

Kinetic Studies on Styrene–Divinylbenzene Copolymerization by Suspension Technique

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ABSTRACT: Kinetic studies on styrene and divinylbenzene (DVB) copolymerization by the suspension technique in a toluene diluent initiated by benzoyl peroxide are reported. Evaluation of the important reaction parameters is carried out. The crosslinked styrene–DVB copolymers can absorb toluene to a maximum swelling ratio of 17. The absorption/desorption took place instantaneously and reached the maximum value within 10 min, and it could be repeated many times, yet gave the consistent result. Rate equations evaluated by both integral and differential methods are investigated. High monomer orders of 1.5–2.3 were obtained. The activation energy for the polymerization was about 40 kcal/mol⁻¹. Autoacceleration was found even at low conversions. The acceleration was influenced by both monomer, crosslinker, and initiator concentrations. The integral and differential methods for the rate evaluation were compared, and the relationship between the rate equation and polymerization behavior was elucidated. The kinetic orders determined for this copolymerization show considerable deviation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1521–1540, 2001

Key words: kinetic studies; styrene; divinylbenzene; ethyl vinylbenzene; rate equation; integral method; differential method

INTRODUCTION

The increasing interest in porous styrene–divinylbenzene (DVB) copolymer beads in recent years is due to their diversified applications. Commercial use of these copolymers is made, for example, for manufacturing resins for gel permeation chromatography, ion exchangers, chromatographic packing for size exclusion chromatography, polymer-supported catalysts, and absorbents

in medical, chemical, and agricultural applications. This work extends its interesting swelling properties for the absorption and desorption of organic solvents, such as toluene. Currently, industrial development is expanding tremendously and rapidly to the convenience of humankind. Unfortunately, almost all industries produce various kinds of pollution problems. One such problem is with the residual solvent that is drained from production lines and discarded, perhaps to community waterlines. In one approach to solve part of the aforementioned problem, absorbent materials must be produced to get rid of some or all of these solvents. The swelling of styrene–DVB copolymers can absorb some organic solvents with

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(Shimadzu) was used. A packed column containing 25% PEG-20M Uniport B was used. High-purity nitrogen (99.99%) was used as the carrier gas under a pressure of 200 kPa. The injection port, oven, and detector temperatures were set at 180, 150, and 200 °C, respectively. The sample solution of 1.0 μL was injected into the GC using a microsyringe. The peak area was calculated using Shimadzu C-R6A software.

The sample solutions were collected at a set interval and were then rapidly quenched with hydroquinone (0.2 g, Merck) in an iodine flask. Toluene (60 cm^3) was added to extract the unreacted monomers. The sample was stored at 4 °C for 20 min. The solid polymer was extracted with acetone in a Soxhlet extractor for 10 h, and the solid portion was then dried in an oven at 50 °C for 24 h. The sample solution including the solution from the Soxhlet extraction was analyzed for unreacted monomers through volumetric determination. The overall conversion of the monomers to the solid copolymer was determined gravimetrically. The residual monomer content in moles was also calculated with reference to the calibration curve. The monomer conversion was obtained from

$$\text{Percent monomer conversion} = \left(1 - \frac{m_r}{m_i}\right) \times 100, \quad (1)$$

where m_r is the mole of the residual monomer as determined by the GC technique, and m_i is the initial mole of the monomer determined by calculation.

Degree of Swelling Ratio

A test tube containing the dry polymer sample of weight m_g and a total added solution weight of m_l was used for the swelling test in toluene. The excess amount of toluene was poured into the test tube and then sealed with aluminum foil and closed with a cap. The swelling test was carried out at room temperature for 24 h. The excess solvent was filtered, and the swollen beads were weighed as m_s . The swelling ratio, G , was calculated by the following equation:

$$G = \frac{m_s - m_l}{m_g} \quad (2)$$

Statistical Analysis of the Effect of Reaction Parameters on Swelling

Part of the data was used to calculate the relationship between the swelling ratio and the reac-

tion parameters by means of the SPSS (Statistical Program for Social Science) program. Both the main parameters and the parameter interaction effects on swelling were considered.

Particle Sizes

The particle sizes (12) of the crosslinked styrene-DVB beads were determined by counting more than 300 grains projected on an SZH 10 stereomicroscope coupled with the Luzex F package (Nireco QJ8500). The Saunter mean diameter was calculated as follows

$$d = \frac{\sum f_i \bar{d}_i^3}{\sum f_i \bar{d}_i^2} \quad (3)$$

where $\bar{d}_i = (d_i + d_{i+1})/2$ is the average diameter in the interval, and f_i the frequency of grains in the size range $d_i - d_{i+1}$.

RESULTS AND DISCUSSION

Parameter Studies and Their Significance

The swelling ratio of styrene-DVB beads in toluene is presented in Table II. The analysis by a

Table II Dependence of the Swelling Ratio on PVA, DVB, and Toluene (%)

PVA (%)	Styrene (%)	DVB (%)	Toluene (%)	Swelling Ratio
0.06	92.5	7.5	100	4.1
0.06	92.5	7.5	100	3.6
0.06	92.5	7.5	100	3.8
0.09	92.5	7.5	100	6.1
0.09	92.5	7.5	100	7.3
0.09	92.5	7.5	100	7.0
0.12	92.5	7.5	100	5.2
0.12	92.5	7.5	100	6.0
0.12	95.0	5.0	100	6.2
0.12	95.0	5.0	100	7.1
0.12	95.0	5.0	100	5.9
0.12	92.5	7.5	100	5.5
0.12	92.5	7.5	100	5.3
0.12	90.0	10	100	4.5
0.12	90.0	10	100	4.2
0.12	90.0	10	100	3.9
0.12	92.5	7.5	30	2.4
0.12	92.5	7.5	60	2.7
0.12	92.5	7.5	60	3.1
0.12	92.5	7.5	100	5.3
0.12	92.5	7.5	100	5.7

^a BPO 0.5%, 70°C, 240 rpm.

Table III Summary of the Multiple-Regression Equation by ANOVA

Method	Appropriate-Regression Equation
1. Forward analysis	$y_1 = 3.681 + 4.97 \times 10^{-2} - 0.44 \text{ DVB}$
2. Backward analysis	$y_1 = -40.319 + 0.44 \text{ Sty} + 4.97 \times 10^{-2} \text{ Tol}$
3. Stepwise analysis	$y_1 = 3.681 + 4.97 \times 10^{-2} - 0.44 \text{ DVB}$

Tol = toluene, DVB = divinylbenzene, and Sty = styrene.

multiple-variable linear regression via variance (ANOVA) shows the relation between the swelling ratio and each reaction parameter. The independent parameters, X_i , are the concentrations of tolu-

ene, styrene, DVB, and PVA, whereas the dependent parameter of interest, y , is the swelling ratio.

The three methods of ANOVA analysis (forward, backward, and stepwise) show that the

Table IV Effect of the Initiator Concentration on the Conversion of Styrene and Divinylbenzene

Sample ^a	Time (min)	Conversion of Individual Monomer (%)			Overall Conversion (%)	Bead Appearance	Swelling Ratio
		Styrene	DVB	EVb			
A (BPO 0.1%)	0	0.0	0.0	0.0	—	—	—
	30	44.1	60.8	72.7	—	—	—
	60	56.7	66.4	76.0	—	—	—
	90	64.8	71.4	78.6	—	—	—
	120	69.1	73.5	80.2	—	—	—
	150	73.8	77.7	83.3	—	—	—
	180	84.7	88.3	91.1	5.5	Fusion	—
	240	87.1	90.2	92.4	6.7	Fusion	—
B (BPO 0.5%)	0	0.0	0.0	0.0	—	—	—
	30	76.4	80.6	85.4	—	—	—
	60	77.5	82.5	86.3	—	—	—
	90	81.4	86.4	88.7	—	—	—
	120	88.4	92.3	93.7	5.6	Fusion	—
	150	92.3	95.3	96.0	9.8	Fusion	—
	180	92.7	95.2	95.7	14.3	Coalescence	5.0
	240	94.6	96.9	96.9	18.9	Coalescence	14.4
C (BPO 1.5%)	0	0.0	0.0	0.0	—	—	—
	30	80.4	85.0	88.0	—	—	—
	60	83.2	87.9	89.6	—	—	—
	90	88.8	92.6	93.4	—	—	—
	120	94.4	97.1	97.2	11.4	Fusion	—
	150	94.7	97.1	96.9	17.1	Coalescence	9.5
	180	94.8	97.4	97.1	19.9	Coalescence	6.6
	240	95.0	97.8	97.2	26.3	Coalescence	15.3
D (BPO 2.0%)	0	0.0	0.0	0.0	—	—	—
	30	81.0	85.9	88.7	—	—	—
	60	84.3	89.0	90.3	—	—	—
	90	89.3	93.2	93.8	—	—	—
	120	95.5	97.9	97.9	14.9	Fusion	—
	150	96.1	98.1	97.9	21.9	Coalescence	6.8
	180	96.9	100.0	98.3	23.0	Coalescence	9.2
	240	97.7	100.0	99.0	31.2	Coalescence	7.5

^a Styrene 92.5%, DVB 7.5, 70°C, 240 rpm; Toluene 100%, PVA 0.09%, monomer: H₂O, 1/7.

swelling ratio depends on the amounts of toluene, styrene, and DVB but not on the concentration of PVA by the F significance criterion of 0.05. The p values of the effects of the independent parameters are 0.377 for PVA, 0.029 for styrene, 0.029 for DVB, and 0.001 for toluene. All parameters are the positive attributes. Our interpretation is that PVA is a suspending agent that only prevents the monomer droplets from coalescing in the aqueous phase. Therefore, the PVA concentration should not be directly related to the swelling ratio. The appropriate regression equations are shown in Table III.

