

Investigations of the Copolymerization of Acrylonitrile with Vinyl Acetate and Sodium Methallylsulfonate

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ABSTRACT: The bulk copolymerizations of acrylonitrile (AN) with vinyl acetate (VAc) initiated by azobisisobutyronitrile (AIBN) and the suspension copolymerization of AN with VAc and sodium methallylsulfonate (SMAS) in water with a $\text{Na}_2\text{S}_2\text{O}_5$ – Na_2ClO_3 redox initiator system at 65°C, were investigated. The copolymer compositions were determined by ¹H-NMR. The reactivity ratios (γ s) for the two copolymerization systems were determined analytically, based on Mayo–Lewis equation, by fitting the calculated curves with the experimental data. The γ s for the AN and VAc bulk copolymerization were found to be $\gamma_{12} = 2.85$ and $\gamma_{21} = 0.11$. The values of the apparent γ s for the suspension copolymerization of AN, VAc, and SMAS were as follows: $\gamma_{12} = 3.58$, $\gamma_{21} = 0.39$, $\gamma_{13} = 1.45$, $\gamma_{31} = 0$, $\gamma_{23} = 0.92$, and the rate constant ratio $R_3 = k_{31}/k_{32} = 0.04$. A simulated result produced with the obtained γ s agreed fairly well with experimental data of bulk copolymerization in a batch reactor. The apparent γ s obtained were also successfully used to analyze the results of suspension polymerization in a continuous pilot reactor. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 854–860, 2001

Key words: acrylonitrile; vinyl acetate; sodium methallylsulfonate; reactivity ratio; suspension copolymerization

INTRODUCTION

Acrylonitrile (AN)–vinyl acetate (VAc) copolymers have proven to be important in the commercial manufacture of acrylic fibers and are also of interest as precursors in the manufacture of carbon fibers. Commercially, the copolymer is often prepared by the slurry technique, which employs a continuous flow reactor. In a typical slurry polymerization, a saturated aqueous solution of the sparingly soluble comonomers is maintained, and the polymer is allowed to precipitate as it forms. Some times, a third comonomer can be added into

the copolymerization to prepare a copolymer. Improved dyeability is expected of the fibers produced this way.

For quite some time, the AN–methyl acrylate (MA)–sodium methallylsulfonate (SMAS) system has consolidated its status in the mainstream of China's technology. However, in recent years, the local petrochemical group has witnessed excessive production of VAc to match market demand. Conceivably, a reformulation of the current technology by replacing MA with VAc should be technologically feasible to balance the VAc overproduction. The AN–VAc binary copolymerization is a well-known process for the manufacture of acrylic fibers. However, the introduction of SMAS, which is widely used in the AN–MA copolymerization system as a third comonomer to im-

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Table I Literature Data^{4–10} of Reactivity Ratios for the AN–VAc System

	γ_{12}	γ_{21}	System	T (°C)	Initiation	References
1	2.85	0.159	Bulk	18 ± 2	Mechanochemical	Oprea and Popa, 1984 ⁴
2	3.88	0.009	DMF ^a solution	25	Irradiating dye-reducing agent combination	Taniyama and Oster, 1957 ⁵
3	5.6	0.02	Bulk	40	triisobutylboron	Ashikari and Nishimura, 1958 ⁶
4	4.05 ± 0.03	0.061 ± 0.013	Bulk	60	peroxides	Mayo et al., 1948 ⁷
5	6 ± 2	0.02	Bulk	60	peroxides	Fordyce et al., 1948 ⁸
6	4.2	1.01	NaSCN	60	Mn(C ₅ H ₇ O ₂)SCN	Jocheska and Petrov, 1994 ⁹
7	2.11 ^b 2.34 ^c	0.044 ^b 0.045 ^c	Bulk	65	AIBN	Mokhtar et al., 1989 ¹⁰

^a Dimethylformamide.

^b Values calculated from same experimental data by the Fineman–Ross method.

