A Method of Calculating Copolymerization Reactivity Ratios

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Synopsis

An improved linearization method is proposed for determining the monomer reactivity ratios of free-radical copolymerizations by fitting the data of cumulative copolymer compositions and overall weight fractional conversions, or cumulative copolymer compositions and residual monomer compositions of the reaction mixture. The reactivity ratios of monomers for four different copolymerization reactions are determined. The results are very close to those of literature reports and account well for the experimental results.

INTRODUCTION

The conventional methods for determining the reactivity ratios of two types of monomers in free-radical copolymerizations are based on the differential forms of the copolymerization equations. A concise summary of these methods has been given by Tidewell and Mortimer.[1] All these techniques encounter a common drawback with respect to the treatment of the experimental data. In each the assumption is made that the relative monomer concentrations do not change significantly from the initial conditions during the copolymerization. This restriction dictates stopping at low conversions and in many cases involves extraordinary experimental conditions. Numerous advantages should therefore accrue from using one of the integrated forms of the copolymerization equation and correcting for the shift in composition of monomers (and copolymers) with conversion. However, the methods[2-4] based on the integrated forms to determine the reactivity ratios of monomers still require time-consuming computation with the aid of a digital computer.

We propose a new integrated form of the copolymer composition equation whereby the reactivity ratios of monomers may be estimated simply by fitting the data of the overall weight conversion of the copolymerization and the cumulative copolymer composition, instead of using those of instantaneous copolymer compositions and residual monomer compositions of the reaction solutions, by the linear least-squares method. The reactivity ratios of four different copolymerization systems are studied. The feasibility of the proposed method is tested by comparing the theoretical cumulative copolymer compositions of these four copolymerization systems at various calculated conversions with our values of the reactivity ratios to those of the experimental results.

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THEORETICAL

Following the reaction scheme for free-radical copolymerizations proposed by Alfrey,[5] Mayo,[2] Simha,[6] and Wall,[7] the rates of disappearance of the two monomers are given as follows:

$$\frac{-dM_1}{dt} = k_{11}M_1^{\cdot}M_1 + k_{21}M_2^{\cdot}M_1 \tag{1}$$

$$\frac{-dM_2}{dt} = k_{12}M_1^{\cdot}M_2 + k_{22}M_2^{\cdot}M_2 \tag{2}$$

They also assumed that the concentrations of active polymers $M_1^{\cdot}$ and $M_2^{\cdot}$ are in the condition of steady state. Thus, eqs. (1) and (2) may be integrated to yield

$$M_1 = M_{1o} \exp[-(k_{11}M_1^{\cdot} + k_{21}M_2^{\cdot})t] \tag{3}$$

$$M_2 = M_{2o} \exp[-(k_{12}M_1^{\cdot} + k_{22}M_2^{\cdot})t] \tag{4}$$

Estimating the magnitude of these terms in the parentheses of eqs. (3) and (4) for many known copolymerization systems, we find that they are all less than an order of magnitude of 10^{-7} min^{-1}. The concentrations of initiator considered are 10^{-2} and $10^{-3}M$ benzoyl peroxide or azobisisobutyronitrile. Therefore, over a wide range of reaction time eqs. (3) and (4) may be safely linearized to be

$$M_1 = M_{1o}[1 - (k_{11}M_1^{\cdot} + k_{21}M_2^{\cdot})t] \tag{5}$$

$$M_2 = M_{2o}[1 - (k_{12}M_1^{\cdot} + k_{22}M_2^{\cdot})t] \tag{6}$$

Equations (5) and (6) are rearranged to become

$$\frac{M_{1o} - M_1}{M_{1o}} = (k_{11}M_1^{\cdot} + k_{21}M_2^{\cdot})t \tag{7}$$

$$\frac{M_{2o} - M_2}{M_{2o}} = (k_{12}M_1^{\cdot} + k_{22}M_2^{\cdot})t \tag{8}$$

