Kinetic Study of the Thermal Decomposition of (2-Phenyl-1,3-dioxolane-4-yl) Methyl Methacrylate and 2-Hydroxyethyl Methacrylate Copolymers

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ABSTRACT: The kinetics of nonisothermal decomposition of (2-phenyl-1,3-dioxolane-4-yl) methyl methacrylate (PDMMA), 2-hydroxyethyl methacrylate (HEMA), and vinyl-pyrrolidone (VPy) copolymers were investigated by thermogravimetry (TG) and differential thermal analysis (DTA). The data indicated that the major weight loss occurs in the range of 270 to 450°C. The decomposition characteristics showed essentially two regimes and varied depending on the temperature and the copolymer composition. The apparent kinetic parameters of the decompositions were estimated from both TG and DTA data by using the alternative calculation methods. The results suggest that the weight loss rates may be represented, depending on the type of sample, by a reaction model of overall order 1.0 to 1.6, with an activation energy of approximately 65–95 kJ mol^{-1}. The DTA data estimated considerably higher values for the overall activation energies, around 198–240 kJ mol^{-1}. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1500–1508, 2005

Key words: thermogravimetric analysis (TGA); decomposition; kinetics (polym.); methacrylate copolymers; activation energy

INTRODUCTION

Thermal analyses provide a rapid quantitative method to examine the thermal decomposition reactions of solid materials under oxidative or nonoxidative conditions. The analyses are carried out, in general, under either isothermal or nonisothermal conditions. If a polymer is heated in an inert atmosphere, it may undergo chain scission (depolymerization) and chain stripping. The depolymerization may not be entirely to the monomer stage and may produce both volatile products and carbonaceous solid residue.[1–7] Depending on conditions, the decomposition reactions may be endothermic or exothermic and these reactions are accompanied with appreciable weight loss and/or temperature changes. The reactions resulting in solid products do not affect the weight loss, and thus could not be registered with thermogravimetry (TG). Therefore, it is more appropriate to use differential thermal analysis (DTA) or differential scanning calorimetry (DSC) to trace such reactions.[8–12] Both TG and DTA data enable estimation of the effective kinetic parameters for the overall decomposition reactions. The global kinetic data provide a clue to the mechanistic steps of the overall process, and thus there is an increasing interest in the literature concerning the global kinetics of polymer decomposition.[4,7,13–18] Holland and Hay[19] discussed in detail the limitations of nonisothermal kinetics in the study of polymer degradation. Howell[5] investigated the degradation mechanisms of polymers and utility of variable temperature techniques in the determination of kinetic parameters.

A number of reports of other studies discuss in detail several methods for analyzing the thermogravimetric data to determine the kinetic rate parameters. Several methods are available for the evaluation of TG data for kinetic purposes but, generally, two main approaches have been used: integral methods, such as the methods of Coats–Redfern, Reich–Stivala, or Ozawa et al.; and differential methods, such as the methods of Freeman–Caroll, Newkirk, Friedman, and others. Some of these methods require a prior knowledge of the reaction order but some of them assume a single first-order reaction. In fact, several data in the literature suggest that the multiple parallel first-order reactions or the combined parallel and consecutive reactions model, with a statistical distribution of activation energies, take place during the decomposition process.[5–9,16,19–22]

Synthetic polymers, such as (2-phenyl-1,3-dioxolane-4-yl) methyl methacrylate (PDMMA) and poly(2-hydroxyethyl methacrylate) (PHEMA), have poten-

tially numerous applications, especially in the bio-medical field and in membrane technology. The objective of this study was to investigate the thermal degradation of PDMMA-*co*-HEMA and PDMMA-*co*-vinyl-pyrrolidone (VPy) copolymers by TG and DTA techniques. Based on these data, a preliminary global kinetic analysis was carried out with an assumption of an *n*th-order reaction model for the overall process. Basically, TG and DTA data were used for the estimation of the effective kinetic parameters. The DSC analyses were used for a brief discussion of the characteristics of the copolymers used.

