Thermal Decomposition Characteristics of Ethyl Methacrylate and Styrene Copolymer

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Abstract : Thermal decomposition characteristics of ethyl methacrylate (EMA) and Styrene (St.) copolymer was investigated with synthesis at 80°C in a continuous stirred tank reacto (CSTR) using toluene and benzoyl peroxide (BPO) as solvent and initiator, respectively. The thermal decomposition was considered to be side scission at below 300°C and estimated 2nd-order reaction kinetics of EMA/St. copolymer. The activation energies of decomposition on this copolymers were in the ranges of 38~43 kcal/mol for EMA/St. and a good additivity rule was observed in each composition. The thermogravimetric trace curves agreed well with the theoretical calculation.

Key words : ethyl methacrylate (EMA), styrene (St), thermal decomposition, kinetics

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 EHA 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_0 : initial absolute temperature [K]
β : heating rate [°C/min]

1. Introduction

Continuous process offers the advantages of improving polymer properties and economies of scale, but the design of continuous systems requires more understanding than that required in designing batch system [1~5]. In the meantime, conversions are generally low in the continuous process, also the kinetics of a polymerization reaction is not simple [3].

Particularly, this continuous copolymerization of EMA and St. has attracted many interests to prevent unzipping polymerization of EMA by incorporating second monomer. Generally, 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 studies revealed that the copolymerization of EMA and St. was followed by 2nd-order kinetics in a CSTR, regardless of the copolymer composition. This paper dealt with the thermal degradation behaviors of the EMA and St. copolymer, which was obtained from our previous CSTR experiments. We have investigated the following axioms; the copolymerization process of EMA and St. may follow a reverse order of the unzipping process during the thermal degradation and then the copolymerization kinics may be almost the same as that of thermal degradation. Since the copolymerization of EMA and St. was folowed by 2nd-order kinetics, of course, the thermal degradation kinetics would be showed by the 2nd-order kinetics. Thus, we have studied the kinetics of the thermal degradation on copolymers between EMA and St. which were obtained in a CSTR, and investigated the validity of our assumptions. The activation energy and order of thermal degradation of the copolymer were analyzed theoretically and experimentally.

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2. Theory

The kinetics of thermal degradation of various polymers has been evaluated from thermogravi-metric anaysis (TGA) at linear rates of temperature rising in many studies [7~11]. In this paper, the kinetic calculations are based on experiments which were carried out at several different rates of temperature rising according to Friedman's method [12]. The general kinetics equation of thermal degradation could be expressed as eq. (1)

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

Taking logarithms of eq. (1) gives

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

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

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

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

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

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

$$1/(n - 1) \cdot [(1 - c_o)^{n-1} - (1 - c)^{n-1}] =$$

$$AE/\beta R \cdot [P(X) - P(X_o)] \tag{5}$$

where, $X = E/RT$, $X_o = E/RT_o$

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

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

After taking the integral term of eq. (7) with a serises

expansion, we could obtain eq. (8) by substituting it to eq. (5) and rearranging the rest.

$$C = 1 - 1/$$

$$\left[\frac{1}{(1 - c_o)^{n-1}} + \frac{RA(n - 1)}{\beta E^2} \right.$$

$$\left. \left(T^2 \frac{(E - 2RT)}{e^{(E/RT)}} - T_o^2 \frac{(E - 2RT_o)}{e^{(E/RT_o)}} \right) \right]^{1/(n-1)} \tag{8}$$

Assuming that the activation energies of copolymers with the additivity rule and activation energies of PEMA, PSt could be obtainable, those could be as the follows.

$$E, \text{copolymer}_{(EMA/St.)} = f \cdot E_{,PEMA} + (1-f) \cdot E_{,PSt} \tag{9}$$

3. Experimental

3-1. Materials

The EMA/St. copolymer were synthesised in a CSTR. Detailed of the CSTR experiments are described elsewhere [6].

The characteristics of the samples used in this work are summarized in Table 1.

3-2. Thermogravimetry

The results of thermogravimetric (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. Fig. 1 shows a schematic diagram of experimental apparatus for thermal analysis.

