

연속반응기(CSTR)에서 비닐 아세테이트와 비닐 벤조에이트의 용액 공중합(1)

김 영 규 · 하 창 식 · 설 수 덕* · 김 동 건* · 조 원 제

부산대학교 고분자공학과 · *동아대학교 화학공학과

(1991년 6월 12일 접수)

Solution Copolymerization of Vinyl Acetate and Vinyl Benzoate in a CSTR(1)

Young Kyoo Kim, Chang Sik Ha, Soo Duk Seul*, Dong Keun Kim*, and Won Jei Cho

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea.

*Department of Chemical Engineering, Dong-A University, Pusan 602-103, Korea

(Received June 12, 1991)

요 약 : 비닐 아세테이트(VAc)와 비닐 벤조에이트(VBz)를 벤젠에서 AIBN을 개시제로 사용하여 60℃에서 라디칼 공중합을 하였다. 자외선 흡수 분광법으로 공중합체 조성을 분석하였으며, 단량체 반응성비 r_1 (VAc)과 r_2 (VBz)는 Kelen-Tüdös 방법(또는 Finneman-Ross 방법)으로 결정하였다; $r_1=0.69(0.66)$, $r_2=1.48(1.46)$. 단량체, 단일중합체 그리고 공중합체의 속도상수를 결정하였다. 회분식 반응기에서 얻은 자료를 바탕으로 벤젠에서 비닐 아세테이트와 비닐 벤조에이트의 공중합을 연속 반응기(CSTR)를 사용하여서 연구하였는데, CSTR연구에 대한 실험조건은 회분식 반응기의 조건과 동일하게 하였고, Residence time과 부피는 각각 7200초와 1.2리터로 하였다.

Abstract : Radical copolymerization of Vinyl acetate(VAc) and Vinyl benzoate(VBz) was carried out with AIBN as an initiator in benzene at 60°C. The copolymer compositions were analyzed by UV spectrophotometry. The monomer reactivity ratios, r_1 (VAc) and r_2 (VBz) were determined by both the Kelen-Tüdös method and the Finneman-Ross method; $r_1=0.69(0.66)$, $r_2=1.48(1.46)$. The rate constants of monomers, homopolymers and copolymers were determined. Based on the data from a batch reactor, a copolymerization of vinyl acetate and vinyl benzoate in benzene was studied using a CSTR. The experimental conditions for CSTR studies were almost the same as that of a batch reactor. The residence time and volume were given as 7200 sec and 1.2L, respectively.

INTRODUCTION

The basic research on the solution copolymerization of vinyl acetate(VAc) and vinyl benzoate

(VBz) is of great interest in both theoretical and practical standpoints, since it is expected that the copolymer can be applied as a heat resistant adhesive or a protective coating. Few studies have been

reported, however, on the solution copolymerization of vinyl acetate and vinyl benzoate.

Studies of polymerization in ideal continuous stirred tank reactors (CSTRs) have received less attention in spite of their theoretical and industrial importances. The studies using continuous copolymerization method to estimate the rate parameters in copolymerization have not been extensively done.¹

In this connection, studies on the solution copolymerization of vinyl acetate and vinyl benzoate in a CSTR will give a useful insight into the kinetic dependences on each monomer, solvent or other experimental variables.

A great care must be taken to carry out investigations on the continuous copolymerization since the rate parameters are strongly dependent on the experimental conditions such as temperature, reaction time, pressure, solvent and so on.

In this work, we synthesized a copolymer of VAc and VBz with AIBN in benzene at 60°C both in a batch reactor and in a CSTR. The rate parameters were calculated from a simple kinetic scheme with experimental data.

THEORY

Based on the classical radical reaction mechanism, it was assumed that the kinetics in this CSTR model are affected by merely the terminal unit in a growing chain. The radical reaction mechanism consists of initiation, propagation, termination and chain transfer to solvent.

To simplify the reactor model, three assumptions have been made. The first assumption is the quasi-steady state approximation that the initiation rates of active intermediates are virtually the same as the rates of termination.^{2~4}

As a second approximation, the long chain approximation assumes that the monomers are consumed predominantly in the propagation step because of the long copolymer chains.

Other assumptions made are as follows: the rate constant in the propagation step has much

larger value than that in the transfer to solvent, i.e. $k_p \gg k_{tr}$. And the rate constant in the propagation step of active intermediates transferred to solvent is equal to the rate constant in the general propagation step: $k_{ps} = k_p$.

