THERMAL DECOMPOSITION OF COPOLYMERS OF METHYL METHACRYLATE AND ALKYL METHACRYLATES OBTAINED FROM A CSTR

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Abstract — Thermal decomposition of the copolymers of methyl methacrylate (MMA) with ethyl methacrylate (EMA) or n-butyl methacrylate (BMA) were investigated. The copolymers were obtained in a continuous stirred tank reactor (CSTR) using toluene and benzoyl peroxide, as solvent and initiator, respectively, at 80°C. The volume was 1.2 litters and residence time was 3 hours. The thermal decomposition followed the second order kinetics for both MMA/EMA and MMA/BMA copolymers, which were almost in accordance with the order of copolymerization in a CSTR. The activation energies of thermal decomposition were in the ranges of 32-37 kcal/mol and 27-37 kcal/mole for MMA/EMA and MMA/BMA copolymers, respectively and a good additivity rule was observed against each composition for both copolymers. The thermogravimetric trace curve agreed well with the theoretical calculation.

INTRODUCTION

Continuous process offers the advantages of improved polymer properties and economies of scale but the design of continuous systems requires more understanding than that required in the design of batch system [1-6]. In the meantime, conversions are generally low in the continuous process and the kinetics of a polymerization reaction are not simple [3].

Our previous work was reported on the continuous copolymerization of methyl methacrylate with alkyl methacrylates [7]. It was also reported that the unzipping property of methyl methacrylate can be prevented by incorporating second monomer through a copolymerization. The previous study revealed that the copolymerization of MMA with EMA or BMA followed the second-order kinetics in a CSTR, regardless of the compositions of the copolymers. The present paper deals with the thermal degradation behavior of the MMA/EMA or MMA/BMA copolymers, which were obtained from our previous CSTR experiments.

We have investigated the following axioms: the copolymerization process of MMA and alkyl methacrylate may follow a reverse order of the unzipping process during the thermal degradation, and then the copolymerization kinetics may be almost the same as

that of thermal degradation. Since the copolymerization of MMA and alkyl methacrylates followed the second-order kinetics, the thermal degradation kinetics would show the second-order kinetics.

Thus, we studied the kinetics of the thermal degradation of the resulting copolymers of MMA/EMA and MMA/BMA, which were obtained from a CSTR and investigated the validity of our assumptions. The activation energy and order of thermal degradation of the copolymers was analyzed theoretically and experimentally.

THEORY

Kinetics of thermal degradation of polymers have been evaluated from thermogravimetric analysis (TGA) at linear rates of temperature rise in a number of studies [8-13]. In the present paper, kinetic calculations are based on the intercomparison of experiments which were carried out at several different rates of temperature rise according to the Friedman's method [10].

The general kinetic equation of thermal degradation of polymers is

$$\frac{dc}{dt} = A \cdot (1-c)^n \cdot \exp\left(-\frac{E}{RT}\right) \tag{1}$$

where, c = degree of conversion

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t = time
A = pre-exponential factor of rate constant
E = activation energy of rate constant
R = gas constant
T = absolute temperature

Taking logarithms of Eq. (1) gives

$$\ln\left(\frac{dc}{dt}\right) = \ln A + \ln(1-c)^n - \frac{E}{R} \cdot \frac{1}{T} \qquad (2)$$

Let the term, $f(1-c)$ be $(1-c)^n$ of Eq. (2) and multiply pre-exponential factor and taking logarithms to both sides, which gives

$$\ln[A \cdot f(1-c)] = \ln A + n \ln(1-c) \qquad (3)$$

where, n is a kinetic order of the thermal degradation.

Taking parameters of the heating rate ($\beta = dT/dt$) in the given conversion, we obtained activation energy, E from the graph slopes which is related to $\ln(dc/dt)$ and $1/T$ of Eq. (2).