Kinetic Studies on Styrene-Divinylbenzene Copolymerization

We performed kinetic studies of the synthesis of styrene-DVB copolymer beads prepared by suspension polymerization using PVA as a suspending agent and toluene as a diluent. The polymer mixture was sampled at various times of 30, 60, 90, 120, 150, 180, and 240 min during polymerization. The condition for copolymerization is shown in Table I. Each parameter was studied as follows.

The Effect of the Initiator Concentration

The effects of initiator concentrations of 0.1, 0.5, 1.5, and 2.0% benzoyl peroxide (BPO) based on the monomer phase on copolymerization were studied using the standard recipe shown in Table I. Four runs (A, B, C, and D) were carried out. The conversion of the individual monomers was followed by the GC technique, and the overall conversion of the solid copolymer was determined by the gravimetric method, as shown in Table IV and Figure 1. The results reveal that the conversion increases with the increasing initiator concentration as a result of more initiator radicals formed in the initiation step. It has been confirmed that DVB is consumed more readily than styrene because of its difunctionality as a comonomer and crosslinker, whereas EVB can compete effectively with styrene because of its inductive effect. At 240 min of polymerization, the polymer formed was clustered and fused into a big lump (no separated beads as shown in Fig. 2). In Figure 2, the high concentrations of the initiator could produce more spherical beads although they fused together. At low initiator concentration, holes were produced because a low crosslinking reaction took place, which could dissolve in toluene. It appears that

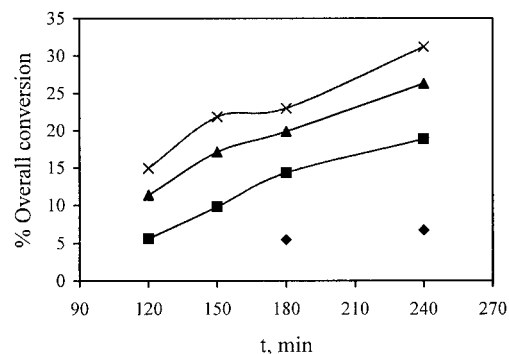


Figure 1 Effect of the initiator concentration on overall conversion of styrene-divinylbenzene. The curves ♦, ■, ▲, and × are for BPO 0.1, 0.5, 1.5, and 2.0%, respectively, for styrene 92.5%, DVB 7.5%, 70 °C, 240 rpm, toluene 100%, PVA 0.09%, and monomer: H₂O, 1/7 are used.

the rate of initiation and the initial viscosity affected the rate of polymerization. The big, clustered lump indicates the high molecular weight as a result of the gel effect at low conversion. We anticipate that a deviation in the kinetic orders could occur, which could be partially attributed to the gel effect. Nevertheless, droplet coalescence can occur when the monomer droplets are not stabilized. This result might indicate that the suspending agent in the aqueous phase is insufficient in stabilizing the monomer droplets.

The Effect of the Temperature

The effect of the temperature was studied using the standard recipe shown in Table I. Three runs (B, E, and F) were carried out using three different temperatures (60, 70, and 80 °C, respectively). The conversion of the individual monomers was followed by the GC technique, and the overall conversion of monomers was tracked by the gravimetric method, as shown in Table V and Figure 3. The conversion increases when the temperature increases. At high temperatures, the initiation rate increases in addition to the crosslinking rate. However, the half-life of the BPO initiator is reduced when the temperature is high. The effect of the temperature on the rate and degree of polymerization is of prime importance in determining the polymerization. Increasing the reaction temperature usually increases the polymerization rate. The high initiation rates accelerate the formation of short polymer chains, leading to a lower molecular weight polymer. Higher temperatures increase all conversions,

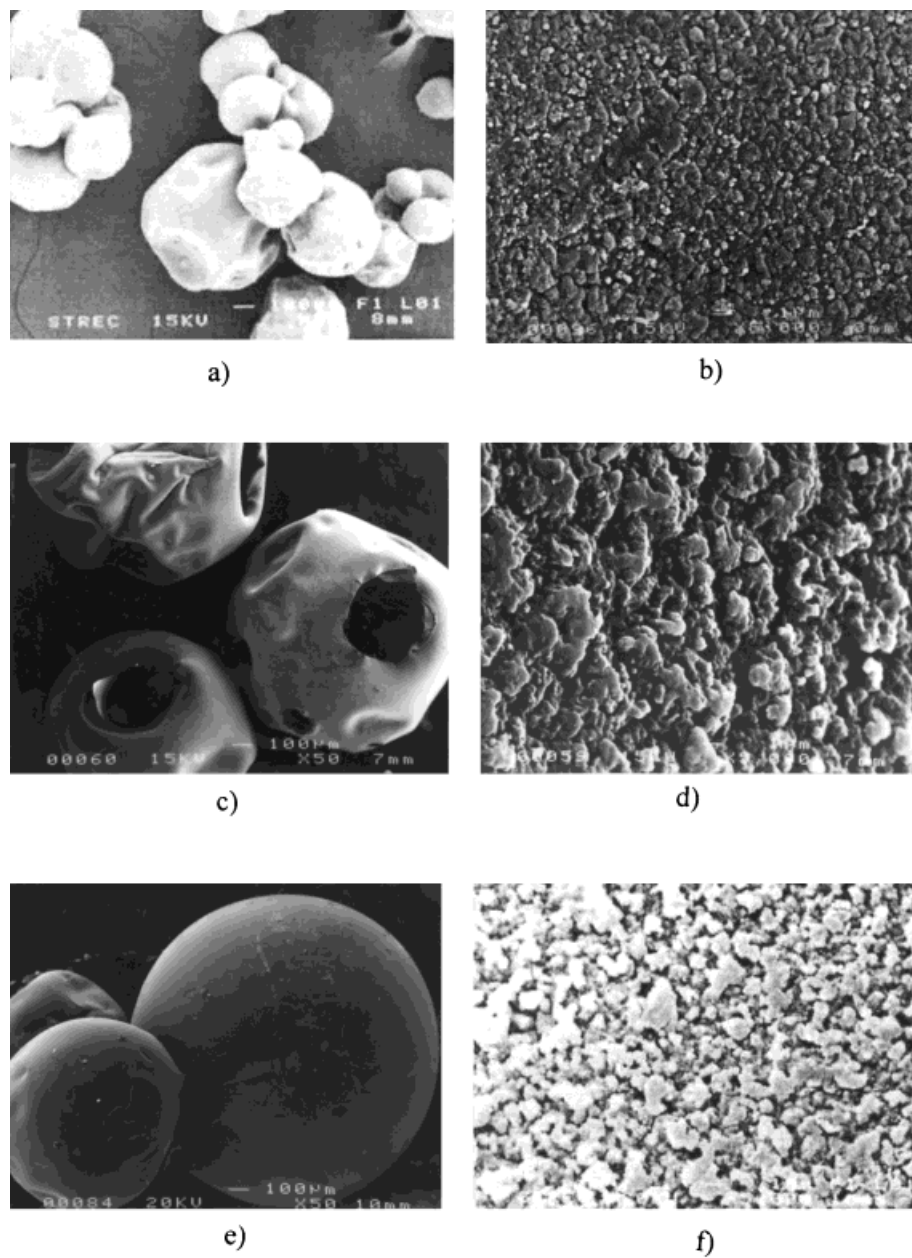


Figure 2 Scanning electron micrographs of the beads under the effect of the initiator concentration: styrene 92.5%, DVB 7.5%, 70 °C, 240 rpm, toluene 100%, PVA 0.09%, and monomer: H₂O, 1/7 at 240 min of the reaction time: a) sample B: BPO 0.5% (×50), b) sample B: BPO 0.5% (×5000), c) sample C: BPO 1.5% (×50), d) sample C: BPO 1.5% (×5000), e) sample D: BPO 2.0% (×50), and f) sample D: BPO 2.0% (×5000).

and the rate of EVB disappearance is especially higher than that of DVB at the three temperatures. Its rate constant increases according to the Arrhenius equation. Nonetheless, the quantitative effect of the temperature is complex because R_p depends on a combination of three rate constants: k_d , k_p , and k_t .

