

Thermal Decomposition of Copolymers of Butyl methacrylate and Styrene Produced in a CSTR

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Abstract : Thermal decomposition of the copolymer of butyl methacrylate(BMA) with styrene(St) was investigated. The copolymer was obtained at 80 °C in a continuous stirred tank reactor(CSTR) using toluene and benzoyl peroxide(BPO), as solvent and initiator, respectively. The reactor volume was 0.3 liters and residence time was 3 hours. The thermal decomposition followed the second order kinetics for BMA/St copolymer. The activation energies of thermal decomposition were in the ranges of 38 ~43 kcal/mol for BMA with St copolymer and a good additivity rule was observed with the composition of copolymer. The thermogravimetric trace curve agreed well with the theoretical calculation.

Keywords : butyl methacrylate(BMA), styrene(St), thermal decomposition, CSTR, kinetics.

1. 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 is not simple[3]. Our previous work reported on the continuous copolymerization of butyl methacrylate(BMA) with styrene(St)[7]. Particularly, this continuous copolymerization of BMA with St has attracted many interests in this laboratory to prevent the unzipping in a polymerization of BMA by incorporating

second monomer.

In general, the acrylates are added to impact film-forming characteristics to copolymer. These polymers and copolymers are used as paints, adhesive and coatings and so on. The previous study revealed that the copolymerization of BMA with St followed the second-order kinetics in a CSTR, regardless of the composition of the copolymer. The present paper deals with the thermal degradation behavior of the BMA with St copolymer, which were obtained from our previous CSTR experiments. We have investigated the following axioms : the copolymerization process of BMA with St 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 BMA with St 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 copolymer of BMA with St, which was obtained in a CSTR, and investigated the validity of our assumptions. The activation energy and the order of thermal degradation of the copolymer were analyzed theoretically and experimentally.

2. Theory

The kinetics of thermal degradation of various polymers has 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 experiments which were carried out at several different rates of temperature rise according to Friedman's method[10]. The general kinetics equation of thermal degradation of polymers is

$$dc/dt = A \cdot (1-c)^n \cdot \exp(-E/RT) \quad (1)$$

$$c = 1 - \frac{1}{\left[\frac{1}{(1-c_0)^{n-1}} + \frac{RA(n-1)}{\beta E^2} \left(T^2 \frac{(E-2RT)}{e^{(E/RT)}} - T_0^2 \frac{(E-2RT_0)}{e^{(E/RT_0)}} \right) \right]^{1/(n-1)}}} \quad (8)$$

where, c =degree of conversion

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

$$\ln(dc/dt) = \ln A + \ln(1-c)^n - E/RT \quad (2)$$

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

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

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

$$dc/(1-c)^n = A/\beta \exp(-E/RT) \quad (4)$$

Taking integration of Eq. (4) in the given boundary condition (from $c=c_0$, $T=T_0$ to $c=c$, $T=T$), which gives

$$\begin{aligned} & 1/(n-1) \cdot (1-c_0)^{n-1} - (1-c)^{n-1}/ \\ & (1-c)^{n-1} - (1-c_0)^{n-1} = \\ & AE/\beta R \cdot [P(X) - P(X_0)] \end{aligned} \quad (5)$$

where, $X=E/RT$, $X_0=E/RT_0$.

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

$$P(X_0) = e^{-X_0} - \int_{X_0}^\infty \frac{e^{-X_0}}{X_0} dX_0 \quad (7)$$

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.

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

$$E_{\text{copolymer(BMA/St)}} = f \cdot E_{\text{PBMA}} + (1-f) \cdot E_{\text{PST}} \quad (9)$$

where, f are mole fraction of BMA in copolymer.

3. Experimental

3.1. Materials

The BMA/St copolymer were produced in a CSTR. Detailed of the CSTR experiments are described elsewhere[7]. Tables 1 and 2 summarize the characteristics of the samples used in the work.