The kinetic order (n) and pre-exponential factor (A) were calculated from the slopes and intercepts of the graph, which are related to $\ln[A \cdot f(1-c)]$ and $\ln(1-c)$ of Eq. (3). Introducing heating rate to Eq. (1) and separating the variables, which gives

$$\frac{dc}{(1-c)^n} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) \qquad (4)$$

Taking integration of Eq. (4) in the given boundary condition (from $c = c_o$, $T = T_o$ to $c = c_o$, $T = T$), which gives

$$\frac{1}{n-1} \cdot \frac{(1-c_o)^{n-1} - (1-c)^{n-1}}{(1-c)^{n-1} \cdot (1-c_o)^{n-1}} = \frac{AE}{\beta R} [P(X) - P(X_o)] \qquad (5)$$

where, $X = \frac{E}{RT}$, $X_o = \frac{E}{RT_o}$

$$P(X) = \frac{e^{-X}}{X} - \int_X^\infty \frac{e^{-X}}{X} \, dX \qquad (6)$$

$$P(X_o) = \frac{e^{-X_o}}{X_o} - \int_{X_o}^\infty \frac{e^{-X_o}}{X_o} \, dX_o \qquad (7)$$

After taking the integral term of Eq. (7) with a series expansion, we could obtain Eq. (8) by substituting it to Eq. (5) and rearranging the rest.

$$c = 1 - \frac{1}{\left[\frac{1}{(1-c_o)^{n-1}} + \frac{RA(n-1)}{\beta E^2}\left(\frac{T^2(E-2RT)}{e^{(E/RT)}} - \frac{T_o^2(E-2RT_o)}{e^{(E/RT_o)}}\right)\right]^{1/(n-1)}} \qquad (8)$$

Assuming that we could obtain the activation energies of copolymers with the additivity rule and activation energies of PMMA, PEMA and PBMA, those could be as the follows,

$$E_{copolymer(MMA,EMA)} = f \cdot E_{,PMMA} + (1-f) \cdot E_{,PEMA} \qquad (9)$$

$$E_{copolymer(MMA,BMA)} = f \cdot E_{,PMMA} + (1-f) \cdot E_{,PBMA} \qquad (10)$$

where, f are mole fractions of MMA in copolymers.

EXPERIMENTAL

1. Materials

The MMA/EMA or MMA/BMA copolymers were obtained from a CSTR. Details of the CSTR experiments are described elsewhere [7]. Tables 1 and 2 summarize the characteristics of the samples used in the work.

2. Thermogravimetry

Thermogravimetry (TG) curves were obtained by using a Rigaku TGA (Model PTC-10A). Samples (10 mg) were degraded in a nitrogen atmosphere (50 ml/min) at linear heating rates of 1-20°C /min.

RESULTS AND DISCUSSION

The DTG (derivative thermogravimetry) curves for poly (methyl methacrylate) (PMMA) at heating rates of 7, 10, and 14°C /min are shown in Fig. 1. It is seen that the rate of weight loss increased as the temperature was increased and reached maxima in the vicinity of the temperatures of 160°C , 250°C , and 380°C . The

Table 1. The monomer composition in copolymers ([M₁]: MMA, [M₂]: EMA)

Feed composition ([M₁]/[M₂]) [mole%]	Element*[wt%]		Copolymer composition [mole%]	
	C	H	[M₁]	[M₂]
0/100	63.135	9.830	0.00	100.00
20/ 80	62.385	9.426	26.34	73.66
40/ 60	61.930	9.296	41.43	58.57
50/ 50	61.668	9.111	49.87	50.13
60/ 40	61.358	9.062	59.61	40.39
80/ 20	60.566	8.990	83.42	16.58
100/ 0	59.984	8.054	100.00	0.00

*By elemental analysis

Table 2. The monomer composition in copolymers
([M$_1$]: MMA, [M$_2$]: BMA)

Feed composition ([M$_1$]/[M$_2$]) [mole%]	Element*[wt%]		Copolymer composition [mole%]	
	C	H	[M$_1$]	[M$_2$]
0/100	67.572	10.923	0.00	100.00
20/ 80	66.489	10.578	19.13	80.87
40/ 60	65.288	10.169	37.95	62.05
50/ 50	64.657	9.908	46.98	53.02
60/ 40	63.760	9.731	58.91	41.09
80/ 20	62.101	9.299	78.58	21.42
100/ 0	59.984	8.054	100.00	0.00