Table 1. The monomer composition in copolymers ([M1] : EMA, [M2] : 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	25.45	74.55
0/100	89.21	10.79	–	0	100

*By elemental analysis
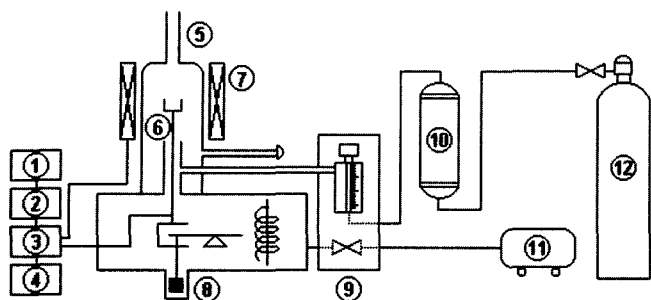
Fig. 1. Schematic diagram of thermogravimetric analyzer.

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 adjust
⑨ Atmosphere control unit ⑩ Drying bottle
⑪ Nitrogen pump   ⑫ Nitrogen cylinder

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

4. Results and Discussion

The DTG (derivative thermo gravimetry) curves for poly (ethyl methacrylate) (PEMA) and polystyrene (PSt.) at heating rates of 4, 12 and 20°C/min are shown in Fig. 2 and 3. In case of PEMA as shown in Fig. 2, the rate of weight loss increased as the temperature was increased and reached maxima in vicinity of the temperatures 160°C, 250°C and 380°C.

The maximum in DTG curves were observed at higher temperature as the heating rate is increasing. The degradation kinetics of PEMA, showing three stages of degradation breakdown, was already reported by Duval [13], and Newkirk [14].
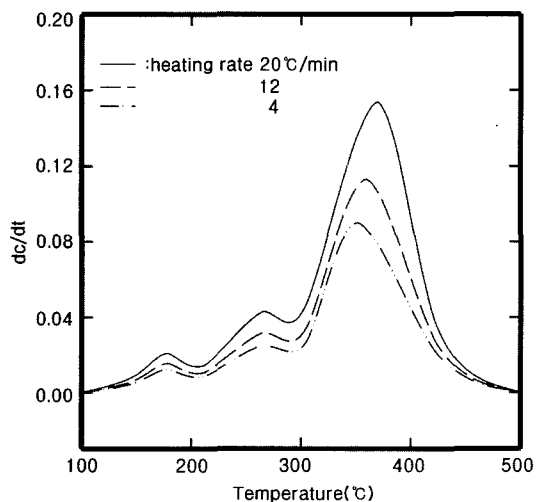
Otherwise, the degradation kinetics of PSt. in Fig. 3 showed one stage of degradation breakdown and the rate of weight loss increased as the temperature was increasing to maximum around 390°C~420°C range. The maximum temperature of PSt. was higher than that of PEMA. The DTG curves for EMA/St. copolymer 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 degradation temperatures of the copolymer were observed between both cases of PEMA and PSt. The result implies that degradation behavior for the copolymers is more complex than that of the homopolymer.

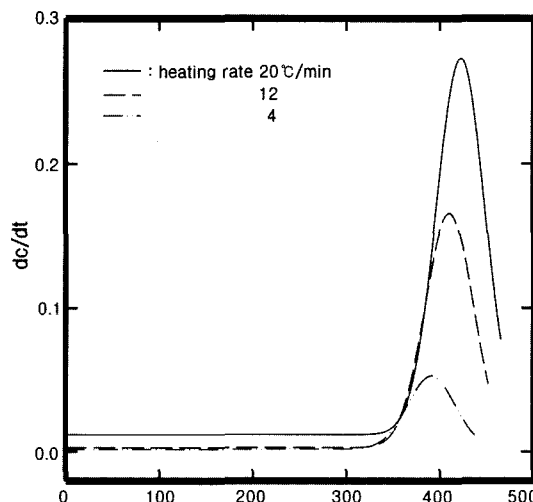The activation energies of copolymer (EMA/St.) which

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

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

Table 2. Activation energy, reaction order and pre exponential factor for the degradation of PEMA, PSt. and those copolymers ([m_1]: EMA, [m_2]: St.)

