Isothermal Gravimetric Analysis of Poly(trimethylene terephthalate)

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ABSTRACT: Poly(trimethylene terephthalate) was investigated by isothermal thermogravimetry in nitrogen at six temperatures, including 304, 309, 314, 319, 324, and 336°C. The isothermal data have been analyzed using both a peak maximum technique and an iso-conversional procedure. Both techniques gave apparent activation energies of 201 and 192 kJ mol^{-1}, respectively, for the isothermal degradation of poly(trimethylene terephthalate) in nitrogen. The decomposition reaction order is calculated to be 1.0. The natural logarithms of the frequency factor based on the peak maximum and the iso-conversional techniques are 36 and 34 min^{-1}, respectively, for poly(trimethylene terephthalate) decomposed isothermally in nitrogen. These isothermal kinetic parameters are in good agreement with those derived by the Kissinger technique on the basis of the dynamic thermogravimetric data reported elsewhere (209 kJ mol^{-1}, 1.0 and 37 min^{-1}). The isothermal decomposition of poly(trimethylene terephthalate) in nitrogen undergoes two processes, a relative fast degradation process in the initial period and a subsequent one with a slower weight-loss rate. The former process may be due to the removal of ester groups, trimethylene groups, and aromatic hydrogen atoms from the chain of poly(trimethylene terethphalate). The latter one may be ascribed to the further pyrolysis of the carbonaceous char. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1600–1608, 2002; DOI 10.1002/app.10476

Key words: poly(trimethylene terephthalate); thermogravimetry; thermostability; degradation kinetics; isothermal gravimetry

INTRODUCTION

Poly(trimethylene terephthalate) (PTT) is a semi-crystalline polymer material currently developed by Shell Chemical Company, DuPont, and others for fiber, film, and engineering thermoplastic applications.[1–3] The outstanding resiliency, relatively low melt temperature, and rapidly crystallizing ability of PTT offer the promise of opportunities for use in carpet, textile, film and packing, engineering thermoplastic and other market places, particularly those dominated by nylons, poly(ethylene terephthalate), and poly(butylene terephthalate).

Thermal stability is of great importance for thermoplastic materials, since they will encounter the elevated temperature at almost every step in the manufacturing, compounding, and processing stages, as well as in services and during recycle. Thermogravimetry (TG) is the most widely used technique to characterize the thermal decomposition of polymer materials. Isothermal TG measures weight change with time at a certain temperature, providing information on material thermal stability and compositional analysis. Since the isothermal condition is a case that more closely simulates the actual fabrication process of thermoplastic materials, the isothermal TG data are of more practical importance than the dynamic ones. In this work, a PTT sample with an intrinsic viscosity of 1.04 dL g^{-1} was investigated by the isothermal thermogravimetry in dynamic nitrogen. The isothermal TG data were analyzed by two kinetic methods, a peak maximum technique and an iso-conversional procedure developed by Flynn.[4] The resulting kinetic parameters were compared with those derived on the basis of nonisothermal TG experiments.[5]

EXPERIMENTAL

Materials

The PTT sample, of which the number-average molar mass ($\bar{M}n$) is 32,000 and the intrinsic viscosity ([η]) is 1.04 dL g^{-1}, was synthesized via transesterification of dimethyl terephthalate with excess 1,3-propanediol.[6] Diactivate catalysts were used. PTT possesses the following molecular structure:
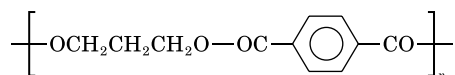
The number-average molar mass, $\bar{M}n$, was determined through end-group analysis by the aid of the ^{1}H nuclear magnetic resonance (^{1}H-NMR) spectrum.[7] The intrinsic viscosity, [η], was measured at a concentration of 0.5 g dL^{-1} in 1,1,2,2-tetrachloroethane/phenol (1:1, w/w) at 20°C. Combining the [η] value with Mark–Houwink parameters (k = 0.00082dL g^{-1} and α = 0.63),[6] the viscosity-average molar mass ($\bar{M}v$) of PTT can be calculated.