*By elemental analysis

Fig. 1. DTG curves of PMMA degraded in the stream of nitrogen gas at various heating rates.
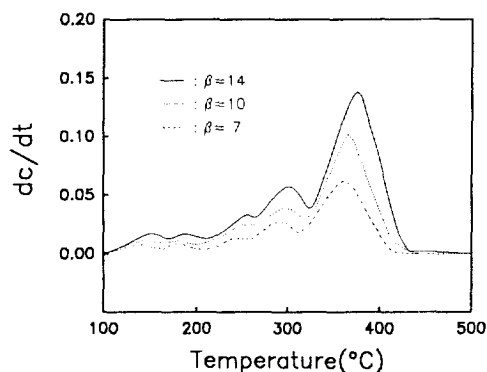

Fig. 2. DTG curves of copolymer (MMA/EMA = 50/50) degraded in the stream of nitrogen gas at various heating rates.

maxima in the DTG curves are observed at higher temperature as the heating rate becomes higher. The degradation kinetics of PMMA, showing three stages of degradation breakdown, was already reported by
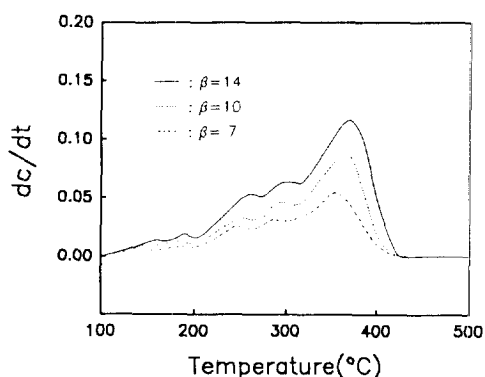

Fig. 3. DTG curves of copolymer (MMA/BMA = 47/53) degraded in the stream of nitrogen gas at various heating rates.
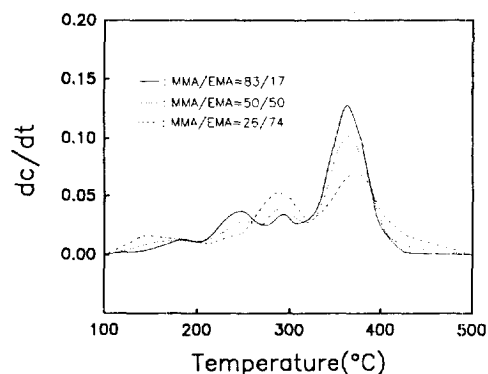

Fig. 4. Variation of DTG curves of copolymer (MMA/EMA) with different copolymer compositions (mol ratio) degraded in the stream of nitrogen gas at the heating rate of 10°C/min.

Duval [14], Newkirk [15] or Lukaszweski and Redfern [16]. The DTG curves for MMA/EMA and MMA/BMA copolymers having compositions of 50/50 and 47/53 (mole%) are shown in Figs. 2 and 3, respectively. The copolymers showed similar behavior except that more maximum peaks were observed for both copolymers than PMMA homopolymer. The result implies that the degradation behavior for the copolymers is more complex than the homopolymer.

Comparison of Figs. 2 and 3 show that the maximum rates of weight loss on DTG curve of the MMA /EMA copolymer are observed to be larger than those of the MMA/BMA copolymer at the same temperature, regardless of the heating rates. In other words, the rate of weight loss is faster in the case of the MMA/EMA copolymer than the MMA/BMA copolymer at the same temperature and heating rate. The
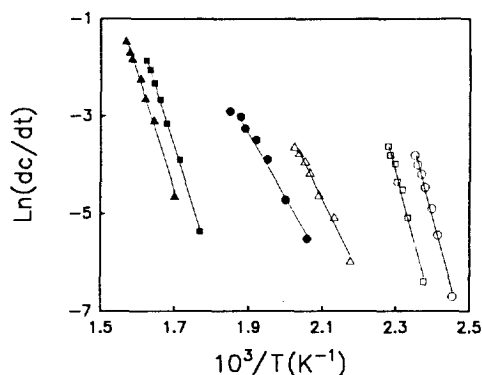
Fig. 5. Friedman plots at the following fractional weight losses for the thermal decomposition of PMMA.
(○: 0.02, □: 0.04, △: 0.1, ●: 0.2, ■: 0.3, ▲: 0.7)

Table 3. Activation energy E, reaction order n and pre-exponential factor A for the degradation of PMMA, PEMA and their copolymers
([M_1]: MMA, [M_2]: EMA)