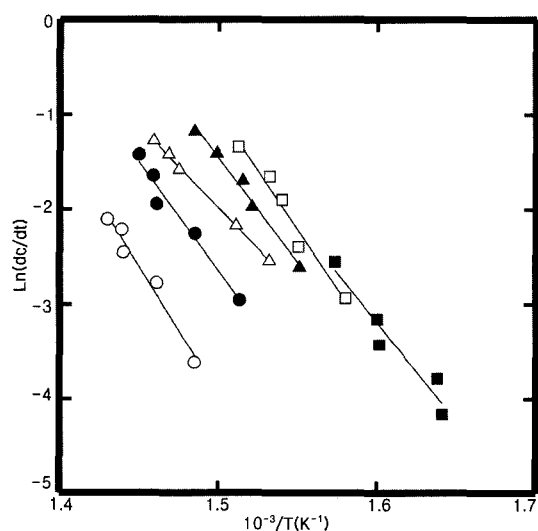| Copolymer composition ([m_1/m_2])	Average E [kcal/mol]	Main stage		
		E [kcal/mol]	n	A [min^{-1}]
100/0	37.0	37.3	1.38	7.56×10^{17}
74.55/25.45	38.1	38.5	1.8	8.90×10^{14}
58.00/42.00	39.3	39.9	1.51	1.20×10^{15}
49.41/50.59	39.9	4.0.5	1.76	1.50×10^{16}
41.13/58.87	41.0	41.9	1.63	2.00×10^{17}
25.50/74.50	42.5	43.2	1.62	6.91×10^{16}
0/100	47.2	46.4	0.92	1.96×10^{13}

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

was derived from Eq. (5) on the plots of Fig. 5, are listed in Table 2. Fig. 5 shows a typical Friedman plots at several fractional weight losses for the degradation of copolymer (EMA/St. = 49/51) to obtain activation energy of copolymer (EMA/St.) degradation. The slope of each line in Fig. 5 is equal to -E/R. Fig. 6 shows the variation of activation energy as a function of EMA composition in EMA/St. copolymer. The activation energy approaches to the value of PSt. homopolymers respect to 0 and 100 wt% at the copolymer and the additivity rule of the results is well consistent. Table 2 shows that the activation energies ranged from 38 to 43 kcal/mole for the EMA/St. copolymers. The values of the frequency coefficient, A, were also shown in the Table 2. The degradation kinetic reaction orders of the copolymers are higher than those of homopolymers. Cascaval *et al.*[15] 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 section and the reaction orders of the degradation kinics were calculated.

It was found that the degradation orders are very similar to that of copolymerization reaction.

The average order of EMA/St. copolymer system was 1.66. The value correspond to the kinetic order of copolymerization of EMA and St. in the CSTR used in our previous work [16]. It was obtained from Fig. 7 that the reaction order and the pre-exponential factor was calculated from the slope and intercept of the graph, which is related to $\ln[A \cdot f(1-c)]$ and $\ln(1-c)$ of Eq. (3) for the EMA/St = 49.41/50.59 copolymer.
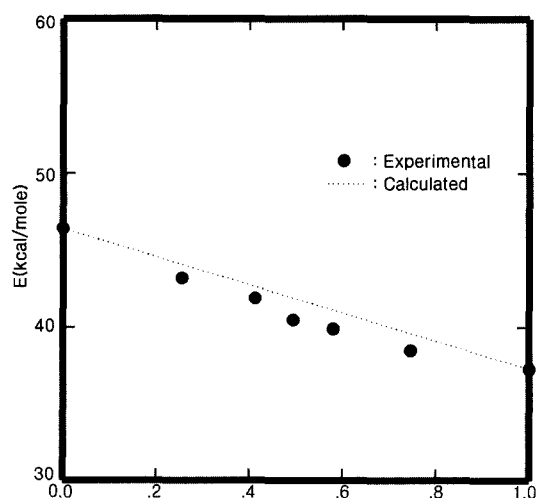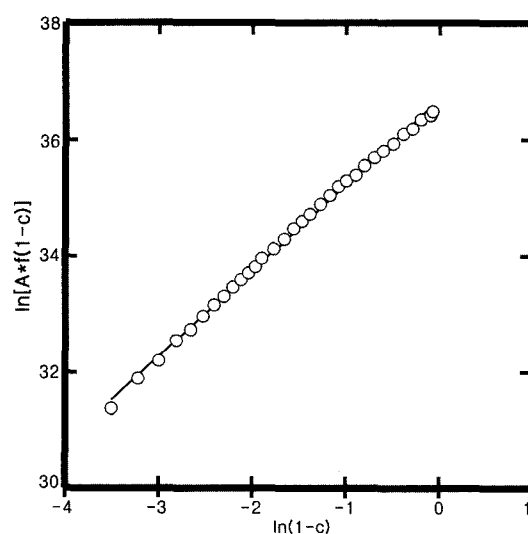

Fig. 6. Dependence of the activation energy of copolymer (EMA/St.) in thermal degradation on copolymer composition.