EXPERIMENTAL

Material

The homopolymers of HEMA and PDMMA, and the copolymers of PDMMA-*co*-HEMA and PDMMA-*co*-VPy were synthesized in the laboratory. HEMA and VPy monomers were supplied as commercial materials, VPy was used as received, but HEMA was purified before use in the syntheses. The monomer of PDMMA was synthesized in two stages. In the first stage, 2-phenyl-5-hydroxy methyl-1,3-dioxolane was synthesized. In the second stage, the dioxolane was reacted with methacroyl chloride to obtain PDMMA monomer. In the preparation of a homopolymer, the monomer and $\alpha\alpha'$-azoisobutyronitrile (AIBN) (0.2% of the monomer weight) in ethanol were mixed in a polymerization tube. The tube was purged with argon, sealed, and inserted into a water bath, and the mixture was then allowed to react for about 1 h at 60°C. The tube was then opened and poured into excess hexane to precipitate the polymer. The dissolution in ethanol and the precipitation in hexane were repeated two times, after which the product was dried under vacuum at 60°C for 24 h. A similar procedure was applied in the preparation of the copolymers. Appropriate amounts of the monomers and AIBN were dissolved in ethanol and reacted for the copolymerization as described above. The copolymers were precipitated in excess ether. The monomers of

PDMMA-co-HEMA   PDMMA-co-VPy
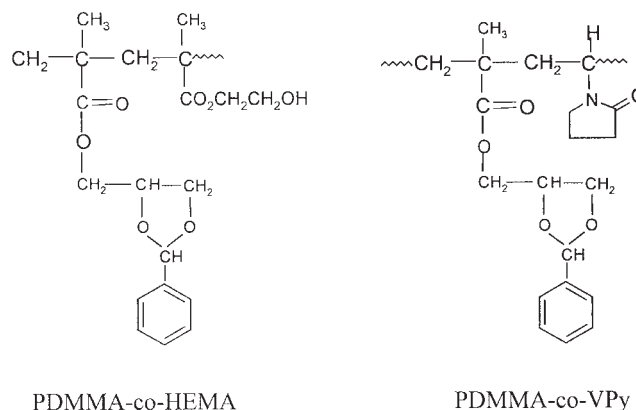
Figure 1 Structural characteristics of the PDMMA copolymers.

PDMMA, HEMA, or VPy were used in various proportions to prepare copolymers with different compositions. The real monomer ratios in the synthesized copolymers were determined by ^{1}H-NMR and the results are given in Table I. The structural characteristics of the PDMMA copolymers are given in Figure 1 and the synthesis and characterization of the polymers are detailed in a previous report.[23]

Thermal analyses

Thermal analyses were carried out with the powdered samples, having a size of about 10 mg, under dynamic nitrogen atmosphere. A Shimadzu TGA-50 instrument (Shimadzu, Kyoto, Japan) was used for the TG and DTA with a heating rate of 10°C/min. Selected samples were heated at a rate of 20°C/min to determine the effect of the heating rate on weight loss. The heating was continued from room temperature to 500°C in TG and to 800°C in DTA. A Shimadzu DSC-50 instrument was used for the DSC analyses, at a heating rate of 10°C/min, from room temperature to 300°C. In the DTA and DSC analyses, α-alumina was used as the reference material. Some analyses were repeated under identical conditions to verify the reproducibility of the results.

RESULTS AND DISCUSSION

DSC analysis

Use of DSC analysis enables one to follow the heat changes arising from both physical (such as melting) and chemical (such as decomposition) processes. Herein, DSC analyses are cited to give the glass-transition temperatures (T_g) of the polymers. The analyses indicated that T_g values vary, depending on the copolymer composition in the range of 105–135°C, as given in Table I. The analyses suggested that the polymers

TABLE I
Monomer Ratios in the Synthesized Copolymers and Their Glass-Transition Temperatures (T_g) by DSC Analysis

Sample	PDMMA	HEMA	VPy	T_g (°C)
Copolymer-I	15.2	84.8	—	105
Copolymer-II	23.5	76.5	—	n/a
Copolymer-III	37.2	62.8	—	109
Copolymer-IV	63.2	36.8	—	118
Copolymer-V	68.7	31.3	—	n/a[a]
Copolymer-VI	7.6	—	92.4	135

[a] n/a, not analyzed by DSC.

are thermally stable and no thermal degradation occurs at temperatures below 250°C.

Differential thermal analysis (DTA)

Several changes that cannot be recorded by TG may be traced by DTA. For example, crystalline transition or melting is not observed by TG but an endothermic peak is observed in the DTA. The chemical decomposition reactions are also not observed by TG unless volatile products are formed.[9–12,15]

   Some representative DTA traces (normalized to unit weight) of the selected copolymers are shown in Figure 2. One observes from the figure that the PDMMA-co-HEMA copolymer shows two exothermic peaks in the relatively high temperature range of 400–500°C. The other PDMMA-co-HEMA copolymers also showed similar DTA traces. These exothermic peaks are relatively sharp, suggesting that the decomposition reactions are relatively fast. An ample free-radical formation, attributed to the degradation, is expected at these temperatures, and most of the crosslinking and free-radical reactions are exothermic.[8,9,12] In fact, some of the decomposition reactions may be endothermic, although the endothermic reactions are masked by the exothermic reactions. The DTA data suggest that the thermal degradation of the copolymers proceed in two successive stages and the degradation of PDMMA-co-VPy copolymer starts at temperatures lower than that of the PDMMA-co-HEMA copolymers.