The rate equations derived by using the three assumptions above are following⁵:

$$R_p = \frac{(r_1 M_1^2 + 2M_1 M_2 + r_2 M_2^2) R_i^{0.5}}{((r_1 \delta_1 M_1)^2 + 2\phi r_1 r_2 \delta_1 \delta_2 M_1 M_2 + (r_2 \delta_2 M_2)^2)^{0.5}} \quad (1)$$

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

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

Further development of the simplified rate equation has been made by Atherton and North⁶ using the assumptions.

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

where $k_{t(12)} = k_{t11}F_1 + k_{t22}F_2$, which is the ideal diffusion model.

In order to find R_p , the monomer reactivity ratios r_1 and r_2 should be predetermined from the composition of each monomer in feed (M_1 and M_2) and in copolymer (m_1 and m_2).

The monomer reactivity ratios can be estimated by the Kelen-Tüdös method.⁷

$$\eta = (r_1 + r_2/\alpha) \varepsilon - r_2/\alpha \quad (3)$$

$$\begin{aligned} \text{where } \eta &= G/(\alpha + F), \quad \varepsilon = F/(\alpha + F), \quad F = X^2/Y, \\ G &= Y(Y-1), \quad \alpha = (F_{\min} F_{\max})^{0.5}, \\ X &= M_1/M_2, \quad Y = m_1/m_2. \end{aligned}$$

The r_1 and r_2 values were also obtained by the following Fineman-Ross method.⁸

$$\frac{f_1(1-2F_1)}{F_1(1-f_1)} = r_2 + \left[\frac{f_1^2(F_1-1)}{F_1(1-f_1)^2} \right] r_1 \quad (4)$$

The reactivities as a function of a comonomer composition in feed (f_1) were correlated with

kinetic parameters by Balaraman et al.⁹ The correlation is given as

$$\frac{K_1}{K_2} = \frac{(r_1 - 1)f_1 + 1}{(1 - r_2)f_1 + r_2} \quad (5)$$

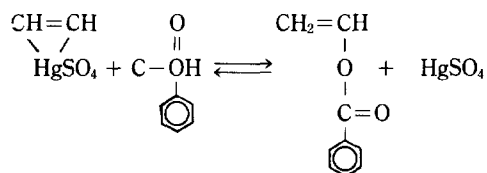
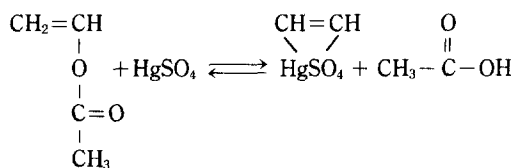
where $K_1 = (2fk_d)^{0.5}/\delta_1$, $K_2 = (2fk_d)^{0.5}/\delta_2$.

EXPERIMENTAL

Materials and Instruments

Vinyl acetate(VAc; Junsei Co.) was purified as the standard procedure. Benzoic acid(Junsei Co.), mercuric acetate(Karasama Chemical Co.), Hydroquinone(Katayama Chemical Co.) and sulfuric acid were used without further purifications in synthesizing vinyl benzoate. Benzene as solvent was distilled prior to use.

The vinyl benzoate was prepared by refluxing 1.5 moles of benzoic acid, 3 moles of vinyl acetate and 15 g of mercuric acetate in the presence of 0.5 cc of conc-sulfuric acid and 7 g of hydroquinone in an oil bath at 60°C for 36 hours. After non-reacted vinyl acetate was removed by using the rotary evaporator, the product obtained was distilled under vacuum(3mmHg) at 73°C. Yield was 87%.



The vinyl benzoate was characterized by Fourier-Transform Infrared Spectroscopy(Perkin-Elmer 130C) and ¹H-NMR(Varian, A60) Spectroscopy.

The vinyl benzoate(VBz) prepared is identified by the characteristic peaks of 3090 cm⁻¹(aromatic

C-H), 1740 cm⁻¹(C=O), 1647 cm⁻¹(C=C), 1260 cm⁻¹, 1140 cm⁻¹ and 1090 cm⁻¹(C-O stretching of ester) and 700 cm⁻¹ (out-of-plane bending of aromatic C-H), as shown in Fig. 1. The VBz was also characterized by ¹H-NMR; 4.31 ppm(H_a), 4.69 ppm(H_b), 7.80 ppm(H_c) and 7.16 ppm(phenyl proton); see Fig. 2.

The copolymer compositions were analyzed by UV Spectrophotometer(Hitachi 220). The analysis was performed by using a characteristic wave length of 284 nm, which is observed only in vinyl benzoate.