^c Values calculated from the same experimental data by the Kelen–Tüdös method.

prove the dyeability of the final fiber product, into the AN–VAc system has not received the proper attention it deserves for its industrial interest.

Many works^{1–10} have been published on the copolymerization of the AN-based copolymerization system. The literature data^{4–10} of the AN and VAc systems present a large amount of diversity concerning the reactivity ratio (γ) values, depending on the initiation mechanism, solvent, reaction temperature, and additive. The differences in the reactivity values cannot be only ascribed to the methods for synthesizing copolymers (see items 1–6 in Table I) but also to the various techniques used for the estimation of copolymerization parameters (see item 7 in Table I).^{1,4} Therefore, for a special system of commercial copolymerization, it is necessary to determine its unique γ under the reaction condition.

The objectives of this study were to investigate the AN–VAc–SMAS slurry copolymerization in water with a Na₂S₂O₅–Na₂ClO₃ redox initiator system and to determine the apparent γ values of this ternary copolymerization system, which is needed for designing optimal conditions for the industrial reaction system. In the experiment, NMR was used to analyze the composition of the copolymer, and an improved algorithm was proposed to evaluate the γ values. To begin, the investigation process was verified by applying it to AN–VAc binary bulk copolymerization system. The γ values so obtained were used to simulate the polymerization in a batch reactor with acceptable agreement. With this background, we came up with the measurement of apparent γ values for the slurry copolymerization in water of AN, VAc, and SMAS. The calculated result of a continuous

reactor for this ternary system with the obtained apparent γ values presented fairly good agreement with the experimental data on a pilot-test scale.

EXPERIMENTAL

Materials

The AN and VAc monomers were dried over calcium chloride and purified by distillation under nitrogen at 77 and 73°C, respectively. The purified monomers were stored in the refrigerator at –10°C until needed. The bulk copolymerization of AN with VAc was initiated by azobisisobutyronitrile (AIBN). The oxidation–reduction initiation system, consisting of Na₂S₂O₅ and Na₂ClO₃, was used for the aqueous suspension copolymerization without further treatment.

Polymerization Procedures

A 500-mL vessel was used to prepare the copolymers for the determination the apparent γ values. For the suspension polymerization, the vessel contained 50 mL of distilled water as a dispersion phase, which was maintained at pH 4 by the addition of a small amount of H₂SO₄. About 16 g monomers with each monomer at its required ratio was added to the vessel, followed by the charging of the initiator system with the designed weight percent of total monomers. For the bulk polymerization, the AN and VAc monomers with their designed proportions and the initiator were added to the vessel to react. Afterward, the mixture was deoxygenated with a stream of nitrogen for

5 min. The vessel was hermetically sealed to maintain a nitrogen blanket over the reaction mixture throughout the experiment and then placed in a thermostat-controlled water bath to maintain the reaction temperature at 65°C. The polymerization of the monomers in the reaction system, subjected to stirring by an electromagnetic agitator, was indicated by the development of a milky color. After a certain reaction time, when a low conversion (<5%) was ensured, the resultant mixture was poured into methanol to end the polymerization and to avoid comonomer composition drift.

To check the validity of the obtained γ values of the AN-VAc bulk polymerization, a batch process was performed. A 2-L reactor with an agitator was flushed with nitrogen, charged with the prescribed quantities of freshly purified monomers and initiator, and then deoxygenated with a stream of nitrogen for 5 min before hermetic sealing. The system was heated to the reaction temperature of 65°C. Copolymers with different compositions were obtained after various reaction times, and the conversions were determined correspondingly.

On a pilot-test scale, a 15-L aluminum continuous tank reactor equipped with an agitator (equivalent to a continuously stirring tank reactor if the mixing was perfect) was employed for the slurry polymerization of the AN-VAc-SMAS ternary system. AN and VAc monomers, an aqueous solution of SMAS and the reduction initiator $\text{Na}_2\text{S}_2\text{O}_5$, and an aqueous solution of the oxidation initiator Na_2ClO_3 were separately fed into the reaction tank from three reservoirs via measuring pumps. The slurry from the reactor flowed into a termination tank, where the pH value was adjusted to around 7 to stop the reaction. The slurry was washed in a centrifugal tank while the effluent was driven out by it.