3.2. Thermogravimetry

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

Table 1. The Monomer Composition in Copolymers ($[M_1]$: BMA, $[M_2]$: St)

Feed composition ($[M_1]/[M_2]$) (mole %)	Element*[wt%]			Copolymer composition	
	C	H	O	$[m_1]$	$[m_2]$
100/0	59.84	8.06	31.96	100	0
80/20	68.44	8.64	22.92	74.55	25.45
60/40	73.84	8.46	17.70	58.00	42.00
50/50	76.63	8.45	14.92	49.41	50.59
40/60	79.29	8.43	12.28	41.13	58.87
20/80	84.27	8.22	7.51	25.50	74.50
0/100	89.21	10.79	-	0	100

* By elemental analysis

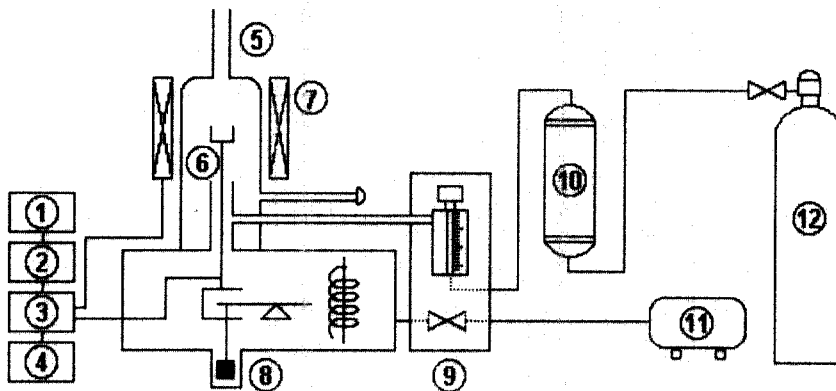


Fig. 1. Schematic diagram of thermogravimetric analyzer.

- | | |
|---------------------------|--------------------------------------|
| ① TG, DTG unit | ② DTA, DSC unit |
| ③ Temperature controller | ④ Pen recorder |
| ⑤ Gas flow attachment | ⑥ Sample holder |
| ⑦ Electric furnace | ⑧ Balance weight adjusting mechanism |
| ⑨ Atmosphere control unit | ⑩ Drying bottle |
| ⑪ Vacuum pump | ⑫ Nitrogen cylinder |

4. Results and Discussion

The DTG(derivative thermogravimetry) curves for poly(butyl methacrylate)(PBMA) and polystyrene(PSt) at heating rates of 4, 12 and 20 °C/min are shown in Fig. 2 and 3, respectively. In the case of PBMA as shown in Fig. 2, 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 maximum in the DTG curves were observed at higher temperature as the heating rate became higher. The degradation kinetics of PBMA, showing three stages of degradation breakdown, was already reported by Duval[14], Newkirk[15] or Lukaszewski and Redfern[16].

Otherwise, the degradation kinetics of PSt. as Fig. 3 showed one stage of degradation breakdown and the rate of weight loss increased as the temperature was increased reaching maximum in the vicinity of the temperatures range of 390°C~420°C. The Maximum temperature of PSt. was higher than that of PBMA. The DTG curves for BMA/St copolymer having the composition of 74.55/25.45 (mole%) is shown in Fig. 4. The degradation behavior for the copolymer showed similar behavior to the PSt homopolymer. The maximum temperatures of the copolymer were observed between the temperatures PBM and PSt. The result implies that the degradation behavior for the copolymers is more complex than that for the homopolymer. The effect of copolymer composition on the DTG curves were shown in Fig. 4. Like in Fig. 3, the higher peaks were observed for copolymers, regardless of their compositions, than PBMA homopolymer.

The activation energies of copolymer (BMA/St) which was derived from Eq. (5) with the help of Fig. 5, are listed in Table 2. Fig. 5 shows a typical Friedman plots at several fraction weight losses for the degradation of copolymer(BMA/St=49/51) to

obtain the activation energy of copolymer (BMA/St) degradation. The slope of each line in Fig 5 is equal to $-E/R$. Fig. 6 shows the change in activation energy as a function of BMA composition in BMA/St copolymer system.