Experimental Procedure

Batch Reactor

Synthesis of poly(vinyl acetate) : Poly(vinyl acetate) was prepared by reacting 0.36 mole of VAc dissolved in 100 ml of benzene with 3×10⁻³

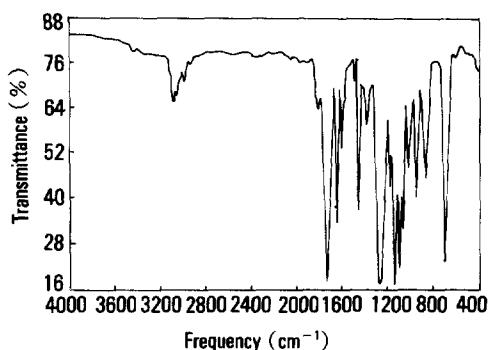


Fig. 1. FT-IR Spectrum of vinyl benzoate (liquid cell).

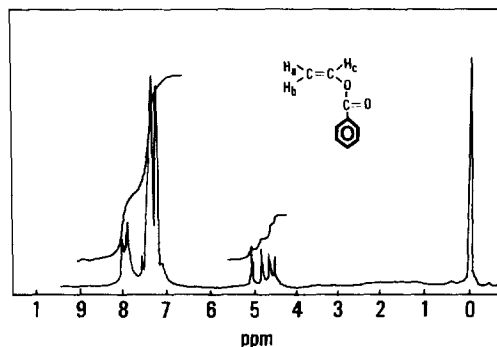


Fig. 2. ¹H-NMR spectrum of vinyl benzoate(CCl₄).

mole of AIBN at 60°C under nitrogen atmosphere in a polymerization tube.

After two hours, the contents were poured into petroleum ether with stirring; the precipitate was filtered and dried in vacuo to constant weight.

Synthesis of poly(vinyl benzoate) : Poly(vinyl benzoate) was prepared by reacting a mixture of 0.36 mole of VBz and 3×10^{-3} mole of AIBN in 100 ml of benzene by the same method as described for preparation of poly(vinyl acetate).

Synthesis of poly(vinyl acetate-co-vinyl benzoate) : A mixture of VAc and VBz at a given mole ratio was dissolved in 100 ml of benzene and then added with 3×10^{-3} mole of AIBN. The tube was sealed after charging with nitrogen. The preparation method was similar as described for the homopolymerization of VBz or VAc.

The copolymerization was carried out at 60°C for a chosen period to assume the conversions below 10%.^{10~12}

CSTR

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, N₂ gas was purged continuously. Continuous purging with nitrogen gas was necessary during copolymerization reaction.

The initiator had been added to the mixture in the reactor just before the pumps were operated. The total fixed flowrate and the residence time were 10 ml/min and 2 hours, respectively.

The sampling was done at 30 minutes intervals. The samples withdrawn were directly analyzed by UV spectrophotometer. The volume fraction of the

solvent was kept constant to allow no gel-effect. The experimental conditions were summarized in Table 1. The schematic diagram of the CSTR is shown in Figure 3.

RESULTS AND DISCUSSION

Copolymer Compositions and Monomer Reactivity Ratios

The copolymer compositions were determined by UV spectrophotometry according to the literatures.^{13,19} Typical UV spectra of copolymers with different compositions in feed in a batch reactor is shown in Fig. 4.

A characteristic equation to find copolymer compositions was obtained from the calibration curve of specific absorbance at 284 nm, which is detectable only for vinyl benzoate, as a function of poly(vinyl benzoate) concentration in feed mixture of poly(vinyl acetate) and poly(vinyl benzoate) with given mole ratios.

$$\epsilon = 0.682X - 1.852 \times 10^{-4}$$

where ϵ is the specific extinction coefficient of copolymer and X is the weight fraction of vinyl benzoate in the copolymer.

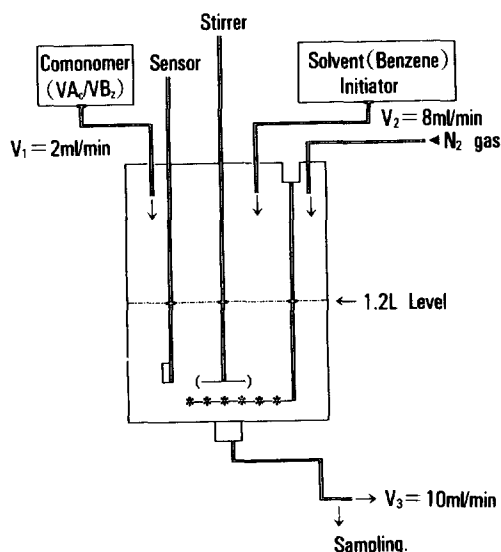


Fig. 3. Schematic diagram of CSTR experiments.

Table 1. Experimental Conditions

Polymerization Temp.	60°C
Solvent	Benzene
Solvent/Comonomer Ratio	4 : 1(v/v)
Initiator Used	AIBN
Initiator Conc.	8.05 mmol/L
Residence Time	7200 s
Reactor Volume	1.2 L

The copolymer compositions obtained by using the characteristic equation were shown in Fig. 5.

