# SOLUTION COPOLYMERIZATION OF METHYL METHACRYLATE AND ALKYL METHACRYLATES IN A CONTINUOUS STIRRED TANK REACTOR(CSTR)

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**Abstract**—Continuous solution copolymerization of methyl methacrylate with ethyl methacrylate or n-butyl methacrylate was carried out in a continuous stirred tank reactor. Solvent and initiator used were toluene and benzoyl peroxide, respectively. Reaction volume was 1.2 litters, residence time 3 hours and polymerization temperature 80°C . The copolymerization conversions were analyzed by UV spectrophotometry and confirmed by measuring the solid weights of copolymers obtained after evaporating solvent. The copolymerization of methyl methacrylate and alkyl methacrylates followed the second order kinetics. The simulated conversions and copolymerization rates were compared with the experimental results. The average time to reach dynamic steady-state was three and half times of the residence time.

## INTRODUCTION

Copolymerization in a batch reactor has been studied for several decades. Even though the batch copolymerization has given lots of useful informations on the kinetics or reactivity, it always involves some technical problems such as high maintenance cost and difficulty in control during operation. In a practical point of view, continuous systems in polymerization process are capable of solving those problems which appeared in a batch copolymerization [1, 2]. The on-lined process include several advantages such as cost reduction, easy polymerization and the like. The process control and the kinetics of polymerization have been main themes of the investigations.

Continuous process offers the advantages of improved polymer properties and economics of scale but the design of continuous systems requires more understanding than is required in the design of batch system [3-5]. In addition, conversions are generally low in a continuous process and the kinetics of a polymerization reaction is not simple [5].

Kinetic studies of copolymerization in a CSTR were made in this work. Particularly, the continuous copolymerization of methyl methacrylate with alkyl methacrylates have attracted much interests in this laboratory to prevent the unzipping in a polymerization of

methyl methacrylate [6]. In case of a polymerization of methyl methacrylate, the efficiency is low in general because of the hyperconjugation effect of methyl group attached to the carbon in the main chain. The unzipping property of methyl methacrylate can be prevented by incorporating second monomer through a copolymerization.

In the present system, two different alkyl methacrylates were selected for copolymerization because they contain the same chemical structure except pendant group. Toluene is used as a solvent to control the "gel effect" from the exothermic heat of copolymerization.

## EXPERIMENTAL

### 1. Materials

Monomers used in the present experiment are methyl methacrylate (Junsei Chemical), ethyl methacrylate (Junsei Chemical) and n-butyl methacrylate (Junsei Chemical). All the monomers were purified by standard procedures. Benzoyl peroxide (Hayashi Chemical) as an initiator was purified by recrystallization from methanol. Toluene was used after distillation.

### 2. Copolymerization in a CSTR

The CSTR used in this study is shown in Fig. 1. The operation principle is basically same as described
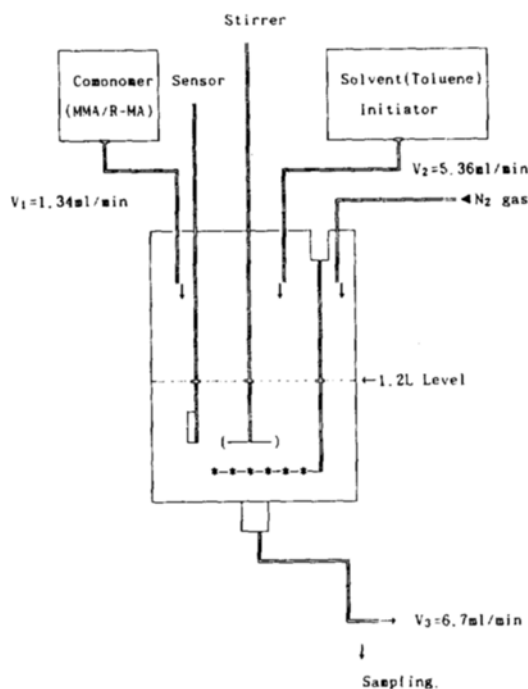
Fig. 1. Schematic diagram of CSTR experiments.
(R-MA denotes alkyl methacrylate)



Fig. 2. UV absorption changes of the mixture MMA/
BMA(40/60) with time.
(The characteristic wavelength of copolymer was
detected at 285 nm).

in the literature [1]. The start-up procedure was to
fill the reactor initially with the desired ratio of the
comonomer in the solvent. While the mixture in the
reactor was being heated up to the desire temperature
$N_2$ gas was purged continuously to prohibit the reacted
materials from oxidizing during copolymerization reac-
tion. The temperature was maintained at 80°C through-
out the copolymerization.