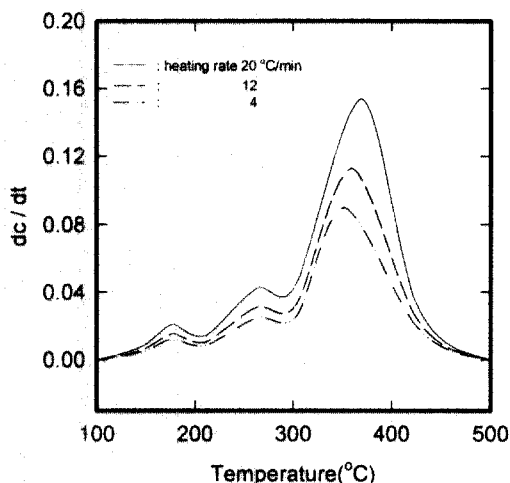


Fig. 2. DTG curves of PBMA degraded in the stream of nitrogen gas at various heating rates.

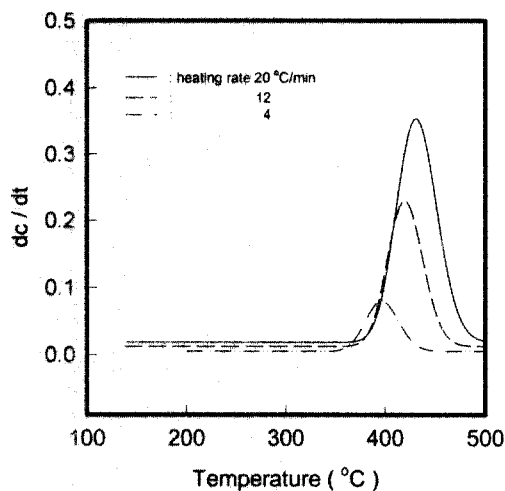


Fig. 3. DTG curves of PSt degraded in the stream of nitrogen gas at various heating rates.

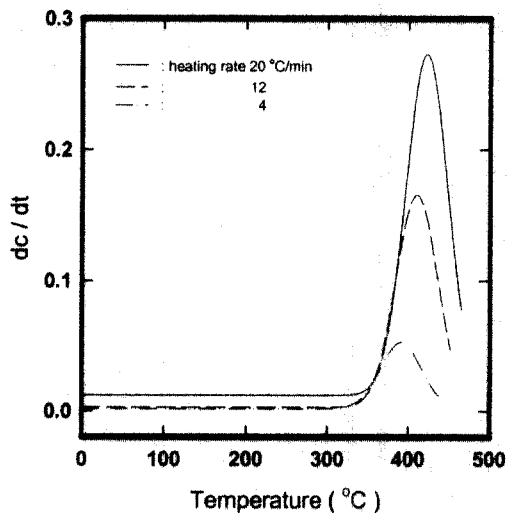


Fig. 4. DTG curves of Poly(BMA-co-St) degraded in the stream of nitrogen gas at various heating rates[BMA/St.=74.55/25.45].

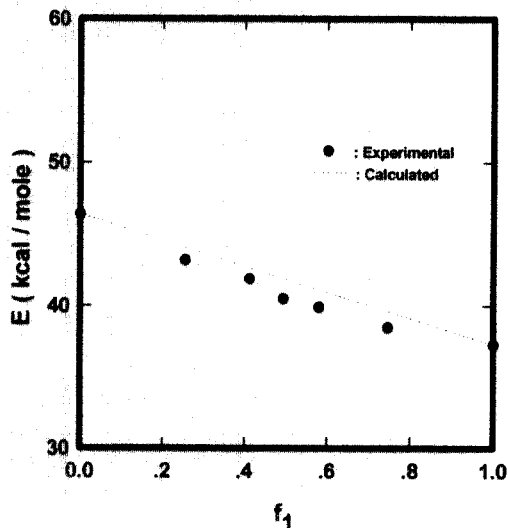


Fig. 6. Dependence of the activation energy of copolymer(BMA/St) in thermal degradation on copolymer composition.