The polymer was obtained as a water-insoluble slurry. It was filtered through a sintered glass funnel, washed thoroughly with cold distilled water and then hot distilled water to remove unpolymerized monomers, and finally dried in a vacuum oven at 50°C.

Analysis

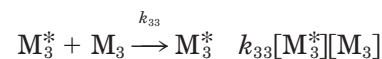
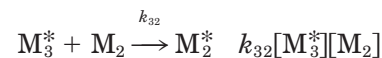
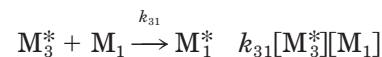
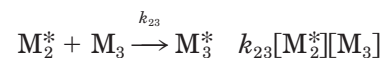
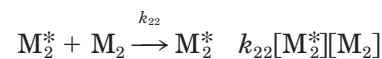
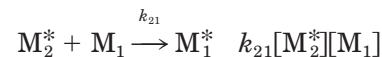
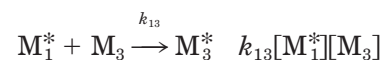
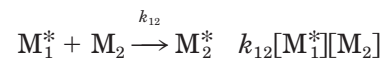
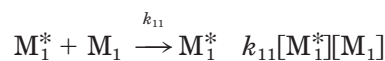
The composition of the copolymer was determined with NMR. All of the resonances were assignable on the basis of the spectra of the corresponding homopolymers and from the data presented in an earlier publication.¹¹ The copolymer composition of the AN copolymers was determined from a

¹H-NMR spectrum through the ratio of the signals of the CHCN methine proton (AN comonomer) at 3.0–3.2 ppm to that of the HC—OCOCH₃ methine proton (VAc comonomer) at 5.1–5.2 ppm or that of the CH₃ methyl proton (SMAS comonomer) at 1.1–1.3 ppm.

RESULTS AND DISCUSSION

Theoretical

Nine propagation equations for copolymerization system M_1 – M_2 – M_3 were considered:



where k_{ij} stands for the rate constants corresponding to the equations.

When the simplified assumption that the concentrations of the growing ends M_1^* , M_2^* , and M_3^* do not change for the steady state is taken into account, the following copolymer composition equations held:¹²

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] \left(\frac{[M_1]}{\gamma_{21}\gamma_{31}} + \frac{[M_2]}{\gamma_{32}\gamma_{21}} + \frac{[M_3]}{\gamma_{23}\gamma_{31}} \right) \times \left([M_1] + \frac{[M_2]}{\gamma_{12}} + \frac{[M_3]}{\gamma_{13}} \right)}{[M_2] \left(\frac{[M_1]}{\gamma_{31}\gamma_{12}} + \frac{[M_2]}{\gamma_{12}\gamma_{32}} + \frac{[M_3]}{\gamma_{13}\gamma_{32}} \right) \times \left(\frac{[M_1]}{\gamma_{21}} + [M_2] + \frac{[M_3]}{\gamma_{23}} \right)} \quad (1)$$

$$\frac{d[M_1]}{d[M_3]} = \frac{[M_1] \left(\frac{[M_1]}{\gamma_{21}\gamma_{31}} + \frac{[M_2]}{\gamma_{32}\gamma_{21}} + \frac{[M_3]}{\gamma_{23}\gamma_{31}} \right) \times \left([M_1] + \frac{[M_2]}{\gamma_{12}} + \frac{[M_3]}{\gamma_{13}} \right)}{[M_3] \left(\frac{[M_1]}{\gamma_{21}\gamma_{13}} + \frac{[M_2]}{\gamma_{12}\gamma_{23}} + \frac{[M_3]}{\gamma_{13}\gamma_{23}} \right) \times \left(\frac{[M_1]}{\gamma_{31}} + \frac{[M_2]}{\gamma_{32}} + [M_3] \right)} \quad (2)$$