Thermogravimetric (TG) analysis

TG may be used to trace the weight changes arising from both physical (such as evaporation) or chemical
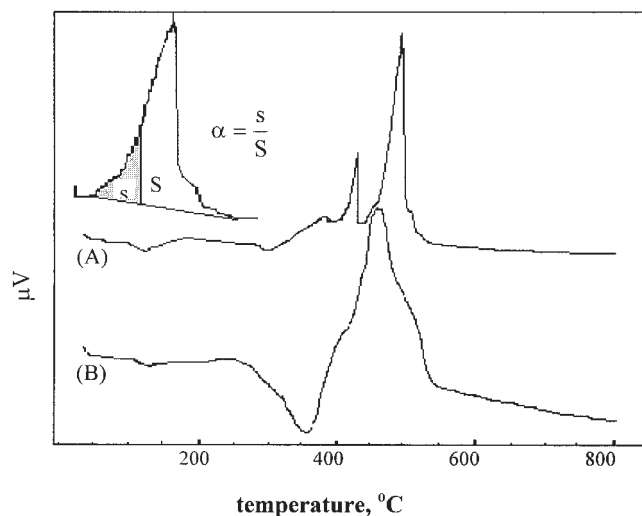
Figure 2   DTA curves of the selected copolymers in nitrogen atmosphere (heating rate 10°C/min): (A) copolymer-I; (B) copolymer-VI.
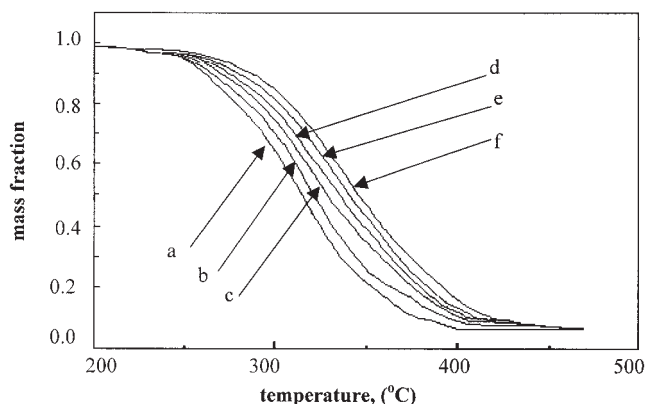
Figure 3   TG curves of the copolymers and homopolymers in nitrogen atmosphere (heating rate 10°C/min): (a) PDMMA homopolymer; (b) copolymer-V; (c) copolymer-III; (d) copolymer-I; (e) copolymer-VI; (f) HEMA homopolymer.

(such as decomposition or oxidation) processes. The crosslink density in the polymer and the diffusion rates of the decomposition products outside of the sample also affect the weight loss characteristics.[5,7,15–18] Nonisothermal weight loss traces of some homopolymers and copolymers of this study are shown in Figure 3. The figure indicates the weight loss below about 260°C is minor, generally less than 10%, and may be attributed to the loss of a small amount of solvent retained in the polymer matrix. The onset of the main weight loss may be used as an indicator for thermal stability. In this respect, Figure 3 suggests that HEMA homopolymer is relatively more stable than either PDMMA homopolymer or PDMMA-co-HEMA copolymers.

   During the thermal degradation of the polymers, a random bond scission may form macroradicals and these radicals may form various types of products, depending on the functional groups in the structure. Several types of degradation reactions are possible, but the first step is expected to be main chain scission initiated by depolymerization. An appreciable amount of dimers is also formed, especially in the case of radical depolymerization. The monomers or dimers formed in this way may also undergo thermal degradation.[15,17,18] The types of these reactions and the formed products affect the weight loss rates. The temperatures corresponding to 20, 40, 50, 70, and 90% weight loss [$T_{(20\%)}$, $T_{(40\%)}$, $T_{(50\%)}$, $T_{(70\%)}$, and $T_{(90\%)}$, respectively] are compared in Table II. The temperatures of the constant weights (T_{max}) are also indicated in the table. An appreciable amount of solid residue ($\sim$ 6.0–8.5%) was observed in almost all cases. This residue may be essentially a carbonaceous material or highly crosslinked polymeric material. The weight loss almost ceases at about 400°C for PDMMA homopolymer and around 450°C for the other cases.