Thermogravimetric Measurement

Isothermally programmed TG analyses of PTT were carried out using a Perkin-Elmer TGA 7 module coupled with a Perkin-Elmer 7 series analyzer. Because of a known dependence of kinetic parameters on sample mass,[8] the sample sizes were standardized at 1.0 ± 0.1 mg. All TG experiments were conducted in nitrogen at a fixed flow rate of 60 mL min^{-1}. The isothermal TG temperatures used were 304, 309, 314, 319, 324, and 336°C. The furnace was heated to a selected temperature at a heating rate of higher than 150 K min^{-1}. As the system reached the selected temperature and the value of the sample weight stopped waving, the variation of sample weight with time was registered. The zero point of weight was adjusted at the same isothermal temperature of TG measurement in advance. The PTT sample used in TG analysis was porous powder, which has been dissolved in trifluoroacetic acid and precipitated by ethyl alcohol to remove the impurities, and then dried in a vacuum oven for 24 h.

Data Analysis

It is convenient to define the conversion α as the reaction coordinate. For a weight-loss process, the conversion (the weight loss) α is given by[9,10]

$$\alpha = \frac{w_o - w}{w_o - w_f} \tag{1}$$

where w is the weight of the sample and the subscripts, o and f, respectively, refer to the values at the beginning and the end of the weight-loss event of interest.

The rate of conversion (the rate of weight loss), $d\alpha/dt$, for isothermal TG experiments at a certain temperature T can be expressed by[9–11]

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{2}$$

where $k(T)$ is the rate constant and is defined as a function of temperature only. The function of conversion, $f(\alpha)$, is a characteristic function that depends upon the mechanism of the decomposition process.[11]

The temperature dependence of the rate is often modeled successfully by the Arrhenius equation[9–12]:

$$k(T) = Z \cdot \exp\left(-\frac{E}{R \cdot T}\right) \tag{3}$$

where E is the activation energy; Z, the preexponential factor (or the frequency factor); R, the gas

constant (8.3136 J mol^{-1} K^{-1}); and T, the absolute temperature (K).

Usually for a simple thermal degradation process of polymer, the conversion-dependence function $f(\alpha)$ can be written as

$$f(\alpha) = (1 - \alpha)^n \qquad (4)$$

where n is the order of the degradation reaction.

Substituting eqs. (3) and (4) into eq. (2), and taking logarithm, one obtains[13]

$$Ln\left(\frac{d\alpha}{dt}\right) = Ln(Z) + n \cdot Ln(1 - \alpha) - \frac{E}{R \cdot T} \qquad (5)$$

In the case of isothermal degradation, the temperature is a constant during the decomposition process. Therefore, drawing the line of the logarithm of weight-loss rate $Ln(d\alpha/dt)$ vs the logarithm of the percentage of undegraded polymer $Ln(1-\alpha)$ enables us to determine the degradation order n from the slope of this straight line.

Provided that the mechanism of the decomposition reaction does not undergo a change in the temperature interval investigated, eq. (5) will be valid at the peak maximum for the TG data obtained at several isothermal temperatures[11,13,14]:

$$Ln\left(\frac{d\alpha}{dt}\right)_{max} = Ln(Z) + n \cdot Ln\,(1 - \alpha_{max})$$

$$- \frac{E}{R \cdot T} \qquad (6)$$

where $(d\alpha/dt)_{max}$ is the maximum rate of conversion (the maximum rate of weight loss), and α_{max} is the correspondent conversion. Provided that the α_{max} is independent of temperature, the plot of the logarithm of the maximum weight-loss rate $Ln(d\alpha/dt)_{max}$ as a function of the reciprocals of the isothermal temperatures $1/T$ permits the determination of the activation energy E from the slope[11,15–17] and the frequency factor Z from the intercept of the straight line, while the n value has been known.

The transposition of term in eq. (2) and followed integration give[10]

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^1 k(T) \cdot dt = k(T) \cdot t \qquad (7)$$

where t is the time to reach a certain weight loss α By combining eq. (3) with eq. (7), and taking logarithm, the following expression is derived[10,12,18]:

$$Ln(t) = Ln\left[\frac{g(\alpha)}{Z}\right] + \frac{E}{R \cdot T} \qquad (8)$$

where

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \xrightarrow{f(\alpha) = (1 - \alpha)^n} g(\alpha)$$

$$= \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \begin{cases} - Ln(1 - \alpha) & n = 1 \quad (9) \\ \dfrac{(1 - \alpha)^{n-1} - 1}{n - 1} & n \neq 1 \quad (10) \end{cases}$$

Provided that the decomposition order n keeps constant in the temperature range and the weight-loss interval, E and $Ln(Z)$ can be respectively calculated in terms of the slope and intercept of the linear relationship of $Ln(t)$ vs $1/T$ for various α values.