where

$$\gamma_{12} = \frac{k_{11}}{k_{12}}, \quad \gamma_{21} = \frac{k_{22}}{k_{21}}, \quad \gamma_{13} = \frac{k_{11}}{k_{13}},$$

$$\gamma_{31} = \frac{k_{33}}{k_{31}}, \quad \gamma_{23} = \frac{k_{22}}{k_{23}}, \quad \gamma_{32} = \frac{k_{33}}{k_{32}}$$

are for the γ s of monomers M_1 , M_2 , and M_3 .

1. When $[M_3] = 0$, representative of the M_1 - M_2 binary copolymerization system, eq. (1) simply reduces to the Mayo-Lewis equation:

$$F_1 = 1 - F_2 = \frac{\gamma_{12}f_1^2 + f_1f_2}{\gamma_{12}f_1^2 + 2f_1f_2 + \gamma_{21}f_2^2} \quad (3)$$

where f_1 and f_2 are the molar ratios of M_1 and M_2 in the mixture:

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]}$$

and F_1 and F_2 are the molar ratios of M_1 and M_2 in the copolymer:

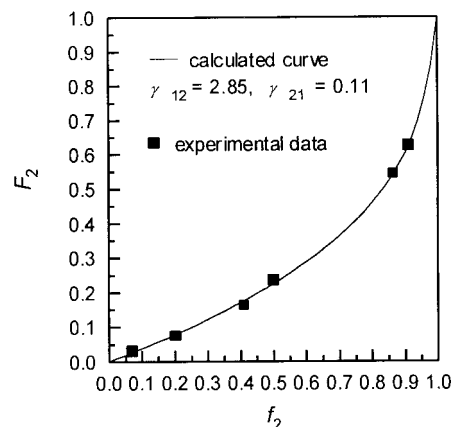


Figure 1 Monomer-copolymer composition curve for the bulk copolymerization of AN-VAc at 65°C (weight ratio of AIBN to monomers = 2.2×10^{-3}).

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]}$$

In a batch reactor, the relationship of f_1 with the conversion (m) can be obtained from the Mayo-Lewis equation and the Skeist equation¹³ as:

$$\frac{[M]}{[M]_0} = 1 - m = \left(\frac{f_1}{f_1^0} \right)^{\gamma_{21}/(1-\gamma_{21})} \left(\frac{1-f_1}{1-f_1^0} \right)^{\gamma_{12}/(1-\gamma_{12})}$$

$$\times \left[\frac{1-\gamma_{21}}{(2-\gamma_{12}-\gamma_{21})f_1^0} \right]^{1-\gamma_{12}\gamma_{21}/(1-\gamma_{12})(1-\gamma_{21})} \left[\frac{1-\gamma_{21}}{(2-\gamma_{12}-\gamma_{21})f_1} \right] \quad (4)$$

where f_1^0 is the molar ratio of M_1 in the original mixture.

whereas the relationship of the average composition of M_1 , \bar{F}_1 versus m , is deduced as the following:

$$\bar{F}_1 = \frac{[M_1]_0 - [M_1]}{[M]_0 - [M]}$$

$$= \frac{[M_1]_0 - f_1(1-m)[M]_0}{m[M]_0}$$

$$= \frac{f_1^0 - f_1(1-m)}{m} \quad (5)$$

2. If $[M_2] = 0$, which describes the M_1 - M_3 binary copolymerization system, eq. (2) reduces to:

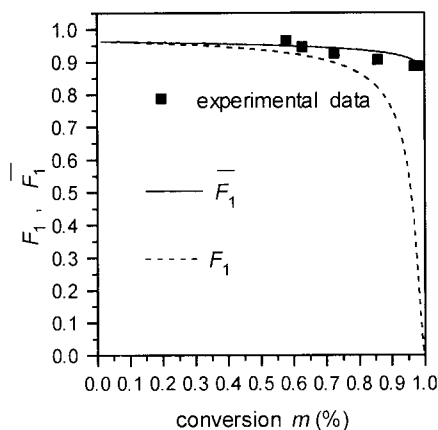
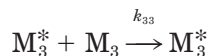