The initiator had been added to the mixture in the
reactor just before the pumps were operated. The total
flow rate was maintained at 6.7 ml/min. The residence
time was 3 hours but a run was typically durated for
about four residence times to achieve steady state.

The sampling was done at intervals of 30 min. The
volume fraction of the solvent in the reaction was kept
constant to allow no gel-effect. The sample were dried
to a constant weight under high vacuum at a room
temperature for several days. The copolymer compo-
sition was determined by $^1$H-NMR spectroscopy (Bru-
ker WP80CW). The on-lined conversion of the samples
withdrawn were also analyzed by measuring the absorb-
ance change with time on UV Spectra (Shimadzu 200
A).

The calibration in the conversion was made by re-
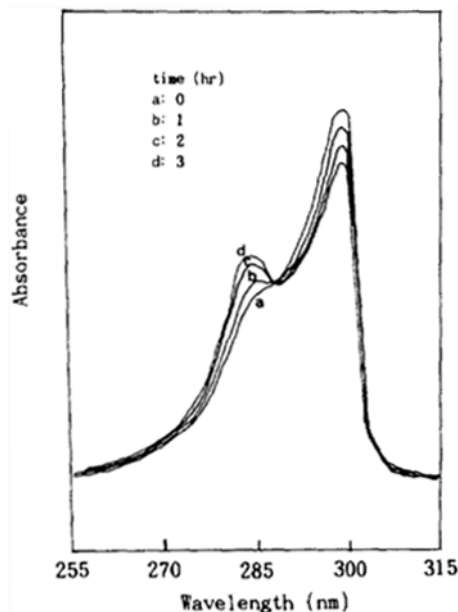peated comparing the UV absorbance change with the

solid weight of the dried products. Repeatability in
the conversion determination by UV spectra was fairly
good. Fig. 2 shows typical UV absorption changes of
the mixture, MMA/BMA(40/60) as a function of time
measured at 285 nm. It is clearly seen that the UV
absorbance of the copolymer increases with time as
the conversion of monomer to copolymer becomes hi-
gher. The experimental conditions were summarized
in Table 1.

**Table 1. Experimental conditions**

| | |
|---|---|
| Polymerization temperature | 80°C |
| Solvent | Toluene |
| Solvent/comonomer ratio | 4 : 1(v/v) |
| Initiator used | Benzoyl peroxide |
| Initiator concentration | 10 mmol/L |
| Residence time | 10800 sec |
| Reaction volume | 1.2 L |

## RESULTS AND DISCUSSION

### 1. Rate Parameters

The rate parameters used in the present study were
taken from the literatures [7-9]. The reactivity ratios
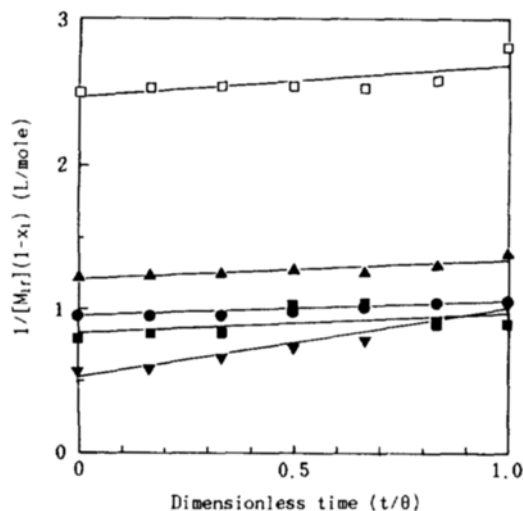[10], $r_1$ and $r_2$, in the copolymerization of methyl meth-

**Table 2. Summary of parameters in the CSTR experiments**

| BPO | Methyl methacrylate | n-Butyl methacrylate | Ethyl methacrylate |
|---|---|---|---|
| $k_d = 4.3 \times 10^{-5}$ | $k_{p11} = 800.00$ | $k_{p22} = 1012.04$ | $k_{p22} = 464.00$ |
| $f = 0.9$ | $k_{t11} = 3.05 \times 10^7$ | $k_{t22} = 1.30 \times 10^7$ | $k_{t22} = 1.21 \times 10^7$ |
| $R_i = 6.45 \times 10^{-9}$ | $k_{p11}/k_{t11} = 2.62 \times 10^{-5}$ | $k_{p22}/k_{t22} = 7.78 \times 10^{-5}$ | $k_{p22}/k_{t22} = 3.84 \times 10^{-5}$ |
| $[I] = 8.33 \times 10^{-5}$ | $\delta_1 = 9.76$ | $\delta_2 = 5.04$ | $\delta_2 = 10.60$ |