At the higher temperature of 70 °C and the reaction time of 240 min, the copolymer can form

beads. The higher temperature and longer reaction time allow more polymeric chains to propagate, crosslink, and form networks that result in the formation of beads as shown in Figure 4.

The Effect of Agitation

The effect of agitation was studied using the standard recipe shown in Table I. Three runs (B, G,

Table V Effect of the Temperature on the Conversion of Styrene and Divinylbenzene

Sample ^a	Time (min)	Conversion of Individual Monomer (%)			Overall Conversion (%)	Bead Appearance	Swelling Ratio
		Styrene	DVB	EVB			
E (60°C)	0	0.0	0.0	0.0	—	—	—
	30	70.9	74.9	81.7	—	—	—
	60	72.6	81.1	86.5	—	—	—
	90	75.4	79.8	84.6	—	—	—
	120	76.0	79.7	84.6	—	—	—
	150	79.1	83.0	86.8	—	—	—
	180	83.5	87.4	90.1	—	—	—
B (70°C)	240	93.0	95.1	96.0	6.7	Fusion	—
	0	0.0	0.0	0.0	—	—	—
	30	76.4	80.6	85.4	—	—	—
	60	77.5	82.5	86.3	—	—	—
	90	81.4	86.4	88.7	—	—	—
	120	88.4	92.3	93.7	5.6	Fusion	—
	150	92.3	95.3	96.0	9.8	Fusion	—
F (80°C)	180	92.7	95.2	95.7	14.3	Coalescence	5.0
	240	94.6	96.9	96.9	18.9	Coalescence	14.4
	0	0.0	0.0	0.0	—	—	—
	30	79.7	84.2	87.8	—	—	—
	60	81.9	87.0	89.3	—	—	—
	90	87.7	91.8	92.8	12.4	Fusion	—
	120	91.7	95.0	95.2	16.4	Coalescence	16.6
150	92.3	95.7	95.5	21.4	Coalescence	15.2	
180	93.7	96.7	96.4	24.9	Coalescence	14.0	
240	96.7	100.0	98.2	37.3	Bead formation	10.5	

^a Styrene 92.5%, DVB 7.5%, BPO 0.5%, and 240 rpm; Toluene 100%, PVA 0.09%, monomer: H₂O, 1/7.

and H) were carried out using three different agitation speeds (180, 240, and 300 rpm, respectively). The conversion of the individual monomers was followed by the GC technique, and the

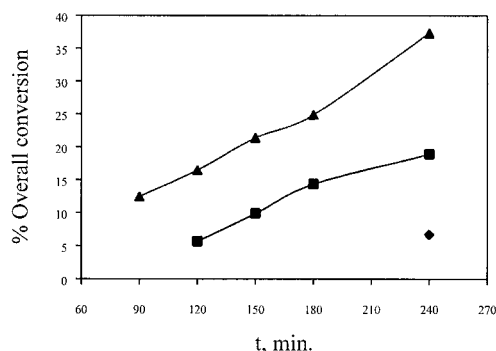


Figure 3 Effect of the temperature on overall conversion of styrene/DVB. The curves ♦, ■, and ▲ are for temperatures 60, 70, and 80 °C, respectively, for styrene 92.5%, DVB 7.5%, BPO 0.5%, 240 rpm, toluene 100%, and monomer: H₂O, 1/7 are used.

overall conversion of the polymer was followed by the gravimetric method, as shown in Table VI. The agitation speed does not cause any vital differences in conversions at longer reaction times. The function of agitation is to develop droplets of monomer phase during the reaction. The agitation rate in suspension polymerization determines the particle size distribution as it changes the stability of monomer droplets in the aqueous phase. An assumption was made that the extent of agitation is sufficient to maintain uniform turbulence throughout the reactor so that the mean drop sizes and size distribution are constant. When two immiscible liquids are agitated, a dispersion of one liquid in the other is formed. In the absence of sufficient concentrations of suspension stabilizers, continuous breakage and coalescence of droplets occur until, after a short time, a dynamic equilibrium is established. At equilibrium, the breakage and coalescence occur at the same rate, and the average size and size distribution of

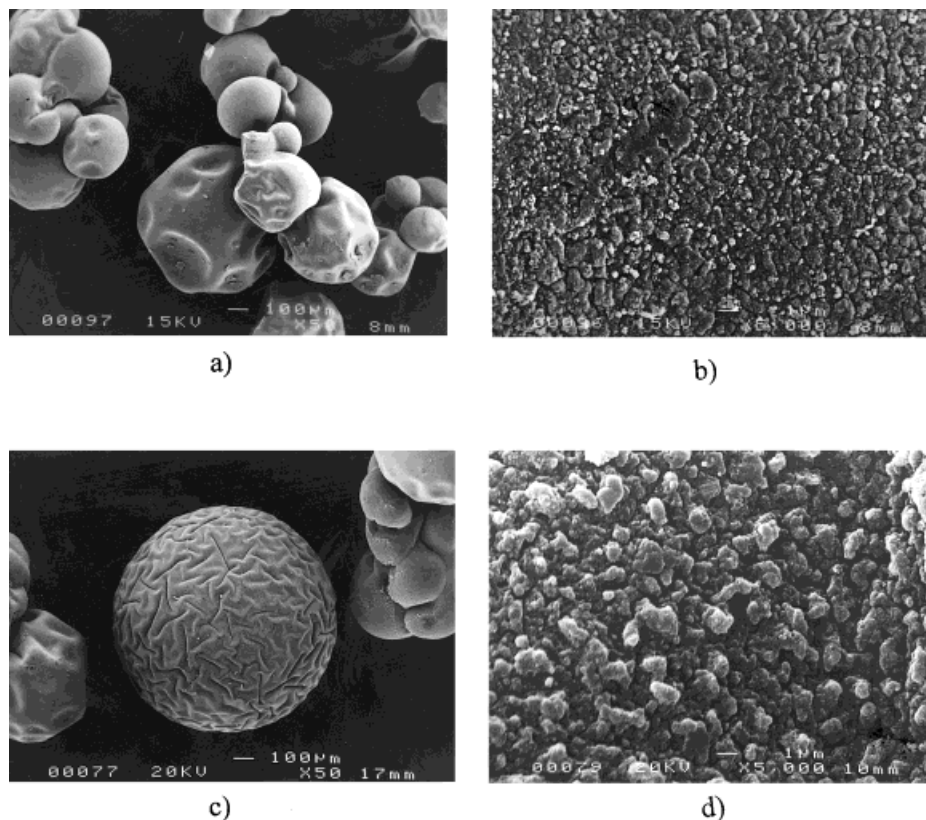


Figure 4 Scanning electron micrographs of the beads under the effect of the temperature: styrene 92.5%, DVB 7.5%, BPO 0.5%, 240 rpm, toluene 100%, PVA 0.09%, and monomer: H₂O, 1/7 at 240 min of the reaction time: a) sample B: 70 °C (×50), b) sample B: 70 °C (×5000), c) sample F: 80 °C (×50), and d) sample F: 80 °C (×5000).

the drops are governed by the type and extent of agitation as well as the physical properties of the two liquids. Under turbulent conditions, breakage occurs as a result of turbulent velocity and pressure variations along the surface of the drop. The coalescence occurs because of the collision of drops in a turbulent field, some of these collisions resulting in coalescence. The coalescence efficiency (defined as the fraction of collisions resulting in coalescence) can approach unity, but it is reduced when a stabilizer is used and it adsorbs on the surface of the droplets. As the bulk concentration of the stabilizer is increased, its surface concentration increases and coalescence efficiency decreases until, at a certain surface coverage called the critical surface coverage, coalescence is completely eliminated. Above this coverage the dispersion is noncoalescing. Table VI also lists the relation between the agitation speed and particle size. When the agitation of the reaction increases, the particle size decreases as confirmed by the McManamey equation.¹² The scanning electron micrographs of the beads are illustrated in Figure 5.