Dividing eq. (7) by eq. (8) and eliminating $M_1^{\cdot}$ and $M_2^{\cdot}$ by the relation

$$k_{12}M_1^{\cdot}M_2 = k_{21}M_2^{\cdot}M_1 \tag{9}$$

we have a new integrated form of the copolymer composition equation:

$$\frac{(M_{1o} - M_1)}{(M_{2o} - M_2)} = \frac{M_{1o}(r_1M_1 + M_2)}{M_{2o}(M_1 + r_2M_2)} \tag{10}$$

By defining the residual monomer compositions of M_1 and M_2 in the reaction solution as

$$f_1 = \frac{M_1}{M_1 + M_2} = 1 - f_2 \tag{11}$$

and the cumulative copolymer compositions of M_1 and M_2 in copolymers formed at f_1 as

$$F_1 = \frac{M_{1o} - M_1}{(M_{1o} - M_1) + (M_{2o} - M_2)} = 1 - F_2 \tag{12}$$

eq. (10) becomes

$$\frac{F_1}{F_2} = \frac{f_{1o}(r_1 f_1 + f_2)}{f_{2o}(f_1 + r_2 f_2)} \tag{13}$$

Rearrangement of eq. (13) yields

$$\frac{F_2 f_{1o} f_2 - F_1 f_{2o} f_1}{F_1 f_{2o} f_2} = r_2 - \frac{F_2 f_{1o} f_1}{F_1 f_{2o} f_2} r_1 \tag{14}$$

where r_1 ($= k_{11}/k_{12}$) and r_2 ($= k_{22}/k_{21}$) are the reactivity ratios of M_1 and M_2, respectively. Equation (14) shows that r_1 and r_2 can be determined from the slope and the intercept of the plot of $(F_2 f_{1o} f_2 - F_1 f_{2o} f_1)/F_1 f_{2o} f_2$ vs. $F_2 f_{1o} f_1 / F_1 f_{2o} f_2$ or by the least-squares method to fit the $F_1 - f_1$ data in eq. (14).

The overall weight fractional conversion X_{wc} are easily and accurately obtained. It is convenient to determine r_1 and r_2 using F_1 and X_{wc} or f_1 and X_{wc} data. Taking material balance to monomers M_1 and M_2, the relationships among F_1, f_1, and X_{wc} are obtained as follows:

$$X_{wc} = \frac{(m_1 - m_2)F_1 + m_2}{(m_1 - m_2)f_{1o} + m_2} \frac{f_{1o} - f_1}{F_1 - f_1} \tag{15}$$

where m_1 and m_2 denote respectively the molecular weights of M_1 and M_2. Therefore, r_1 and r_2 can be determined with using the F_1 and X_{wc} data from eqs. (14) and (15). On the other hand, after r_1 and r_2 are determined, eqs. (14) and (15) may be used to calculate the cumulative copolymer composition and the residual monomer composition at various X_{wc}. The predicted F_1, f_1, and X_{wc} values can be compared with those of the experimental data. Thus, the r_1 and r_2 values obtained may be tested to see if they describe the copolymerization reaction.

If the data available are those of the initial monomer composition of the reaction mixture and the composition of copolymer formed initially, eq. (14) may be reduced to be the Fineman–Ross instantaneous copolymer composition equation[19]

$$\frac{f_{1o}(1 - 2F_1)}{F_1(1 - f_{1o})} = r_2 + \frac{f_{1o}^2(F_1 - 1)}{F_1(1 - f_{1o})^2} r_1 \tag{16}$$

by putting $f_1 = f_{1o}$ and $f_2 = f_{2o}$.