$k_{pii}$, $k_{tii}[=]$l/mole·sec, $k_d[=]$sec$^{-1}$, $R_i[=]$mole/1·sec, $[I][=]$mole/1

$R = $n-butyl, $r_1 = 0.52$, $r_2 = 2.11$

$R = $ethyl, $r_1 = 0.81$, $r_2 = 0.86$
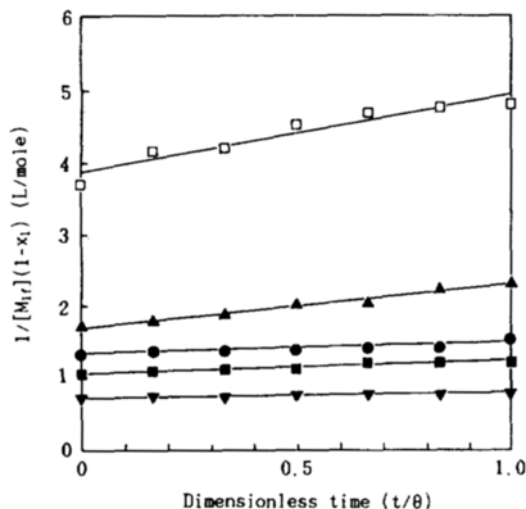


Fig. 3. The correlation of the 2nd-order kinetics in the copolymerization of MMA/BMA series(correlation coefficient : 0.96).
(□ : 20/80, ▲ : 40/60, ● : 50/50, ■ : 60/40, ▼ : 80/20)



Fig. 4. The correlation of the 2nd-order kinetics in the copolymerization of MMA/EMA series(correlation coefficient : 0.92).
(□ : 20/80, ▲ : 40/60, ● : 50/50, ■ : 60/40, ▼ : 80/20)

acrylate (MMA) with n-butyl methacrylate (BMA) are 0.52 and 2.11, respectively. This means that BMA is more reactive toward homopolymerization than MMA. In case of MMA and ethyl methacrylate (EMA) [11], however, the reactivity ratios of the two monomers were similar; $r_1$(MMA) = 0.81 and $r_2$(EMA) = 0.86. In this work, the reactivity ratios measured at 60℃ were taken. Even though the CSTR experiments in this study were carried out at 80℃, we assumed that the temperature dependences of the reactivity ratios were negligible, since the ceiling temperature of MMA is relatively high as 135-155.5℃. Thus, the copolymer compositions are considered to be not much different from those in feed within tolerable significances. The rate parameters are summarized in Table 2.

## 2. Rate of Copolymerization

In general, the polymerization reaction in a batch reactor follows first-order kinetics [12, 13], especially for homopolymerization. Our present system showed that the continuous copolymerization of MMA with BMA or EMA followed second-order kinetic behavior, as shown in Figs. 3 and 4. In the copolymerization of MMA and BMA in a CSTR, as shown in Fig. 3, the inverse of $[M_{1f}]$ $(1 - x_1)$ increased linearly with time. In this figure, $[M_{1f}]$ and $x_1$ denote the mole of MMA in feed and the conversion of MMA to polymer, respectively. Fig. 3 implies that the copolymerization reaction of MMA and BMA in a CSTR follows the second-order kinetics. The slope of the solid line in the figure, which obtained from the linear regression, decreased remarkably as the MMA composition in feed increased up to 0.5 but thereafter levelled off with further increasing MMA composition in feed. The trends in the rate of copolymerization is more clearly seen in the plot of rate constant of copolymerization against MMA composition (Fig. 5), where the rate con-
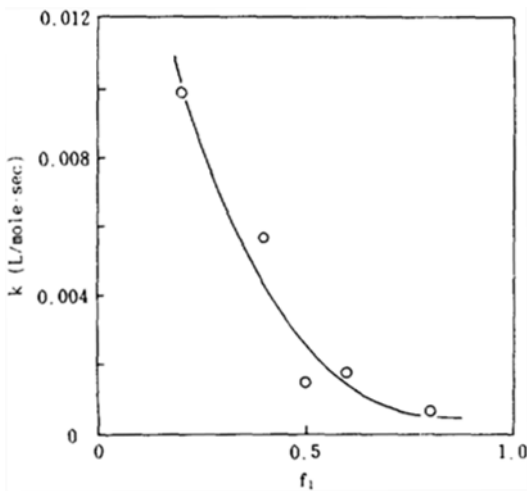
Fig. 5. Dependence of the rate constant on the composition of MMA in the copolymerization of MMA and BMA.