Composition ([M_1]/[M_2]) [mole%]	Average [kcal/mol]	Main stage		
		E[kcal/mol]	n	A[min^{-1}]
0/100	31.9	34.1	1.41	8.67×10^9
26/ 74	34.0	32.1	3.41	3.68×10^{21}
41/ 59	33.2	31.2	2.71	1.40×10^{22}
50/ 50	35.4	41.9	1.90	1.57×10^{20}
60/ 40	36.2	45.2	1.77	8.61×10^{20}
83/ 17	36.9	35.1	1.49	6.75×10^{18}
100/ 0	37.3	49.8	1.38	7.56×10^{17}

Table 4. Activation energy E, reaction order n and pre-exponential factor A for the degradation of PMMA, PBMA and their copolymers
([M_1]: MMA, [M_2]: BMA)

Composition ([M_1]/[M_2]) [mole%]	Average [kcal/mol]	Main stage		
		E[kcal/mol]	n	A[min^{-1}]
0/100	27.5	28.2	1.33	1.35×10^9
19/ 81	28.7	29.1	2.05	5.91×10^{20}
38/ 62	32.1	35.2	1.93	4.22×10^{20}
47/ 53	32.5	35.4	1.64	9.04×10^{18}
59/ 41	32.9	33.2	1.75	2.53×10^{17}
79/ 21	34.1	35.1	1.26	4.54×10^{15}
100/ 0	37.3	49.8	1.38	7.56×10^{17}

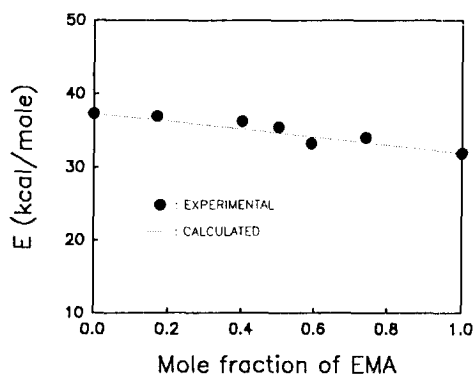
Fig. 6. Dependence of the activation energy of copolymer (MMA/EMA) in thermal degradation on copolymer composition.

result may be due to the bulkier property of butyl group of BMA than ethyl group of EMA.

The effect of copolymer composition on the DTG curves were shown in Fig. 4. Like in Figs. 2 and 3, more maximum peaks were observed for copolymers, regardless of their compositions, than PMMA homopolymer. The maximum peaks in the degradation rate show just the overlap of the degradation behavior of PMMA, poly (ethyl methacrylate) (PEMA) and poly (n-butyl methacrylate) (PBMA) homopolymers depending on their compositions. That is, the copolymer having more MMA composition follows the behavior of PMMA homopolymer whereas the copolymers having more EMA composition follows the behavior of PEMA homopolymer. Similar trend was observed for the MMA/BMA copolymers.

The activation energies of PMMA which were derived from Eq. (5) with the help of Fig. 5, are listed in Tables 3 and 4. Fig. 5 shows a typical Friedman

plots at several fractional weight losses for the degradation of PMMA to obtain the activation energy of PMMA degradation. The slope of each line in Fig. 5 is equal to $-E/R$.

Figs. 6 and 7 show the change in activation energy as a function of MMA composition in MMA/EMA copolymer systems. It is seen that the activation energy approaches to the value of that of PMMA or PEMA homopolymers at the copolymer composition of 0 and 100 wt% and the additivity rule well holds. It is seen in Tables 3 and 4 that the activation energy ranged from 32 to 37 kcal/mole for the MMA/EMA copolymer and from 27 to 37 kcal/mole for the MMA/BMA copolymers, respectively.

