

THERMOGRAVIMETRIC STUDIES ON POLY(METHYL METHACRYLATE), POLY(TETRAHYDROFURAN) AND THEIR BLENDS

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Abstract

TG studies are given for PMMA prepared by radical polymerization, PTHF prepared by cationic polymerization, and their blends. A procedure is proposed for determining the activation energy, frequency factor, and the order of events corresponding to the respective stages of the multistage TG curves. The order of the initial event of PMMA is not the 1st. It is shown for this discussion that the relationship between mass loss and time of the 2nd order reaction is similar to that of the depolymerization including the vaporization process at the earlier times. Some of TG curves of PTHF are not dependent on the heating rate. This independence depends on the size of sample. The order of event of PTHF, which is obtained from TG curves dependent on the heating rate, is the 0th. The event order equal to the 0th reflects major contribution of vaporization in the event. The TG behaviors shown by the procedure mentioned above for the PMMA/PTHF blends with the smaller PMMA or PTHF contents cancel those of PMMA or PTHF.

Keywords: kinetic parameters, PMMA, PTHF, TG of multiple stages

Introduction

Integrative isoconversional TG analyses are used in most of studies on kinetic parameters obtained from non-isothermal TG data on polymers, because of convenience for model independence. However, this model independence makes the obtained kinetic parameters to be uncertain in sense of kinetics, particularly in analysis of TG curves consisting of two or more stages. Moreover, dependence of activation energy on conversion if any so, leads to errors in kinetic parameters determined by this method [1]. Recent TG studies for poly(vinyl chloride) [2], and benzimidazolyl-substituted aromatic polyamides [3] show that the maximum of the activation energies obtained by Ozawa plots [4] for various mass losses appears in vicinity of 30% mass loss. This is extraordinary behavior in kinetics of thermal decomposition of polymers. Thus a modification of this method is necessary to analyze complicated TG curves.

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In our previous paper [3], the observed TG data are successfully fitting equations derived from independent two or three first-order rate equations. However, a detailed discussion was not given, because little is known about the mechanism of thermal decomposition of the sample polymers.

In the present paper, we propose a procedure to fit the observed TG data rate equations for several independent events on a poly(methylmethacrylate) (PMMA), a poly(tetrahydrofuran) (PTHF). The thermal decompositions of PMMA and PTHF proceed by depolymerization [5] and by random decomposition [6], respectively. The TG curves of PMMA prepared by initiator initiation have three discrete stages [7, 8], and however, to our knowledge, the activation energies corresponding to respective stages still have not been obtained from their TG curves. Previously, we reported that the thermal decomposition of PTHF proceeds by random scission of ether linkages, accompanied by evolution of the major products with formyl and/or methyl in the chain ends and that the TG curves depend on the thermal history and the size of sample [6].

Experimental

PMMA (Tokyo Kasei Co., Inc., $M_n=608000$, radical polymerization using azobisisobutyronitril) and PTHF (de Pont de Nemours & Co., $M_n=2900$, ring-opening polymerization), purchased commercially were used without purification. All samples were prepared by casting in acetone solution. All TG measurements were performed using Perkin Elmer 7 series with UNIX TGA 7.

Nitrogen gas flow rates were checked prior to each run and were maintained at $25 \text{ cm}^3 \text{ min}^{-1}$ in the balance area and $50 \text{ cm}^3 \text{ min}^{-1}$ in the furnace. A platinum pan used was flame-cleaned prior to each run. The TG data were recorded at the heating rates of 2, 5, 10 or 20 K min^{-1} . About 2 or 1 mg of sample was precisely weighted.

Analysis procedure

The order rate equation, the Ozawa plots [4], and the Doyle approximation [9] for p -function are used for the analysis of TG data by the following procedure. At first, the activation energy, $E1$, is estimated from Ozawa plots for the initial mass loss (associated with event 1), and then the frequency factor, $A1$, the starting mass, $W1_0$, and the order of event, $n1$, are estimated for event 1. Thereby the mass of residue due to event 1, $W1$ is determined at a given temperature, T , as a function of the estimated parameters: $W1=f(E1, A1, W1_0, n1)$. Next, the TG curve independent of event 1 is obtained by subtraction of $W1$ from the overall sample mass, W . The procedure mentioned above is conducted for the TG curve independent of event 1. The resulting parameters give the mass of residue due to event 2 at T , $W2=f(E2, A2, W2_0, n2)$. Similarly and successively, the mass of residues due to event 3, event 4, and etc. are determined until a sum of the respective starting masses, $W1_0+W2_0+W3_0+\dots$, becomes close to the starting overall sample mass, W_0 .

Results and discussion

PMMA

Figure 1 shows the observed TG plots recorded with heating rate of 2, 5, 10 and 20 K min⁻¹ for 2.0 mg sample size of PMMA, together with the calculated curves. The observed plots seem to have three stages, as shown in the literature [7, 8]. The kinetic parameters in Table 1 were determined in order of the initial event (event 1), the middle event (event 2), and the final event (event 3).