RESULTS AND DISCUSSION

Thermal Stability

The weight loss of the PTT sample ($\bar{M}n = 3 \times 10^4$) during isothermal heating in nitrogen was measured in a temperature range from 304 to 336°C. The isothermal TG traces obtained are shown in Figure 1. The corresponding time derivatives of weight loss $d\alpha/dt$ are plotted against the heating time and the weight loss α, respectively, in Figures 2 and 3. Since the maximum weight-loss rate $(d\alpha/dt)_{max}$ of PTT degraded isothermally at 336°C (1.77% · min^{-1}) is much higher than those at lower temperatures (0.19 % · min^{-1} ~0.66 % · min^{-1}), the time derivatives of weight loss $d\alpha/dt$ as functions of heating time and weight loss α for PTT degradation by isothermal heating at 336°C are omitted in Figures 2 and 3. The maximum decomposition rate $(d\alpha/dt)_{max}$ and the char yield at 400 min are listed in Table I.

It can be indicated from Figure 1 that the higher the isothermal TG temperature, the faster the sample decomposition, and the lower the char yield at a certain time. Figures 2 and 3 show that the higher the isothermal TG temperature, the higher the value of peak maximum $(d\alpha/dt)_{max}$ and the higher the rate of weight loss $(d\alpha/dt)$ at a
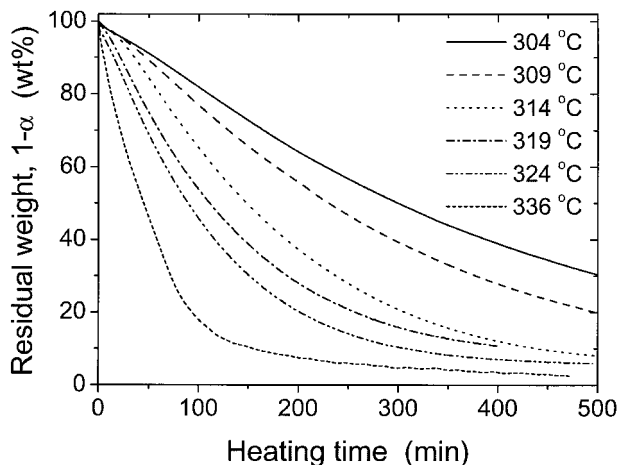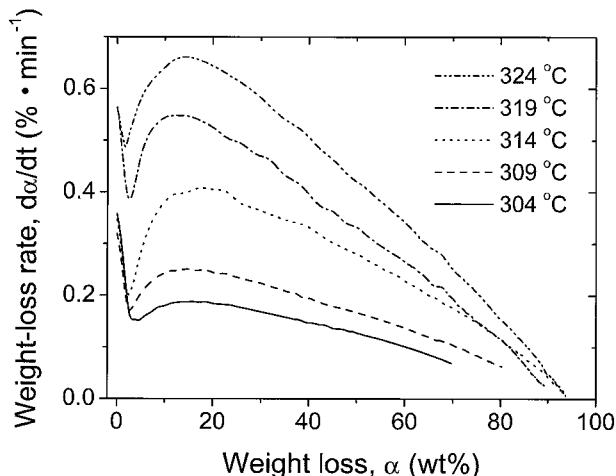
Figure 1 Weight-loss curves of PTT degraded in nitrogen by isothermal heating at the temperatures indicated (sample mass: 1.0 ± 0.1 mg; purge gas rate: 60 mL min^{-1}).