The Effect of the Crosslinking Agent

The effect of the crosslinking agent was investigated using the standard recipe shown in Table I. Three runs (I, B, and J) were carried out using three different crosslinking agent concentrations (5.0, 7.5, and 10.0% DVB based on the monomer phase). The conversion of the individual monomers measured by GC and the overall conversion of polymers measured by the gravimetric method are summarized in Table VII. The conversion was not affected by the crosslinking monomer concentration at the same reaction time. At 5.0% DVB (the solubility parameter, $\delta_{5\% \text{ DVB}} = 17.4$ and $\delta_{\text{toluene}} = 18.2$ (MPa)^{1/2},¹³ for the copolymer prepared by 95/5% of styrene/DVB in toluene), the polymeric product formed was clustered and fused, and no bead formation was observed. Thus, a small amount of the crosslinking agent is not sufficient to copolymerize with styrene and lead to bead formation. We suggest adding an organic-phase inhibitor such as monoethyl hydroquinone for suppression of the secondary nucleation. At a

Table VI Effect of Agitation on the Conversion of and Divinylbenzene

Sample ^a	Time (min)	Conversion of Individual Monomer (%)			Overall Conversion (%)	Bead Appearance	Swelling Ratio
		Styrene	DVB	EVB			
G (180 rpm)	0	0.0	0.0	0.0	—	—	—
	30	58.4	65.9	74.5	—	—	—
	<i>b</i>	60	69.0	76.3	81.6	—	—
	90	81.4	87.3	89.9	—	—	—
	120	82.7	88.3	90.5	4.4	Fusion	—
	150	90.0	93.4	94.5	11.4	Fusion	11.3
	180	92.4	95.0	95.7	13.0	Fusion	13.1
B (240 rpm)	240	95.1	97.6	97.6	16.8	Coalescence	13.1
	0	0.0	0.0	0.0	—	—	—
	30	76.4	80.6	85.4	—	—	—
	<i>c</i>	60	77.5	82.5	86.3	—	—
	90	81.4	86.4	88.7	—	—	—
	120	88.4	92.3	93.7	5.6	Fusion	—
	150	92.3	95.3	96.0	9.8	Fusion	—
H (300 rpm)	180	92.7	95.2	95.7	14.3	Coalescence	5.0
	240	94.6	96.9	96.9	18.9	Coalescence	14.4
	0	0.0	0.0	0.0	—	—	—
	30	77.5	82.4	87.0	—	—	—
	<i>d</i>	60	80.7	86.6	90.1	—	—
	90	84.6	89.5	92.3	—	—	—
	120	85.7	91.9	93.9	3.3	Fusion	—
<i>d</i>	150	91.2	94.7	95.8	8.0	Fusion	—
	180	91.6	94.8	95.8	8.1	Fusion	16.5
	240	93.4	96.0	96.4	14.4	Coalescence	14.3

^a Styrene 92.5%, DVB 7.5, BPO 0.5%, 70°C, Toluene 100%, PVA 0.09%, monomer: H₂O, 1/7. Particle sizes of *b* = 0.94 mm, *c* = 0.78 mm, and *d* = 0.44 mm at 240-min polymerization.

high percentage of DVB (7.5–10%), bead formation is relatively better, as shown in Figure 6, in terms of spherical beads with some dimples or dented areas on the bead surfaces. Solubility parameters of toluene and the copolymers prepared from various amounts of DVB, as previously mentioned ($\delta_{5\% \text{ DVB}} = 17.4$, $\delta_{10\% \text{ DVB}} = 15$, and $\delta_{\text{toluene}} = 18.2 \text{ MPa}^{1/2}$), may be an attribute to the extent of bead formation because the difference in the δ values between toluene and the copolymers increase (=3.2), which could allow the beads to form separately as a result of the lesser swelling and harder surfaces.

The Effect of the Diluent Concentration

The effect of the diluent concentration was analyzed using the standard recipe given in Table I. Four runs (K, L, B, and M) were carried out using four different dilutions to values of 20, 60, 100, or 140% toluene relative to the monomer phase. The

conversions of the individual monomers measured by the GC technique and the overall conversion determined by the gravimetric method are listed in Table VIII. The conversion decreased as a result of the increase in the diluent content by the effect of the diluent. The higher the solvency concentration, the greater the number of shorter kinetic chains. As a result of the solvency power of toluene toward the copolymer of styrene/DVB, the surface of the copolymer softens and may possibly stick the other beads together to precipitate as a lump, as shown in Figure VII.

Because the solubility parameter values of toluene, styrene, and DVB monomers with respect to the copolymers are very similar ($\delta_{\text{toluene}} = 18.2$, $\delta_{\text{styrene}} = 19.0$, $\delta_{\text{DVB}} = 17.2$, and $\delta_{\text{styrene/DVB}} = 18.6 \text{ MPa}^{1/2}$),¹³ solvation, dilution, and droplet formation could possibly occur simultaneously. A large number of monomer droplets were generated and distributed throughout the system,

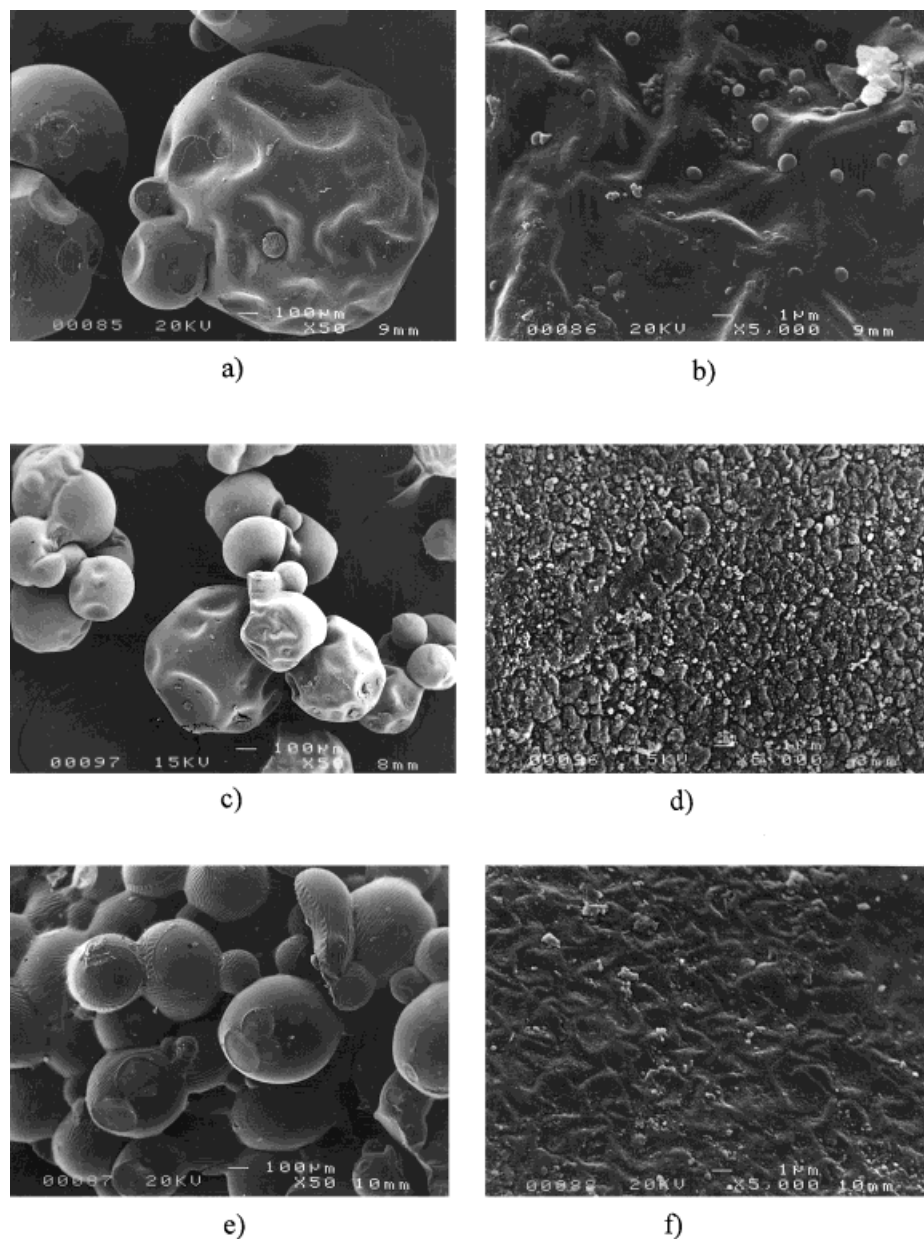


Figure 5 Scanning electron micrographs of the beads under the effect of the agitation: styrene 92.5%, DVB 7.5%, 70 °C, BPO 0.5%, toluene 100%, PVA 0.09%, and monomer: H₂O, 1/7 at 240 min of the reaction time: a) sample G: 180 rpm (×50), b) sample G: 180 rpm (×5000), c) sample B: 240 rpm (×50), d) sample B: 240 rpm (×5000), e) sample H: 300 rpm (×50), and f) sample H: 300 rpm (×5000).

whereas the liquid medium responsible for the heat transfer was consequently reduced. This caused the accumulation of heat inside the vessel, and the small beads were forced to coagulate.