DISCUSSION

Verification of the Assumption

Inherent in our approach is that those values of $k_{11}M_1'$, $k_{12}M_1'$, $k_{22}M_2'$, and $k_{21}M_2'$ are assumed to be so small that over a wide range of reaction time eqs. (3) and (4) may be linearized to eqs. (5) and (6). This assumption is tested here as follows: Applying the steady-state assumption to active polymers M_1' and M_2', we can obtain M_1' and M_2' by the following two equations[8,9]:

$$M_1' = \frac{1}{k_{12}} \left[\frac{R_i}{r_1^2 \delta_1^2 + 2\phi r_1 r_2 \delta_1 \delta_2 (f_2/f_1) + r_2^2 \delta_2^2 (f_2/f_1)^2} \right]^{1/2} \tag{17}$$

$$M_2' = \frac{1}{k_{21}} \left[\frac{R_i}{r_1^2 \delta_1^2 (f_1/f_2)^2 + 2\phi r_1 r_2 \delta_1 \delta_2 (f_1/f_2) + r_2^2 \delta_2^2} \right]^{1/2} \qquad (18)$$

where R_i denotes the rate of the initiation, $\phi = k_{t12}/[2(k_{t11}k_{t22})]^{1/2}$, $\delta_1^2 = 2k_{t11}/k_{11}^2$, and $\delta_2^2 = 2k_{t22}/k_{22}^2$. Consequently, the magnitudes of the $k_{ij}M_i'$ terms may be estimated. Table I shows the computed $k_{ij}M_i'$ values for three different copolymerization reactions, i.e., the methyl methacrylate (MMA)–styrene (St), methyl methacrylate–vinyl acetate (VAc), and acrylic acid (AA)–acrylamide (AAm) systems. The initiators and their concentrations considered are $10^{-2}M$ benzoyl peroxide for the first two systems and $10^{-3}M$ $K_2S_2O_8$ for the last system; the r_i and k_{tij} values used for the evaluation are picked up from the literature.[10,11] From Table I we may see that the order of the magnitudes of $k_{ij}M_i'$ values is not greater than 10^{-7} min^{-1}. Furthermore, the residual monomer concentrations of M_1 and M_2 at 1 and 6 hr of reaction time for these three systems are separately computed by use of eqs. (3)–(6) and listed in Table II. We may find that the possible maximum error caused by using eqs. (5) and (6) is less than 0.7%. Therefore, this assumption is sound for low and moderate conversions.

TABLE I
Estimated Values of $K_{ij}M_i'$ for Four Different Copolymerizations

	MMA–St	MMA–VAc	AA–Am	VCl–VAc
$K_{11}M_1'$, min^{-1}	1.26×10^{-8}	2.75×10^{-7}	8.85×10^{-8}	1.06×10^{-7}
$K_{21}M_2'$, min^{-1}	6.38×10^{-8}	3.21×10^{-8}	5.73×10^{-8}	1.47×10^{-7}
$K_{22}M_2'$, min^{-1}	3.60×10^{-8}	1.29×10^{-11}	7.91×10^{-8}	3.37×10^{-9}
$K_{12}M_1'$, min^{-1}	2.97×10^{-8}	3.70×10^{-10}	2.46×10^{-8}	6.28×10^{-8}

TABLE II
Monomer Concentration at Various Conversions for MMA–VAc, AA–AAm, and MMA–St Copolymerization Systems Calculated by the Original and Linearized Monomer Concentration Equations

	MMA–VAc	AA–AAm	MMA–St
Initial monomer concentration, mole/l.			
M_{1o}	3.112	0.300	2.672
M_{2o}	7.262	0.700	6.234
Monomer concentration at 1 hr, mole/l.			
M_1 eq. (3)	2.768	0.293	2.599
eq. (5)	2.768	0.293	2.599
Δ^a	0.000	0.000	0.000
M_2 eq. (4)	7.261	0.674	6.087
eq. (6)	7.261	0.674	6.087
Δ^b	0.000	0.000	0.000
overall conversion, % by mole	4	3	2.5
Monomer concentration at 6 hr, mole/l.			
M_1 eq. (3)	1.616	0.260	2.261
eq. (5)	1.612	0.258	2.258
Δ^a	0.004	0.002	0.003
M_2 eq. (4)	7.118	0.559	5.410
eq. (6)	7.118	0.556	5.408
Δ^b	0.000	0.003	0.002
overall conversion, % by mole	18	20	15

[a] $\Delta = M_{1 \text{ eq. (3)}} - M_{1 \text{ eq. (5)}}$.
[b] $\Delta = M_{2 \text{ eq. (4)}} - M_{2 \text{ eq. (6)}}$.