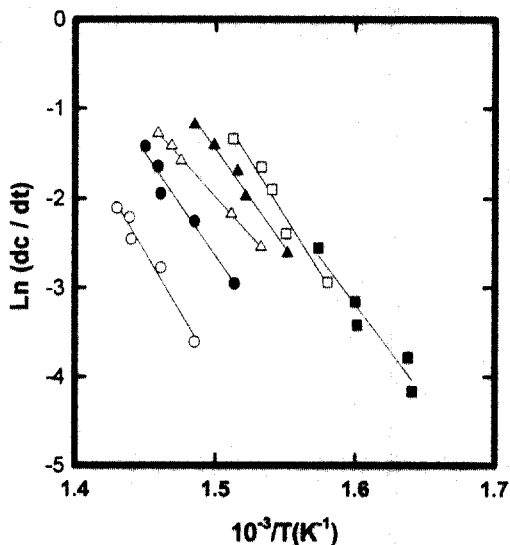


Fig. 5. Friedman plots at the following fractional weight losses for the thermal decomposition of copolymer (BMA/St=49/51)[○ : 0.9, ● : 0.8, △ : 0.7, ▲ : 0.5, □ : 0.3, ■ : 0.1].

It is seen that the activation energy approaches to the value of that of PSt. homopolymers at the copolymer composition of 0 and 100 wt% and the additivity rule well holds. It is seen in Table 2 that the activation energy ranged from 38 to 43 kcal/mole for the BMA/St. copolymers. The value of the frequency coefficient, A, was also shown in the Table 2. 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 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

Table 2. Activation Energy E, Reaction Order n and Pre-Exponential Factor A for the Degradation of PBMA, PSt and Their Copolymers ([m₁] : BMA, [m₂] : St)

Copolymer composition ([m ₁]/[m ₂]) (mole %)	Average E [kcal/mol]	Main stage		
		E[kcal/mol]	n	A[min^{-1}]
100/0	37.0	37.3	1.38	7.56×10^{11}
74.55/25.45	38.1	38.5	1.80	8.90×10^{14}
58.00/42.00	39.3	39.9	1.51	1.20×10^{15}
49.41/50.59	39.9	40.5	1.76	1.50×10^{16}
41.13/58.87	41.0	41.9	1.63	2.00×10^{17}
25.50/74.50	42.5	43.2	1.62	6.91×10^{16}
0/100	47.2	46.4	0.92	1.96×10^{13}

of BMA/St copolymer system was 1.66. The value correspond to the kinetic order of copolymerization of BMA with St in the CSTR used in our previous work⁷. It was obtained from Fig. 7 that the reaction orders and the pre-exponential factors 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) for the BMA/St=49.41/50.59 copolymers.

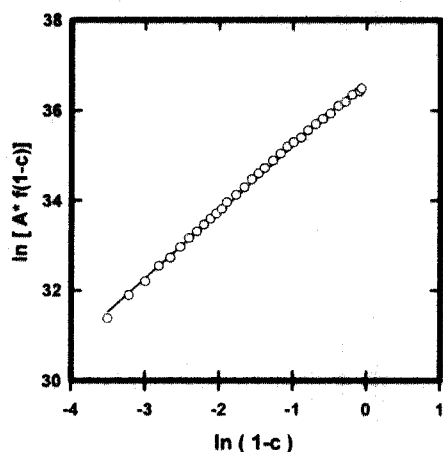


Fig. 7. Plot of the determination of A and kinetic order of copolymer(BMA/St=49/51) at main stage.

Finally, it was also observed that there is a good correlation between experiments and theory for our copolymer systems. Fig. 8 shows a typical thermograms obtained, theoretically and experimentally, for the BMA/St copolymer of 25.50/74.50 composition. In this figure, the theoretical curve was drawn by Eq. (8) with the data of E, A and n in Table 2. One can see that the experimental TGA curves are well fitted by the theoretical calculation. Fig. 9 show pyrogram of pyrolysis gas chromatography (PGC) of BMA/St=49.41/50.59 copolymer, pyrolyzed at 300°C, 1% of gaseous mixtures, 50% of St. monomer and 48% of BMA monomers were observed. The copolymer showed less light gases and the withdrawing rate of monomer was more than 90%. Fig. 10 is the FT-IR spectra of copolymer (BMA/St=49.41/50.59) copolymer, thermally decomposed with temperature change of copolymers. From this figure, the intensity of characteristic absorption stretching vibration of aromatic C-H(3050cm^{-1}), strong bending vibration of aromatic C-H(700cm^{-1}), strong stretching vibration of C=O(1750cm^{-1}) and strong stretching vibration of C-O(1200cm^{-1}) were decreased slowly as the temperature