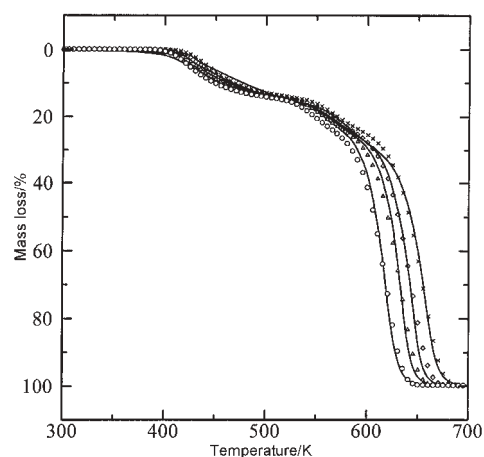


Fig. 1 TG curves of PMMA. The sample size is 2 mg. The plots are the observed data, recorded with the heating rate of 2 (x), 5 (◇), 10 (△) and 20 (○) K min⁻¹. The solid lines are the calculated curves

Table 1 Kinetic parameters of PMMA

Event	$E/\text{kJ mol}^{-1}$	A/s^{-1}	n	W_0/mg
1	122.8 ± 32.2	$6.8 \pm 0.55 \cdot 10^{13}$	4	0.35
2	179.4 ± 76.6	$1.4 \pm 0.15 \cdot 10^{14}$	1	0.20
3	204.1 ± 4.7	$3.7 \pm 0.35 \cdot 10^{14}$	1	1.60

Many activation energy values have been reported for thermal decomposition of PMMA, though there have been no report on the activation energy values obtained from TG curves of PMMA prepared by radical polymerization using an initiator. And these values depend on the structure of PMMA molecular chain (degree of polymerization, head-to-head linkage, double-bonding chain-end, etc.). Jellinek and Luh provided the values of activation energy equal to about 120 kJ mol⁻¹ for end-initiation depolymerization and about 300 kJ mol⁻¹ for random-initiation depolymerization for PMMA [10]. These values are in fair agreement with the values of activation energy obtained in the present studies. However the order of event 1, that is higher than the

1st order, seems to reflect some additional events besides depolymerization reaction. Here, we assume the following consecutive process.

Polymer (liquid) → radical chain (liquid) initiation
 Radical chain (liquid) → radical chain (liquid) + monomer (liquid) →
 Monomer (liquid) depropagation
 Monomer (liquid) → monomer (gas) vaporization

From this consecutive process, the following relationship between mass and time is derived.

$$W/W_0 = C_i \exp(-k_i t) + C_d \exp(-k_d t) + C_v \exp(-k_v t) \quad (1)$$

$$C_i = k_v k_d / (k_d - k_i)(k_v - k_i)$$

$$C_d = k_v k_i / (k_i - k_d)(k_v - k_d)$$

$$C_v = k_i k_d / (k_i - k_v)(k_d - k_v)$$

where k_i , k_d and k_v are the rate constants of initiation, depropagation, and vaporization, respectively, and t is time.

The order of depolymerization initiated by cleavage of chain end or head-to-head linkage is the 1st, and the order of depolymerization initiated by random scission is the 1.5th [11] (for the exponential distribution of molecular mass of chain radicals), when k_v is larger than k_d . Figure 2 shows representative relationships between mass and time drawn according to the 2nd order reaction (a), the 1st order reaction (b), and Eq. 1 (c). The slope of curve c is larger than that of curve b and close to that of curve a in most of time before $t=1$. This suggests that kinetic equations including contribution of vaporization process are approximated to those of reactions of the order higher than the 1st order. Therefore, we speculate that a deviation from the 1st order reaction of event 1 reflects contribution of vaporization process to event 1. The events 2 and 3

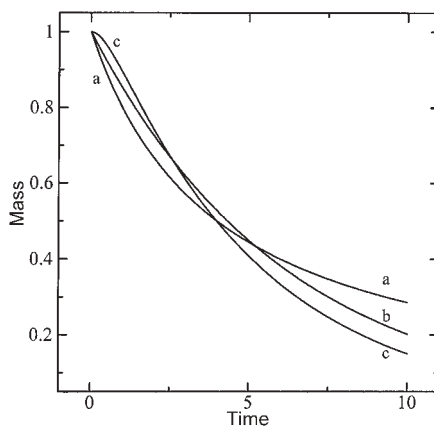


Fig. 2 Plots of mass (W/W_0) vs. time (t). a – $W/W_0 = (1 + 0.25t)^{-1}$, b – $W/W_0 = \exp(-0.16t)$ and c – $W/W_0 = 1.11 \exp(-0.20t) - 0.11 \exp(-2.00t)$ (C_d is neglected, because k_d is very large)

seem to correspond to depolymerization initiated at end or head-to-head linkages and depolymerization initiated randomly, respectively.

