

연속반응기(CSTR)에서의 비닐 아세테이트와 페닐 아크릴레이트 및 비닐벤조에이트의 용액 공중합 : 2. 회분식 반응기에서의 반응성

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Solution Copolymerization of Vinyl Acetate and Phenyl Acrylate or Vinyl Benzoate in a CSTR : 2. Reactivity in a Batch Reactor

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요 약 : 회분식 반응기를 사용하여 비닐 아세테이트(VAc)와 페닐아크릴레이트(PA)를 벤젠에서 AIBN을 개시제로 사용하여 60°C에서 라디칼 공중합을 하였다. 자외선 흡수 분광법으로 공중합체 조성을 분석하였으며, 단량체 반응성비 r_1 (VAc)과 r_2 (PA)는 Kelen-Tuřs 방법으 로 결정하였다 ; $r_1=0.22$, $r_2=2.48$. 공중합체의 ϕ 값은 VAc의 전조성에 걸쳐 0.02~11.56 범위의 값을 가졌고, 공중합체내의 PA조성이 증가할수록 ϕ 값은 증가하였다. VAc와 PA의 반응성, 공중합속도 등을 VAc와 비닐벤조에이트(VBz)의 반응성, 공중합속도 등과 비교 검토하였다. 통계적인 분석과 반응성 검토 결과 VAc와 PA 공중합체는 VAc와 VBz 공중합체보다 더 많은 교호구조를 가지는 것으로 밝혀졌다.

Abstract : Radical copolymerization of vinyl acetate(VAc) and phenyl acrylate(PA) was carried out with AIBN as an initiator in benzene at 60°C in a batch reactor. The copolymer compositions were analyzed by UV spectrophotometry. The monomer reactivity ratios, r_1 (VAc) and r_2 (PA) were determined by the Kelen-Tuřs method ; $r_1=0.22$, $r_2=2.48$. The ϕ factors of the copolymer over the entire VAc compositions ranged from 0.02 to 11.56. The ϕ factors of the VAc-PA copolymer increased with increasing PA compositions.

The rate of copolymerization and monomer reactivity ratios of VAc and PA were compared with those obtained from VAc and vinyl benzoate(VBz). It was found that the VAc-PA copolymer system has more alternating tendency than the VAc-VBz copolymer system by statistical analyses and reactivity values.

INTRODUCTION

In our previous work,¹ we studied the solution copolymerization of vinyl acetate(VAc) and vinyl benzoate(VBz) in a Continuous Stirred Tank Reactor(CSTR). The reactivity ratios of the two monomers were determined by the Kelen-Tűrkő method as follows ; $r_1(\text{VAc})=0.69$, $r_2(\text{VBz})=1.48$. The copolymerization rate was estimated by using the following equation (1) or, in more simplified form, equation (2).

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

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

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

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

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

Based on the classical radical reaction mechanism, it was assumed that the kinetics in this CSTR model were 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 quasisteady state approximation that the initiation rates of active intermediates are virtually the same as the rates of termination.^{2,3} 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. $k_p \gggg k_{tr}$. 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 solution copolymerizations of vinyl acetate (VAc) and vinyl benzoate(VBz) or phenyl acrylate (PA) in a CSTR has been attracted much interests in this laboratory for years, since it is expected that the copolymers of VAc and VBz or PA can be applied as heat resistant adhesives or protective coatings. Moreover, it is interesting to note that PA and VBz have same structure except $-C=O$ and $-O-$ pendant group in each side chain.

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.^{4,5}

The aim of this programme of work is to find optimal operating conditions of a CSTR to obtain copolymers of VAc and VBz or PA. The series of work consists of four main categories ; 1) solution copolymerization of VAc and VBz in a CSTR, 2) solution copolymerization of VAc and PA in a CSTR, 3) Reactivity in a solution copolymerization of VBz or PA with VAc in a CSTR, and 4) Determination of optimal conditions to obtain copolymers of VAc and VBz or PA in a CSTR. Parts of category 1) work are already published.¹ Before going to the Category 2) work, it would be of great importance to have informations about the reactivity differences of VBz and PA in the copolymerization with VAc in a batch reactor, which is very closely related to the Category 2) and 3) works.