The value of the frequency coefficient, A, was also shown in the Tables 3 and 4. In this table, the term 'stage' in the third column means that the number of maximum peaks on DTG curves show the different degradation kinetic stages. The degradation kinetic
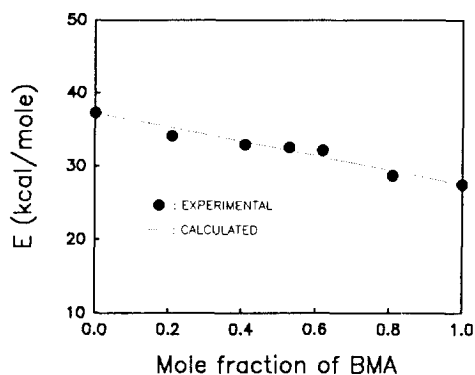
Fig. 7. Dependence of the activation energy of copolymer (MMA/BMA) in thermal degradation on copolymer composition.
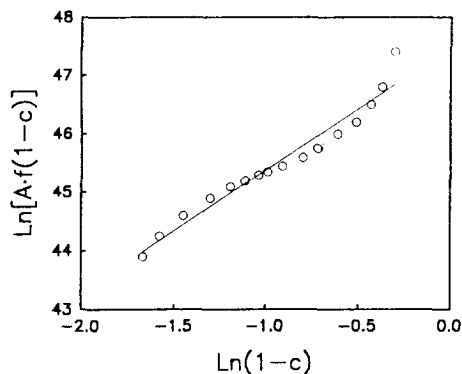

Fig. 9. Experimental and calculated TG curves of copolymer (MMA/BMA = 19/81) in the heating rate of 10°C/min.
(correlation coefficient is 0.993)

Fig. 8. Plot of the determination of A and kinetic order of copolymer.
(MMA/BMA = 19/81)

orders of the copolymers are higher than those of homopolymers. Calahorra et al. [17] reported that the degradation kinetics of copolymers are significantly affected by the copolymer composition.

The DTG curves of the copolymers were analyzed. Data from the degradation experiments were put into the Eq. (5) presented in the theory section and the orders of the degradation kinetics were calculated. It was found that the degradation orders are very similar to that of copolymerization reaction. The average order of MMA/EMA and MMA/BMA copolymer system was 2.26 and 1.73, respectively. These values correspond to the kinetic order of copolymerization of MMA and EMA or BMA in the CSTR used in our previous work [7].

It was obtained from Fig. 8 that the reaction orders and the pre-exponential factors were calculated from the slopes and intercepts of the graph, which are rela-
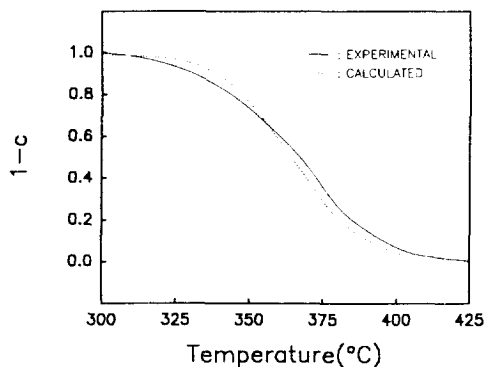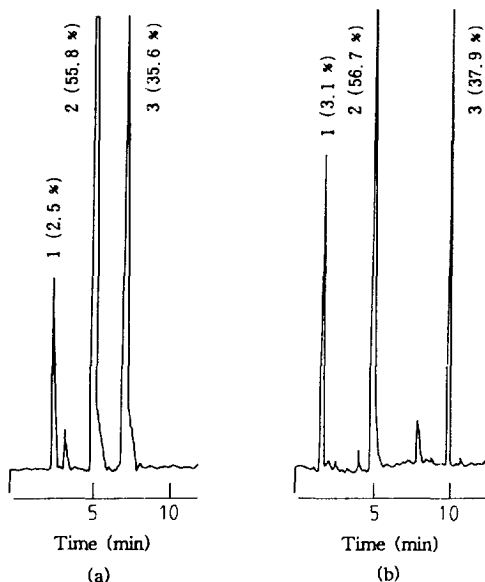

Fig. 10. Pyrograms of copolymers (a) MMA/EMA = 60/ 40 and (b) MMA/BMA = 59/41, pyrolyzed at 300 °C, where 1, 2 and 3 denote light gases, MMA and EMA or BMA monomer peaks, respectively. [pyrolysis conditions: oven temp.; 30C (7 min hold) to 300℃ (5 min hold), temp. program; 20 ℃/min, pyro. time; 10 sec]

ted to $\ln[A \cdot f(1-c)]$ and $\ln(1-c)$ of Eq. (3) for the MMA/BMA = 19/81 copolymers.