Fig. 6. Dependence of the rate constant on the composition of MMA in the copolymerization of MMA and EMA.

stant of copolymerization is estimated from the slope of the straight line in Fig. 3. The large difference in reactivity ratios of BMA and MMA implies that the rates of copolymerization as well as homopolymerization increases rapidly with increasing BMA composition whereas those rates increase steadily with increasing MMA composition. Thus, the rate of copolymerization decreases rapidly with increasing MMA composition or decreasing BMA composition up to 50/50 composition but the composition of MMA becomes higher, the increase of copolymerization rate due to increasing MMA composition counterbalances the decrease of the rate due to decreasing BMA composition. Then, it may be thought that the rate of copolymerization has the levelling-off tendency, shown in Fig. 5, beyond the composition of 50/50 MMA/BMA. This tendency is in a good accord with the result of dynamic steady state approach, which will be discussed later.

The continuous copolymerization of MMA and EMA follows also second order kinetics, as shown in Fig. 4. The slope represents the bulk rate constant of copolymerization. One can see that the rate of copolymerization went through a minimum at a composition of 50/50 MMA/EMA in Fig. 6. The trend is more severe in the copolymerization of MMA and BMA than of MMA and EMA, since the difference in reactivity ratios in case of MMA/BMA is larger than that in case of MMA/EMA.

## 3. Dynamic Steady State

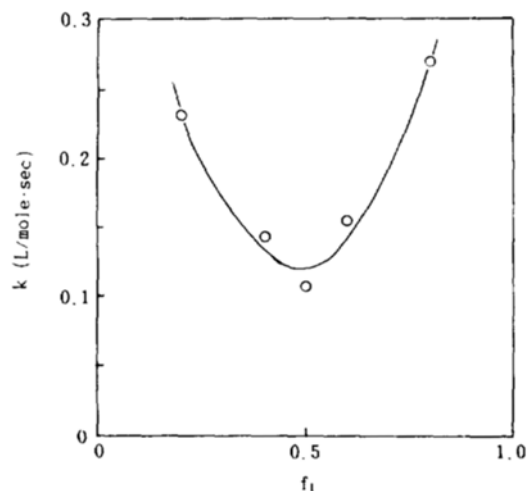Studies on the dynamic steady-state in a continuous polymerization process have not been widely carried out while the stationary steady-state in a batch system have been extensively investigated. It is considered that the dynamic steady-state is able to be realized only in a continuous system, which is concerned on the continuous increment of conversion with time as far as the reactants are active.

The dynamic steady-state modeling is sourced from the steady state approximation [14] and general mole balance equation [15].

The overall general mole balance with steady state copolymerization is given as

$$[M_{ij}] - [M_j] = R_i\theta, \quad R_i = k_i[M_i][I]^{0.5},$$

$$Fl_{ij} - Fl_i + \int^V r_i dV = dN_i/dt \tag{1}$$

The mole balances for each component, $M_1$, $M_2$ and I, are

$$V(d[M_1]/dt) = ([M_{1i}] - [M_1]) - R_1V,$$
$$R_1 = k_1[M_1][I]^{0.5}$$
$$V(d[M_2]/dt) = ([M_{2i}] - [M_2]) - R_2V,$$
$$R_2 = k_2[M_2][I]^{0.5}$$
$$V(d[I]/dt) = ([I_i] - [I]) - k_d[I]V,$$
$$[I] = [I_i]/(1 + k_d\theta) \tag{2}$$

Introducing several parameters for simple manipulation,

$$t_1 = t/\theta, \quad \theta = V/v, \quad f_A = [M_{1i}]/[M_{2i}], \quad f_B = [I_i]/[M_{2i}],$$
$$DB = k_1/k_2, \quad DR = k_d/(k_2[I_i]^{0.5}), \quad DA = k_2[I_i]^{0.5}\theta. \tag{3}$$
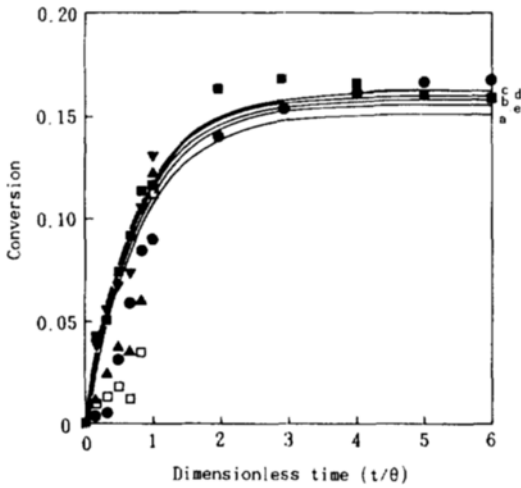
By definition,