certain weight loss α. Correspondingly, the $(d\alpha/dt)_{max}$ value listed in Table I increases and the char yield at 400 min decreases with increasing isothermal TG temperature. Although the time to reach the maximum weigh-loss rate t_{max} reduces significantly with increasing isothermal temperature (see Fig. 2), the value of α_{max}, which is the weight-loss correspondent to the maximum weight-loss rate, varies only a little with the isothermal temperature (see Fig. 3). There are other reports[11,19–21] where this α_{max} shows a temperature independence.
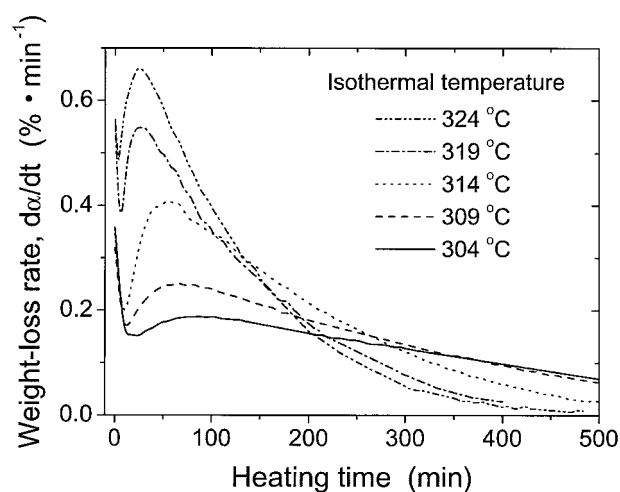
Figure 2 Dependence of weight-loss rate $d\alpha/dt$ on heating time t for PTT degraded isothermally in nitrogen at various temperatures (sample mass: 1.0 ± 0.1 mg; purge gas rate: 60 mL min^{-1}).

Figure 3 Dependence of weight-loss rate $d\alpha/dt$ on weight loss α for PTT degraded in nitrogen by isothermal heating at various temperatures (sample mass: 1.0 ± 0.1 mg; purge gas rate: 60 mL min^{-1}).

For PTT decomposed isothermally at 304 and 309°C, the sample mass loses almost linearly with heating time, and the variation of weight-loss rate $d\alpha/dt$ with weight loss α is less notable than that for PTT degraded at higher isothermal temperature. As the isothermal TG temperature increases from 314 to 336°C, the decomposition of PTT becomes faster within a period from the beginning, whereas after this initial period, subsequent decomposition gets much slower. Generally, the group that contains more oxygen and hydrogen atoms is of poorer thermal stability, since its degradation products are easier to volatilize. Accordingly, the ester groups and the aliphatic groups in PTT chain are easier to degrade thermally than the aromatic ones.[22] The transition point of PTT decomposition from fast to slow is nearby the weight-loss value of 65%, which is equal to the summation of the weight percentages of ester groups, trimethylene groups, and aromatic hydrogen atoms in PTT chains. Therefore, the relatively faster degradation of PTT in the initial period of isothermal heating could be attributed to the removal of the ester groups, trimethylene groups, and aromatic hydrogen atoms. During this initial period, an intermolecular condensation (probably due to the recombination of aromatic radicals formed) occurs to form carbonaceous char.[23] The slower subsequent decomposition of PTT in nitrogen by an isothermal heating may be ascribed to the further pyrolysis of the carbonaceous char.

When PTT undergoes an isothermal degradation in nitrogen, the rate of weight loss $d\alpha/dt$

Table I   The Maximum Rate of Weight Loss and Char Yield for PTT Degraded Isothermally at Various Temperatures, and the Decomposition Order _n_

Isothermal Temperature (°C)	$(d\alpha/dt)_{max}$ (% · min^{-1})	Char Yield at 400 min (wt %)	Degradation Order n	r^a
304	0.19	39.0	0.8	0.9990
309	0.25	28.0	0.9	0.9981
314	0.41	12.2	1.0	0.9983
319	0.55	10.8	1.1	0.9982
324	0.66	7.3	1.1	0.9980
336	1.77	3.6		

[a]Symbol r is the linear correlation coefficient corresponding to Ln($d\alpha/dt$) vs Ln(1-α).

decrease at first. After reaching a minimum $(d\alpha/dt)_{min}$, the weight-loss rate increases with degradation time and weight loss, then approaches a maximum $(d\alpha/dt)_{max}$. It can be known from the data of high-resolution TG[7] that the degradation of PTT starts from the chain ends; therefore the residual catalysts and the decomposition products of chain ends, including 1,3-propanadiol and carbon dioxide, escape from the sample at first. The fraction of residual catalysts and terminal units estimated by ^{1}H NMR for the PTT sample ($\bar{M}n$ = 32,000, [η] = 1.04 dL g^{-1}) is 2% approximately,[7] which approaches to the weight loss corresponding to minimum rate of weight loss $(d\alpha/dt)_{min}$. So the degradation process of PTT before the minimum of weight-loss rate may be attributed to the volatilization of the residual catalysts and the decomposition products of chain ends. With the escape of residual catalysts and the consumption of chain ends, the weight-loss rate decreases. The main chains of PTT start to pyrolysis while the undegraded chain ends and residual catalysts are exhausted.