The monomer reactivity ratio was determined by the Kelen-Tüdös method with several parameter values listed in Table 2. The Kelen-Tüdös plot gives the reactivity ratios of $r_1(\text{VAc})$ and $r_2(\text{VBz})$ as 0.69 and 1.48, respectively. The result means that VAc has much lower tendency to homopolymerize than VBz and the copolymerization is dominant over the homopolymerization of each monomer.

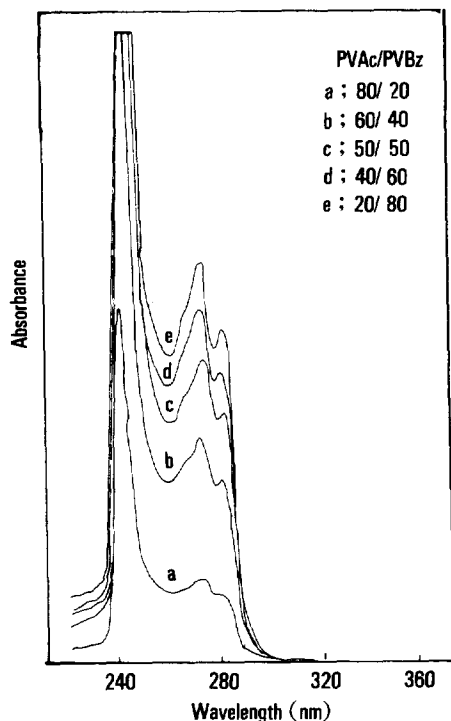


Fig. 4. UV spectra of poly(VAc-co-VBz)'s with different feed ratios.

In order to confirm the monomer reactivity ratios, the Fineman-Ross calculation^{8,14} was also carried out using equation (4). The monomer reactivity ratios of $r_1(\text{VAc})$ and $r_2(\text{VBz})$ were determined as 0.66 and 1.46, respectively. It is noteworthy that the two different approaches lead to the very similar results in the monomer reactivity ratios.

Parameter Estimation Procedure

In order to find the rate equations of homopolymerization or copolymerization of vinyl acetate and vinyl benzoate in benzene, the rate parameters included in the equation (1) should be estimated. The kinetic parameters for vinyl acetate at 60°C were easily obtained from the Polymer Handbook.¹⁵ Table 2 shows the list of such rate parameters.

The rate parameters for vinyl benzoate, how-

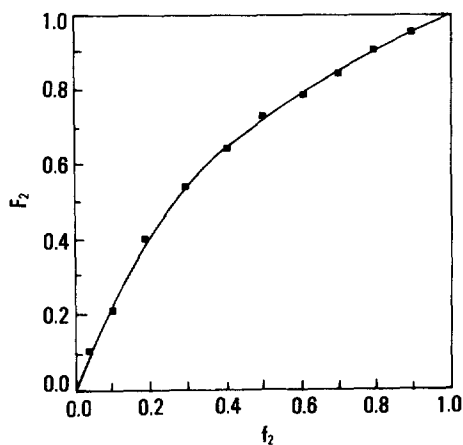


Fig. 5. Graphic analysis of copolymer compositions obtained from batch data($r_1=0.69$, $r_2=1.48$).

Table 2. Summary of Parameters

AIBN	Vinyl Acetate	Vinyl Benzoate
$k_d = 8.45 \times 10^{-6} \text{ sec}^{-1}$	$k_{p11} = 7730.0 \text{ L/mole} \cdot \text{sec}$	$k_{p22} = 16619.5 \text{ L/mole} \cdot \text{sec}$
$f = 0.6$	$k_{t11} = 342 \times 10^6 \text{ L/mole} \cdot \text{sec}$	$k_{t22} = 735 \times 10^6 \text{ L/mole} \cdot \text{sec}$
$R_i = 81.63 \times 10^{-9}$	$k_{p11}/k_{t11} = 22.6 \times 10^{-6}$	$k_{p22}/k_{t22} = 22.6 \times 10^{-6}$
mole/L \cdot sec	$\delta_1 = 3.38$	$\delta_2 = 2.31$
$\phi = (2.15 - 1.15F_1)/2.93$		

ever, were available neither from the Polymer Handbook nor from the literatures. It might be expected that the rate parameters of vinyl benzoate can be estimated from the corresponding values of vinyl acetate by considering the difference between reactivity ratio of each monomer.

Since the reactivity ratio, r_2 , of vinyl benzoate is 2.15 times of the reactivity ratio, r_1 , of vinyl acetate, it may be assumed that the kinetic parameters of VBz can be obtained by multiplying 2.15 times to each corresponding parameter of VAc. The rate parameters thus obtained were also summarized in Table 2.