**Fig. 7. Variation of the experimental conversions with the different feed compositions in MMA/EMA mixtures : Solid lines represent the simulation results against dimensionless time with various feed compositions.**
(a : 20/80, b : 40/60, c : 50/50, d : 60/40, e : 80/20)
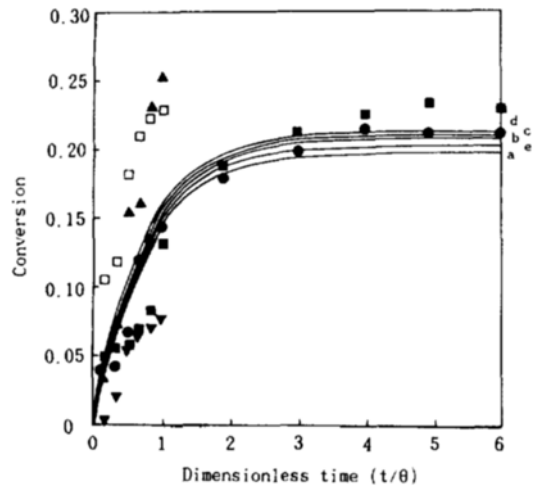(□ : 20/80, ▲ : 40/60, ● : 50/50, ■ : 60/40, ▼ : 80/20)

**Fig. 8. Variation of the experimental conversions with the different feed compositions in MMA/BMA mixtures : Solid lines represent the simulation results against dimensionless time with various feed compositions.**
(a : 20/80, b : 40/60, c : 50/50, d : 60/40, e : 80/20)
(□ : 20/80, ▲ : 40/60, ● : 50/50, ■ : 60/40, ▼ : 80/20)

$$x_1 = ([M_{1f}] - [M_1])/[M_{1f}]$$
$$x_2 = ([M_{2f}] - [M_2])/[M_{2f}]$$
$$x_3 = ([I_f] - [I])/[I_f] \qquad (4)$$

Rearranging several variables into other parameters, coupled with the rate equation of copolymerization described later in Eq. (5).

$$k_1 = [r_1(1-x_1)f_A + (1-x_2)]/T_A^{0.5}$$
$$k_2 = [(1-x_1)f_A + (1-x_2)r_2]/T_A^{0.5}$$
$$T_A = T/(2fk_d)$$
$$T = [r_1\delta_1(1-x_1)f_A]^2 + [r_2\delta_2(1-x_2)]^2 + T_B$$
$$T_B = 2\phi r_1 r_2 \delta_1 \delta_2(1-x_1)(1-x_2)f_A.$$

Finally, consequential dimensionless modeling equations are estimated as

$$dx_1/dt_1 = -x_1 + (1-x_1)(1-x_3)^{0.5}DA \cdot DB$$
$$dx_2/dt_1 = -x_2 + (1-x_2)(1-x_3)^{0.5}DA$$
$$dx_3/dt_1 = -x_3 + (1-x_3)DA \cdot DR \qquad (5)$$

As shown in Fig. 7, the conversions in the copolymerization of MMA and EMA varied with dimensionless time. This dimensionless time is the reaction time divided by residence time. Solid lines in this figure represent the conversions by computer simulation. The comonomer mixtures of the two compositions, 50/50 and 60/40, were selected to react for six resi-

dence times. The conversions for the copolymer of EMA-rich compositions show negative deviation from the simulated results. It was observed that the average time to reach dynamic steady-state was three and half times of the residence time. The conversions of the mixtures are well approached to the simulated values up to six residence times.

However, larger deviation of conversions were observed from simulation results in the copolymerization of MMA and BMA, as shown in Fig. 8. The copolymerizations of MMA with BMA having the composition ratios of 50/50 and 60/40 were durated for six residence times. As the reaction proceeds, the experimental conversions are largely diverged from the simulated values except the copolymers having the compositions around 50/50.