TABLE III
Experimental[13] and Theoretical Results on Compositions of Copolymer and Reaction Mixture
for Methyl Methacrylate and Styrene Copolymerization

Reaction time, hr	X_{wc}	f_1	F_1	$F_{1,calc}$	$f_{1,calc}$
0.5	0.012	0.299	0.345	0.346	0.299
1.0	0.024	0.299	0.345	0.345	0.298
2.0	0.052	0.298	0.345	0.345	0.298
3.0	0.076	0.297	0.345	0.344	0.297
4.0	0.106	0.296	0.344	0.344	0.297

Determination of the Relative Monomer Reactivity Ratios

Methyl Methacrylate–Styrene Copolymerization

The MMA–St system is known to have similar relative monomer reactivity ratios; the shift in the monomer composition with conversion in the system is negligible. Thus, both differential and integrated forms of the copolymer composition equations are equally suitable for determining the monomer reactivity ratios.

Table III, which is obtained from our previous work,[12] lists F_1, f_1, and X_{wc} data for the MMA–St copolymerization at 60°C. Fitting the F_1, f_1 data into eq. (14), we obtain a linear plot of $(F_2 f_{1o} f_2 - F_1 f_{2o} f_1)/F_1 f_{2o} f_2$ vs. $F_2 f_{1o} f_1/F_1 f_{2o} f_2$, shown in Figure 1. Thus, the reactivity ratios of MMA and St monomers are determined by employing the linear least-squares method. The results are $r_1 = 0.53$ and $r_2 = 0.47$, where subscripts 1 and 2 express the MMA and St monomers, respectively. Substituting these values of 0.53 and 0.47 into eqs. (14) and (15), F_1 and f_1 at various X_{wc} values are calculated and shown in the fifth and sixth columns of Table III. Both theoretical and experimental F_1 and f_1 are found in very good agreement with each other. Meanwhile, our observation values of r_1 and r_2 are very much comparable to those reported in the literature.[13,14]

Methyl Methacrylate–Vinyl Acetate Copolymerization

The relative monomer reactivity ratios of this system at 60°C are 20 for MMA monomer and 0.015 for VAc monomer.[15] The shifts of monomer compositions with conversion in the system become quite significant; hence, the integrated forms of the copolymer composition equations are preferred for determination of the monomer reactivity ratios.