   Plots of the derivative weight loss data [by differential thermogravimetry (DTG)] allow one to compare

Sample	Percentage weight loss at temperatures (°C) of					T_{max} [a] (°C)	Percentage residue (%)
	20	40	50	70	90		
HEMA[b]	310	332	350	375	430	465	8.5
Copolymer-I	297	325	343	368	420	460	7.5
Copolymer-III	285	318	334	352	408	455	7.0
Copolymer-V	278	310	330	345	390	445	6.5
Copolymer-VI	290	325	338	360	416	440	6.5
PDMMA[b]	270	300	320	335	375	410	6.0

[a] T_{max}, temperature of the constant weight.
[b] Homopolymer.

the temperatures of maximum rate of the weight losses. The DTG curves for some of the samples are demonstrated in Figure 4 and the temperatures of the peak maxima are given in Table III. From the figure one can observe that the homopolymers show essentially one characteristic peak maximum, but they are not sharp, but rather relatively wider and flattened. This suggests that some decomposition reactions are fast over a narrow temperature interval. The DTG plots also show that there are generally two distinct maxima for the copolymers, which indicates that at least two main routes exist during the thermal degradation of the copolymers and these maximum temperatures change only negligibly with the composition of the copolymers.

A kinetic approach based on TG data

A TG curve involving a single weight loss may be represented by a single kinetic equation. In general, the bond scission proceeds by first-order kinetics, although if the depolymerization is initiated at chain ends and the zip length of the depropagation reaction is much shorter than the polymeric main length, then a large portion of the reaction follows zero-order kinetics. If the zip length is much larger than polymer chain length, then the reaction follows first-order kinetics. Radical combination or termination reactions are second order.[1] In fact, because of the large number of interacting processes, it is difficult to develop a realistic mechanistic kinetic model, and so generally only pseudokinetic models are developed to estimate the kinetic parameters.

The kinetic analysis of nonisothermal degradation data is based essentially on the following three equations[7,8–13,20–22]:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

$$k = A \exp\left(\frac{-E}{RT}\right) \tag{2}$$

$$T = T_0 + qt \tag{3}$$

where α is the fraction decomposed, $f(\alpha)$ is a function of the degree of the reaction, t is time, k is the rate constant, T is absolute temperature, E is the activation energy, A is the preexponential factor, R is the gas
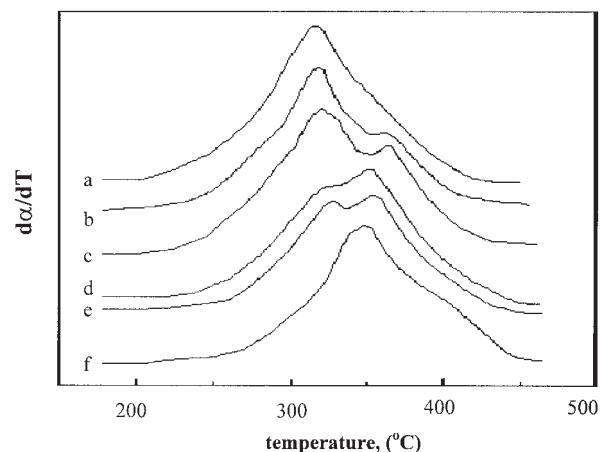

Figure 4 Derivative TG curves of the homopolymers and copolymers in nitrogen atmosphere (see Fig. 3 for the nomenclature).

TABLE III
Characteristic Temperatures in the Derivative Weight Loss (DTG) Data[a]

Sample	T_0 (°C)	T_{max1} (°C)	T_{max2} (°C)
PDMMA[b]	260	325	—
Copolymer-I	270	325	355
Copolymer-III	265	325	360
Copolymer-V	260	325	375
Copolymer-VI	260	330	360
HEMA[b]	280	355	—

[a] T_0, starting temperature for the thermal decomposition; T_{max1}, T_{max2}, the maximum weight loss rate temperatures.
[b] Homopolymer.
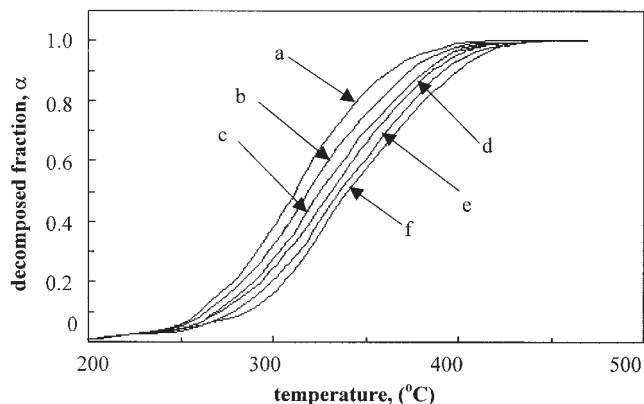
Figure 5 Modified TG data for the homopolymers and copolymers (see Fig. 3 for the nomenclature).

