

연속 반응기(CSTR)에서 Methyl Methacrylate와 Styrene의 라디칼 공중합 반응 속도론

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The Kinetics of Radical Copolymerization of Methyl Methacrylate and Styrene in a Continuous Stirred Tank Reactor(CSTR)

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요 약 : 메틸 메타크릴레이트(MMA)와 스티렌(St)을 등온하에서 라디칼 공중합에 대한 반응속도론적 고찰에 대하여 연속반응기(CSTR)를 사용하여 연구하였다. 용매로 톨루엔 중에서 BPO를 개시제로 사용하였으며, 반응물부피, 체류시간 및 중합온도는 각각 0.3L, 3시간 및 80°C로 하였다. 중합은 반응성비를 결정하기 위하여 적절히 높은 전환율에 도달될때 까지 수행되었다. 공중합체의 전환율은 FT-IR, EA, GPC, DSC 및 TGA 등으로 분석 되었으며, 단량체의 반응성비 r_1 (MMA)과 r_2 (St)는 Kelen-Tüdös법으로 결정하였다. $r_1=0.59$, $r_2=0.61$. 공중합체의 ϕ 값은 St의 전체조성에 걸쳐 0.46에서 0.55의 범위였으며, St의 조성이 증가할수록 증가 하였다. MMA와 St의 공중합 반응은 2차 반응 속도론에 따랐으며, 시뮬레이션 한 전환율과 공중합속도를 실험결과와 비교하였다. 동적인 정상상태에 도달하는 평균시간은 체류시간의 3배였으며, 반응기내에서 정상상태에 접근하는 특성이 주어졌다. ϕ 의 단일값으로서는 실험값과 시뮬레이션 값과의 좋은 일치점을 얻는 것은 어려웠다.

Abstract : The kinetics of isothermal and radical copolymerization of methyl methacrylate(MMA) with styrene(St) has been investigated using a continuous stirred tank reactor(CSTR). Solvent and initiator used were toluene and benzoyl peroxide. Reaction volume, residence time and polymerization temperature were 0.3 liters, 3 hours and 80°C, respectively. Polymerizations were carried out to reach moderately high conversions to determine the reactivity ratios. The copolymerization conversions were analyzed by FT-IR, EA, GPC, DSC and TGA. The monomer reactivity ratios, r_1 (MMA) and r_2 (St) were determined by the Kelen-Tüdös method ; $r_1=0.59$, $r_2=0.61$. The ϕ factors of the copolymer over the entire St compositions ranged from 0.46 to 0.55 and increased with increasing St compositions. The copolymerization of MMA and St followed the second order kinetics. The simulated conversions and copolymerization rates were compared with the experimental results. The average time to reach dy-

dynamic steady-state was three times of the residence time. The approach to steady-state in the reactor was characterized. It was not possible to obtain good agreement between experiment and simulation with a single value of the ϕ factor.

INTRODUCTION

For copolymerization in a CSTR, there have been a little reported experiments and very little analysis of the reactor dynamics because it has been known that the CSTR as a experimental reactor system for free radical polymerization may exhibit complex steady-state characteristics and dynamic behavior such as multiple steady-states.¹ The use of continuous copolymerization methods to estimate rate parameters in copolymerization has not been extensively studied. The majority of the investigations in copolymerization have been carried out at low conversions using batch reactors. However, industrial processes are carried out high conversions due to economical reason, kinetic studies conducted under such conditions are of prime importance. Solution polymerization in a CSTR offers an elegant method for producing chemically homogeneous copolymers at high conversions. Provided the solvent concentrations kept well above the "critical solvent concentration", the "gel effect" can be ignored. The kinetics and mechanism of solution polymerization are determined primarily by the type of initiation used and by the type of solvent employed.

The solvent can influence the rate and molecular weight. The extent of that influence is determined by the solvent chain transfer constant. Such chain transfer is not usually taken into consideration in copolymerization rate equations.² And the existence of steady state under isothermal conditions has received considerable attention in reaction engineering literature. Both theoretical and experimental studies in this field have been reviewed Schintuch, Schmitz and Slinko.^{3,4} Most of these analyses were confined to nonviscous systems and relatively little attention has been paid to analysis of viscous systems such as might be

encountered in continuous polymerizations. Knorr and O'Driscoll⁵ were the first to consider the "gel effect" in order to predict steady state under isothermal conditions for styrene polymerization.^{1,6} Kinetic studies of copolymerization in a CSTR were made in this work. Particularly, the continuous copolymerization of MMA and St have attracted many interests in this laboratory to prevent the unzipping in a polymerization of MMA.⁷

In the case of a homopolymerization of MMA, 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 MMA can be prevented by incorporating second monomer through a copolymerization. Toluene is used as a solvent to control the "gel effect" from the exothermic heat of copolymerization.