changed. Consequently, from the results of PGC and FT-IR analyses, 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.

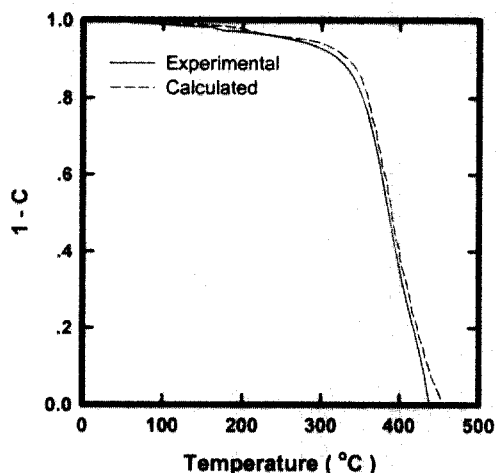


Fig. 8. Experimental and calculated TG curves of copolymer (BMA/St=25.50/74.50) in the heating rate of 10°C/min (correlation coefficient is 0.99).

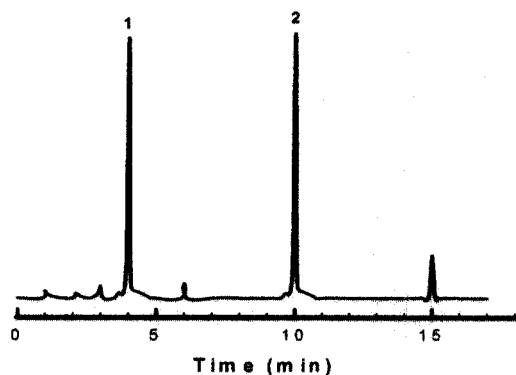


Fig. 9. Pyrogram of poly(BMA-co-St) pyrolyzed at 300°C, where 1 and 2 denote BMA and St monomer peaks, respectively [pyrolysis conditions : oven temp.: 30°C (7min hold) to 300°C(5min hold), temp. program ; 20/min, pyro. time ; 10sec].

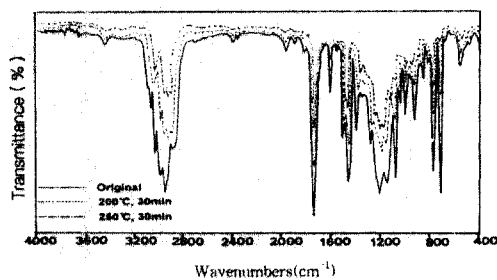


Fig. 10. FT-IR spectra of thermally decomposed poly(BMA-co-St.) at various temperature.

5. Conclusions

The thermal decomposition of the copolymer followed the second order kinetics for BMA/St copolymer, which was almost in accordance with the order of copolymerization in a CSTR. The activation energy of thermal decomposition was in the range of 38~43 kcal/mol and a good additivity rule was observed with each composition of copolymer.

In conclusion, it was found that the kinetic order of copolymerization and that of degradation shows the corresponding correlation. The average order of BMA/St system was 1.66 and the thermogravimetric trace curve agreed well with the theoretical calculation. Finally, the thermal degradation of copolymer was considered to occur by the random scission at an environment temperature below 300°C.

Nomenclature

- A : pre-exponential factor [min^{-1}]
- c : degree of conversion [-]
- c_0 : initial degree of conversion [-]
- E : apparent activation energy [kcal/mol]
- f : mole fraction of BMA 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]
 T₀ : initial absolute temperature [K]
 β : heating rate [°C/min]

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