constant, q is the heating rate, and T_0 is the starting temperature. By combining eqs. (1)–(3), the decomposition rate may be expressed as

$$\frac{d\alpha}{dT} = f(\alpha)\frac{A}{q}\exp\left(\frac{-E}{RT}\right) \qquad (4)$$

Various definitions have been used in the literature for α; one of the most widely used is defined as[6,11,12,13]

$$\alpha = \frac{1 - f_i}{1 - f_\infty} \qquad (5)$$

where f_i and f_∞ are the instantaneous and the final values of the weight fractions, respectively. A graph of α versus temperature gives a modified TG plot, which can be used for kinetic analysis. The modified TG plots or the estimated α-values for the polymers are represented in Figure 5.

Several approximations are given in the literature to represent the function of $f(\alpha)$, although in general it is defined as $f(\alpha) = (1 - \alpha)^n$ (n is overall reaction order) with singular E and A values.[7,10,11,13,14,19] The same definition is used in this study. Inserting this definition into eq. (4) gives

$$\frac{d\alpha}{dT} = \frac{A}{q}\exp\left(-\frac{E}{RT}\right)(1 - \alpha)^n \qquad (6)$$

Equation (6) is the basic expression to estimate the kinetic parameters on the basis of TG data. Various approaches are given in the literature to estimate the global kinetic parameters from this equation.[1,7,10,13,20–22] Some of those widely used approaches are applied in this study to compare the result for the thermal decomposition of the polymers. The preliminary calculations indicated that the convergence was poor or the correlation coefficients of the approximated straight lines were low when the TG

data of whole temperature region were processed together. Therefore, it seemed to be more convenient to carry out the main kinetic analyses for the temperature ranges corresponding to the degradation range of approximately $0.15 < \alpha < 0.95$. A similar approximation is also used by other investigators.[1] Under these limitations, four different approaches were used in this study to determine the apparent kinetic parameters through eq. (6).

In the first approach, the Coats–Redfern method was used. By integrating eq. (6)—by expanding it into series and then ignoring the higher-order terms—they obtained, for the case of $n \neq 1$, the following equation[12,19]:

$$\frac{1 - (1 - \alpha)^{1-n}}{(1 - n)T^2} = \frac{AR}{qE}\left(1 - \frac{2RT}{E}\right)\exp\left(\frac{-E}{RT}\right) \qquad (7)$$

Equation (7) may be further simplified if it is assumed that $2RT \ll E$. Based on this assumption, eq. (7) is modified as

$$\ln\left[\frac{1 - (1 - \alpha)^{1-n}}{(1 - n)T^2}\right] = \ln\left(\frac{AR}{qE}\right) - \frac{E}{RT} \qquad (8a)$$

With the same assumptions as given above, the integration of eq. (6) for the first-order reaction model ($n = 1$) gives

$$\ln\left[\frac{-\ln(1 - \alpha)}{T^2}\right] = \ln\left(\frac{AR}{qE}\right) - \frac{E}{RT} \qquad (8b)$$

By using the α-values from Figure 5, a plot of the left-hand side of eq. (8) versus $1/T$ should give a straight line for a correct value of n. The A and E values can then be estimated from the intercept and the slope of this line. In the evaluation of eq. (8a), the best value for n was tracked by a computer program in the range from 0.4 to 2. A regression analysis with the least-squares method was used in the estimation of n. The n value, giving a straight line with the highest correlation coefficient, was assumed to be concomitant with the order of the overall degradation reactions. The values of E and A were then calculated from the slope and the intercept of the line, respectively. Some representative plots of eq. (8) are presented in Figure 6 and the estimated kinetic data from these plots are summarized in Table IV.