Finally, it was also observed that there is a good correlation between experiments and theory for our copolymer systems. Fig. 9 shows a typical thermograms obtained, theoretically and experimentally, for
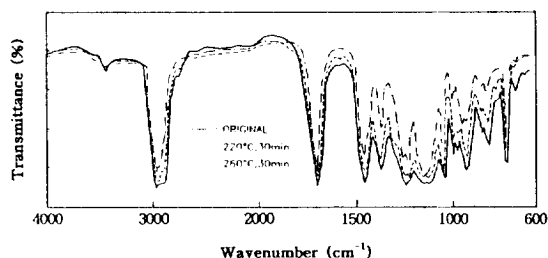
Fig. 11. Infrared spectra of thermal-decomposed copolymer (MMA/EMA = 60/40) at various temperatures.
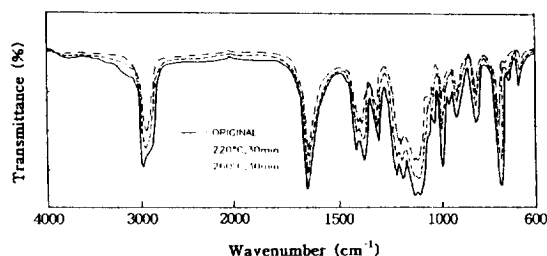

Fig. 12. Infrared spectra of thermal-decomposed copolymer (MMA/BMA = 59/41) at various temperatures.

the MMA/BMA copolymer of 19/81 compositions. In this figure, the theoretical curve was drawn by Eq. (8) with the data of E, A, and n in Table 3. One can see well that the experimental TGA curves are well fitted by the theoretical calculation.

Fig. 10 shows pyrograms of pyrolysis gas chromatography (PGC) of MMA/EMA = 60/40 copolymers and MMA/BMA = 59/41 copolymers, pyrolyzed at 300℃. 2.5% of gaseous mixtures, 55.8% of MMA monomers, and 35.6% of EMA monomers were observed at (a), and 3.1% of gaseous mixtures, 56.7% of MMA monomers, and 37.9% BMA monomers were observed at (b), respectively.

Both of two copolymers showed less light gases, and the withdrawing rate of monomer was more than 90%.

Figs. 11 and 12 are the infrared spectra of MMA/EMA = 60/40 copolymers and MMA/BMA = 59/41 copolymers, thermally decomposed with temperature changes of copolymers. From these figures, the intensity of characteristic absorption stretching vibration of C-H (2900 cm⁻¹), strong stretching vibration of C=O (1750 cm⁻¹), and stretching vibration of C-O of ester group (1279 cm⁻¹) was decreased slowly as the temperature changed.

Consequently, from the results of PGC and IR ana-

lyses, it is considered that the thermal decomposition of the synthesized copolymers is seemed to be hardly the scissions of side chains, instead, the random scissions of main chains.

CONCLUSIONS

The thermal decomposition of the copolymers followed the second order kinetics for both MMA/EMA and MMA/BMA copolymers, which were almost in accordance with the order of copolymerization in a CSTR. The activation energies of thermal decomposition were in the ranges of 32-37 kcal/mol and 27-37 kcal/mole for MMA/EMA and MMA/BMA copolymers, respectively and a good additivity rule was observed against each composition for both copolymers.

In conclusion, it was found that the kinetic order of copolymerization and that of degradation shows the significant corresponding correlations. The average order of MMA/EMA and BMA system was 2.26 and 1.73, respectively and the thermogravimetric trace curve agreed well with the theoretical calculation. Finally, the thermal degradation of copolymers were considered to occur by the random scission at an environment temperature below 300℃.

NOMENCLATURE

A : pre-exponential factor [min⁻¹]
c : degree of conversion [-]
c_o : initial degree of conversion [-]
E : apparent activation energy [kcal/mol]
f : mole fraction of MMA in copolymers [-]
k : rate constant [min⁻¹]
n : apparent order of reaction [-]
R : gas constant [1.987 cal/(g·mole·K)]
t : time [min]
T : absolute temperature [K]
T_o : initial absolute temperature [K]
β : heating rate [℃/min]

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