Such approach to estimate the unknown rate parameters of vinyl benzoate from the reactivity difference is approximative and should be proved with more concrete experimental data. Fortunately, however, one can see that the approximative approach is not unreasonable, assuming the Balaraman equation (5) holds for the system in this work; if we put experimental data into f_1 , r_1 and r_2 in equation (5), we can calculate K_1/K_2 . The mean value of the right-hand term in the equation is calculated as 0.68 with the standard deviation of 0.005. Then, $K_1 = 0.68 K_2$ and in turn $\delta_2 = 0.68 \delta_1$. From the definition and the known values of δ_1 , δ_2 is estimated as 2.31 and consequently $(2k_{t22}/k_{p22}^2)^{0.5} = 2.31$. The δ_2 value is in accordance with that calculated from the assumed $k_{p22} = 2.15k_{p11}$ and $k_{t22} = 2.15k_{t11}$. The diffusion-controlled termination constant ($k_{t(12)}$) and cross termination factor (ϕ) was also determined by the rate parameters of vinyl benzoate thus obtained.

The somewhat rough method shown above enables us to obtain the unknown parameters of VBz without any great ambiguity, even though the significance of the experimentally-determined reactivity ratios should be accounted. Of course, however, more accurate and credible methods to obtain unknown rate parameters should be investigated from both theoretical and experimental standpoints. In general, only the values of $2k_t/k_p^2$ have been reported with experimental data.¹⁶⁻¹⁸

Rate of Homopolymerization and Hydrolysis

Figure 6 shows the difference in the rate of homopolymerization (R_p) between that of vinyl benzoate and that of vinyl acetate as a function of time. In this figure the slope of R_p for vinyl benzoate is stiffer than that of vinyl acetate. The result is due to the fact that the reactivity of vinyl benzoate is much greater than that of vinyl acetate, as expected from their reactivity ratios.

The difference in the reactivity of the copolymer as well as their homopolymers are also observed in the hydrolysis of the polymers with KOH. The hydrolytic study was also made to compare their reactivity difference by hydrolyzing the polymers with KOH at 60°C. 0.414g of each polymer was dissolved in 100 ml of DMF and diluted with hundred-fold excess KOH. The analysis of hydrolysis rate was made using a characteristic wavelengths of 273 nm. The details of analysis were given elsewhere.¹⁹

Figure 7 shows the plot of $\ln(a/(a-x))$ vs reaction time for the reaction of poly(vinyl acetate), poly(vinyl benzoate) and poly(vinyl acetate-co-

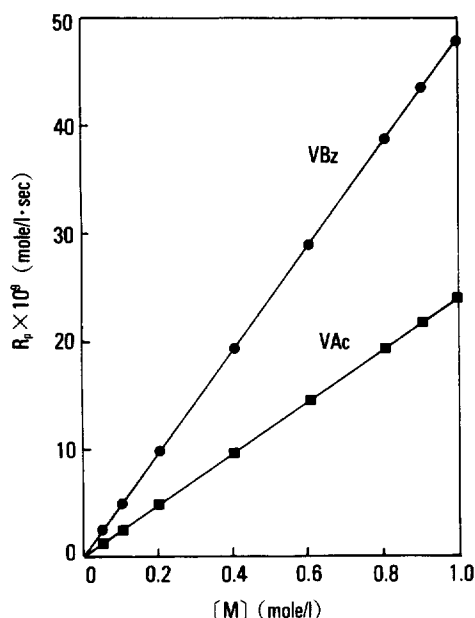


Fig. 6. Plot of R_p vs $[M]$ for VAc and VBz.

Solution Copolymerization of Vinyl Acetate and Vinyl Benzoate in a CSTR(1)

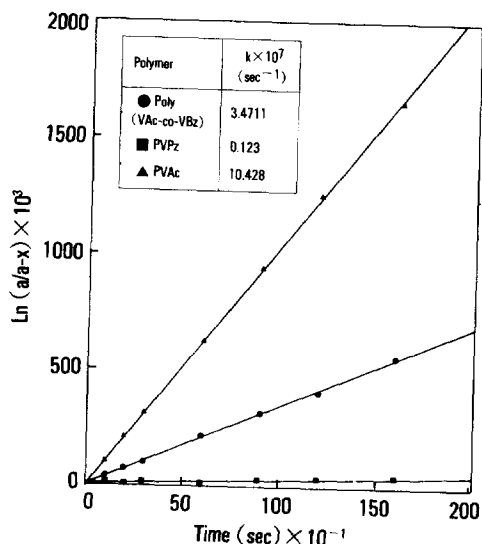


Fig. 7. Plot of $\text{Ln}(a/(a-x))$ vs reaction time for the reaction of PVAc, PVBz and poly(VAc-co-VBz) with KOH at 60°C.

vinyl benzoate) (50/50 by wt.% in feed) with KOH at 60°C, where a is an initial concentration of each monomer and x is a conversion. The rate constants for each polymer are shown in the table of the left-upper part in figure 7. As expected, the rate constant of the copolymer has the intermediate value between the two homopolymers. The linearity in this figure implies that all of the polymer and copolymer follow the first order-kinetics. For reference, the rate constant of copolymer of VBz and VAc at 60°C was given as $3.47 \times 10^{-7} \text{ sec}^{-1}$.