Toluene Swelling Ratio of Styrene–Divinylbenzene Beads

All beads prepared from the recipes and reaction conditions in Table I (samples A–M) were swollen

in toluene, a good solvent, for crosslinked styrenic–DVB copolymers. In Table III evaluation of the solvent swelling ratio by three methods of ANOVA indicates that the solvent swelling ratio depends on toluene diluent, styrene, and DVB concentrations. Although the polymers coalesced into a fuse mass, toluene swelling ratios are still of significant interest. The maximum solvent swelling ratio is in a range of 16–17 times. The

Table VII Effect of the Crosslinking Agent Concentration on the Conversion of Styrene and Divinylbenzene

Sample ^a	Time (min)	Conversion of Individual Monomer (%)			Overall Conversion (%)	Bead Appearance	Swelling Ratio
		Styrene	DVB	EVB			
I (DVB 5%)	0	0.0	0.0	0.0	—	—	—
	30	75.4	83.5	85.2	—	—	—
	60	77.8	85.5	86.3	—	—	—
	90	80.7	87.5	88.0	—	—	—
	120	81.8	89.4	89.7	—	—	—
	150	87.4	93.7	93.8	—	—	—
	180	90.5	95.6	95.5	10.6	Fusion	—
	240	95.9	100.0	98.0	15.0	Fusion	13.1
B (DVB 7.5%)	0	0.0	0.0	0.0	—	—	—
	30	76.4	80.6	85.4	—	—	—
	60	77.5	82.5	86.3	—	—	—
	90	81.4	86.4	88.7	—	—	—
	120	88.4	92.3	93.7	5.6	Fusion	—
	150	92.3	95.3	96.0	9.8	Fusion	—
	180	92.7	95.2	95.7	14.3	Coalescence	5.0
	240	94.6	96.9	96.9	18.9	Coalescence	14.4
J (DVB 10%)	0	0.0	0.0	0.0	—	—	—
	30	70.6	76.5	81.9	—	—	—
	60	76.9	81.4	86.0	—	—	—
	90	81.0	85.9	88.6	—	—	—
	120	85.7	90.3	92.1	10.5	Fusion	—
	150	91.0	93.7	94.8	12.1	Fusion	—
	180	93.2	95.4	96.0	14.7	Coalescence	8.6
	240	94.2	96.4	96.6	18.1	Coalescence	14.1

^a BPO 0.5%, 70°C, 240 rpm. Toluene 100%, PVA 0.09%, monomer: H₂, 1/7.

most interesting swelling ratio found is imposed by the diluent effect. On a closer examination of the bead surface morphology, they are composed of tiny particles of a fraction of micrometers fused and formed holes on the surfaces and pores inside the beads. The solvent swelling behavior is interesting because the polymers can also deswell to their original volume. The swelling-deswelling behavior repeats many times without bead distortion or dissolution. The higher initial swelling-deswelling rate occurs within 10 min. As previously stated, the δ values for toluene and styrene/DVB are very close with a difference in δ of less than 0.5 MPa^{1/2}. This is one reason for the high swelling ratio of the crosslinked copolymers in toluene. For other types of solvents, the solvent absorption/desorption will vary according to the difference in solubility parameters between the solvent and the polymer beads.

Rate Equations

On the basis of the aforementioned experimental results, correlations between independent parameters and the dependent parameter of reaction time were tested for a significance level of $\alpha = 0.05$. The coefficients of partial correlation of the parameters show relationships of styrene, DVB, and EVB with the reaction time (α significance of less than 0.0001). Interestingly, the correlation between DVB or EVB and the reaction time is very high ($R^2 = 0.9985$), whereas the correlation between styrene and DVB is -1.0 and between styrene and EVB is -0.9985 . This negative correlation implies that the three monomers are competing among themselves during copolymerization. In addition, the correlation between the individual or overall conversion and the polymerization time is also significant with α values of 0.001 or less than 0.001, respectively.

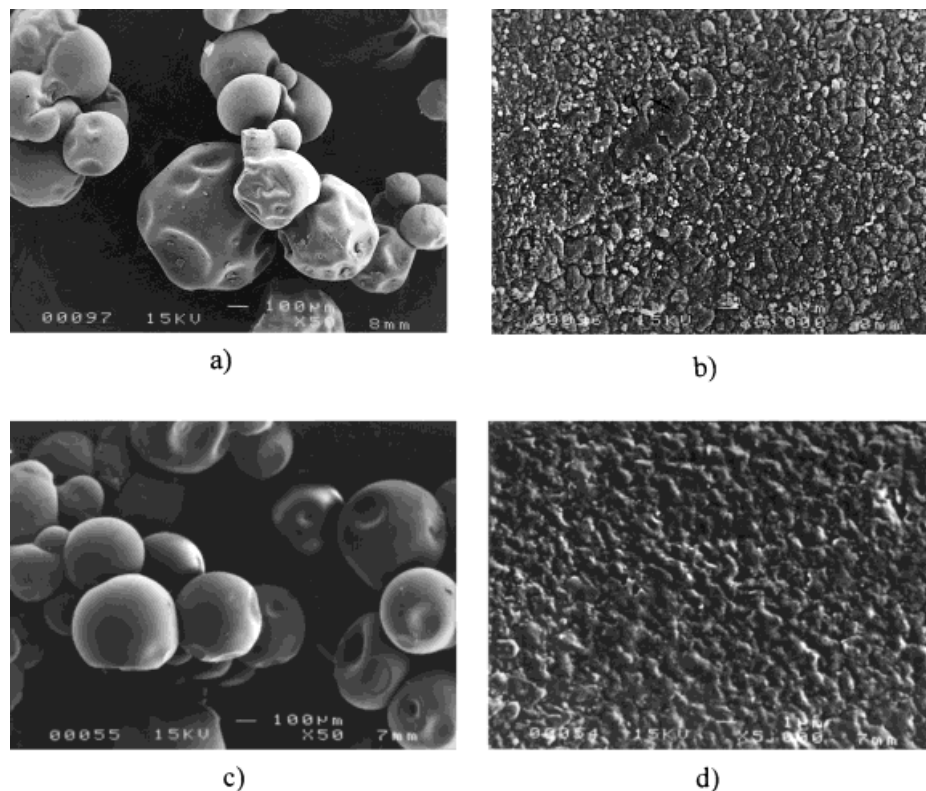


Figure 6 Scanning electron micrographs of the beads under the effect of the crosslinking agent: 70 °C, BPO 0.5%, 240 rpm, toluene 100%, PVA 0.09%, and monomer: H₂O, 1/7 at 240 min of the reaction time: a) sample B: DVB 7.5% (×50), b) sample B: DVB 7.5% (×5000), c) sample J: DVB 10.0% (×50), and d) sample J: DVB 10.0% (×5000).

Integral Method of Analysis of Data

The integral method of analysis always puts a particular rate equation to the test by integration and comparing the predicted C versus t curves with the experimental C versus t data. If the fit is unsatisfactory, another rate equation is suggested and tested. In a constant-volume system, the examination for fitting simple reaction types usually corresponds to elementary reactions. The concentrations of styrene, DVB, and EVB in samples A, B, C, D, G, and H were averaged to search for a rate equation that fits well the experimental data.

Irreversible Bimolecular-Type Second-Order Reaction

Tables IX and X present the concentration changes of styrene, DVB, and EVB with time at the reaction temperatures of 60, 70, and 80 °C. It is important to obtain a rate expression for the principal reaction of styrene polymerization be-

cause the concentrations of DVB and EVB are very small. The experimental data were found to correlate well with a second-order rate equation that offers the following implications.

If one considers the following reaction:¹⁴



with the corresponding rate equation

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 \quad (5)$$

where k is the rate constant whose value depends on the reaction temperature. Integration of eq 5 gives

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt \quad (6)$$

Table VIII Effect of the Diluent Concentration on Kinetics of the Copolymerization of Styrene and Divinylbenzene

Sample ^a	Time (min)	Conversion of Individual Monomer (%)			Overall Conversion (%)	Bead Appearance	Swelling Ratio
		Styrene	DVB	EVB			
K (Tol 20%)	0	0.0	0.0	0.0	—	—	—
	30	80.5	83.9	87.8	—	—	—
	60	83.4	87.4	90.1	—	—	—
	90	89.3	91.9	93.4	8.0	Coalescence	—
	120	92.5	94.9	95.6	11.5	Coalescence	12.6
	150	93.7	96.1	96.4	15.5	Coalescence	13.6
	180	96.9	98.1	97.9	19.9	Coalescence	12.3
	240	98.1	100.0	100.0	29.4	Coalescence	8.6
L (Tol 60%)	0	0.0	0.0	0.0	—	—	—
	30	76.4	81.1	85.6	—	—	—
	60	78.9	83.7	87.1	—	—	—
	90	85.2	89.5	91.5	6.1	Fusion	—
	120	90.6	93.6	94.7	11.2	Fusion	—
	150	94.2	96.5	96.9	12.3	Fusion	12.7
	180	94.9	96.9	97.1	15.7	Coalescence	14.3
	240	95.5	97.7	97.6	20.3	Coalescence	12.7
B (Tol 100%)	0	0.0	0.0	0.0	—	—	—
	30	76.4	80.6	85.4	—	—	—
	60	77.5	82.5	86.3	—	—	—
	90	81.4	86.4	88.7	—	—	—
	120	88.4	92.3	93.7	5.6	Fusion	—
	150	92.3	95.3	96.0	9.8	Fusion	—
	180	92.7	95.2	95.7	14.3	Coalescence	5.0
	240	94.6	96.9	96.9	18.9	Coalescence	14.4
M (Tol 140%)	0	0.0	0.0	0.0	—	—	—
	30	50.2	58.6	67.6	—	—	—
	60	62.1	70.0	76.2	—	—	—
	90	67.1	72.9	78.9	—	—	—
	120	71.4	80.1	83.3	—	—	—
	150	75.7	85.4	87.9	—	—	—
	180	84.2	89.6	90.8	10.9	Fusion	14.2
	240	93.1	95.5	95.9	13.9	Fusion	15.0

^a Styrene 92.5%, DVB 7.5%, BPO 0.5%, 70°C, 240 rpm, PVA 0.09%, monomer: H₂O, 1/7.

where C_{A0} and C_A are the initial and instantaneous concentrations of styrene, respectively. The validity of eq 6 is illustrated in Figure 8. The rate constants at different temperatures were calculated from the regression analysis of these data (see Table XI). These data fall on a reasonably straight line passing through the origin with an R^2 value of 0.97 (Fig. 8); therefore, the equation of this reaction is second-order kinetic, and the slope or k value is 2.1×10^{-2} . Therefore, the rate of the second-order reaction is

$$-r_A = 0.021C_A^2 \quad (7)$$

The Arrhenius plot (Figs. 9 and 10) based on the rate constants from Table XI gave an activation energy of 42 kJ/mol⁻¹ for styrene-DVB copolymerization.