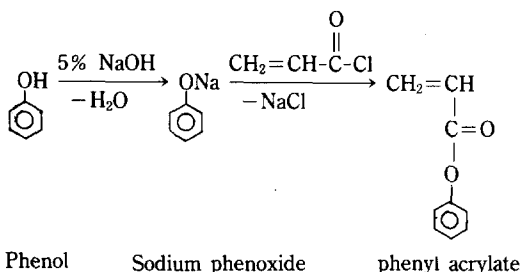
Thus, the aim of this paper is to copolymerize VAc and PA in benzene in a batch reactor and discuss differences in the copolymerization kinetics and reactivity between VAc and VBz or VAc and PA. In this work, we synthesized copolymers of VAc and PA with AIBN in benzene at 60°C in a batch reactor.

EXPERIMENTAL

Materials and Instruments

Vinyl acetate(VAc ; Junsei Co.) was purified as the standard procedure. Phenol(Hayashi) and acryloyl chloride(Aldrich) were used without further purifications in synthesizing phenyl acrylate. Benzene as solvent was distilled prior to use. The vinyl benzoate(VBz) was prepared by the same method as described in our previous work.

Phenyl acrylate(PA) was prepared from phenol by the following reaction scheme⁶ ;



0.5 mol of phenol was added dropwise to the 500 ml of aqueous solution of 5% NaOH in 1L of three-neck flask. The mixture was quenched to 0°C and then 0.5 mol of acryloyl chloride was added dropwise and stirred for 1 hr in an ice bath. After 30 minutes, the product was washed with 5% NaOH and water subsequently, dehydrated with magnesium sulfonate anhydride, and distilled under reduced pressure(b. p. 80~85°C/11 mmHg) in the presence of sulfur powder(yield ; 80%).

The PA prepared was identified on IR spectrum (Perkin-Elmer 130C) by the characteristic peaks of 3070 cm⁻¹(aromatic C-H), 1730 cm⁻¹(C=O), 1637 cm⁻¹(C=C), 1250 cm⁻¹, 1200 cm⁻¹ and 1160 cm⁻¹ (C-O stretching of ester) and 690 cm⁻¹(out-of-plane bending of aromatic C-H), as shown in Fig. 1. The PA was also characterized by ¹H-NMR spectrum(Varian A60) ; 5.78 ppm(H_a), 6.23 ppm(H_b and H_c) and 7.14 ppm(phenyl proton), see Fig. 2.

Experimental Procedures

Syntheses of poly(vinyl acetate)(PVAc), poly(vinyl benzoate)(PVBz), and poly(VAc-co-VBz)

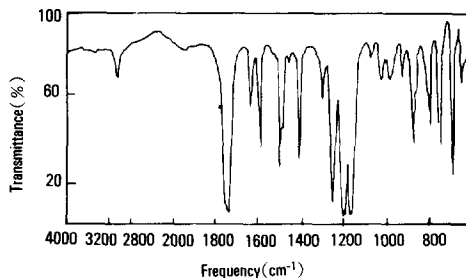


Fig. 1. IR spectrum of phenyl acrylate ; liquid phase.

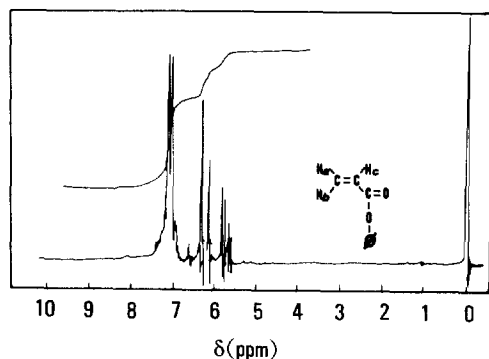


Fig. 2. NMR spectrum of phenyl acrylate.(CCl₄).