Figs. 9 and 10 present the rate of copolymerization (Rp) of the MMA/EMA and MMA/BMA systems, respectively. It was assumed that the termination process in this copolymerization is chemically controlled [see Eq. (7)] and the copolymerization rate Eq. (6) was applied.

$$R_p = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)R_i^{0.5}}{[(r_1\delta_1[M_1])^2 + 2\phi r_1 r_2 \delta_1 \delta_2[M_1][M_2] + (r_2\delta_2[M_2])^2]^{0.5}} \qquad (6)$$
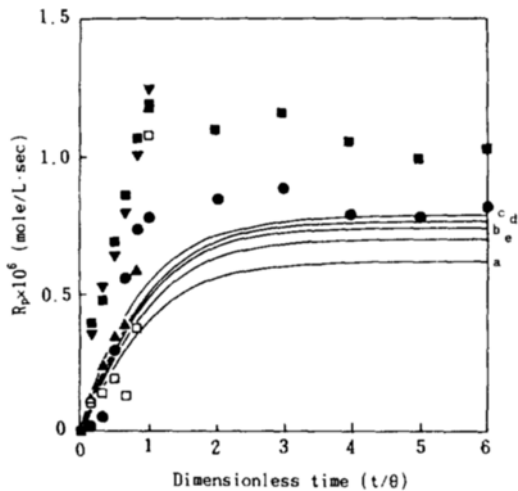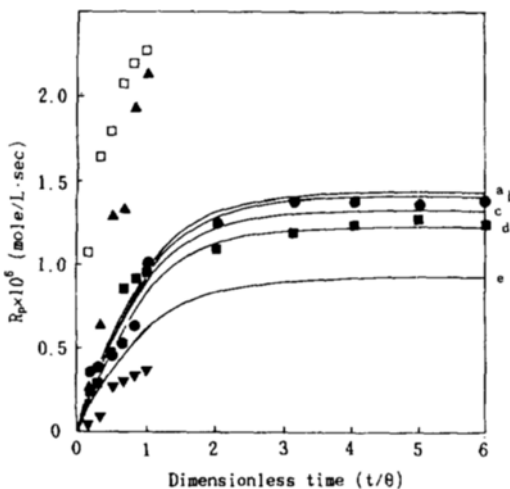
Fig. 9. Variation of the experimental rates of copolymeri-
zation with the different feed compositions in
MMA/EMA mixtures : Solid lines represent the
simulation results against dimensionless time with
various feed compositions.

(a : 20/80, b : 40/60, c : 50/50, d : 60/40, e : 80/20)
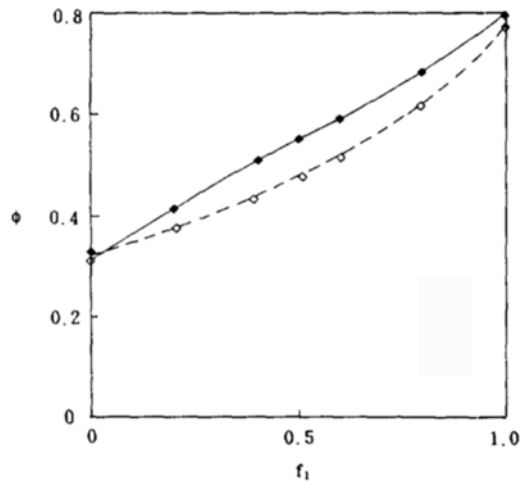(□ : 20/80, ▲ : 40/60, ● : 50/50, ■ : 60/40, ▼ : 80/
20)



Fig. 11. φ-factor varied with comonomer composition.
(◇ : MMA/BMA, ◆ : MMA/EMA)

where

$$r_1 = k_{p11}/k_{p12}, \quad r_2 = k_{p22}/k_{p21}$$
$$\delta_1 = (2k_{t11}/k_{p11}^2)^{0.5}, \quad \delta_2 = (2k_{t22}/k_{p22}^2)^{0.5}$$
$$\phi = k_{t12}/[2(k_{t11}k_{t22})^{0.5}]$$
$$R_i = 2fk_d[I].$$

Subscripts 1 and 2 refer to monomer 1 and monomer
2, respectively. In order to obtain the $R_p$, rate parame-
ters summarized in Table 2 was used.

It is noticeable that merely the initial rate of copo-
lymerization for the monomer mixtures of around 50/
50 composition shows a good agreement with the sim-
ulated solid line and that the durated rate data oscil-
late and have a tendency of convergency to the simu-
lated rate. In other words, both of the two systems
show large or small positive and negative deviation
in comparison of the experimental rates with the sim-
ulations. Thus the assumption of chemically control-
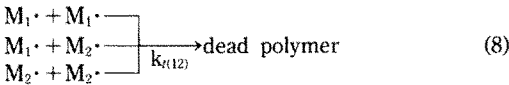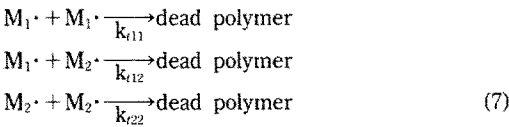led termination has to be reconsidered.