The F_1, f_1 data in Table IV, which are taken from the same reference as the above MMA–St system, are fitted into eq. (14), whereupon we obtain Figure 2. The plot of $(F_2 f_{1o} f_2 - F_1 f_{2o} f_1)/F_1 f_{2o} f_2$ versus $F_2 f_{1o} f_1/F_1 f_{2o} f_2$ is linear. The relative monomer reactivity ratios determined are 21 for MMA monomer and 0.016 for VAc monomer. These values are very close to those of the literature.[15] By using $r_1 = 21$ and $r_2 = 0.016$, the theoretical compositions versus conversions are calculated. The computed results are shown in the fifth and sixth columns of Table IV. Both theoretical F_1 and f_1 obtained are in good agreement with those of our experimental data.
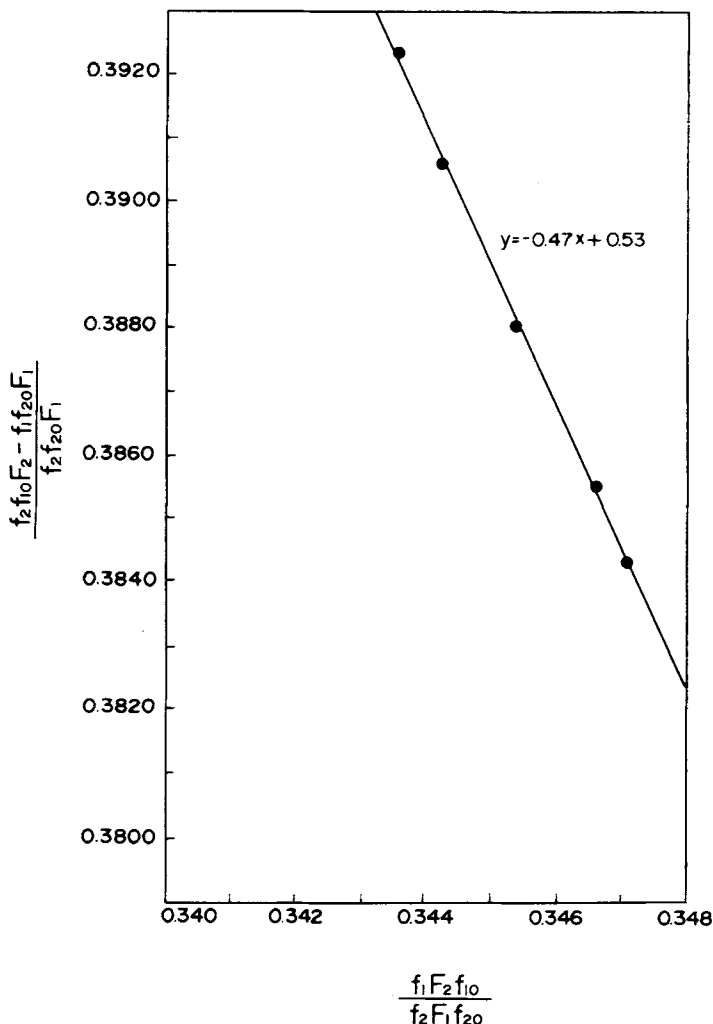
Fig. 1. Evaluation of monomer reactivity ratios of methyl methacrylate–styrene copolymerization at 60°C by the improved linearization method.

Vinyl Chloride–Vinyl Acetate Copolymerization

Montgomery and Fry[16] obtained $r_1 = 2.5$ for VCl monomer and $r_2 = 0.3$ for VAc monomer, which are determined by using the integrated equation due to Mayo and Lewis[2]:

$$r_2 = \frac{\log (M_{2o}/M_2) - (1/P) \log \left[\dfrac{1 - pM_1/M_2}{1 - pM_{1o}/M_2}\right]}{\log (M_{1o}/M_1) + \log \left[\dfrac{1 - pM_1/M_2}{1 - pM_{1o}/M_{2o}}\right]} \tag{19}$$

$$p = \frac{1 - r_1}{1 - r_2}$$

and employing a computer technique. Using their values of r_1 and r_2, they cal-

TABLE IV
Experimental[13] and Theoretical Results on Compositions of Copolymer and Reaction Mixture
for Methyl Methacrylate and Vinyl Acetate Copolymerization

Reaction time, hr	X_{wc}	f_1	F_1	$F_{1,calc}$	$f_{1,calc}$
0.5	0.020	0.287	0.912	0.912	0.287
1.0	0.040	0.276	0.911	0.910	0.275
2.0	0.075	0.250	0.907	0.907	0.250
3.0	0.108	0.228	0.904	0.904	0.228
4.0	0.136	0.205	0.901	0.900	0.204

culated the theoretical composition at various conversions which are fitted well to the experimental points after about 20% conversion, but the initial points do not fall on the line. They attributed this deviation to the presence of impurities.