EXPERIMENTAL

Materials. Methyl methacrylate (Junsei Chem. Co., Japan) was washed twice with aq. 5% NaOH and twice with water. Dried with CaCl_2 , then with CaH_2 under nitrogen at reduced pressure. The distillate was stored at low temperatures and redistilled before use. Styrene (Junsei Chem. Co., Japan) was also washed with aq. 5% NaOH to remove inhibitors, then with water, dried for several hours with MgSO_4 and distilled at 25°C under reduced pressure in the presence of 0.005% p-tert-butylcatechol. Benzoyl peroxide (Hayashi Chem. Co., Japan) as an initiator was purified by recrystallization from methanol. It was dissolved in CHCl_3 at room temperature and precipitated by adding an equal vol of MeOH. Toluene was used after distillation.

Copolymerization in a CSTR. The CSTR used in this study is shown in Fig. 1. The operation princi-

ple is basically the same as described in the literature. The start-up procedure was to fill the reactor initially with the intended ratio of the comonomer in the solvent. While the mixture in the reactor was being heated up to the desired temperature, N₂ gas was purged continuously to prohibit the reacted materials from oxidizing during copolymerization reaction. The temperature was maintained at 80°C throughout the copolymerization. The initiator was added to the mixture in the reactor just before the pumps are operated. The total flow rate was maintained at 1.67 ml/min. The residence time was 3 hours but a run was typically durated about three times to achieve steady state. The samplings were done at intervals of 30 min. The volume fraction of the solvent in the reaction was kept constant to allow no geleffect. Samples were dried to a constant weight under high vacuum at a room temperature for several days. The copolymer composition was determined by elemental analyzer (Carlo Erba Instrument, EA-1108). The experimental conditions were summarized in Table 1.

Table 1. Experimental Conditions

Description	Condition
Polymerization temperature	75, 80, 85°C
Solvent	Toluene
Solvent/comonomer ratio	4 : 1(v/v)
Initiator used	Benzoyl peroxide
Initiator concentration	5, 10, 15mmol/L
Residence time	120, 180, 240min
Reaction volume	0.3L

RESULTS AND DISCUSSION

Rate parameters. The reactivity ratios, r_1 and r_2 , in the copolymerization of MMA with St are 0.59 and 0.61, respectively. It was determined by the Kelen-Tüdös method, Eq. (1). This means that the monomers have low tendency to homopolymerize.

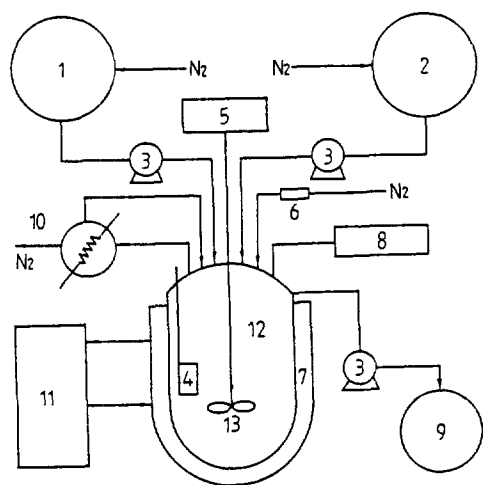
$$\eta = (r_1 + r_2/\alpha) \varepsilon - r_2/\alpha \quad (1)$$

where $\eta = G/(\alpha + F)$, $\varepsilon = F/(\alpha + F)$, $F = X^2/Y$

$$G = X(Y-1)/Y, \quad \alpha = (F_{\min} \times F_{\max})^{1/2}$$

$$X = F_1/F_2, \quad Y = f_1/f_2$$

The cross termination factor ϕ is ranged from 0.46 to 0.55 for this system. 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 styrene feed ratio. In the present studies of the rate of copolymerization, the terminal model was adapted. A $\phi < 1$ means that cross termination is not favored, while $\phi > 1$ means that cross termination is favored. The tendency toward cross-termination parallels the tendency toward cross propagation (i. e., toward alternation) in that the ϕ increases as $r_1 r_2$ approaches zero.^{8,9} Another approach by North and co-workers^{10,11,12} have suggested that the termination modes of the propagating chains are affected by the diffusion of the chain segments.¹³ A more applicable kinetic expression for the diffusion controlled rate equation of copolymerization should be considered.