are described elsewhere.¹

Synthesis of Poly(Phenyl Acrylate) : Poly(phenyl acrylate)(PPA) was prepared by reacting a mixture of 3.6M of PA and 3×10⁻² 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-phenyl Acrylate) : A mixture of VAc and PA at a given mole ratio was dissolved in 100 ml of benzene and then added with 3×10⁻² mole of AIBN. The tube was sealed after charging with nitrogen. The preparation method was similar as described for the copolymerization of VAc and VBz. The copolymerization was carried out at 60°C for a chosen period to assume the conversions below 12%. The conversion data were summarized in Table 2. The prepared poly(VAc-co-PA) was identified by an IR spectrum, as shown in Fig. 3.

Rate Parameter Estimation

The rate constants k_p and k_t have been obtained

for phenyl acrylate by using a simple dilatometric method.⁷ All polymerization runs were prepared

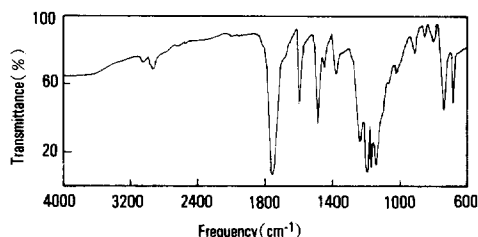


Fig. 3. IR spectrum of poly(vinyl acetate-co-phenyl acrylate) ; solid phase, KBr.

Table 1. The Solubility of Homopolymers and Copolymers in Various Solvents

Solvent	Homo- or copolymers				
	PVAc	PPA	PVBz	P(VAc-co-PA)	P(VAc-co-VBz)
Methanol	●	○	○	○	◐
Ethanol	◐	○	○	○	○
Acetone	●	●	●	●	●
Acetonitrile	●	◐	◐	◐	●
n-Hexane	○	○	○	○	○
Benzene	●	◐	●	◐	●
Toluene	●	◐	●	◐	●
Carbon tetrachloride	◐	○	○	○	○
Chloroform	●	●	●	●	●
Dioxane	●	◐	◐	◐	◐
DMF	◐	◐	◐	◐	◐

● ; good soluble spontaneously, ◐ ; soluble within 15 minutes, ◑ ; soluble within 30 minutes, ○ ; insoluble.

using the standard high vacuum techniques. The size of the cylindrical dilatometers is 1 cm of diameter and 10 cm of length. The movement of the meniscus in the dilatometer stem was observed using a travelling microscope fitted with an eyepiece containing a graduated scale of length equivalent to 0.25 cm.

RESULTS AND DISCUSSION

Characterization

Solubility : Both Poly(VAc-co-PA) and poly(VAc-co-VBz) were well soluble in acetone and chloroform but insoluble in n-hexane and CCl₄. Table 1 shows typical solubility data of poly(VAc-co-VBz) and poly(VAc-co-PA).

Copolymer Compositions and Monomer Reactivity Ratios

The copolymer compositions were determined by UV Spectrophotometry according to the literature.¹ Fig. 4 shows UV spectra of the PVAc/PPA mixtures with various concentrations. To determine the compositions of monomer units in poly(VAc-co-PA), a calibration curve was obtained by using the specific absorbance at 259 nm, which is detectable only for phenyl acrylate, as a function of PPA concentration in feed(Fig. 5).

The copolymer compositions were determined from the calibration curve by the following characteristic equation.

$$\varepsilon = 0.75X + 0.025 \quad (3)$$

where ε is the specific extinction coefficient of co-

Table 2. The Conversion of Copolymerization of Poly(VAc-co-PA) ; VAc : M₁ and PA : M₂

Experimental values	Experimental No.						
	1	2	3	4	5	6	7
Wt.(g) of M ₁	6.227	2.179	1.868	1.556	1.245	0.934	0.000
Wt.(g) of M ₁ +M ₂	6.227	3.798	4.026	4.255	4.488	4.711	10.793
Mole fraction of PA in the monomer mixture	0.000	0.280	0.390	0.500	0.610	0.720	1.000
Wt.(g) of copolymer		0.290	0.381	0.500	0.206	0.158	
Conversion(%)		7.650	9.480	11.760	6.610	3.360	