Here, we fit Montgomery and Fry's F_1–X_{wc} data[16] into eqs. (14) and (15), which are listed in Table V. A linear plot, shown as Figure 3, is obtained. The relative monomer reactivity ratios thus determined are r_1 = 1.70 for VCl monomer and r_2 = 0.24 for VAc monomer. These values differ quite from those of Montgomery and Fry but are close to r_1 = 1.68 ± 0.08 and r_2 = 0.23 ± 0.02 reported by Mayo
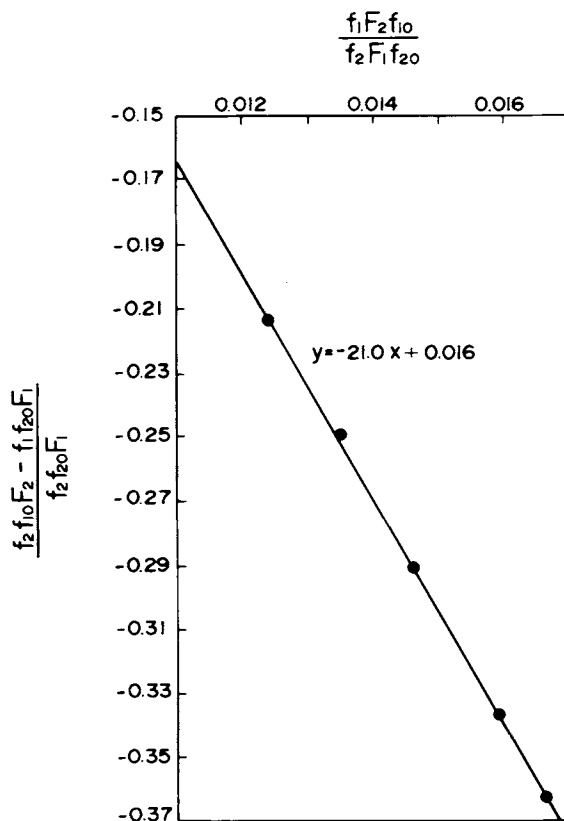

Fig. 2. Evaluation of monomer reactivity ratios of methyl methacrylate–vinylacetate copolymerization at 60°C by the improved linearization method.

Experimental Data for Vinyl Chloride–Vinyl Acetate Copolymerization obtained from
Montgomery and Fry's Work[17]

X_{wc}	F_1	f_1
0.075	0.908	0.796
0.120	0.907	0.790
0.180	0.905	0.782
0.250	0.904	0.770
0.390	0.902	0.740
0.480	0.894	0.718
0.610	0.886	0.669
0.695	0.881	0.616
0.760	0.873	0.567

et al.[15]   Substituting $r_1 = 1.70$ and $r_2 = 0.24$ into eqs. (14) and (15), we obtain
the predicted F_1 values at various X_{wc}, shown as the solid line in Figure 4.   It
may be seen that the theoretical F_1–X_{wc} line are coincident with all Montgomery
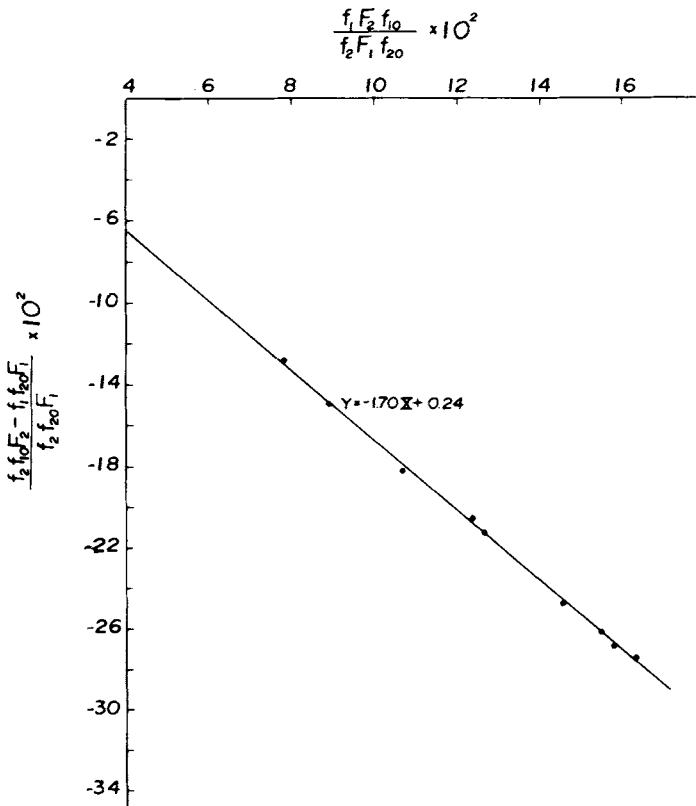and Fry's experimental points.