In the second approach, eq. (6) was rearranged as

$$\frac{(d\alpha/dT)}{(1 - \alpha)^n} = \frac{A}{q}\exp\left(-\frac{E}{RT}\right) \qquad (9a)$$

$$\ln\frac{(d\alpha/dT)}{(1 - \alpha)^n} = \ln\frac{A}{q} - \frac{E}{RT} \qquad (9b)$$
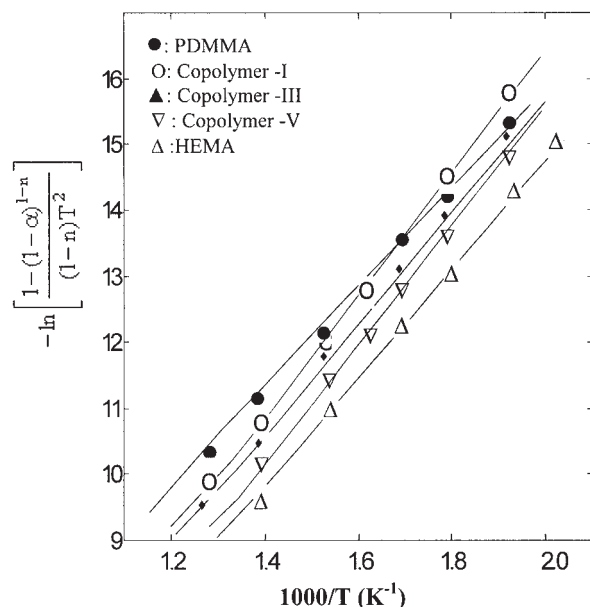
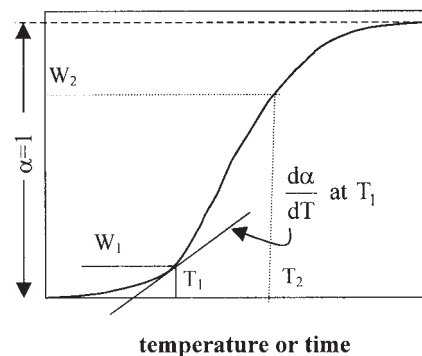Figure 6 Determination of the kinetic parameters from TG data, according to eq. (8).

Figure 7 Schematic representation of the estimation of $d\alpha/dT$ for the numerical calculations.

$$\ln \left(\frac{d\alpha}{dT}\right)_2 = \ln\frac{A}{q} + n \ln(1 - \alpha)_2 - \frac{E}{RT_2} \quad (10b)$$

Subtracting eq. (10a) from eq. (10b), and then rearranging, gives

$$\frac{\Delta \ln(d\alpha/dT)}{\Delta \ln(1 - \alpha)} = -E \frac{\Delta(1/T)}{R\Delta \ln(1 - \alpha)} + n \quad (11)$$

Equation (9) indicates that plotting of $\ln[(d\alpha/dT)/(1 - \alpha)^n]$ versus $1/T$ should give a straight line with a correct value for n. In the evaluation of eq. (9), the values of $d\alpha/dT$ were determined from Figure 5, as schematically represented in Figure 7, and the best values for n was tracked by a computer program as mentioned above. The estimated values of E and A are given in Table IV.

In the third approach, a modified Friedman method was used.[21] Equation (6) is written for a certain temperature of T_1 as

$$\ln \left(\frac{d\alpha}{dT}\right)_1 = \ln\frac{A}{q} + n \ln(1 - \alpha)_1 - \frac{E}{RT_1} \quad (10a)$$

Similarly, it may be rewritten for another temperature T_2 as

Equation (11) represent a line of $Y = -EX + n$. To obtain the plot of the straight line, the random points may be selected on the weight loss curve. From these points, X and Y values are calculated and plotted. In these calculations $d\alpha/dT$ values were evaluated from the modified TG as mentioned above. Equation (11) suggests that two points may be enough for the evaluation; however, the calculations indicated that, at least, more than five or six data points should be selected to obtain a good correlation. The estimated n values, in particular, may fluctuate from negative to positive values if the selected number of data points is not sufficient. Several authors concluded that this method is sufficient to estimate the activation energies but it may not be valid in the determination of the reaction order n and for the preex-

TABLE IV
Kinetic Parameters Estimated from TG Data by Alternative Calculation Methods (heating rate 10°C/min)[a]

	Equation (8)			Equation (9)			Equation (11)		Runga–Kutta solution		
Sample	n	$A \times 10^{-5}$	E (kJ/mol)	n	$A \times 10^{-5}$	E (kJ/mol)	n	E (kJ/mol)	n	$A \times 10^{-5}$	E (kJ/mol)
PDMMA[b]	1.0	1.82	66.84	1.2	1.03	62.72	1.0	61.34	1.0	1.48	63.78
Copolymer-I	1.2	2.31	69.81	1.2	2.26	69.95	1.3	66.94	1.2	2.29	71.03
Copolymer-III	1.2	1.53	62.41	1.2	1.05	61.78	1.5	84.41	1.2	1.41	63.05
Copolymer-V	1.2	8.45	61.35	1.4	2.07	65.79	1.6	89.40	1.2	2.17	65.08
Copolymer-VI	1.2	16.49	76.83	1.2	6.40	74.28	1.6	95.02	1.4	5.24	73.05
HEMA[b]	1.2	5.83	75.53	1.2	2.29	69.76	1.5	87.51	1.2	3.68	73.65