Irreversible Trimolecular-Type Third-Order Reaction

If one considers the reaction



with the corresponding rate equation

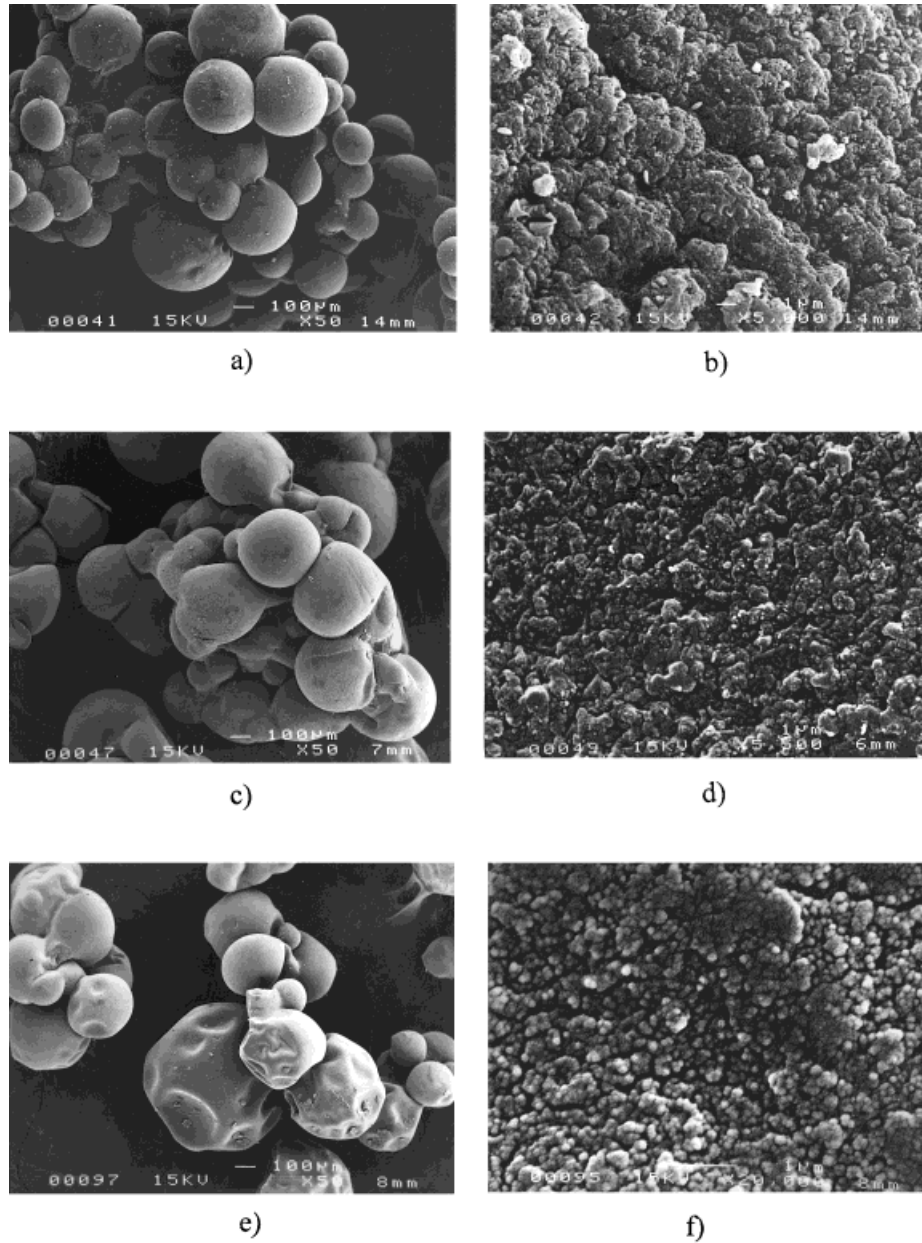


Figure 7 Scanning electron micrographs of the beads under the effect of the diluent concentration: styrene 92.5%, DVB 7.5%, 70 °C, BPO 0.5%, 240 rpm, PVA 0.09%, and monomer: H₂O, 1/7 at 240 min of the reaction time: a) sample K: toluene 20% (×50), b) sample K: toluene 20% (×5000), c) sample L: toluene 60% (×50), d) sample L: toluene 60% (×5000), e) sample B: toluene 100% (×50), and f) sample B: toluene 100% (×5000).

$$-r_A = -\frac{dC_A}{dt} = kC_A C_B^2 \quad (9)$$

the integration form is

$$\frac{(2C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0}C_B} + \ln \frac{C_{A0}C_B}{C_{B0}C_A} = (2C_{A0} - C_{B0})^2 kt \quad (10)$$

These data fall on a reasonably straight line passing through the origin ($R^2 = 0.97$); therefore, the equation of this reaction is third-order kinetic, and the slope is 3.25 (Fig. 11). The rate constant can be obtained as follows

$$(2C_{A0} - C_{B0})^2 k = 3.25$$

Table IX The Concentration of Each Component at the Polymerization Intervals of 30, 60, 90, 120, 150, 180, and 240 min at a Polymerization Temperature of 70°C

Time (min)	Styrene (C_A) (mol L ⁻¹)	DVB (C_B) (mol L ⁻¹)	EVB (C_D) (mol L ⁻¹)
0	3.938	0.159	0.079
30	0.762	0.023	0.009
60	0.667	0.020	0.008
90	0.515	0.015	0.006
120	0.404	0.011	0.004
150	0.301	0.009	0.003
180	0.231	0.006	0.003
240	0.183	0.004	0.002

$$k = \frac{3.25}{(3.94 - 0.16)^2} = 0.23$$

Therefore, the rate of the third-order reaction is

$$-r_A = 0.23C_A C_B^2 \quad (11)$$

where C_A is the concentration of styrene, and C_B is the concentration of DVB.

Differential Method for Analysis of Data

The differential method of analysis deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative dC/dt and testing the goodness of fit of the equation with the experiment. We used the experimental program to test the reaction in question to give the complete rate equation. We considered a reaction carried out in a constant

Table X Styrene Monomer-Concentration Dependence on the Reaction Time at Polymerization Temperatures of 60 and 80°C for Styrene

Time (min)	Styrene (C_A) (mol L ⁻¹) 60°C	Styrene (C_A) (mol L ⁻¹) 80°C
0	3.938	3.938
30	0.698	0.516
60	0.667	0.480
90	0.651	0.363
120	0.647	0.245
150	0.608	0.227
180	0.488	0.188
240	0.208	0.099

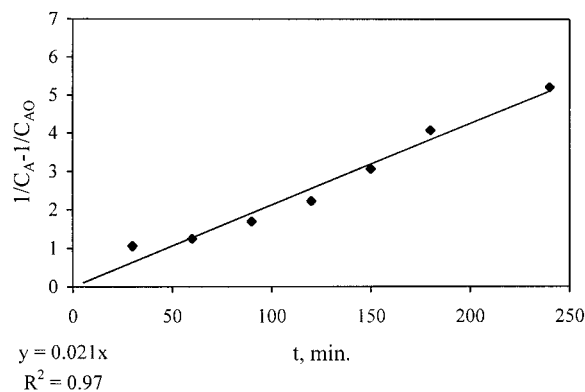


Figure 8 Test for the second-order reaction of eq 6.

volume, and the concentration was recorded as a function of time as shown in Table VIII. Additionally, this method uses all types of vinyl monomer concentrations for the determination of the following rate equation regardless of their quantities, as we consider that it is not appropriate to eliminate any component with vinyl unsaturation that can undergo polymerization:¹⁵

$$-\frac{dC_A}{dt} = kC_A^\alpha \quad (12)$$

After taking the natural logarithm of both sides of eq 20, the equation of rate reaction is

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A \quad (13)$$

The reaction order can now be found from a plot of $\ln(-dC_A/dt)$ as a function of $\ln C_A$. One uses the line through the data points in Figures 12–14 to calculate the slope and k values for styrene, DVB, and EVB that are 1.9 and 1.97×10^{-2} , 1.8 and 2.91×10^{-1} , and 1.8 and 7.76×10^{-1} , respectively. The rate constant of each monomer conversion indicates that EVB is more reactive than the others.