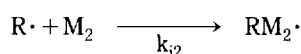
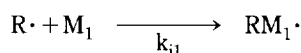
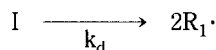


- | | |
|---------------------------------------|---------------------------------|
| 1. Monomer storage tank | 8. Thermometer |
| 2. Initiator and solvent storage tank | 9. Receiver for product |
| 3. Peristaltic pump | 10. Reflux condenser |
| 4. Baffle rod | 11. Temperature control unit. |
| 5. Variable speed stirrer | 12. CSTR polymerization reactor |
| 6. Gas flow meter | 13. Impeller |
| 7. Heating jacket | |

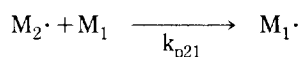
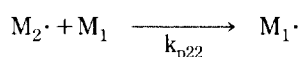
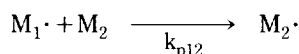
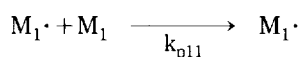
Fig. 1. Schematic diagram of CSTR experiments.

Dynamic steady-state. Studies on the stationary steady-state in a batch system have been extensively investigated but the dynamic steady-state in a continuous polymerization process have not been widely carried out. 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 kinetic mechanism assumed in the reactor model is based on the classical terminal model, which asserts that only the terminal unit in a growing chain will affect the kinetics of the process.⁶ 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. The scheme is shown here :

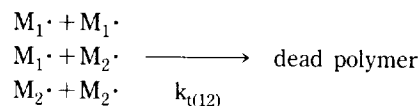
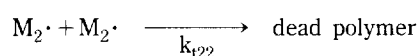
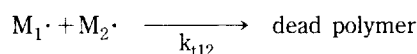
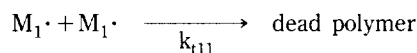
Initiation :



Propagation :



Termination :



The dynamic steady-state modeling is sourced from the steady state approximation¹⁴ and general mole balance equation. The overall general mole balance with steady state copolymerization is given as

$$\begin{aligned} [M_{if}] - [M_i] &= R_i \theta, \quad R_i = k_i [M_i] [I]^{0.5}, \\ F I_{if} - F I_i + \int V r_i dV &= dN_i/dt \end{aligned} \quad (2)$$

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

$$\begin{aligned} V(d[M_1]/dt) &= ([M_{1f}] - [M_1]) - R_1 V, \\ V(d[M_2]/dt) &= ([M_{2f}] - [M_2]) - R_2 V, \\ V(d[I]/dt) &= ([I_f] - [I]) - k_d [I] V, \end{aligned} \quad (3)$$

where θ is the residence time in the reactor. The rates of polymerization, R_1 and R_2 , are defined as

$$\begin{aligned} R_1 &= k_1 [M_1] [I]^{0.5} \\ R_2 &= k_2 [M_2] [I]^{0.5} \\ \text{and } [I] &= [I_f]/(1 + k_d \theta) \end{aligned} \quad (4)$$

The constants k_1 and k_2 are dependent on the monomer ratio and independent of the total concentration of monomers. Introducing several parameters for simple manipulation,

$$\begin{aligned} t_1 &= t/\theta, \quad \theta = V/v, \quad f_A = [M_1 f]/[M_{2f}], \\ f_B &= [I_f]/[M_{2f}], \quad DB = k_1/k_2, \\ DR &= k_d/(k_2 [I_f]^{0.5}), \quad DA = k_2 [I_f]^{0.5} \theta \end{aligned} \quad (5)$$

By definition,

$$\begin{aligned} x_1 &= ([M_{1f}] - [M_1])/[M_1 f] \\ x_2 &= ([M_{2f}] - [M_2])/[M_{2f}] \\ x_3 &= ([I_f] - [I])/[I_f] \end{aligned} \quad (6)$$

Rearranging several variables into other parameters, coupled with the rate equation of copolymerization described later in Eq. (13).

$$\begin{aligned}
 k_1 &= (r_1(1-x_1)f_A + (1-x_2))/T_A^{0.5} \\
 k_2 &= ((1-x_1)f_A + (1-x_2)r_2)/T_A^{0.5} \\
 T_A &= T/(2fk_d) \\
 T &= (r_1\delta_1(1-x_1)f_A)^2 + (r_2\delta_2(1-x_2))^2 + T_B \\
 T_B &= 2\phi r_1r_2\delta_1\delta_2(1-x_1)(1-x_2)f_A
 \end{aligned}
 \quad (7)$$

where f is the efficiency of the initiator.