[a] n, overall reaction order; A, preexponential factor for Arrhenius statement (min^{-1}); E, energy of activation.
[b] Homopolymer.
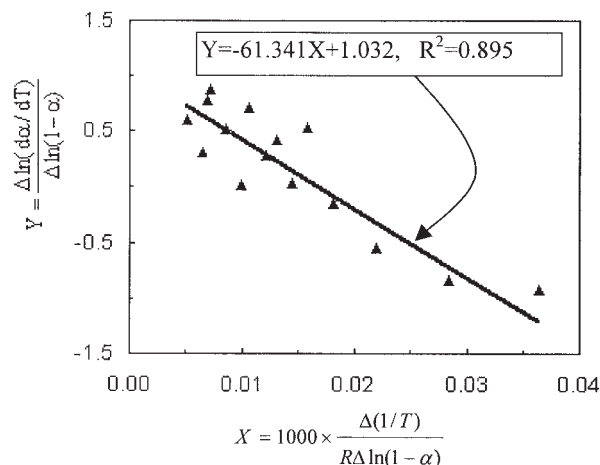
Figure 8 Determination of the kinetic parameters from TG data for PDMMA homopolymer, according to eq. (11).

ponential factor A. The application of this calculation procedure was recently discussed in detail by Liu and Fan.[21] A representative plot of eq. (11) is given in Figure 8 and the estimated n and E values are given in Table IV.

In the fourth approach, a computer program using the fourth-order Runge–Kutta algorithm was developed to estimate A, E, and n values. Bockhorn et al.,[13] Varhegyi et al.,[22] and others also used the same approach for the estimation of these kinetic parameters. The experimental data and predicted values are compared by using a reference error criterion to assess the agreement between them. The error criterion is defined as

$$\varepsilon = \frac{1}{N}\sum_{i=1}^{N}[\alpha_{i(\exp)} - \alpha_{i(p)}]^2 \qquad (12)$$

where $\alpha_{(\exp)}$ is an experimental value, $\alpha_{(p)}$ is a calculated value, and N is the number of the data chosen in the calculations. A, E, and n values were tracked to minimize the error criterion and results are given in Table IV.

The data in the literature indicate that the estimated kinetic parameters for the nonisothermal decomposition of polymers vary in a relatively wide range, depending on the type of sample, the analysis conditions, and the calculation methods. The reported values for E vary from 63 to 268 kJ/mol and the kinetic order n varies from 0.8 to 2.0, although generally $n \approx 1$.[1,4,5,7,16,19–22] The A values also vary accordingly, depending on the E and n values. The estimated activation energies and the kinetic orders by the different calculation methods are generally consistent and in accord with those given in the literature for various polymers.[5–7,19,21]

The correlation coefficients (R^2) were sufficiently high ($R^2 > 0.99$) for all cases herein except for eq. (11). Indeed, the energies estimated from the TG data are essentially the apparent energies for the sum of different reactions that occur simultaneously. During the stages of decomposition, the types of reactions may change and thus the effective activation energies change. Several authors discussed that the thermal decomposition of polymers proceeds through initiation, propagation, and termination stages with different activation energies. The global activation energies for a conversion level, $E_{(\alpha)}$, vary depending on the α, and the trend of α versus temperature may reflect these stages.[6,7,12,13] The phases of the degradation for a selected sample (PDMMA homopolymer) are schematically represented in Figure 9, indicating that the range of approximately $0.15 \leq \alpha \leq 0.92$ corresponds to the propagation stage of the decomposition. If the above-discussed calculation methods are applied for the initiation stage, a lower activation energy and a lower kinetic order ($n < 0.8$) are estimated. These results also confirm that the thermal degradation proceeds through the kinetic stages as represented in Figure 9. The probable decomposition mechanisms and the products of the polymers of this study will be discussed in a subsequent report.

