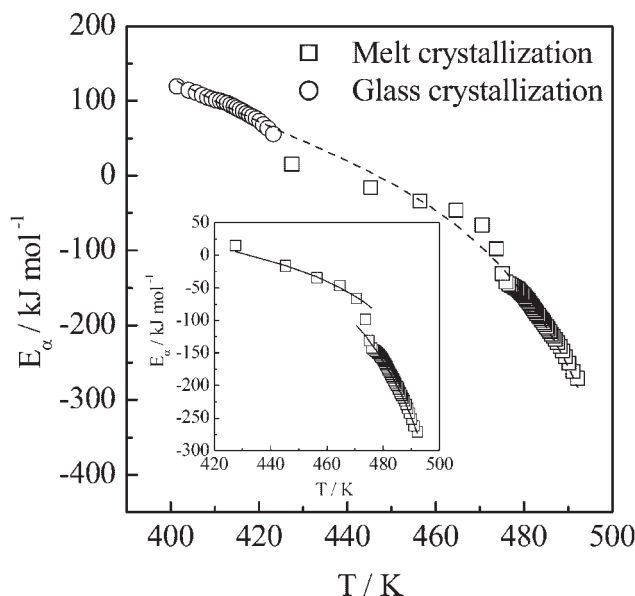


Figure 8. Experimental E on T data for melt (squares) and glass (circles) crystallization of poly(ethylene terephthalate). Inset: solid line represents a fit [Equation (23)] for the melt data. Dashed line has been obtained by fitting combined (melt and glass) crystallization data.

poly(trimethylene terephthalate). It is noteworthy that the decreasing E_α dependencies are also found in crystallization of inorganic glasses^[135] that reflects the kinetic similarity of the crystallization process in the systems of a different nature. For the melt crystallization data, the E_α values are negative, but increasing with increasing α , because T is decreasing. By converting the dependencies of E_α versus α into the dependencies of E_α versus T , one can clearly see (Figure 8) the decrease predicted by Equation (23).

A remarkable feature of the E_α dependence for the melt crystallization is a breakpoint around $\alpha = 0.85$ (Figure 7) or around $T = 475 \text{ K}$ (Figure 8) that indicates a possible change in the crystallization mechanism. By separately fitting the above and below 475 K portions of the E_α versus T dependence to Equation (23), the K_g values of 3.2 and $1.9 \times 10^5 \text{ K}^2$ have been respectively obtained.^[130] The closeness of these values ratio to 2 suggests that the breakpoint is likely due to the change in the crystallization mechanism from regime I to regime II. Vyazovkin et al. have also used this method to derive K_g and U^* values for the melt crystallization of poly(ethylene oxide)^[112] and poly(ethylene 2, 6-naphthalate)^[109] and observed good agreement with the literature values.

The proposed isoconversional approach to evaluating the Hoffman–Lauritzen parameters has been applied successfully by other workers. Achilias et al.^[119] have employed it to determine K_g and U^* for the melt crystallization of poly(propylene terephthalate) and poly(butylene naphthalate), Cai et al.^[122] for syndiotactic 1,2-polybutadiene,

Botines and Puiggali^[127] for poly[(glycolic acid)-*alt*-(6-aminohexanoic acid)], and Run et al.^[128] for poly(trimethylene terephthalate)/poly(ethylene 2,6-naphthalate) blends. In all cases good correspondence with the parameters derived from the classical macroscopic measurements has been reported.

Vyazovkin and Dranca^[109] have recently suggested that Equation (23) can be used to simultaneously fit combined melt and glass crystallization data. Figure 8 shows an example of such fit for poly(ethylene terephthalate) that yields $K_g = 3.6 \times 10^5 \text{ K}^2$ and $U^* = 7.5 \text{ kJ} \cdot \text{mol}^{-1}$. Compared to the individual fit to the melt data, the K_g value has not changed much, whereas the U^* value has increased from $4.3 \text{ kJ} \cdot \text{mol}^{-1}$ getting closer to the universal value $6.3 \text{ kJ} \cdot \text{mol}^{-1}$. Similar effect has been observed^[109] for poly(ethylene 2,6-naphthalate) crystallization. It has been concluded that the use of the combined data sets improves the precision of the fit and accuracy of the U^* value.

Conclusion

Over the past decade the isoconversional kinetic analysis has come a long way, successfully opening up new opportunities in traditional areas of application such as polymer degradations and curing as well as efficiently delving into uncharted application areas such as glass transition and crystallization. The efficacy of the analysis originates from its ability of disclosing and handling the complexity of the respective processes. As a matter of fact, the isoconversional analysis provides a fortunate compromise between the oversimplified but widely used single-step Arrhenius kinetic treatments and the prevalent occurrence of processes whose kinetics are multi-step and/or non-Arrhenius. Although the resulting activation energies tend to be effective or composite values and tend to vary with the extent of conversion and temperature, they can be employed to make reliable kinetic predictions, to get information about complex mechanisms, and, ultimately, to access intrinsic kinetic parameters. It is highly gratifying to see that the isoconversional analysis has been of help and value to a number of polymer researchers. Based on considerable progress and impact made over a decade, it is expected that the isoconversional methodology will continue developing as well as expanding to novel application areas in order to adequately serve the ever-growing needs of the polymer community in the understanding of thermally stimulated processes.

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