Finally, consequential dimensionless modeling equations are estimated as,

$$\begin{aligned}
 dx_1/dt_1 &= -x_1 + (1-x_1)(1-x_3)^{0.5}DA \cdot DB \\
 dx_2/dt_1 &= -x_2 + (1-x_2)(1-x_3)^{0.5}DA \\
 dx_3/dt_1 &= -x_3 + (1-x_3)DA \cdot DR
 \end{aligned}
 \quad (8)$$

In the case of homopolymerization,

$$\begin{aligned}
 k_1 &= (2fk_d)^{0.5}/\delta_1 \\
 k_2 &= (2fk_d)^{0.5}/\delta_2
 \end{aligned}
 \quad (9)$$

Combining Eq. (7), we obtain an expression which can be used to estimate the reactivity ratios

$$\frac{k_1}{k_2} = \frac{(r_1(1-x_1)f_A + (1-x_2))}{((1-x_1)f_A + (1-x_2)r_2)} \quad (10)$$

Eq. (10) has been derived under steady state conditions and is therefore applicable at different levels of conversion in the reactor. A differential form of the copolymer composition equation derived by Mayo and Lewis⁶ has been widely used for estimating reactivity ratios in copolymer systems. The method assumes that the feed composition in the reactor does not change as the reaction proceeds. This is valid only at very low conversions. The equation they derived was

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \quad (11)$$

The number average degree of polymerization in a CSTR (if one assumes termination by coupling) is defined as

$$\bar{X}_n = ([M_{1p}] + [M_{2p}])/[I_p] \quad (12)$$

where M_{1p} , M_{2p} , I_p represent the molar concentrations of monomers M_1 , M_2 , and the initiator I in the polymer.

The rate expression by incorporating the assumptions in the reaction scheme is

$$R_p = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)R_i^{0.5}}{((r_1\delta_1[M_1])^2 + 2\phi r_1r_2\delta_1\delta_2[M_1][M_2] + (r_2\delta_2[M_2])^2)^{0.5}} \quad (13)$$

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

Subscripts 1 and 2 refer to monomer 1 and monomer 2, respectively.

In order to obtain the R_p , rate parameters summarized in Table 2 was used. 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. (14) of Atherton and North.

$$R_p = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)R_i^{0.5}}{k_{t(12)}^{0.5}(r_1[M_1]/k_{p11} + r_2[M_2]/k_{p22})} \quad (14)$$

$$\text{Where } k_{t(12)} = F_1k_{t11} + F_2k_{t22}$$

Table 2. The Monomer Composition in Copolymers($[M_1]$: MMA, $[M_2]$: St)

Feed composition ($[M_1]/[M_2]$)[Mole %]	Element*[Wt. %]			Copolymer composition[Mole %]	
	N	C	H	$[M_1]$	$[M_2]$
20/80	0.068	84.274	8.217	25.48	74.52
40/60	0.056	79.293	8.434	41.12	58.88
50/50	0.055	76.634	8.454	49.40	50.60
60/40	0.053	73.845	8.463	58.02	41.98
80/20	0.045	68.437	8.644	74.56	25.44

* By elemental analysis.

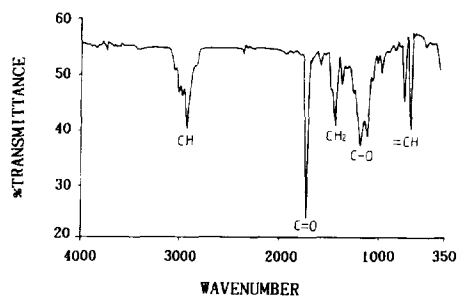


Fig. 2. FT-IR spectrum of copolymer in the present studies: solid phase, KBr.