Fig. 3. Evaluation of monomer reactivity ratios of vinyl chloride–vinyl acetate copolymerization
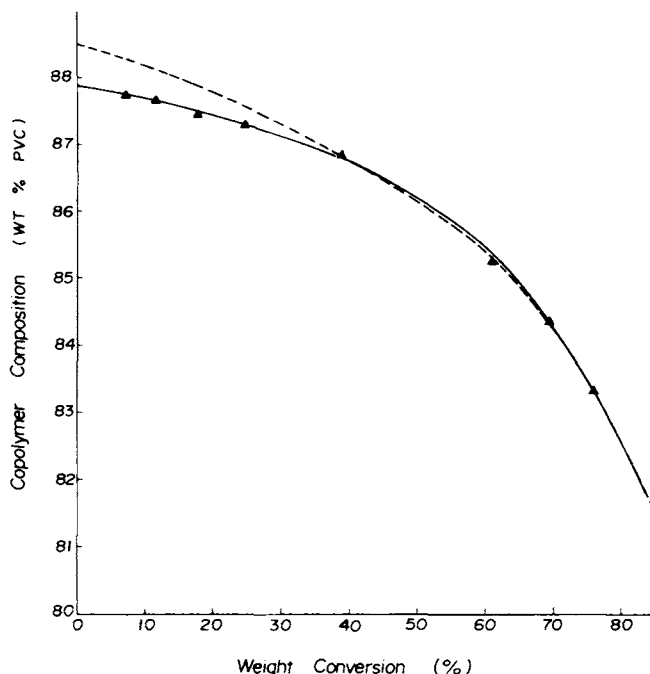by the improved linearization method.

Fig. 4. Composition vs. conversion for vinyl chloride–vinyl acetate copolymerization; initial monomer composition 75:25 by weight: (▲) experimental points; (- - -) Montgomery and Fry's theoretical curve for $r_1 = 2.5$ and $r_2 = 0.3$; (—) our theoretical curve for $r_1 = 1.7$ and $r_2 = 0.24$.

Acrylic Acid–Acrylamide Copolymerization

Table VI lists the cumulative copolymer composition–fractional molar conversion $(F_1–X)$ data which are reported by Shawski and Hamielec,[4] where subscript 1 refers to the acrylic acid monomer. The experimental conditions of these data are: $1.0M$ = total monomer concentration, $10^{-3}M$ $K_2S_2O_8$ = initiator concentration; and reaction temperature = 40°C. The residual monomer composition of reaction mixture f_1 given in the fourth column of Table VI is calculated by the following equation[17]:

$$f_1 = \frac{f_{1o} - F_1 X}{1 - X} \qquad (20)$$

Substituting the $F_1–f_1$ data into eq. (14), a linear plot is obtained, which is shown in Figure 5. The reactivity ratios of the monomers obtained are $r_1 = 1.36$ and $r_2 = 0.67$, which are consistent with those of Hamielec et al.[4] and Bourdais et al.[18] With these reactivity ratios we compute F_1 at various X using both eqs. (14) and (20); these values are given in the fifth column of Table VI. Comparing the values listed in the third and fifth columns of Table VI, we find both theoretical and experimental F_1 values in good agreement.