PTHF

There are some TG studies on PTHF, in which the sample size dependence was neglected [6, 12, 13]. Figure 3 shows TG curves, recorded with 2, 5, 10 and 20 K min⁻¹ of heating rates for 1 and 2 mg of PTHF. Some TG curves (sample size, 1 mg, heating rate, 10 and 20 K min⁻¹; sample size, 2 mg, heating rate, 5, 10 and 20 K min⁻¹) are independent of the heating rate. Others depend on the heating rate, and give the activation energy equal to 105.8±8.2 kJ mol⁻¹, the frequency factor equal to 1.8±0.52·10⁶ s⁻¹, and the order equal to 0th. These values suggest that the decrease in mass proceeds by the vaporization of monomer. In our previous isothermal TG study [6], the TG curves fit to the random decomposition equation [14] given by

$$dC/dt=(L-1)(1-C)-[(N-L)(L-1)/N]\exp(-L\tau)$$

where $\tau=kt$, $N=40$, k is the rate constant, t is the time, C is the conversion equal to $(W_0-W)/W_0$, and $(L-1)$ is the degree of polymerization of the largest evaporated compound. And the activation energy equal to 61.6 kJ mol⁻¹ and $L=4$ have been derived. The Ozawa method for the non-isothermal TG curves have not worked well because of dependence of L on temperature.

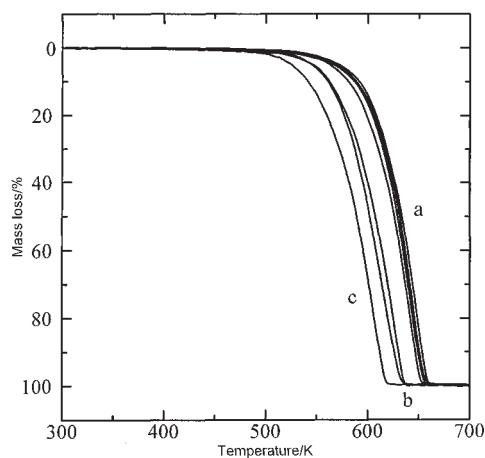


Fig. 3 TG curves of PTHF: a – sample size, 1 mg, heating rate, 10 and 20 K min⁻¹; sample size, 2 mg, heating rate, 5, 10 and 20 K min⁻¹, b – sample size, 1 mg, heating rate, 5 K min⁻¹; sample size, 2 mg, heating rate, 2 K min⁻¹ and c – sample size, 1 mg, heating rate, 2 K min⁻¹

PTHF thermally decomposes at 353 K without vaporization [6]. When most of the decomposition products become the compound with $L=4$, before the boiling temperature, non-isothermal TG curves express its vaporization behavior, that is, depend

on the heating rate, and derive the 0th-order of change. When the decomposition products with $L=3, 4, 5$ or etc. are remaining in the sample pan, the vaporization occurs at the individual boiling temperatures, and TG curves are independent of the heating rate. The former is more subjective for smaller sample. These explain reasonably the experimental results.

PMMA/PTHF blends

As shown in Table 2, the kinetic parameters of PMMA/PTHF blends with mass ratio equal to 2/1 and 1/1 are close to those of PMMA. The TG curves of the blend with mass ratio equal to 1/2 are single curves similar to those of PTHF. This is similar to the composition dependence of the glass transition temperature of PMMA/PTHF blends: the glass transition temperature of a PMMA/PTHF blend containing the richer polymer above 70 mass% is close to that of the richer polymer in the blend [15].

Table 2 Kinetic parameters of PMMA/PTHF blends

PMMA/PTHF mass ratio=2/1				
Event	$E/\text{kJ mol}^{-1}$	A/s^{-1}	n	W_0/mg
1	124.3±26.2	$3.5\pm 1.7\cdot 10^{14}$	4	0.18
2	155.8±10.9	$7.8\pm 0.76\cdot 10^{11}$	1	0.40
3	211.0±4.3	$2.1\pm 0.25\cdot 10^{15}$	1	1.50
PMMA/PTHF mass ratio=1/1				
Event	$E/\text{kJ mol}^{-1}$	A/s^{-1}	n	W_0/mg
1	109.1±7.4	$1.1\pm 0.2\cdot 10^{13}$	4	0.18
2	137.8±4.3	$2.9\pm 0.18\cdot 10^{10}$	1	0.40
3	172.2±2.9	$1.6\pm 0.49\cdot 10^{12}$	1	1.50

Conclusions

Kinetic parameters of multiple events are determined by successive subtraction of mass from TG curves of multiple stages. The obtained values of these parameters explain well event that each stage is associated with. The initial stage of TG of PMMA is not able to be explained only in terms of depolymerization and is able to be explained in terms of depolymerization including vaporization. TG behaviors of PTHF are able to be explained in terms of vaporization process. These conclusions are very reasonable, because mass loss reflects only liberation of small compounds from the sample pan.

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