Table XI Rate Constants of Second-Order Reactions versus Temperature

T (K)	$1/T$ (K ⁻¹)	k (L mol ⁻¹ s ⁻¹)	Rate Equation	R^2 Value
333	0.0030	0.014	$r_A = 0.014 C_A^2$	0.63
343	0.0029	0.021	$r_A = 0.021 C_A^2$	0.97
353	0.0028	0.034	$r_A = 0.034 C_A^2$	0.88

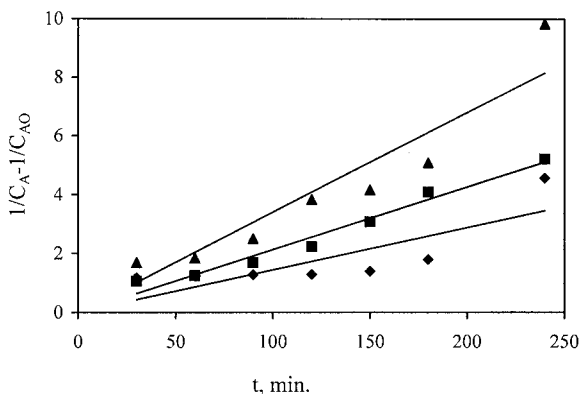


Figure 9 Second-order kinetic plot for styrene polymerization. The curves \blacklozenge , \blacksquare , and \blacktriangle are for temperatures 60, 70, and 80 °C for styrene 92.5%, DVB 7.5%, BPO 0.5%, 240 rpm, toluene 100%, and monomer: H_2O , 1/7 used.

Comparison of the Rate Equations by Integral and Differential Methods

Table XII summarizes the results of the rate equations from experiments and calculations of the reactants. Almost all the rates for EVB are faster than those for DVB and styrene except Sample A. The rate from calculation was compared with the rate from experiment when the concentration of each monomer was substituted in eq 13 with the results shown in Figure 15. The rate from experiment is close to the rate from calculation with deviation for Sample A with the initiator concentration of 0.1%. The complete simple-rate equation of the reaction is probably

$$-r\alpha C_{styrene}^{1.9} C_{DVB}^{1.8} C_{EVB}^{1.8} \quad (14)$$

The rate from calculation in eq 7 was compared with the rate from experiment. The concentra-

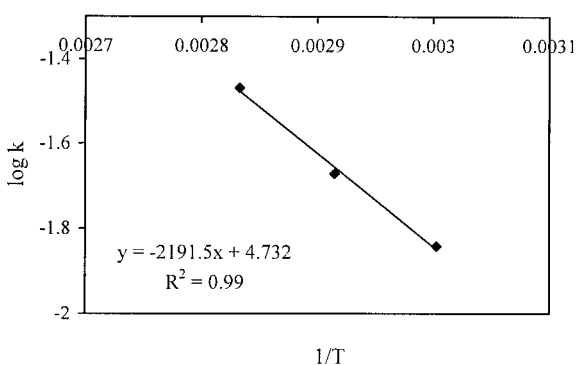


Figure 10 Temperature dependence of the rate constant.

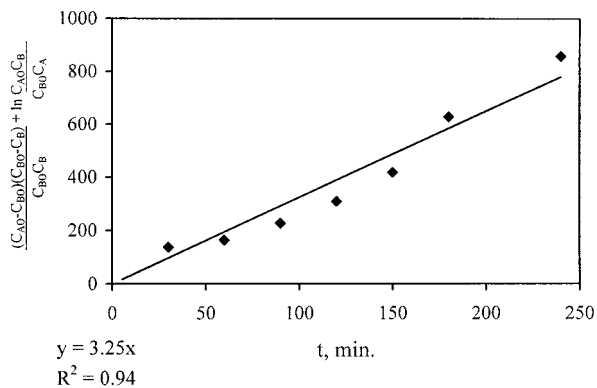


Figure 11 Test for the third-order reaction of eq 11.

tions of each monomer were substituted in the equation (see results in Fig. 16). The deviations were observed for Samples A and D with the initiator concentrations of 0.1 and 2.0%, respectively. From Table XII, the total rate constant for each sample agreed well with the polymerization behavior mentioned in the previous sections of each parameter effect, for example, initiator concentration and agitation effect. The rate from calculation of the differential method is therefore somewhat more accurate than the rate from calculation by the integral method. Thus, the complete simple-rate equation of the polymerization reaction could be eq 14.

Relationship between the Rate Equation and the Polymerization Behavior

In a radical-chain polymerization, the rate of polymerization or conversion depends on the monomer concentration to first-order, with a square-root dependence on initiator concentration. According to Table XII, high monomer orders may

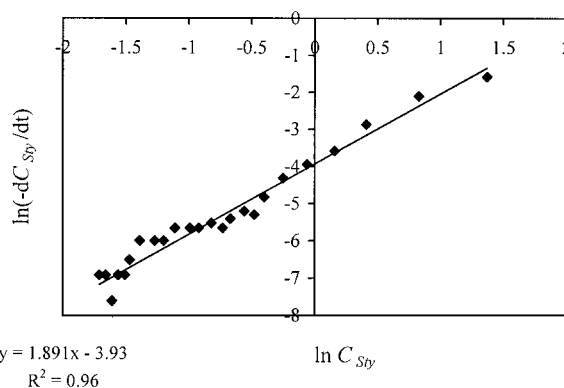


Figure 12 Differential method for determining the reaction order of styrene.

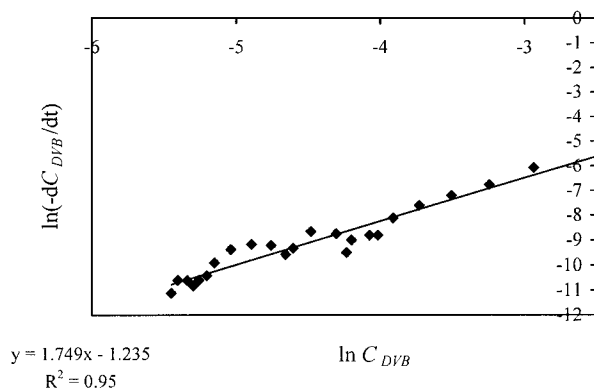


Figure 13 Differential method for determining the reaction order of DVB.

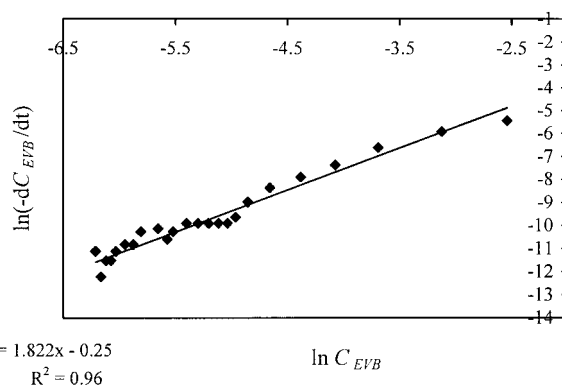


Figure 14 Differential method for determining the reaction order of EVB.

result from a low initiator efficiency, for which the initiator efficiency is affected by the monomer concentration. The dependence of the initiation rate on the monomer concentration could be in error because of the assumption that the rate of initiation is independent of $[M]$. The initiation rate can be monomer-dependent in several ways (Fig. 17). One way is that the second step of the initiation (adding one monomer molecule to the primary radical) could be the rate-determining step instead of the first step of decomposition of the initiator. The increased decomposition rate in the BPO-styrene system could occur by a molecular-induced homolysis reaction, which is first-order in both styrene and BPO. Such an initiation reaction would result in a second-order dependence of R_p on $[M]$.