Figure 2 Simulated curves of copolymer composition versus conversion and the experimental data of bulk copolymerization of AN-VAc in a batch reactor at 65°C (weight ratio of AIBN to monomers = 2.2×10^{-3}).

$$\frac{d[M_1]}{d[M_3]} = \frac{[M_1]}{[M_3]} \cdot \frac{(\gamma_{13}[M_1] + [M_3])}{(\gamma_{31}[M_3] + [M_1])} \quad (6)$$

If M_3 does not self-polymerize, that is,



does not occur, which means $k_{33} = 0$ or $\gamma_{31} = 0$, eq. (6) becomes

$$\frac{d[M_1]}{d[M_3]} = \gamma_{13} \cdot \frac{[M_1]}{[M_3]} + 1 \quad (7)$$

3. For the M_1 - M_2 - M_3 ternary copolymerization system, if M_3 does not self-polymerize, which causes k_{33} to be zero, the copolymer composition can be obtained by a similar version to which eqs. (1) and (2) were reduced:

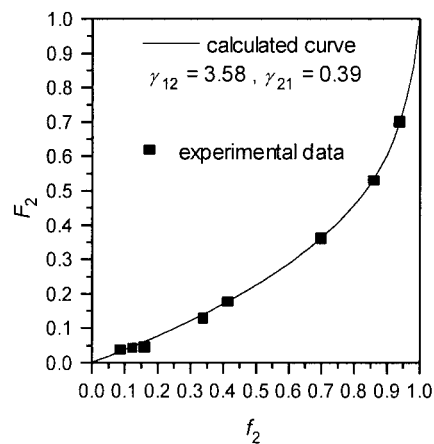


Figure 3 Monomer-copolymer composition curve for the suspension copolymerization of AN-VAc at 65°C (weight ratio of NaClO_3 to $\text{Na}_2\text{S}_2\text{O}_5$ = 1:5; weight ratio of initiators to monomers = 7.2×10^{-3}).

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] \left(R_3 \frac{[M_1]}{\gamma_{21}} + \frac{[M_2]}{\gamma_{21}} + R_3 \frac{[M_3]}{\gamma_{23}} \right) \times \left([M_1] + \frac{[M_2]}{\gamma_{12}} + \frac{[M_3]}{\gamma_{13}} \right)}{[M_2] \left(R_3 \frac{[M_1]}{\gamma_{12}} + \frac{[M_2]}{\gamma_{12}} + \frac{[M_3]}{\gamma_{13}} \right) \times \left(\frac{[M_1]}{\gamma_{21}} + [M_2] + \frac{[M_3]}{\gamma_{23}} \right)} \quad (8)$$

$$\frac{d[M_1]}{d[M_3]} = \frac{[M_1] \left(R_3 \frac{[M_1]}{\gamma_{21}} + \frac{[M_2]}{\gamma_{21}} + R_3 \frac{[M_3]}{\gamma_{23}} \right) \times \left([M_1] + \frac{[M_2]}{\gamma_{12}} + \frac{[M_3]}{\gamma_{13}} \right)}{[M_3] \left(\frac{[M_1]}{\gamma_{21}\gamma_{13}} + \frac{[M_2]}{\gamma_{12}\gamma_{23}} + \frac{[M_3]}{\gamma_{13}\gamma_{23}} \right) \times (R_3[M_1] + [M_2])} \quad (9)$$

Table II Values of γ_s for the Bulk Copolymerization of AN-VAc and the Apparent γ_s for the Suspension Copolymerization of the AN-VAc, AN-SMAS, and AN-VAc-SMAS Systems