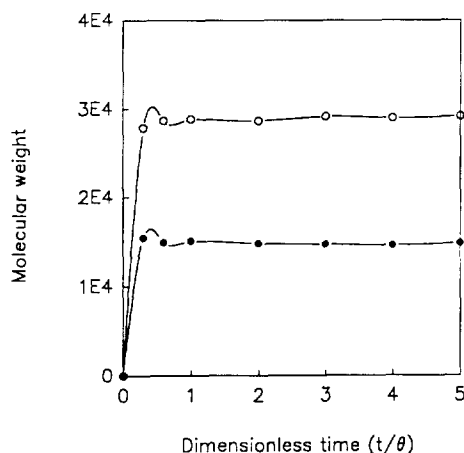


Fig. 3. Variation of the molecular weight against dimensionless time in MMA/Styrene mixtures in toluene as a solvent at 80°C. (○: \bar{M}_w , ●: \bar{M}_n)

But the factor $k_{t(12)}$ as a function of copolymer composition appears to be qualitatively but not quantitatively valid.

The composition of the copolymer samples was determined by elemental analysis and correlated with respective IR spectra. The wavenumbers corresponding to strongly absorbing MMA and styrene were determined as 1730 and 700 cm^{-1} , representing the C=O and =CH. Fig. 2 shows the IR spectrum of copolymer in the present studies. And, in the case of free radical polymerizations, the polymer chains grow in a very short period of time.⁶ As is evident from Fig. 3, the value of \bar{M}_w rapidly approaches a steady state. \bar{M}_n behaves in similar fashion, implying that the polydispersity is cons-

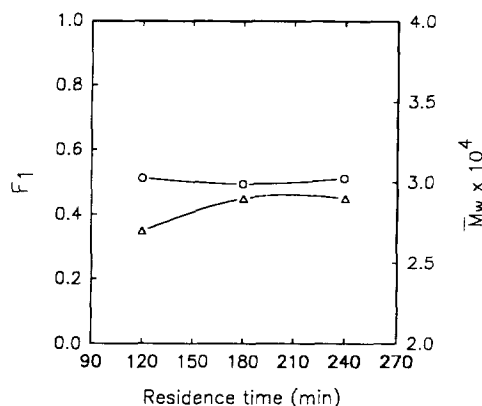


Fig. 4. Variation of the compositions of copolymers and \bar{M}_w with the different residence time in MMA/Styrene mixtures in toluene as a solvent at 80°C. (○: F1, △: \bar{M}_w)

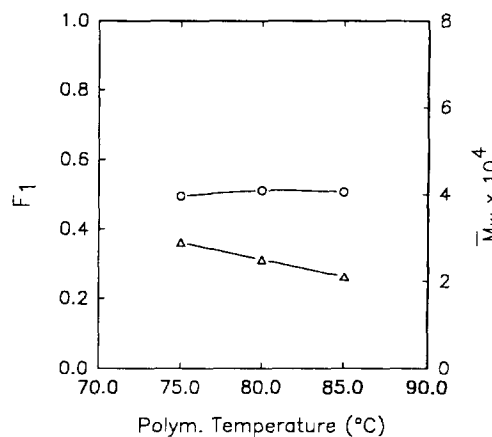


Fig. 5. Variation of the compositions of copolymers and \bar{M}_w with the different reaction temperature in MMA/Styrene mixtures in toluene as a solvent at 80°C. (○: F1, △: \bar{M}_w)

tant after the initial brief period of rapid chain growth.

The composition drift in the copolymerization of MMA with styrene is shown from Fig. 4 to Fig. 8. The compositions have been estimated while the CSTR is operating at steady state and a uniform copolymer is obtained in the exit stream of the reactor. The concentrations and the polymerization rates of the individual monomers are determined from the conversion and the copolymer composi-

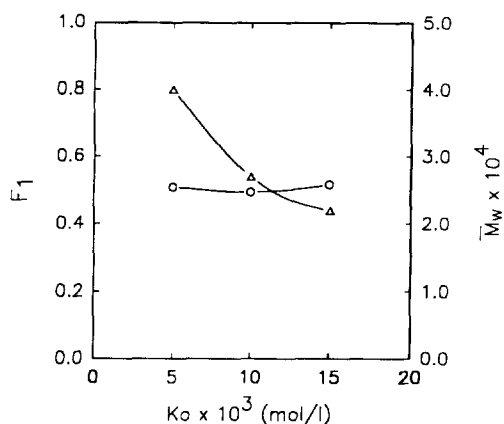


Fig. 6. Variation of the compositions of copolymers and \bar{M}_w with the different initiator concentration in MMA/Styrene mixtures in toluene as a solvent at 80 °C. (○ : F_1 , △ : \bar{M}_w)