Kinetics Analysis

The plots of weight-loss rate $d\alpha/dt$ vs the weight loss α (Fig. 3) are similar with one another, which pass through a maximum value between α = 10% to α = 20% before decreasing. According to eq. (5), the reaction order n can be determined by plotting Ln($d\alpha/dt$) against Ln(1-α) as shown in Figure 4. The calculated reaction order n for PTT degraded isothermally at different temperatures and the linear correlation coefficients are summarized in Table I.

Good linear relations were observed in Figure 4. All of the linear correlation coefficients shown in Table I are higher than 0.998. The reaction

order n varies from 0.8 to 1.1 with an average value of 1.0 for the degradation of PTT by isothermal heating at different temperatures.

Peak Maximum Technique

For the purpose of determining activation energy E, the maximum reaction rate $(d\alpha/dt)_{max}$ has been used in a variety of studies.[11–17] This method represents a simple approach to the determination of E from the slope of the plot of Ln($d\alpha/dt$)$_{max}$ against 1/T as described in the aforementioned eq. (6). An application of this technique to the isothermal data of PTT in nitrogen is displayed in Figure 5, which gives a value of 201 ± 8 kJ mol^{-1} for the activation energy.

As shown in Figure 3, the weight loss correspondent to the maximum weight-loss rate, α_{max}, varies from 10 to 20% for PTT degraded isother-
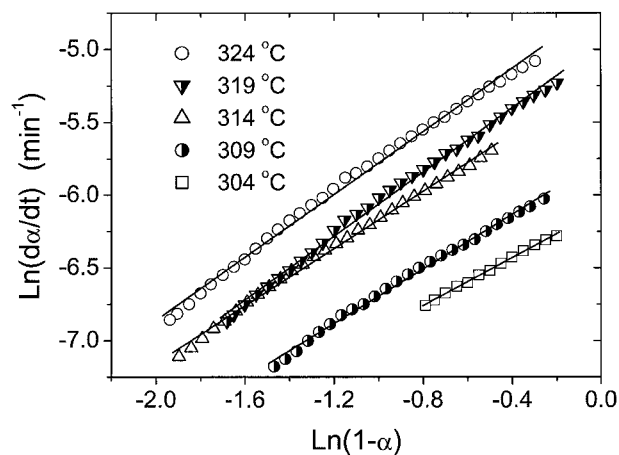
Figure 4 Plots of Ln($d\alpha/dt$) vs Ln(1 − α) for the isothermal degradation of PTT at the indicated temperatures.
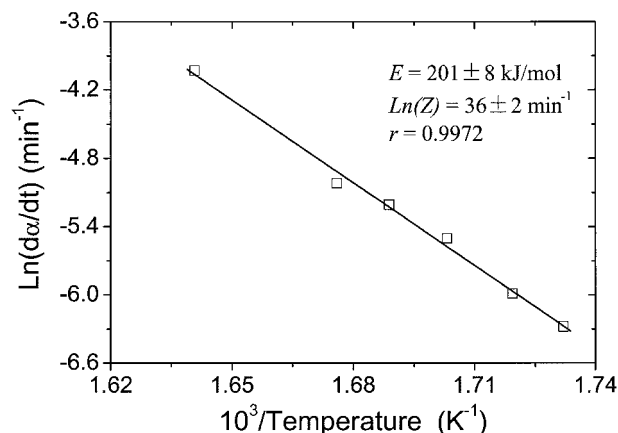
Figure 5 Plot of Ln($d\alpha/dt$)max vs $1/T$ for the isothermal degradation of PTT at several temperatures.