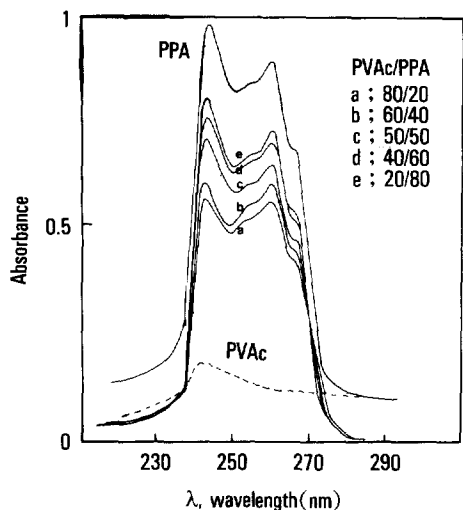


Fig. 4. UV spectra of poly(phenyl acrylate), poly(vinyl acetate) and poly(vinyl acetate-co-phenyl acrylate).

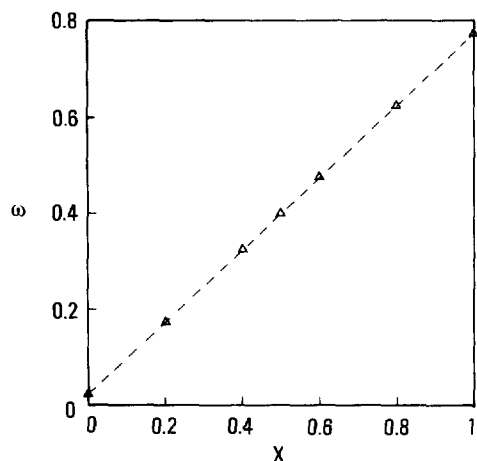


Fig. 5. Dependence of the specific extinction coefficient of PPA at the wavelength of 259 nm on the weight fraction of PPA in the mixture of PPA and PVAc.

polymer and X is the weight fraction of phenyl acrylate in the copolymer.

Fig. 6 illustrates the copolymer compositions. In this figure, the composition in VAc-VBz copolymer system is plotted with a solid line, for comparison.

The monomer reactivity ratio was determined by the Kelen-Tüdös method⁸(see Table 3). The

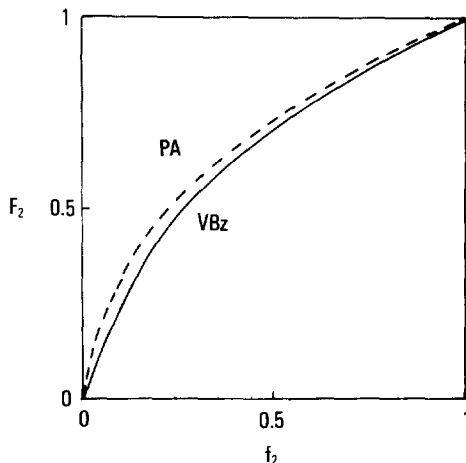


Fig. 6. Compositions of phenyl acrylate(----) and vinyl benzoate(—) in feed(f_2) and in copolymers(F_2) in benzene as a solvent at 60°C.

Table 3. Summary of Kelen-Tüdös Parameters in the Determination of Monomer Reactivity Ratios for the Copolymerization of Vinyl Acetate(M_1) and Phenyl Acrylate(M_2) in Benzene at 60°C : $\alpha=2.974$