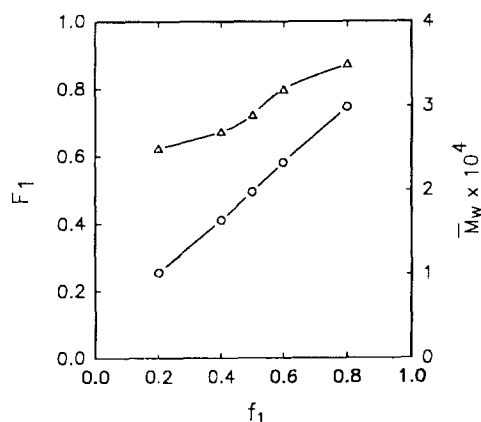


Fig. 7. Variation of the compositions of copolymers and \bar{M}_w with the different feed compositions in MMA/Styrene mixtures in toluene as a solvent at 80 °C. (○ : F_1 , △ : \bar{M}_w)

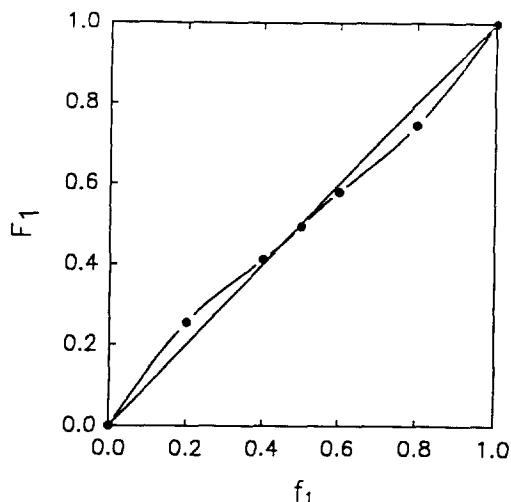


Fig. 8. Compositions of MMA in feed (f_1) and in copolymers (F_1) in a CSTR.

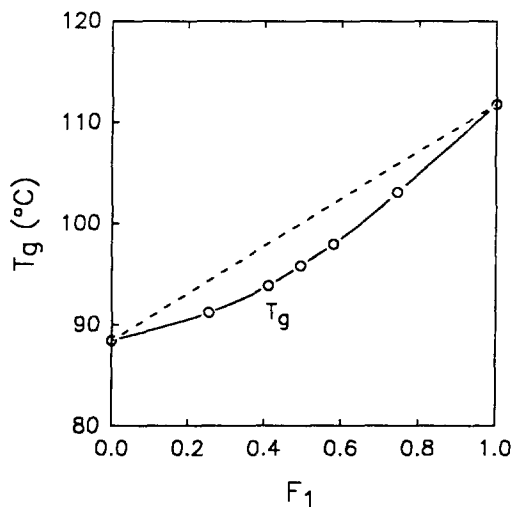


Fig. 9. Plot of glass transition vs. mole ratio of MMA in copolymers.

tion.

Fig. 9 implies that the glass transition temperature of the copolymers increases with MMA-rich compositions in copolymers. Our present system showed that the continuous copolymerization of MMA with St followed second-order kinetic behavior, as shown in Fig. 10. In the copolymerization of MMA and St in a CSTR, as shown in Fig. 10, 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. Copolymerization reaction of MMA and St in a CSTR follows the second-order kinetics. And the time to reach dynamic steady state was about three times of the residence time in our present system. Table 2 shows the EA data and the monomer composition in copolymers. In Fig. 11, The Kelen-Tüdös plot gives the reactivity ratios, r_1 and r_2 , in the copolymerization of MMA

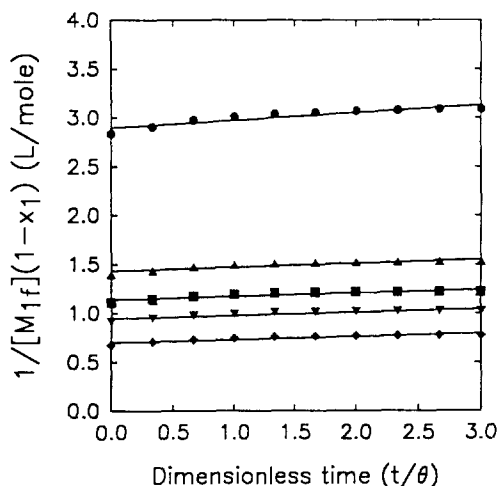


Fig. 10. The correlation of the 2nd-order kinetics in the copolymerization of MMA/Styrene (correlation coefficient : 0.985). (● : 20/80, ▲ : 40/60, ■ : 50/50, ▼ : 60/40, ◆ : 80/20)