Rate of Copolymerization

In Figure 8, the rate of copolymerization R_p was plotted against the comonomer feed composition f_2 . The copolymerization rate was obtained by using the simplified rate equation(2) proposed by Atherton and North. The rate of copolymerization decreases initially and increases remarkably with the comonomer feed ratio. The minimum was observed in R_p . The occurrence of this minimum point was also observed in other works,^{20,21} Palit²¹ has investigated the conditions under which the mini-

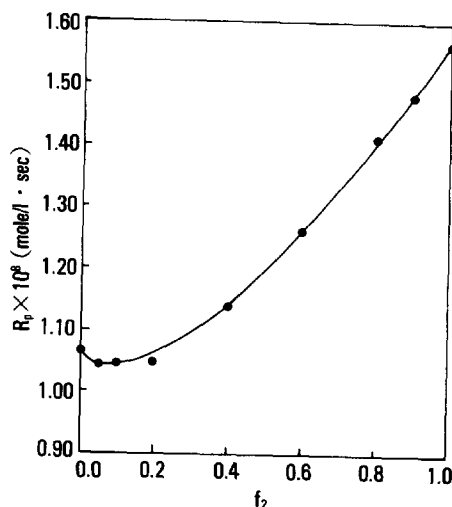


Fig. 8. Dependence of the rate of copolymerization on the comonomer feed composition. (assuming $k_{t(12)} = k_{t11} (2.15-1.15F_1)/2.93$ followed by substituting into Atherton and North equation).

um occurs in the rate of copolymerization curve. According to him, the necessary condition for the minimum to occur is $M_2/M_1 = (r_2/r_1)^{0.5}$. If $r_2 \gg r_1$, the minimum occurs close to a monomer mixture of pure M_1 .

The result may be related to ϕ factor, which is shown in Figure 9. From this Figure, the ϕ factors are ranged from 0.34 to 0.73. 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 ratio. In the equation (1) the terminal model was adapted. However, some researchers suggested that the terminal model is a special case of the penultimate model and the complex model.

Ma et al. proposed that their styrene/methyl methacrylate system follows the $\phi = 1$ model in the termination step when it comes to numerical values and the penultimate model is well-fitted in the propagation step.^{16,17} In other cases, Brown et al. have compared the three models¹⁸: the terminal model, the penultimate model and the complex model. They concluded that the penultimate model was more realistic than any other models.

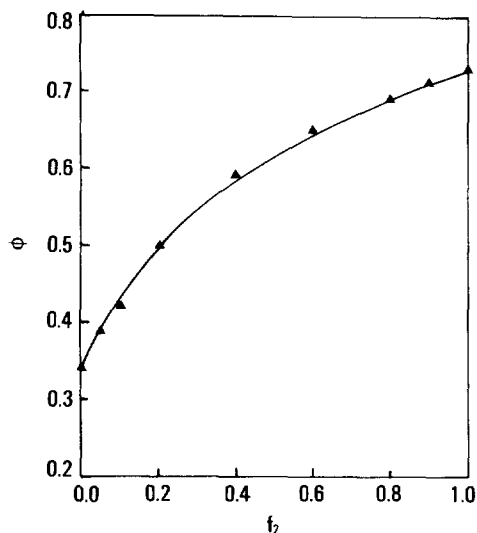


Fig. 9. The dependence of ϕ -factor on the comonomer feed ratio.

In our work, the simple terminal model was used because the available data were limited. Another reason to use the terminal model is for simplification, since a series of the works in our laboratory mainly concerns a CSTR, not the copolymerization kinetics. It should be pointed out, however, that since it was roughly assumed to develop the rate equation in this study that the ϕ factor is only dependent on extremely few parameters like the copolymer compositions and the rate constants, the speculation in explaining the result of Fig. 8 may lead to somewhat erroneous conclusions.

More detailed studies on the ϕ factor should be performed to reveal the accurate relation among ϕ factor, comonomer feed ratio and rate of copolymerization. The ϕ values reported by Burnett and Gersmann²² for vinyl acetate-methyl methacrylate copolymer system were widely scattered over the range 100–800.