Parameters	Experimental No.				
	2	3	4	5	6
$\bar{X} = M_1/M_2$	2.314	1.487	0.991	0.661	0.425
$Y = m_1/m_2$	0.685	0.531	0.382	0.221	0.159
X^2	5.355	2.213	0.983	0.437	0.180
$Y-1$	-0.315	-0.469	-0.618	-0.779	-0.841
$F = X^2/Y$	7.816	4.168	2.571	1.976	1.131
$G = X(Y-1)/Y$	-1.063	-1.314	-1.601	-2.328	-2.236
$\alpha + F$	10.789	7.142	5.545	4.950	4.105
$\eta = G/(\alpha + F)$	-0.098	-0.184	-0.288	-0.470	-0.544
$\xi = F/(\alpha + F)$	0.724	0.583	0.463	0.399	0.275
$\alpha = (F_{min} \times F_{max})^{1/2}$					

Kelen-Tüdös plot in Fig. 7 gives the reactivity ratios of r_1 (VAc) and r_2 (PA) as 0.22 and 2.48, respectively. The result means that VAc has much lower tendency to homopolymerize than PA and the copolymerization is dominant over the homopolymerization of each monomer. The monomer reactivity ratios also imply that the copolymer has block structure to some extent. The Alfrey-Price

scheme gives $Q=0.10$ and $e=0.56$ for PA.

The monomer reactivity ratios of $r_1(\text{VAc})$ and $r_2(\text{VBz})$ in the copolymerization of VAc and VBz were reported as 0.69 and 1.48, respectively, in our previous work¹($Q=0.25$, $e=0.36$ for VBz). Similar data of the reactivity ratios of $r_1(\text{VAc})$ and $r_2(\text{VBz})$ were also reported in the literatures.^{9,10} The different reactivity of VBz and PA with VAc should be noted.

Relative Reactivities of PA and VBz with VAc

Table 4 shows the values of monomer reactivity ratios r_1 and r_2 for the copolymerization of vinyl acetate(M_1) and other monomers(M_2). It is seen that styrene radical is more readily reacted with styrene monomer than vinyl acetate monomer and the copolymerization of styrene and vinyl acetate is not easy, since $r_1 \ll 1$, $r_2 \gg 1$, and $1/r_2=0.02$.

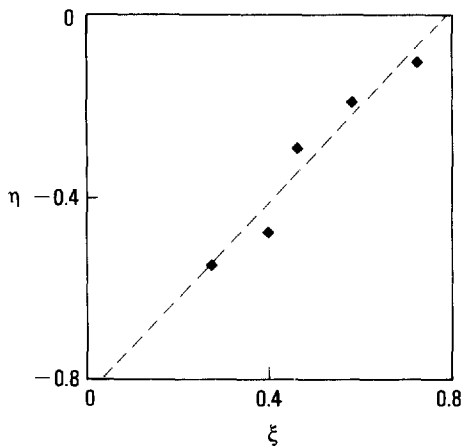


Fig. 7. Kelen-Tirfs plot of poly(vinyl acetate-co-phenyl acrylate) ; $r_1=0.22$ and $r_2=2.48$.

This may be due to the fact that the growing styrene radical can be resonance-stabilized but the growing vinyl acetate radical cannot be resonance-stabilized. The reactivity of acrylate monomers to the vinyl acetate radical follows the order methyl acrylate>methyl methacrylate>phenyl acrylate.

In the copolymerization of VAc with PA or VBz, the reactivity of PA to vinyl acetate radical is larger than VBz. This may be ascribed to the fact that the PA radical is readily resonance-stabilized whereas VBz radical is not resonance stabilized.

Monomer Sequence Length In Copolymers

In order to analyze the difference in copolymer structures of poly(VAc-co-VBz) and poly(VAc-co-PA) from their monomer reactivity ratios, monomer sequence length was calculated by several statistical methods. Fig. 8 shows the mean sequence length of monomers on its feed composition.