T (°C)	Bulk Polymerization		Suspension Copolymerization					
	AN-VAc		AN-VAc		AN-SMAS		AN-VAc-SMAS	
	γ_{12}	γ_{21}	γ_{12}	γ_{21}	γ_{13}	γ_{31}	γ_{23}	R_3
65	2.85	0.11	3.58	0.39	1.45	0	0.92	0.04

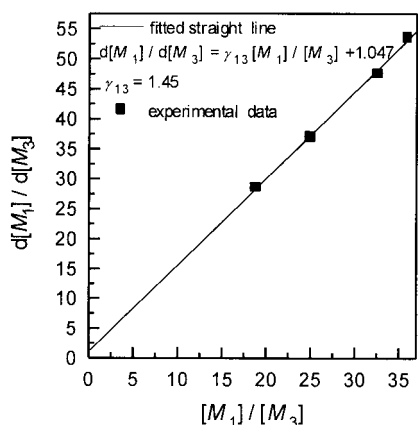


Figure 4 Monomer-copolymer composition curve for the suspension copolymerization of AN-SMAS at 65°C (weight ratio of NaClO_3 to $\text{Na}_2\text{S}_2\text{O}_5 = 1:5$; weight ratio of initiators to monomers = 7.2×10^{-3}).

where

$$R_3 = \frac{k_{31}}{k_{32}}$$

is for the rate constant ratio of k_{31} and k_{32} .

Evaluation Procedure

To obtain the values of γ_{12} , γ_{21} , γ_{13} , γ_{23} , and R_3 for the M_1 - M_2 - M_3 ternary copolymerization system without the self-polymerization of M_3 , such as AN-VAc-SMAS, where $\gamma_{31} = 0$, the evaluation procedure we propose comprises two steps. First, γ_{12} , γ_{21} , and γ_{13} should be determined according to eqs.(3) and (7) on the basis of the binary copolymerization of M_1 - M_2 and M_1 - M_3 , respectively. Afterward, γ_{23} and R_3 can be estimated with eq. (8) for the copolymerization of the three monomers, M_1 , M_2 , and M_3 .

Miller et al.¹ investigated the copolymerization in dimethylformamide of AN-vinyl chloroacetate systems, determined the composition of the copolymer by analysis for chlorine content, and evalu-

ated the reactivity values by various procedures, such as the Fineman-Ross method, Kelen-Tüdös method, and Mayo-Lewis copolymer composition integral equation. However, the reactivity values obtained by various methods differed considerably. For the AN-vinyl dichloroacetate and AN-vinyl trichloroacetate systems, even negative values were obtained with the Fineman-Ross method. The negative values of reactivity coefficients determined by the Fineman-Ross method were explained as being caused by certain errors in elementary analysis determinations. Differences in the γ_{12} and γ_{21} values obtained by the two quoted linear methods for the same experimental data could have been caused by the different statistical weights of the experimental points considered in the Kelen-Tüdös and Fineman-Ross methods. With the Mayo-Lewis copolymer composition integral equation for the same experimental data, considerable scattering of the intersection points of the different experimentally derived straight lines was observed.

Considering all these existing discrepancies, in this study we estimated the γ s by the simplex method¹⁴ for fitting experimental data. For the M_1 - M_3 binary system without the self-polymerization of M_3 , we determined γ_{13} by fitting the experimental data in linear eq. (7). The bivariate simplex technique was used to determine $(\gamma_{12}, \gamma_{21})$ and (γ_{23}, R_3) , respectively. For instance, when $(\gamma_{12}, \gamma_{21})$ are calculated, a series of copolymers with different compositions $[F_2(i)]$ are prepared under various $f_2(i)$. When a set of estimated values for $(\gamma_{12}, \gamma_{21})$ are given, the calculated compositions $[F_2^c(i)]$ corresponding to $f_2(i)$ can be derived by eq. (3). The set of estimated values for $(\gamma_{12}, \gamma_{21})$ that minimize the objective function $D_2 = \sum [F_2(i) - F_2^c(i)]^2$ indicate the accepted γ values.