A kinetic approach based on DTA data

The literature data indicate that DTA data also enable one to estimate the apparent kinetic parameters.[8,10,12,24–26] Haddadin and Tawarah[10] and Ceylan et al.[12] used the nth-order rate model, as given in eq. (9b), to estimate the kinetic parameters for the peak regions in the DTA curves. In this approach, however, the extent of the decomposition α should be defined conveniently. The theory based on the idea that the area under a DTA peak is directly propor-
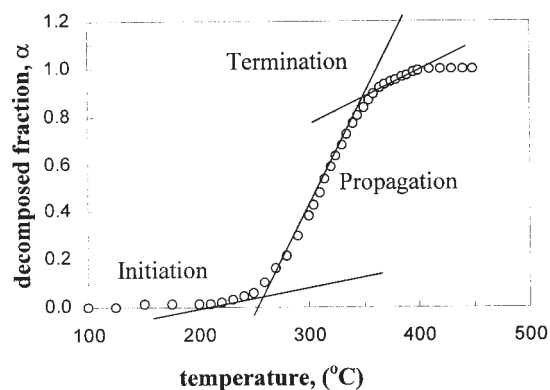
Figure 9 Representation of the stages of the decomposition reactions for PDMMA homopolymer.

tional to the corresponding enthalpy changes and can be used to study the kinetics of the reactions. Therefore, the α-values may be defined as the ratio of the partial peak area at temperature T to the total peak area, as schematically demonstrated in Figure 2. The total peak area is generally defined as the area enclosed between the peak and the interpolated base line. In this definition, the value of α ranges from 0.0 to 1.0 for each peak region. The same approach is used in this study to estimate the kinetic parameters from DTA data. The correct n value was tracked by a computer program as mentioned earlier. As an example, the plots of an nth-order rate model for the exothermic peak of HEMA homopolymer are given in Figure 10. Similar plots were obtained for each exothermic peak of the other samples. The results indicated that generally a reaction model of order 1.2 gives straight lines with high correlation coefficients. The kinetic parameters of A and E were estimated from the intercept and the slope of these lines as mentioned earlier. The estimated kinetic parameters from the second exothermic peaks of the DTA data of the polymers are summarized in Table V.

A comparison of the data given in Tables IV and V indicates that the apparent activation energies estimated from the two methods (i.e., TG and DTA) are considerably different. These differences essentially originate from the differences in the basic data obtained by these methods: in TG, the differences pertain to the weight losses; in DTA, however, the temperature changes are registered versus temperature or time. The above results imply that a substantial portion of the degradation reactions at higher-temperature regions are accompanied by temperature changes. Some of these reactions are also accompanied by weight loss, but some are not. The reactions that produce volatile products seem to have lower activa-
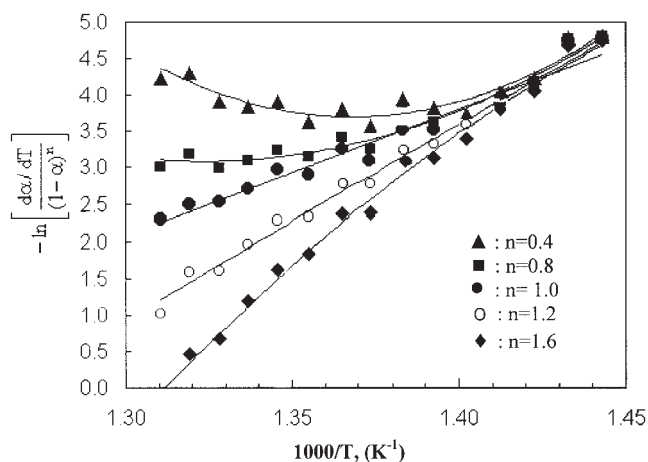
TABLE V
Kinetic Parameters Estimated from the Exothermic DTA Peak (heating rate 10°C/min)

Sample	n	E (kJ/mol)	ln A	$R^{2\,a}$
PDMMA[b]	1.2	220.57	34.803	0.976
Copolymer-I	1.2	205.57	32.257	0.986
Copolymer-III	1.2	199.75	32.153	0.995
Copolymer-V	1.2	198.91	32.053	0.989
Copolymer-VI	1.2	240.00	38.685	0.973
HEMA[b]	1.2	225.74	36.303	0.966

[a] R, correlation coefficient; see Table IV for the other nomenclature.
[b] Homopolymer.

tion energies compared to those reactions that do not produce volatile products.

CONCLUSIONS

The thermogravimetric data discussed above suggest that the initial fragmentation starts around 270°C, depending on the type of sample. The degradation involves at least two kinetically active steps and the order of overall reaction changes depending on the steps. The apparent activation energies estimated from TG data by different methods are consistent, although the DTA-derived energies are considerably higher than the TG-derived energies. This result implies that some of the higher-temperature reactions that do not result in the weight loss proceed with higher activation energies. The exothermic effects may be related to the free-radical combination or polycondensation reactions at the high-temperature regions. The above-discussed results suggest that HEMA homopolymer is thermally more stable than PDMMA homopolymer and PDAMMA copolymers.

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Figure 10 Plots of nth-order equation for the exotherm of DTA curve of HEMA homopolymer.

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