Table 3. Summary of Parameters in the CSTR Experiments

BPO	Methyl methacrylate	Styrene
$k_d = 4.30 \times 10^{-5}$	$k_{p11} = 800.00$	$k_{p22} = 340.19$
$f = 0.90$	$k_{t11} = 30.50 \times 10^6$	$k_{t22} = 44.20 \times 10^6$
$R_i = 6.45 \times 10^{-8}$	$k_{p11}/k_{t11} = 2.62 \times 10^{-5}$	$k_{p22}/k_{t22} = 7.70 \times 10^{-6}$
$[I] = 8.33 \times 10^{-4}$	$\delta_1 = 9.76$	$\delta_2 = 27.64$
$k_{pij}, k_{tij} = \text{mole/l} \cdot \text{sec}, k_d = \text{sec}^{-1}, r_1 = 0.59, r_2 = 0.61$		

with St are 0.59 and 0.61, respectively. This means that St has a little more tendency to homopolymerize than MMA. The rate parameters are summarized in Table 3. The polymerization reaction in a batch reactor follows first-order kinetics, especially for homopolymerization.

The cross termination factor ϕ , which is shown in Fig. 12, are ranged from 0.46 to 0.55 for this system. 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 styrene feed ratio. In the present studies of the rate of copolymerization, the terminal model was adapted. A $\phi < 1$ means that cross termination is not favored, while $\phi > 1$ means that cross termination is favored.

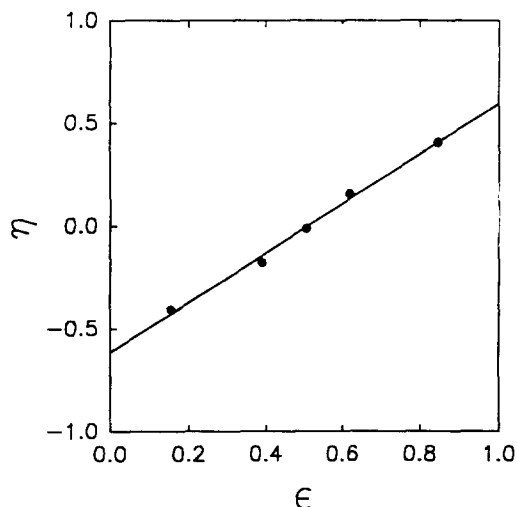


Fig. 11. Kelen-Tüdös plot of poly(methyl methacrylate-co-styrene) : $r_1 = 0.59$ and $r_2 = 0.61$ (correlation coefficient : 0.995).

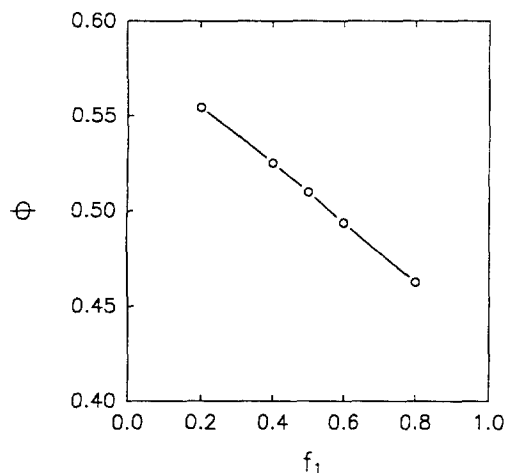


Fig. 12. Variation of ϕ -value with the feed composition of MMA.

nation is favored. The tendency toward cross-termination parallels the tendency toward cross propagation (i. e., toward alternation) in that the ϕ increases as $r_1 r_2$ approaches zero.^{15,16} Another approach by North and co-workers^{11,17,18} have suggested that the termination modes of the propagating chains are affected by the diffusion of the chain segments.¹⁹ A more applicable kinetic expression for the diffusion-controlled rate equation of copol-