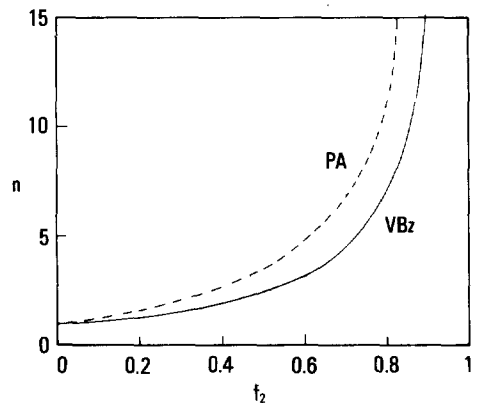


Fig. 8. Dependence of the mean sequence length of monomers on its feed composition.(— : vinyl benzoate, ---- : phenyl acrylate)

Table 4. The Monomer Reactivity Ratios($r_1 \cdot r_2$) and the Derivative Values for the Copolymerization of Vinyl Acetate(M_1) and Other Monomers(M_2)

Monomer(M_2)	r_1	r_2	$1/r_1$	$1/r_2$	$r_1 \cdot r_2$	Ref.
Styrene	0.010	55.000	100.000	0.018	0.550	16
Methyl acrylate	0.030	6.700	33.333	0.149	0.201	17
Methyl methacrylate	0.072	22.210	13.889	0.045	1.599	18
Phenyl acrylate	0.220	2.480	4.545	0.403	1.599	this work
Vinyl benzoate	0.690	1.480	1.449	0.676	1.021	1,20,21
Vinyl chloride	0.600	1.800	1.670	0.560	1.080	19

nce length of monomers(n_i) as a function of the mole fraction of vinyl benzoate and phenyl acrylate in feed, where n_1 was estimated from the following Miller and Nielsen equation.¹¹

$$n_1 = (r_1 f_1 + f_2) / f_2 \quad (4)$$

where f_1 and f_2 are mole fractions of 1 and 2 monomer in feed, r_1 is reactivity ratio of 1 monomer. It is seen that the n_i in the copolymer of VAc and VBz is smaller than 5 up to the $f_1=0.7$ and thereafter n_1 increases remarkably, whereas n_1 in the copolymer of VAc and PA is smaller than 5 up to $f_1=0.6$ and thereafter increases rapidly.

The probability(w_n) that exact n of 1 and 2 monomers are arranged sequentially in a block [i. e. $-(1-2)_n-$] is related to the monomer fraction in feed as followings¹¹;

$$w_1 = [r_1 f_1 / (r_1 f_1 + f_2)]^{n-1} \times f_2 / (r_1 f_1 + f_2) \quad (5)$$

Fig. 9 shows the dependence of $w_{(n)}$ on n in the copolymers of VBz or PA with VAc having the 1 :

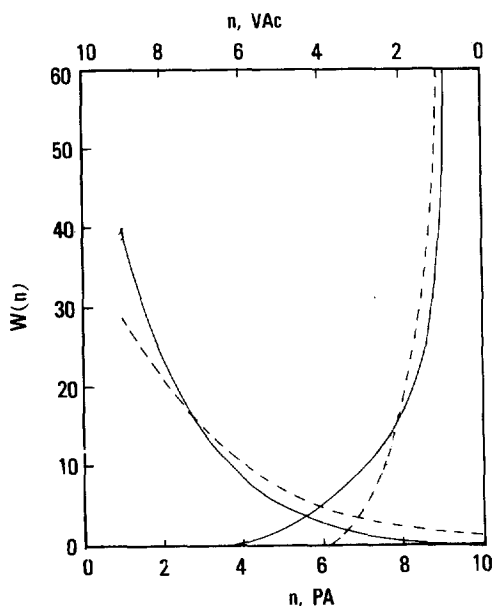
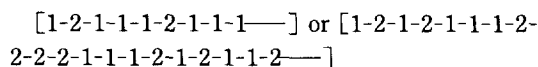
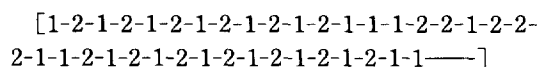


Fig. 9. Plot of the probability $W(n)$ versus the mean sequence length(n) of the copolymers in the fifty-fifty feed mixtures. (— ; vinyl benzoate and ---- : phenyl acrylate)