The results may be related to φ factor, which is
shown in Fig. 11. From this figure, the φ factors are
ranged from 0.20 to 0.80 for both systems. Therefore,
the experimental result cannot be described merely
by a single value of the φ factor. It is seen that the
φ factor also increases with increasing comonomer
feed composition. In the present studies of the rate
of copolymerization, the terminal model was adapted.
A φ<1 means that cross termination is not favored,
while φ>1 means that cross-termination is favored.
The tendency toward cross-termination parallels the
tendency toward cross propagation (i.e., toward alter-
nation) in that the φ increases as $r_1r_2$ approaches zero



Fig. 10. Variation of the experimental rates of copolym-
erization with the different feed compositions in
MMA/BMA mixtures : Solid lines represent the
simulation results against dimensionless time with
various feed compositions.

(a : 20/80, b : 40/60, c : 50/50, d : 60/40, e : 80/20)
(□ : 20/80, ▲ : 40/60, ● : 50/50, ■ : 60/40, ▼ : 80/
20)

[16, 17].

Another approach by North and co-workers [3, 18, 19] have suggested that the termination modes of the propagating chains are affected by the diffusion of the chain segments (8). A more applicable kinetic expression for the diffusion-controlled rate equation of copolymerization should be considered.

## 4. Chemically Controlled and Diffusion-controlled Rate Model

Termination mode by chemical-controlled concept has three different termination rate constants, $k_{t11}$, $k_{t12}$ and $k_{t22}$, while that by diffusion-controlled concept has a single constant, $k_{t(12)}$, in termination reaction.

$$M_1 \cdot + M_1 \cdot \xrightarrow[k_{t11}]{} \text{dead polymer}$$
$$M_1 \cdot + M_2 \cdot \xrightarrow[k_{t12}]{} \text{dead polymer}$$
$$M_2 \cdot + M_2 \cdot \xrightarrow[k_{t22}]{} \text{dead polymer} \qquad (7)$$

$$\left. \begin{array}{l} M_1 \cdot + M_1 \cdot \\ M_1 \cdot + M_2 \cdot \\ M_2 \cdot + M_2 \cdot \end{array} \right\} \xrightarrow[k_{t(12)}]{} \text{dead polymer} \qquad (8)$$

Especially, the difficulties in obtaining the value of $k_{t12}$ have been occurred in this experiment. This was settled by putting $k_{t(12)}$ instead of $k_{t12}$ into the Eq. (6), which gives the following rate Eq. (9) of Atherton and North.

$$R_f = \frac{(r_1 M_1^2 + 2M_1 M_2 + r_2 M_2^2) R_i^{0.5}}{k_{t(12)}^{0.5}(r_1 M_1/k_{p11} + r_2 M_2/k_{p22})} \qquad (9)$$

Where $k_{t(12)} = F_1 k_{t11} + F_2 k_{t22}$.

But the factor $k_{t(12)}$ as a function of copolymer composition appears to be qualitatively but not quantitatively valid [20]. At a first glance, it is not easy to obtain the value of the factor $k_{t12}$ presented in the chemical-controlled termination model. It is requested, consequently, that the factor of $k_{t(12)}$ is used instead of $k_{t12}$. This is considered as the chemically diffusion-controlled rate model. The simulation results of these two models were compared with the experimental data at 3 hours after start-up of reaction.

In Fig. 12, the comparison of these two different models on the rates estimated from experiments was shown for the copolymerization of MMA and EMA. They show similar trends but not the same values over all the compositions. The value of the chemically controlled rate model is slightly lower than that of diffusion controlled model. The experimental data lies between the two simulated models with different histories. The minimum point of the experimental rate is presented in the composition of 0.5, and also the same in MMA/BMA series shown in Fig. 13. This min-
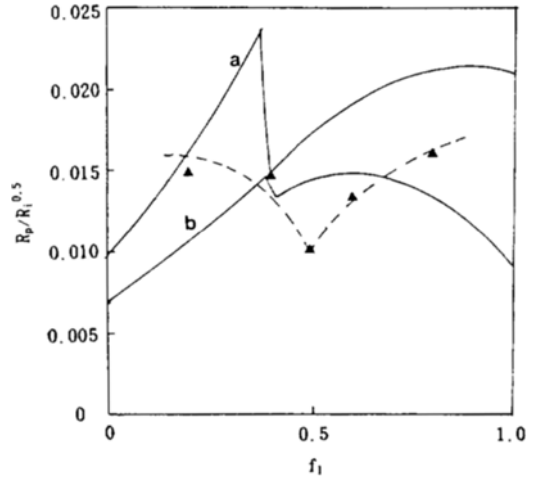