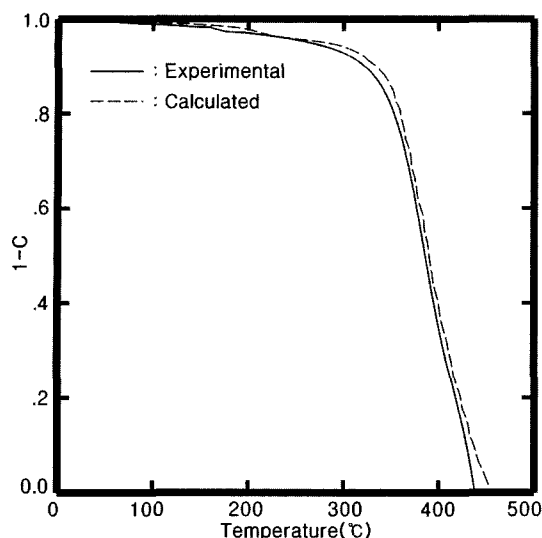**Fig. 7.** Plot of the determination of A and kinetic order of copolymer (EMA/St. = 49/51) at main stage.

Fig. 8. Expeimental and calculated TG curves of copolymer (EMA/St .= 25.50/74.50) in the heating rate of 10°C/min (C.R. = 0.99)
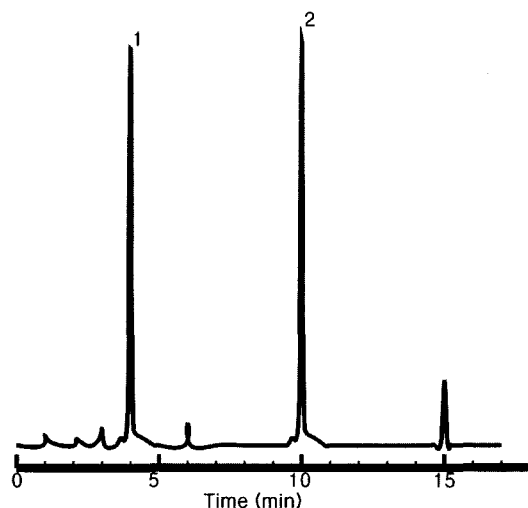

Fig. 9. Pyrogram of poly(EMA-co-St.) pyrolyzed at 300°C, where 1 and 2 denote EMA and St. monomer peaks, respectively. [pyrolysis conditions : oven temp.; 30°C (7 min hold) to 300°C(5 min hold), temp. program; 20°C/min, pyro.time; 10 sec]

We was observed a good correlation between experimental and theoretical results for our copolymer systems. Fig. 8 shows a typical thermograms obtained from the EMA/St. copolymer of 25.50/74.50 composition theoretically and experimentally.

In the Fig. 8 the theoretical curve was plotted by Eq. (8) on the data of E, A and n in Table 2. One can see well that the experimental TGA curves are well fitted by the theoretical calculation.

Fig. 9 shows pyrogram of pyrolysis gas chromatography (PGC) of EMA/St. = 49.41/50.59 copolymer, pyrolyzed at 300°C, 1% of gaseous mixtures, 50% of St. and 48% of
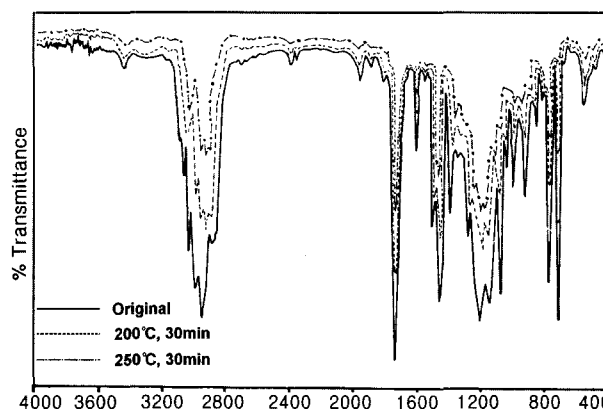

Fig. 10. FT-IR spectra of thermally decomposed poly(EMA-co-St.) at various temperature.

EMA monomers were observed. This shows that copolymer producted small amount of light gases and the withdrawing rate of monomer was more than 90%. Fig. 10 is the FT-IR spectra of EMA/St.(49.41/50.59) copolymer by decomposing with temperature variation. From the FT-IR analysis the intensity of characteristic absorption stretching vibration of aromatic C-H (3050 cm^{-1}), strong bend vibration of aromatic C-H (700 cm^{-1}) strong stretching vibration of C = O (1750 cm^{-1}) and stretching vibration of C-O of ester group (1200 cm^{-1}) was decreased slowly as the temperature changed. Consequently, the results of PGC and FT-IR analyses were considered that the thermal decomposition of the synthesized copolymers was seemed to be hardly the scission of side chains, instead of the random scission of main chains.