γ for the AN-VAc Bulk-Copolymerization System

In Mokhtar et al.'s study,¹⁰ the copolymer compositions were calculated on the basis of nitrogen

Table III Experimental Data of the Suspension Copolymerization of AN-VAc-SMAS in a Continuous Pilot Reactor

Wt. % of Monomers in Feed Solution (w_m)	Wt. % of Copolymer in Outlet Slurry (w_s)	Conversion (m , %)	AN/VAc/SMAS Monomer Weight Ratio		AN/VAc/SMAS Mole Ratio in Copolymer	
			In Feed ($W_1 : W_2 : W_3$)	In Outlet ($W_1^0 : W_2^0 : W_3^0$)	Experimental ($M_1 : M_2 : M_3$)	Calculated ($M_1^c : M_2^c : M_3^c$)
3.2	28.2	85	89.29 : 10.48 : 0.23	76.68 : 23.01 : 0.31	94.55 : 5.35 : 0.10	94.85 : 5.06 : 0.09

content of the copolymers from infrared spectra, and the copolymerization parameters were calculated by the Fineman–Ross and the Kelen–Tüdös methods (see item 7 in Table I). The obtained values of γ for the bulk copolymerization of AN and VAc in this study were somewhat larger than Mokhtar et al.'s.¹⁰ A simulated curve of the average copolymer composition (\bar{F}_1) versus conversion (m) in a batch reactor according to eqs.(4) and (5) with the obtained reactivity values fit closely with the experimental data (see Fig. 2), demonstrating the precision of the investigative procedure of this study.

Apparent γ of the AN Suspension Copolymerization

Izumi et al.¹⁵ studied the copolymerization of AN and methyl acrylate in three types of polymerizations: emulsion polymerization in water with a water-soluble initiator, suspension polymerization in water with an oil-soluble and a water-insoluble initiator, and solution polymerization in dimethyl sulfoxide. Experimental results showed that the emulsion polymerization of AN with a water-soluble initiator existed both in the polymer particles and in water, and the loci of the suspension polymerization with an oil-soluble initiator were restricted to the polymer particles because the initiator did not dissolve in water.

In these experiments, the suspension copolymerization rates of AN with VAc or SMAS with a water-soluble redox initiator system were readily shown to be affected by an increase in the feed concentration of the monomers, regardless of the fact that the aqueous solution of monomers was saturated. This may lead to the conclusion that the loci of the suspension copolymerization of AN with a water-soluble initiator existed both in the particles and in water when the aqueous solution was saturated. In industrial continuous production, the suspension copolymerization with a water-soluble initiator is always operated under the condition that the reaction mixture is saturated with the monomers. Consequently, the apparent γ s obtained from the saturated system, as in this work, should be used for optimal production design. The values of the apparent γ s of the AN–VAc–SMAS suspension copolymerization system are listed in Table II. γ_{12} , γ_{21} , and γ_{13} were obtained from the binary copolymerizations of AN and VAc and AN and SMAS, respectively (Figs. 3 and 4). γ_{23} and R_3 were determined subsequently

from the ternary polymerization of AN, VAc, and SMAS.

For a continuous pilot reactor at a steady state, the slurry outlet comprises a liquid phase of water and monomers and a solid phase of copolymer. The material balance for each monomer component gives

$$\frac{M_i M_i^0}{M_1 M_1^0 + M_2 M_2^0 + M_3 M_3^0} w_s F^0 + W_i^0 (1 - w_s) F^0 = W_i w_m F^0 \quad (10)$$

where M_i^0 is the molecular weight of comonomer i and F^0 is the mass flow rate of the feed and outlet. Substituting the experimental data of M_i , w_s , w_m , and W_i listed in Table III into eq. (10) makes it possible to calculate the weight percent of each monomer in slurry (W_i^0). By inserting the mole fractions of each monomer in slurry and the accepted apparent γ values into eqs.(8) and (9), the compositions of copolymer (M_i^c) could be eventually derived. Such calculated M_i^c s were compared with the experimental data and shown to have fairly good agreement as shown in Table III.

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