Conversion of Copolymer

The absorbance changes in UV spectra with time for the copolymer obtained from CSTR were shown in Figure 10. The conversion was obtained

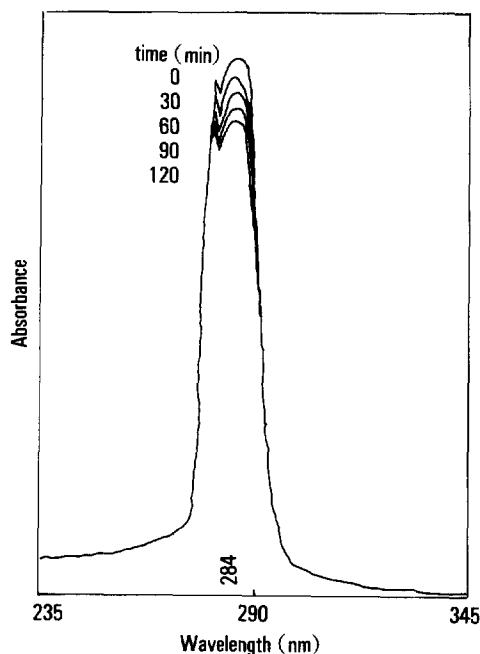


Fig. 10. Absorbance change in UV spectra with time for the copolymers with various comonomer feed ratio, f_2 ($X = 1 - A_t/A_0$).

by the ratio of the absorbance of reacted vinyl benzoate in the copolymer at time t (A_t) to that of unreacted vinyl benzoate in feed mixture at time 0 (A_0). The 284 nm was used as a characteristic wavelength to study conversion of copolymer. The sampling was taken for every thirty minutes, as mentioned in the introduction. Great precautions were taken for measuring UV spectra of the samples. Since the conversions of copolymers were very low, the copolymer solutions of benzene were analyzed on UV spectra. Even though the cut-off range of the benzene as a solvent might affect these spectra in spite of our careful sample treatment when sampling or measuring, we relied on the raw UV spectra of the copolymer solutions to find conversion. We believe that the result is of great importance since no other data for the solution copolymerization of VAc and VBz in a CSTR in benzene at 60°C has been reported.

From this UV spectral data, the conversions of copolymerization were calculated by the same

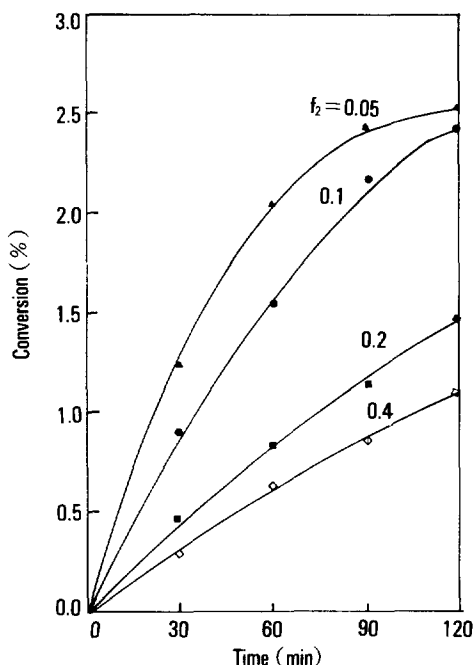


Fig. 11. Plot of conversion vs time for the copolymers with various comonomer feed ratios obtained from CSTR data.

method in the determination of copolymer compositions. In Figure 11, the conversion changes against time were plotted. It is seen that the conversion varies from 0.23 to 2.54% when the f_2 is in the range of 0.05 to 0.4. The conversions increase with time and decrease with the comonomer feed composition based on monomer 2 (f_2). It is of no doubt that the conversion increases monotonically with the monomer feed ratio of $M_1(f_1)$. More careful attention should be paid to the results for $f_2=0.05$ and 0.1, which is the sophisticated consequential character of this system.

At $f_2=0.05$ and 0.1, the conversions increase with time but level off after a certain time. It means that the conversions reach steady states within the residence time of the CSTR used in the work (i. e. 7200sec) when the f_2 is equal to 0.05 or 0.1. The conversions at the higher comonomer feed ratios do not, however, reach the steady state value within the residence time. It should take longer time (up to 8-10 hrs) to approach to a

steady state as vinyl benzoate composition in feed exceeds 0.2.

The result may be attributed to the fact that the polar solvent affects on vinyl benzoate with polar aromatic ring more than vinyl acetate without such a polar structure. Similar results were already reported by Plavljanić and Janović.¹⁰

More careful explanations are assigned now and will be reported elsewhere.