1 mole ratio in feed. The figure illustrates qualitatively the structure of a copolymer and how 1-2 monomer sequences are aligned in the copolymer. In the case of poly(VAc-co-VBz), the probability that one or two of 1-2 monomers aligned sequentially in one block (such as



sequence and the like) is 64.3% and that of more than five 1-2 sequences in a block (such as



sequence and the like) are 7.5%, whereas in the case of poly(VAc-co-PA), w_n of one or two 1-2 sequences [$-(1-2)_1-$ or $-(1-2)_2-$] are 49.2% and that of more than five 1-2 sequences [$-(1-2)_n-$ sequence, $n>5$] is 18.4%. The statistical data mean that poly(VAc-co-PA) has relatively more alternating tendency than poly(VAc-co-VBz).

This type of statistical monomer sequence length can be also confirmed by the Sakaguchi¹² or Berger¹³ analysis. All of these kinds of statistical analyses exhibit that the copolymer of VAc and PA has relatively more alternating tendency than the copolymer of VAc and VBz. The products of reactivity ratios ($r_1 \times r_2 = 1.02$ for poly(VAc-co-VBz) and $r_1 \times r_2 = 0.55$ for poly(VAc-co-PA) proves well our speculations by statistical analyses.

Rate of Copolymerization

In Fig. 10, 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). The rate parameters of PA were measured by using dilatometry ; $k_{p22} = 862.7 \text{ L/mole} \cdot \text{sec}$, $k_{t22} = 0.64 \times 10^6 \text{ L/mole} \cdot \text{sec}$, $k_{p22}/k_{t22} = 13.48 \times 10^{-4}$. The rate parameters of VAc and AIBN were taken from our previous work.¹ The rate of copolymerization decreases initially and increases steadily with the comonomer feed ratio up to $f_2=0.9$, although the increase is not large. The minimum was observed at $f_2=0.4$. The occurrence of this minimum point was also ob-

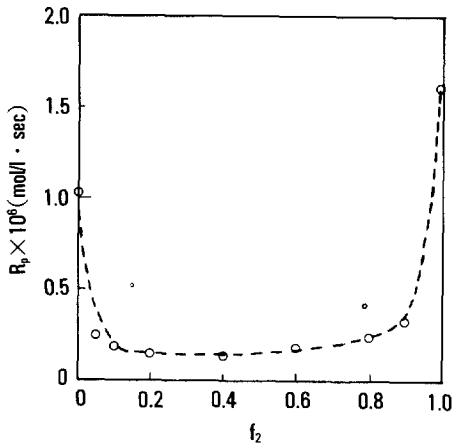


Fig. 10. Effect of the mole fraction in the comonomer mixture on the rate of copolymerization.

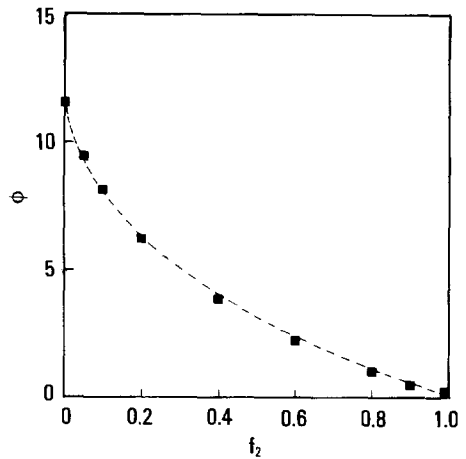


Fig. 11. Variation of ϕ -value with the feed composition of phenyl acrylate.

served in other copolymerization systems.^{5,14} Palit¹⁴ has investigated the conditions under which the minimum occurs in the rate of copolymerization curve. According to his study, 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 . In the case of the copolymerization of VAc and VBz, the minimum was observed around $f_2=0.1$. But, in this case, the R_p increases remarkably with f_2 .