Figure 18 shows the plot of conversion versus $[M]$, which is not a straight line. Horikx and Hermans¹⁶ found that the BPO-initiated polymeriza-

tion of styrene in toluene at 80 °C showed an increasing order of dependence of R_p on $[M]$ as $[M]$ decreased. The dependence is 1.18-order at $[M] = 1.8$ and increases to 1.36-order at $[M] = 0.4$. These effects may be caused by a dependence of the initiation rate on the monomer concentration as previously mentioned. One additional exception to the first-order dependence of the polymerization rate on the monomer concentration occurs when termination is not by the bimolecular reaction of propagating radicals, which could lead to a second-order dependence of R_p on $[M]$ for primary termination.¹⁷

We observed an induction period at low reaction times of 120 and 150 min and at low initiator concentration. At a low polymerization time, initiator radicals were consumed perhaps by inhibition as a result of the contamination of oxygen gas or a radical recombination. This copolymerization of styrene and DVB was influenced by the un-

Table XII Rate Equation from Experiment and from Calculation

Sample	Rate Equation ($-r$) for			Total k
	Styrene	DVB	EVB	
A	$0.0086C^{1.8}$ (0.77)	$0.1368C^{1.8}$ (0.80)	$0.0590C^{1.9}$ (0.86)	7.1×10^{-5}
B	$0.0247C^{2.1}$ (0.91)	$0.3556C^{1.8}$ (0.83)	$0.6327C^{1.8}$ (0.92)	5.5×10^{-3}
C	$0.0288C^{2.5}$ (0.84)	$0.5860C^{1.9}$ (0.91)	$1.3468C^{1.9}$ (0.89)	2.3×10^{-2}
D	$0.0313C^{1.6}$ (0.95)	$0.0667C^{1.2}$ (0.88)	$0.3567C^{1.5}$ (0.95)	7.4×10^{-4}
G	$0.0142C^{2.2}$ (0.96)	$0.0951C^{1.4}$ (0.94)	$0.1718C^{1.5}$ (0.91)	2.3×10^{-4}
H	$0.0207C^{2.3}$ (0.88)	$1.4055C^{2.2}$ (0.84)	$1.966C^{2.0}$ (0.95)	5.7×10^{-2}
Cal	$0.0197C^{1.9}$ (0.96)	$0.2908C^{1.8}$ (0.95)	$0.7756C^{1.8}$ (0.96)	4.4×10^{-3}

Cal = from calculation. The figures in the parentheses are the values for R^2 . k is a unit of $L \text{ mol}^{-1} \text{ s}^{-1}$. A, B, C, and D are the samples having the BPO concentrations of 0.1, 0.5, 1.5, and 2.0%, respectively; the polymerization was performed at 240 rpm. Samples G and H were both prepared by 0.5% BPO with an agitation of 180 and 240 rpm, respectively.

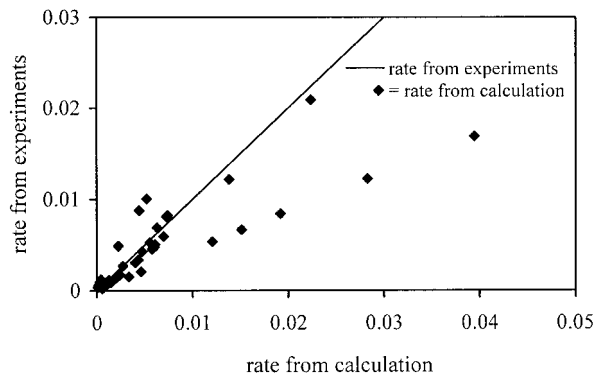


Figure 15 Test for the rate from experiment compared with the rate from the calculation of eq 11.

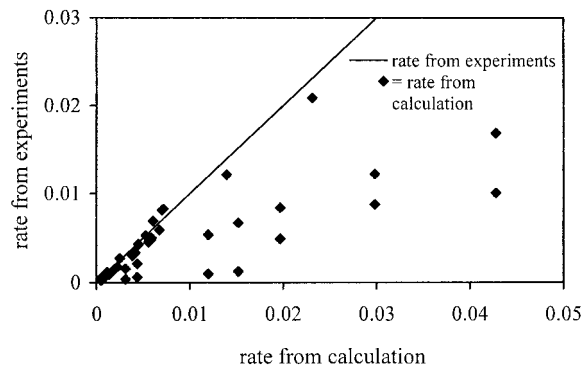


Figure 16 Test for the rate from experiment compared with the rate from the calculation of eq 7.

equal reactivity of the two function groups of unsaturation; instead, r_1 for styrene is 0.26 ± 0.25 and r_2 for DVB is 1.18 ± 0.17 .¹⁸ When the double bonds of the diene (DVB) are more reactive than that of styrene ($r_2 > r_1$), crosslinking occurs in the early stages of copolymerization. Thus, we observed autoacceleration even at a low conversion. As shown in Table IX, crosslinking takes place rapidly within the first 30 min of copolymerization. Gel formation, afterwards, slowly increases compared with the beginning of the reaction. This general behavior is presumably attributed to the wastage of the diene monomer as a result of a possibly intramolecular cyclization.¹⁹ For every parameter studied, we found the overall conversion is relatively low although the concentrations of all the monomers depleted rapidly from about 180 to 240 min of polymerization. We postulate that a soluble portion of noncrosslinked polymers

can dissolve in the good solvent of toluene, as shown in all tables and especially in Table VIII, with high concentrations of toluene. Considering Table IX, there is an indication that the reactivity of the second double bond in DVB is decreased with respect to the reactions of the first double bond as a consequence of its presence in a polymer chain. Our observation is in agreement with the work of Hild and Okasha.²⁰ The decrease of the DVB concentrations compared with those of EVB is slower, although the latter is very much less concentrated either because EVB is competing with styrene for DVB crosslinking monomer or EVB can react with both styrene and DVB at the later stage of the reaction. This behavior confirms that the differential method is a better method for evaluating the rate equation, which takes into account all types of vinyl monomer concentrations.

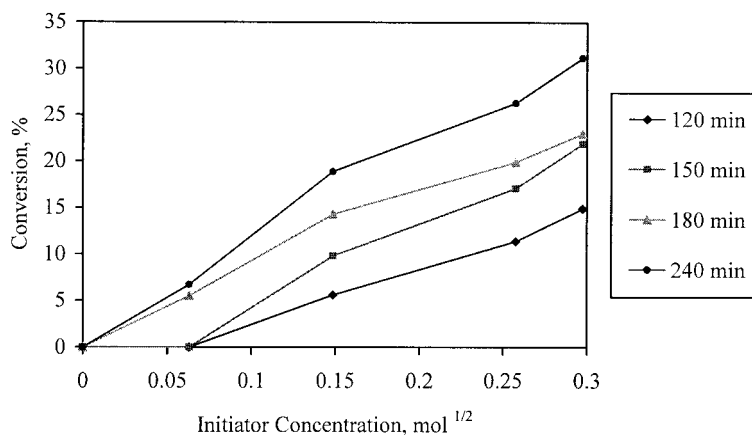


Figure 17 Plot of the conversion versus $[I]$ (BPO) concentration in styrene–DVB (92.5/7.5) copolymerization in toluene at 70 °C.

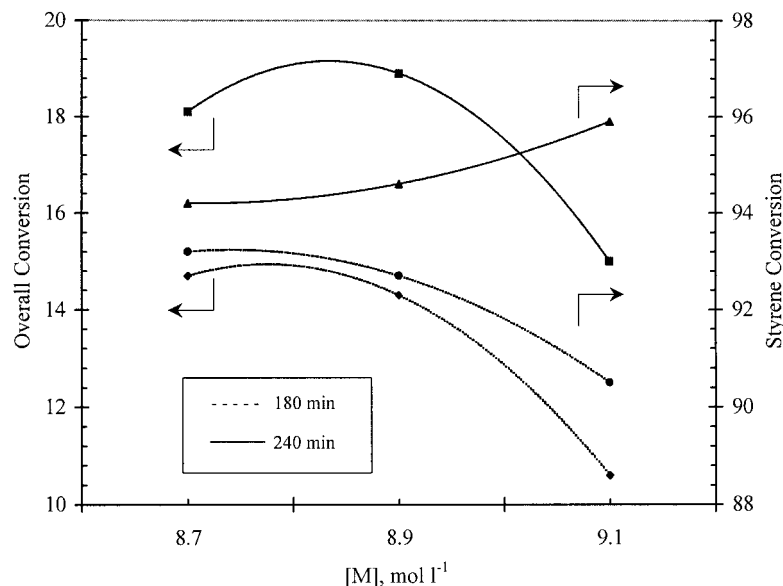


Figure 18 A plot of overall conversion versus $[M]$ in styrene-DVB copolymerization in toluene at 70 °C, $[I]$ (BPO) = 6×10^{-2} mol L⁻¹.

CONCLUSIONS

On the basis of the ANOVA analysis, the concentrations of styrene monomer, DVB as a comonomer and crosslinking agent, and toluene diluent are the reaction parameters that affect the copolymer swelling in toluene. In addition, the reaction temperature and agitation rate also affect the kinetics of the suspension copolymerization for styrene/DVB. The kinetic orders determined for this copolymerization show considerable deviations from the first-order monomer concentration and the square-root order of the initiator concentration. The gel effect might give a partial contribution to the polymerization rate of a lower than square-root dependence on the initiator concentration, as indicated by the calculated rate equation for the monomer concentration dependence of greater than first-order. The autoacceleration in the copolymerization rate along with crosslinking polymerization is dependent on both monomer and initiator concentrations. Comparison of the rate equations determined by integral and differential methods indicates that the latter is a better method for this type of suspension-crosslinking copolymerization. The rate equation obtained by the differential method agrees better with the polymerization behavior.

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