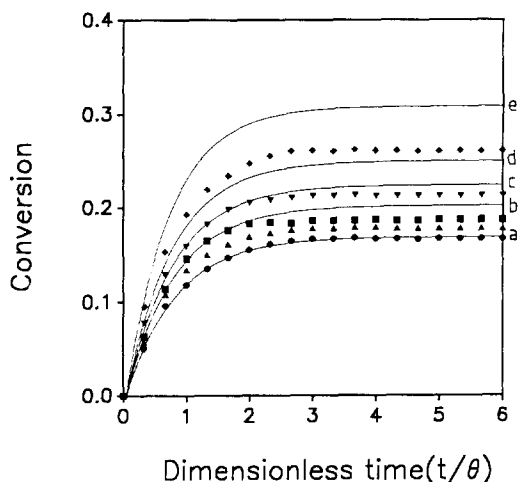


Fig. 13. Variation of the experimental conversions with the different feed compositions in MMA/Styrene mixtures : Solid lines represent the simulation results against dimensionless time with various feed compositions. (a : 20/80, b : 40/60, c : 50/50, d : 60/40, e : 80/20) (● : 20/80, ▲ : 40/60, ■ : 50/50, ▼ : 60/40, ◆ : 80/20)

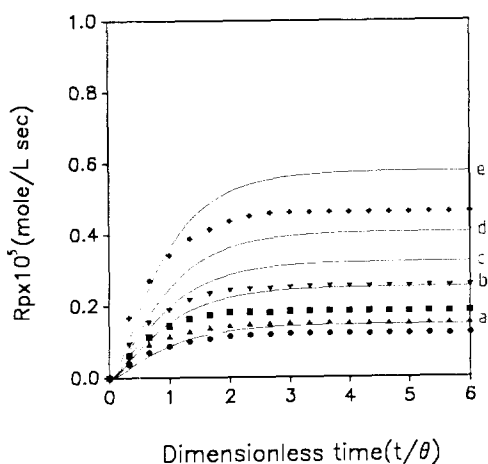


Fig. 14. Variation of the experimental rates of copolymerization with the different feed compositions in MMA/Styrene mixtures : Solid lines represent the simulation results against dimensionless time with various feed compositions. (a : 20/80, b : 40/60, c : 50/50, d : 60/40, e : 80/20) (● : 20/80, ▲ : 40/60, ■ : 50/50, ▼ : 60/40, ◆ : 80/20)

merization should be considered. In Fig. 13, the conversions in the copolymerization of MMA and

St varied with dimensionless time. This dimensionless time is the reaction time divided by residence time. The solid lines in this figure represent the conversions by computer simulation. The conversions for the copolymer of MMA-rich compositions show negative deviation from the simulated results. It was observed that the average time to reach dynamic steady state was three times of the residence time. The conversions of the mixtures are well approached to the simulated values up to six times of the residence time. As shown in Fig. 14, a large deviation of the rate of copolymerization (R_p) were observed from simulation results in the copolymerization of MMA and St. As the reaction proceeds, the experimental conversions and the rate of copolymerization (R_p) were largely diverged from the simulated values except the copolymers having the styrene-rich compositions.

CONCLUSIONS

The radical copolymerization of MMA and St with BPO as a initiator in toluene at 80°C in a continuous stirred tank reactor (CSTR) were carried out.

The followings are some of the important results.

1. The monomer reactivity ratios, r_1 (MMA) and r_2 (St) were determined by the Kelen-Tüdös method ; $r_1 = 0.59$, $r_2 = 0.61$.

2. The copolymerization corresponding to well the second order kinetics (the correlation coefficients 0.985) in the present system.

3. The time to reach dynamic steady state was about three times of the residence time in the present system.

4. The experimental rates of copolymerization and copolymer conversions showed a good correlation with simulated results in 20/80 feed composition of MMA/St, but large deviation other feed compositions was observed.

5. The cross termination factor ϕ of the copolymer over the entire styrene compositions strongly depends on the composition of the comonomer

feed ratio, ranged from 0.46 to 0.55 and increased with increasing styrene compositions.

6. The optimum condition of present copolymerization was determined as just around the composition of 20/80 for MMA/St system.

NOMENCLATURE

f_1 : Composition of monomer 1 in feed.
 F_1 : Copolymer composition of monomer 1.
 Fl_i : Molar flow rate of component i.
 Fl_{if} : 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.
 ϕ : Cross-termination factor, i.e., chemically diffusion-controlled cross termination factor.
 δ_1, δ_2 : Rate parameters used in Eq. 13.

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