mally in the temperature range from 304 to 324°C. The n value calculated by eq. (5) and Figure 4 changes from 0.8 to 1.1 while the isothermal TG temperature increases from 304 to 324°C. As a result, the value of $n \cdot \mathrm{Ln}(1 - \alpha_{max})$ is estimated to be about -0.2. Therefore, the contribution of $n \cdot \mathrm{Ln}(1 - \alpha_{max})$ to the intercept consisting of $n \cdot \mathrm{Ln}(1 - \alpha_{max})$ and $\mathrm{Ln}(Z)$ in eq. (6) is negligible. Consequently, the logarithm of the frequency factor $\mathrm{Ln}(Z)$ can be determined from the intercept value of the line shown in Figure 5, and 36 ± 2 min^{-1} is obtained.
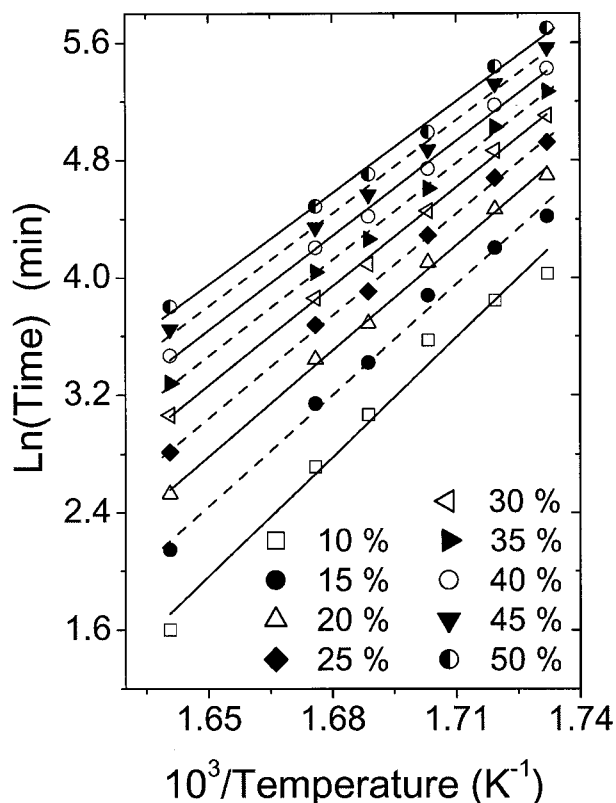
The isothermal kinetic parameters determined at the maximum reaction rate ($E = 201 \pm 8$ kJ $\cdot$ mol^{-1}, $n = 1.0$, $\mathrm{Ln}(Z) = 36 \pm 2$ min^{-1}) are very close to those ($E = 209$ kJ mol^{-1}, $n = 1.0$, $\mathrm{Ln}(Z) = 37$ min^{-1}) obtained on the basis of dynamic TG data,[5] which are also derived at the maximum rate of weight loss (the Kissinger technique) for PTT degradation by heating at a constant rate ranging from 2 to 40 K min^{-1}. This good agreement suggests that a similar kinetic process occurred at the maximum rate points for both the isothermal and the nonisothermal degradation of PTT.

Flynn Technique

If phase-boundary or diffusion-controlled reaction is involved in the decomposition, the maximum reaction rate method for determining the activation energy may result in error.[12,24] The determination of kinetic parameters over a series of weight losses would be more precise. Figure 6 shows the iso-conversional plots for the pyrolysis of PTT in nitrogen in the temperature range of

isothermal TG employed. The average value of the reaction order n calculated from different isothermal TG temperatures is 1.0, thus a substitution of eq. (9) into eq. (8) permits the determination of the preexponential factor Z from the intercept of the lines in Figure 6. The resulting kinetic parameters, i.e., the activation energy E and the frequency factor Z together with their standard errors and the linear correlation coefficient are all summarized in Table II.

It can be seen that most of the data in Figure 6 show good linearity. The linear correlation coefficients listed in Table II are all higher than 0.991. The slope of these straight lines in Figure 6 decreases with increasing weight loss α over the range of 10 ~ 50 %, implying a conversion dependency of activation energy. The dependence of the activation energy E derived from isothermal data upon the weight loss α is shown in Figure 7. The activation energy E^5 calculated by Flynn–Wall technique on the basis of the nonisothermal TG data has also been plotted as a function of the weight loss α in Figure 7.


Figure 6 Flynn diagrams of Ln(time to fixed weight loss) vs $1/T$ calculated from the date of Figure 1 at the indicated weight-loss values.

Table II Kinetic Parameters of the Isothermal Degradation of PTT in Nitrogen (Decomposition Order n = 1.0)

Weight Loss (wt %)	10	15	20	25	30	35	40	45	50	Average
E (kJ·mol⁻¹)	226 (±15)[a]	210 (±9)	200 (±5)	193 (±4)	188 (±3)	183 (±4)	179 (±5)	176 (±6)	173 (±6)	192
$\mathrm{Ln}(Z)$ (min⁻¹)	41 (±3)	37 (±2)	35 (±1)	34 (±1)	33 (±1)	32 (±1)	31 (±1)	31 (±1)	30 (±1)	34
r[b]	0.9913	0.9966	0.9987	0.9993	0.9993	0.9990	0.9985	0.9976	0.9973	0.9975