**Fig. 12. Plot of $R_p/R_i^{0.5}$ vs feed compositions in MMA/ EMA series at 3 hours.**

(a : Atherton and North equation, b : Classical rate equation of copolymerization, ▲ : Experimental result)
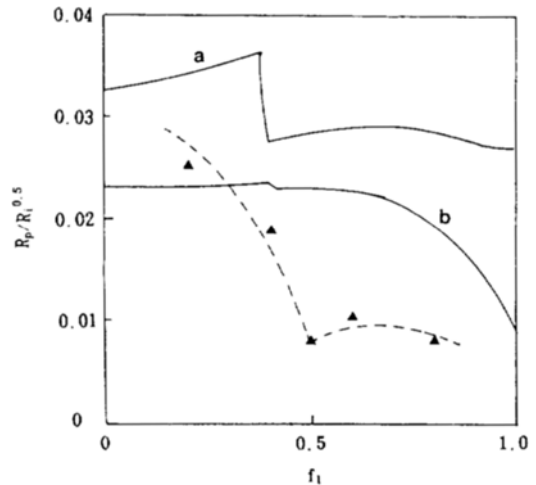


**Fig. 13. Plot of $R_p/R_i^{0.5}$ vs feed compositions in MMA/ BMA series at 3 hours.**

(a : Atherton and North equation, b : Classical rate equation of copolymerization, ▲ : Experimental result)

imum behavior at the composition of 0.5 in both systems is totally in accordance with that in the trends of conversion and copolymerization rate.

From these minimum trendency, it is assumed that the optimum rate of copolymerization exists around the composition of 50/50 MMA/EMA or MMA/BMA.

## CONCLUSIONS

Continuous solution copolymerizatioin of methyl methacrylate with ethyl methacrylate or n-butyl methacrylate was carried out in a continuous stirred tank reactor (CSTR). The second order kinetics well-described the copolymerization in the present systems. The correlation coefficients of MMA/EMA and MMA/BMA system were 0.92 and 0.96, respectively.

Copolymer conversions showed a good correlation with simulated results in 50/50 feed composition of MMA/EMA or BMA. But somewhat larger deviation in the rate of copolymerization was observed. The time to reach dynamic steady state was about three and half residence times in both systems.

After 3 hours, the experimental rate was deviated from the simulated results and the optimum condition of present copolymerization was determined as just around the composition of 50/50 for both MMA/EMA and MMA/BMA systems.

## NOMENCLATURE

f     : initiator efficiency
$f_1$    : composition of monomer 1 in feed
$F_1$    : copolymer composition of monomer 1
$Fl_i$    : molar flowrate of component i
$Fl_{ij}$   : initial molar flow rate of component i
[I]    : initiator concentration
k     : bulk rate constant of copolymerization in second order kinetics
$k_d$    : decomposition rate constant of initiator
$k_{p11}$   : rate constant of propagation between monomer 1
$k_{p22}$   : rate constant of propagation between monomer 2
$k_{p12}$   : rate constant of propagation of monomer 1 to monomer 2
$k_{p21}$   : rate constant of propagation of monomer 2 to monomer 1
$k_{t11}$   : rate constant of termination between monomer 1
$k_{t22}$   : rate constant of termination between monomer 2
$k_{t12}$   : rate constant of chemical-controlled cross-termination between monomer 1 and monomer 2
$k_{t(12)}$  : rate constant of diffusion-controlled cross-termination between monomer 1 and monomer 2
$[M_i]$  : concentration of monomer i in monomer mixture

$M_i\cdot$   : radical species of monomer i
n     : reaction order
$N_i$    : mole number of component i
$r_1$    : reactivity ratio of monomer 1 to monomer 2
$r_2$    : reactivity ratio of monomer 2 to monomer 1
$r_i$    : reaction rate ($R_1$ and $R_2$ are presented)
$R_i$    : reaction rate of initiation
$R_p$    : reaction rate of propagation, so called rate of copolymerization
t     : reaction time
$t_1$    : dimensionless reaction time
V    : reaction volume
v     : volumetric flow rate
$x_i$    : conversion of component i

### Greek Letters

$\theta$    : ratio of V to v, i.e., residence time
$\phi$    : cross-termination factor, i.e., chemically diffusion-controlled cross termination factor
$\delta_1, \delta_2$ : rate parameters used in Eq. (6).

### Subscript
    : the initial property

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