In the above four examples, the $F_1–f_1$, $F_1–X$, or $F_1–X_{wc}$ data used for determination of r_1 and r_2 were obtained from copolymerization reactions of significantly dissimilar or fairly similar monomer reactivity, with extents of reactions from low to moderate or low to rather high conversions. The r_1 and r_2 values of the examples determined by the method proposed in this work are in very good agreement with those of the literature. The predicted copolymer and monomer

TABLE VI
Experimental[18] and Theoretical Results on Compositions of Copolymer and Reaction Mixture
for Acrylic Acid–Acrylamide Copolymerization

f_{10}	X	F_1	f_1	$F_{1,calc}$
0.08	0.164	0.128	0.071	0.128
	0.241	0.115	0.069	0.117
	0.380	0.117	0.057	0.116
	0.509	0.111	0.048	0.113
	0.583	0.103	0.048	0.101
	0.689	0.096	0.045	0.098
0.15	0.234	0.217	0.130	0.216
	0.318	0.204	0.125	0.207
	0.472	0.210	0.097	0.205
	0.521	0.194	0.102	0.193
	0.602	0.186	0.096	0.186
	0.711	0.180	0.076	0.178
0.20	0.197	0.288	0.178	0.288
	0.276	0.273	0.172	0.275
	0.381	0.264	0.161	0.263
	0.490	0.266	0.137	0.268
	0.583	0.256	0.122	0.253
	0.621	0.239	0.136	0.241
0.25	0.228	0.335	0.225	0.336
	0.340	0.334	0.207	0.332
	0.449	0.323	0.191	0.325
	0.512	0.313	0.184	0.311
	0.618	0.309	0.146	0.306
	0.661	0.297	0.158	0.293

compositions of the reaction solution made by our r_1 and r_2 values coincide well
with the experimental results, in spite of the fact that the proposed method was
developed from the approximation solutions of the rate equations of the disap-
pearance of the two types of monomers.   It is important to note in our method
that the data needed are mainly those cumulative copolymer compositions and
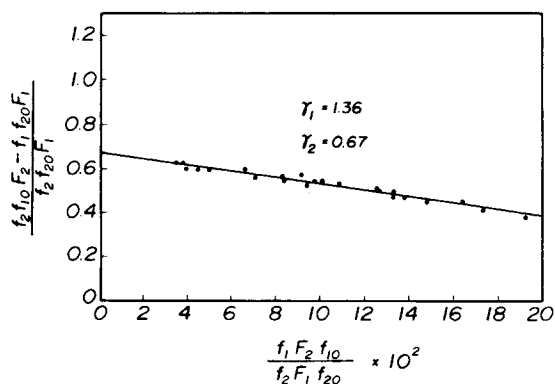overall weight fraction conversions that are easily obtained in the experimental

Fig. 5. Evaluation of monomer reactivity ratios of acrylic acid–acrylamide copolymerization at
40°C by the improved linearization method.

work, and the technique required for fitting is simply the linear least-squares or graphic method.

Nomenclature

K_{11} rate constant of propagation for active growing polymers M_1' reacted with monomer 1, mole/l.-sec

K_{12} rate constant of propagation for active growing polymers M_1' reacted with monomer 2, mole/l.-sec

K_{21} rate constart of propagation for active growing polymers M_2' reacted with monomer 1, mole/l.-sec

K_{22} rate constant of propagation for active growing polymers M_2' reacted with monomer 2, mole/l.-sec

F_1 molar composition of the monomer 1 unit in copolymer product

F_2 molar composition of the monomer 2 unit in copolymer product

f_1 molar composition of monomer 1 in the reaction solution

f_2 molar composition of monomer 2 in the reaction solution

M_1 molar concentration of monomer 1 in the reaction solution, mole/l.

M_2 molar concentration of monomer 2 in the reaction solution, mole/l.

M_1' molar concentration of total active species, the last unit of the chain being monomer 1 unit, mole/l.

M_2' molar concentration of total active species, the last unit of the chain being monomer 2 unit, mole/l.

r_1 monomer reactivity ratio of monomer 1 (defined as K_{11}/K_{12})

r_2 monomer reactivity ratio of monomer 2 (defined as K_{22}/K_{21})

t reaction time

X molar conversion of copolymerization

X_{wc} weight conversion of copolymerization

Subscripts

o for initial quantities

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