[a] The data in parentheses are the standard errors.
[b] Symbol r is the linear correlation coefficient corresponding to $\mathrm{Ln}(t)$ vs $1/T$.
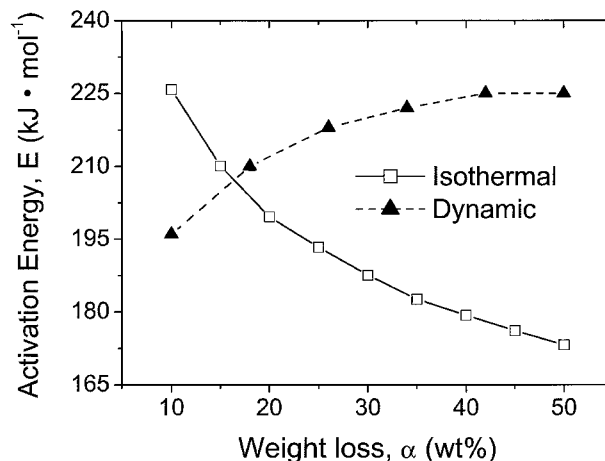
Figure 7 Dependence of activation energy E on weight loss α for PTT degraded isothermally and nonisothermally in nitrogen (sample mass: 1.0 ± 0.1 mg; isothermal temperature range: 304–336°C; purge gas rate: 60 mL min⁻¹; nonisothermal heating rate range: 2–40 K min⁻¹; purge gas rate: 40 mL min⁻¹).

In the case of dynamic heating, the higher the weight loss, the larger the activation energy is. In the case of isothermal heating, the activation energy decreases with increasing weight loss. Day and co-workers[12] found that the activation energy reduces with increasing weight loss for poly(aryl-ether-ether-ketone) degraded both dynamically and isothermally in nitrogen. Generally, the variation of activation energy with the weight loss reveals the change of thermal degradation mechanism, i.e., transformation from the diffusion-controlled kinetics into the decomposition-controlled kinetics, or vice versa.[12,13]

The variation of weight-loss rate ($d\alpha/dt$) with weight loss α for PTT decomposition in nitrogen by dynamic heating in the heating rate range from 2 to 40 K min⁻¹ is displayed in Figure 8. As the weight loss α increases from 10 to 50%, the ($d\alpha/dt$) value decreases in the case of isothermal heating but increases in the case of dynamic heating. Additionally, the ($d\alpha/dt$) value is quite larger for PTT degradation under the nonisothermal condition. An excessively large rate of weight loss may lead to the change of degradation mechanism from decomposition-controlled kinetics to the diffusion-controlled kinetics, resulting in higher value of activation energy. In the initial period of the isothermal degradation of PTT, the sample is subjected to an elevated temperature suddenly; thus the decomposition immediately takes place in both the surface and the inside of the PTT
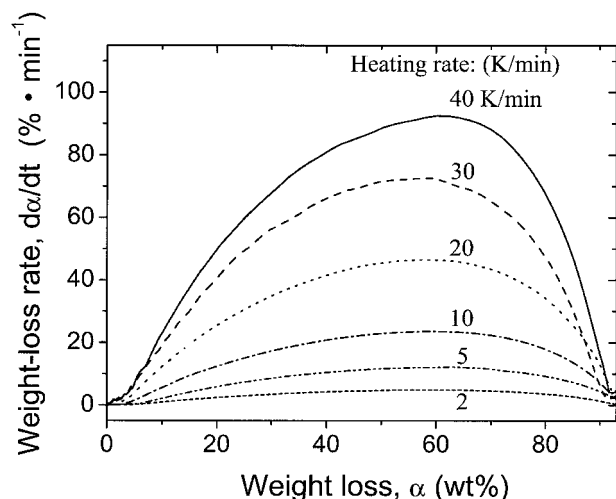
Figure 8 Dependence of weight-loss rate $d\alpha/dt$ on weight loss α for PTT degraded dynamically in nitrogen at various heating rates (sample mass: 1.0 ± 0.1 mg; purge gas rate: 40 mL min^{-1}).

sample, which probably suggests a diffusion-controlled kinetics. Therefore, higher value of apparent activation energy E is observed at the beginning in the case of the isothermal degradation of PTT.