CONCLUSIONS

The radical copolymerizations of vinyl acetate and vinyl benzoate with AIBN in benzene at 60°C in a batch reactor and in a CSTR were carried out. The kinetic studies of the homopolymerization and copolymerizations have been reported. The following are some of the important results.

1. The reactivity ratios of the two monomers were determined by the Kelen-Tüdös method (or re-checked by the Fineman-Ross method) as follows; $r_1(\text{VAc}) = 0.69(0.66)$, $r_2(\text{VBz}) = 1.48(1.46)$.

2. The hydrolysis of the copolymer of vinyl acetate and vinyl benzoate in benzene followed the first-order reaction. The rate constant at 60°C was given as $3.47 \times 10^{-7} \text{ sec}^{-1}$.

3. In a CSTR, the conversion of the copolymer was characterized by UV spectra and varied from 0.23 to 2.54% under different comonomer compositions.

4. The rate of copolymerization of vinyl acetate and vinyl benzoate approached to steady state within the residence time (7200 sec) of the CSTR when the comonomer composition of vinyl benzoate was below 0.1, whereas that does not approach to a steady state as vinyl benzoate composition exceeds above 0.2.

NOMENCLATURES

- A_t ; The UV absorbance of reacted vinyl benzoate in a copolymer at time t .
 A_0 ; The UV absorbance of unreacted vinyl benzoate in feed mixture at time 0.

f ; Initiator efficiency.
 f_1 ; Composition of monomer 1 in feed.
 F_1 ; Composition of monomer 1 in copolymer.
 I ; Initiator concentration.
 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 cross-termination between monomer 1 and monomer 2.
 M_1 ; Concentration of monomer 1 in monomer mixture.
 M_2 ; Concentration of monomer 2 in monomer mixture.
 m_1 ; Concentration of monomer 1 in copolymer.
 m_2 ; Concentration of monomer 2 in copolymer.
 r_1 ; Reactivity ratio of monomer 1.
 r_2 ; Reactivity ratio of monomer 2.
 R_i ; Reaction rate of initiation.
 R_p ; Reaction rate of propagation.
 ϕ ; Cross-termination factor.
 F_{\max} ; Maximum value of F over the feed monomer composition ranges.
 F_{\min} ; Minimum value of F over the feed monomer composition ranges.

REFERENCES

1. S. Das and F. Rodriguez, *J. Appl. Polym. Sci.*, **32**, 5981 (1986).
2. K. G. Denbigh, *Trans. Faraday Soc.*, **43**, 648 (1947).
3. W. H. Ray, *Can. J. Chem. Eng.*, **47**, 503 (1969).
4. A. D. Schmidt and W. H. Ray, *Chem. Eng. Sci.*, **36**, 1401 (1981).
5. F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).
6. J. N. Atherton and A. M. North, *Trans. Farad. Soc.*, **58**, 2049 (1962).
7. T. Kelen and F. Tüdös, *J. Macromol. Sci. -Chem.*, **A-9**, 1 (1975).
8. M. Finneman and S. D. Ross, *J. Polym. Sci.*, **66**, 1594 (1944).
9. K. S. Balaraman, B. D. Kulkarni, and R. A. Mashelkar, *J. Appl. Polym. Sci.*, **27**, 2815 (1982).
10. A. M. North, "Structure and Mechanism in Vinyl Polymerizations", Ch. 4, T. Tsuruta and K. F. O' Driscoll, Eds, Dekker, New York, 1969.
11. B. Plavljanić and Z. Janović, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 1795 (1981).
12. M. Kamachi, J. Satoh, and S. Nazakura, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 1798 (1978).
13. C. C. Price, B. D. Halpera, and S. T. Voong, *J. Polym. Sci.*, **6**, 575 (1953).
14. R. MacFarlane, et al., *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 251 (1980).
15. J. Brandrup and E. H. Immergut, "Polymer Handbook", 3rd Ed., II (1989).
16. T. Fukuda, Y. D. Ma, and H. Inagaki, *Macromolecules*, **18**, 17 (1985).
17. Y. D. Ma, T. Fukuda, and H. Inagaki, *Macromolecules*, **18**, 26 (1985).
18. Brown, Fujimori, and Craven, *J. Polym. Sci. Polym. Chem. Ed.*, **27**, 3315 (1987).
19. Duck Won Kim, *M. S. Thesis*, Pusan National University (1981).
20. S. Das and F. Rodriguez, *J. Appl. Polym. Sci.*, **39**, 1309 (1990).
21. S. R. Palit, *Trans. Farad. Soc.*, **51**, 1129 (1955).
22. G. M. Bennett and H. R. Gersmann, *J. Polym. Sci.*, **28**, 655 (1958).