The unusual behavior of R_p in the VAc-PA copolymer system cannot be easily interpreted at the present moment. The result, however, may be related to ϕ factor, which is shown in Fig. 11. From this figure, the ϕ factors are ranged from 0.02 to 11.56. Therefore, the experimental result cannot be described merely by a single value of the ϕ factor. It is seen that the ϕ factor decreases with increasing comonomer feed ratio (f_2). In the present studies of the copolymerization rate, the terminal model and the quasi-steady state approximation were adapted. For the purpose of the present discussion, it is believed that not much error is introduced by taking the quasi-steady approximation, even though it has been known that the approximation is valid strictly when the conversions are very low (ca. below 5%) in a copolymerization and

a little higher conversions (up to about 12%) were observed in some of the VAc-PA copolymers. 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.^{15,16}

Another interesting feature is that in the case of VBz and VAc the ϕ factor was reported to increase with increasing comonomer feed ratio.¹ The difference in ϕ factor-behavior as a function of f_2 may be ascribed to the more flexible nature of VBz than PA, even though the difference in flexibility is not large. It has been observed in several copolymer systems that the ϕ factor rises with increasing size of the side group and the ϕ factor is related to the flexibility of the chain; For instance, in the copolymerization of 2-ethylhexyl acrylate (EHA) and vinyl chloroacetate (VCLAC), ϕ factor increased with increasing EHA concentration, whereas in the copolymerization of VAc and VCLAC, ϕ factor decreased with VAc concentrations, since EHA is much more flexible than VAc because of its bulkier pendant group.^{4,5}

The ϕ values over the entire f_2 composition, ho-

wever, are relatively small for both VAc-VBz(0.3~0.8) and VAc-PA(0.02~11.56) copolymer systems, whereas the ϕ factors strongly dependent on the composition of comonomer feed ratio in other VAc-MMA(100~800), VCLAC-VAc(75~400) or EHA-VCLAC(100~400) copolymer systems.^{4,5,17} The result indicates that the chain-termination step in VAc-VBz or VAc-PA copolymer systems is possibly chemically controlled and the chain transfer to the solvent is negligible, implying the validity of our assumptions of the termination model. Finally, it should be noted that the dependence of the ϕ values on the f_2 composition could be interpreted more accurately when the effects of reaction medium as well as the chemical structure of polymer chains on the ϕ values as a function of the f_2 composition are definitely revealed, especially at very low f_2 composition.

CONCLUSIONS

The radical copolymerization of vinyl acetate (VAc) and phenyl acrylate(PA) with AIBN in benzene at 60°C in a batch reactor were carried out. The reactivity and copolymerization kinetics of VAc and PA have been reported. The results were compared with those from the VAc-vinyl benzoate (VBz) copolymer system. Some of the experimental data were taken from our previous work.¹ The followings are some of the important results.

1. The reactivity ratios of the VAc and PA monomers were determined by the Kelen-Tudos method as follows : $r_1(\text{VAc})=0.22$, $r_2(\text{PA})=2.48$.

2. The reactivity of PA to VAc radical was larger than that of VBz with VAc radical.

3. It was found that the VAc-PA copolymer system has relatively more alternating tendency than the VAc-VBz copolymer system by statistical analyses and reactivity values.

4. The ϕ factors of the copolymers over the entire VAc compositions ranged from 0.02 to 11.56 for the VAc-PA copolymer or from 0.3 to 0.8 for the VAc-VBz copolymer, respectively.

5. The ϕ factors of the VAc-PA copolymer inc-

reased but those of the VAc-VBz decreased with increasing each PA or VBz compositions.

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NOMENCLATURES

- A_i ; The absorbance of reacted vinyl benzoate in a copolymer at time t .
- A_0 ; The absorbance of unreacted vinyl benzoate in feed mixture at time 0.
- f ; Initiator efficiency.
- f_i ; Composition of monomer i in feed ($i=1$ or 2)
- F_i ; Composition of monomer i in copolymer ($i=1$ or 2)
- 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.
- n_i ; Mean sequence length of monomers.
- n_1 ; Mean sequence length of monomer 1.
- 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.
- ϵ ; Specific extinction coefficient of copolymer.
- X ; Weight fraction of phenyl acrylate in the copolymer.