The average value of activation energy E obtained from different weight losses (10∼ 50%) is 192 kJ mol^{-1} for isothermal TG measurement and 216 kJ mol^{-1} for nonisothermal TG measurement. It should be noted that the dynamic TG experiments were conducted in nitrogen at a flowing rate of 40 mL min^{-1}, which is lower than 60 mL min^{-1} used in isothermal TG experiments. A faster rate of purge may lead to lower value of activation energy, since fast rate of purge gas is helpful for the volatilization of decomposed products.

The average values of kinetic parameters calculated on the basis of different weight losses (E = 192 kJ mol^{-1}, Ln(Z) = 34 min^{-1}) for PTT degraded isothermally in nitrogen agree well with those derived at the maximum rate of weight loss aforementioned (E = 201 kJ mol^{-1}, Ln(Z) = 36 min^{-1}). Therefore, the kinetic parameters derived from the iso-conversion method and peak maximum method are reliable.

At the processing temperature, the initial step of thermal degradation of poly(alkylene terephthalate) is a random scission at ester linkages of chains, resulting in the formation of unsaturated ester groups and carboxyl end-groups.[25–30] The unsaturated ester groups are unstable, which

may further result in acetaldehyde (or formaldehyde)[25–27] and tetrahydrofuran (or butadiene)[28–30] respectively for polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). Many researchers have studied the thermal degradation kinetics of PET and PBT by analyzing the carboxyl group content. For example, Zimmermann[25,26] gave the activation energy values of 170 and 162 kJ/mol respectively for the isothermal degradation of PET (280 ∼ 300°C) and PBT (250 ∼ 280°C) in nitrogen flow. When the isothermal degradation temperature increases, the carboxyl groups are no longer stable, and carbon monoxide and carbon dioxide replace acetaldehyde and formaldehyde as the main volatile degradation products of PET.[27] Lum[30] investigated the thermal decomposition of PBT *in vacuo* under dynamic heating (3 ∼ 10 K/min) and presented activation energies for each volatile degradation products. The outcomes are E = 117 kJ/mol for tetrehydrofuran (235 ∼ 360°C), E = 209 kJ/mol for 1,3-butadiene (275 ∼ 360°C), E = 221 kJ/mol for carbon dioxide (250 ∼ 360°C) and E = 252 kJ/mol for carbon monoxide (325 ∼ 360°C).[30] In this work, the isothermal degradation temperatures are about 80°C higher than the processing temperature of PTT, and an activation energy value of 192 kJ/mol is obtained, which is relatively higher than those for PET and PBT derived from the increase of carboxyl groups. Both the higher activation energy and the higher isothermal degradation temperature suggest that the isothermal decomposition of PTT (304 ∼336 °C) consists of not only the random scission at ester linkages, but also the further decomposition of unsaturated ester groups and carboxyl end-groups evolving carbon oxides and aliphatic hydrocarbons.

CONCLUSIONS

Poly(trimethylene terephthalate) has been carefully investigated by thermogravimetry in nitrogen under the isothermal condition. Six isothermal temperatures, including 304, 309, 314, 319C, 324, and 336°C, were used. The higher the isothermal TG temperature, the faster the sample decomposes, the lower the char yield, and the shorter the time to reach the maximum weight-loss rate. PTT loses weight almost linearly with heating time at 304 and 309°C. At higher temperatures, PTT decomposes more rapidly within the initial period, whereas after this initial period,

subsequent decomposition gets much slower. The relative fast decomposition of PTT in the initial period under isothermal condition may be ascribed to the removal of the ester groups, trimethylene groups, and aromatic hydrogen atoms. The subsequent slow degradation may be due to the further pyrolysis of carbonaceous char, which forms during the former decomposition process.

The isothermal data have been analyzed using both a peak maximum technique and an iso-conversional procedure developed by Flynn. These two techniques gave quite accordant results. The degradation order n is determined at each isothermal temperature, which varies in the range from 0.8 to 1.1 with an average value of 1.0. The activation energy E and the logarithm of the frequency factor $Ln(Z)$ are 201 kJ mol^{-1} and 36 min^{-1}, respectively, based on the peak maximum method, and are 192 kJ mol^{-1} and 34 min^{-1}, respectively, based on the iso-conversional technique in the weight-loss range of $10 \sim 50\%$. These isothermal kinetic parameters are in good agreement with those calculated by the Kissinger technique on the basis of the dynamic thermogravimetric data ($E = 209$ kJ mol^{-1}, $n = 1.0$ and $Ln(Z) = 37$ min^{-1}).

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