5. Conclusions

The thermal decomposition characteristics of copolymers on EMA/St. synthesised in CSTR was investigated by TGA and DTG. The activation energy and the order of thermal degradation of the copolymer were analyzed theoretically and experimentally. The results are as below follows.

1. The activation energies of thermal decomposition were in 38~43 kcal/mol and a good additivity rule was observed in each composition of copolymer.

2. The reaction order of EMA/St. system was estimated as 1.66 and the thermogravimetric trace curve agreed well with the theoretical calculation.

3. The thermal degradation of copolymer was considered as the side scission at below 300°C.

References

[1] Ogorkiewicz, R. H./ICL Ltd. "Engineering Proper-

tiesof Thermoplastics", Wiley-Inters-cience, New York, pp. 215, 1970.

[2] W. H. Ray and R. L. Laurence, "Polymerization Reactor Engineering in Chemical Reactor Theory, Amundson", N. R. and Lapidus, Esd., Prentice-Hall, Englewood Cliffs, New Jersey, 1977.

[3] P. Lorenzini1, M. Pons1 and J. Villermaux, "Free-radical polymerization engineering-IV Modelling homogeneous polymerization of ethylene: determination of model parameters and final adjustment of kinetic coefficients", Chem. Eng. Sci., Vol. 47, pp. 3981~3988, 1992.

[4] V. Prasad, M. Schley, L. P. Russo and B. W. Bequette, "Product property and production rate control of styrene polymerization", J. Proce. Cont., Vol. 12, pp. 353~372, 2001.

[5] S. Das and F. Rouriguez, "Diffusion-Conrolled Kinetics for the Solution Copolymerization of 2-Ethylehxyl Acrylate with Vinyl Chloroacetate in a CSTR" J. Appl. Poly. Sci., Vol. 39, pp. 1309~1323, 1990.

[6] B. S. Shin and S. D. Seul, "The Kinetis of Radical Copolymerization of Methyl Methacrylate and Styrene in Continuous Stired Tank Reactor (CSTR)" J. Polymer (Korea), Vol. 17, No. 4, pp. 452~462, 1993.

[7] H. E. Kissinger, "Reaction kinetics in Differential Thermal Analysis", Anal. Chem., Vol. 29, No. 11, pp. 1702~1706, 1957.

[8] M. J. Fernandez and M. M. Fernandez, "Thermal degradation of copolymers of styrene and 4-nitrostyrene",

Polym. Degrad. & Stab., Vol. 60, pp. 257~263, 1998.

[9] T. C. Chang, H. B. Chen, Y. S. Chiu and S. Y. Ho, "Degradation of poly dimethylioxane - block - polystyrene copolymer", Polym. Degrad. & Stab., Vol. 57, pp. 7~14, 1997.

[10] D. A. Anderson and E. S. Freeman, "The Kinetics of the Thermal Degration of Polystyrene and Polyethylene" J. Polym. Sci., Vol. 54, pp. 253~260, 1961.

[11] T. Ozawa, "A New Method of Analyzing Thermogravimetric Data." Bull. Chem. Soc., Jpn., Vol. 38, No. 11, pp. 1881~1886, 1965

[12] W. I. Kim, S. D. Kim, S. B. Lee and I. K. Hong, "Kinetics Characteristics of Thermal Degradation Process for Commercial Rubbers", J. Ind. Eng. Chem., Vol. 6, No. 5, pp. 348~355, 2000.

[13] C. Duval, "Precautions a prendre dans l'emploi des thermobalances" Anal. Chem. Acta, Vol. 31, pp. 301~314, 1964.

[14] A. E. Newkirk, "Thermogravimetric Measurement", Anal. Chem., Vol 32, No.12, pp. 1558~1564, 1960

[15] C. N. Cascaval, G. Chitanu and A. Carpov, "On the thermal decomposition of copolymers of maleic anhydride with styrene", Thermo. Acta., Vol. 275, pp. 225~233, 1996.

[16] N. S. Kim, S. D. Seul, T. E. Cheong and J. J. Chol, "The kinetics of Radical copolymerization of Styrene with Alkyl Methacrylate in a CSTR", J. Korea Ind. Eng. Chem., Vol. 10, pp. 796~803, 1999.