Evaluation of the Terpolymer Composition Equation

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INTRODUCTION

Copolymerization of two or more vinyl monomers ordinarily yields polymers whose composition differs from that of the starting monomer mixture. The theory governing the feed composition–polymer composition relationship has been developed and used extensively for two-component systems. For the three-monomer system, a mathematical treatment has been developed which predicts the composition of the initially formed terpolymer from the initial feed composition.[1-3] Special cases involving three-component systems in which one or two of the monomers are unreactive toward themselves or with each other have also been described by modified terpolymer composition equations.[4,5] In both the general and special cases the predicted relationship between the initially formed terpolymer and the feed composition has been experimentally verified.[3,6-8] Several methods have been suggested for calculating the average terpolymer composition as a function of feed conversion, both for the special simplified cases[5] and the general case.[3,9] No experimental data have yet been published which show the variation of polymer composition with degree of conversion for a three-component system and permit the verification of the terpolymerization equation for high conversion polymers.

In this paper the terpolymerization equation is integrated both numerically and analytically. The calculations were applied to the three-component system involving vinyl acetate (VAc), dioctyl fumarate (Fum), and N-vinyl pyrrolidone (NVP). The calculated compositions were compared with experimental results obtained by polymerizing two feed mixtures to various degrees covering the entire range of fumarate conversion. Good agreement was found over the entire conversion range, proving the usefulness of the equation for high conversion polymerizations.

The treatment of the three-component system requires reactivity ratios determined from the individual two-component systems. (A reactivity ratio is a relative reaction rate constant indicating the frequency with which a radical will react with a monomer of its own kind relative to a monomer of another kind.) In the course of the present work, reactivity ratios were determined for the two-component systems VAc-NVP and Fum-NVP. Reactivity ratios had been determined previously for the VAc-Fum system[10] and the VAc-NVP system.[11,12] In the latter case, however, there was some disagreement concerning the proper values.

The six reactivity ratios and feed composition were inserted in the terpolymer equation in order to predict the initially formed terpolymer composition from each of the two feeds selected for study. The equation was then programed on a digital computer for stepwise numerical integration. By means of the program the changes in instantaneous and average terpolymer composition, and in feed composition, were calculated with respect to initial feed composition and reactant conversion. To evaluate the accuracy of the calculations a series of eight terpolymerizations were carried out to various levels of monomer conversion for each of two feeds. The 16 terpolymers obtained were analyzed, and the average composition was plotted as a function of Fum conversion.

EXPERIMENTAL

Materials

The monomers, which polymerized quite satisfactorily as obtained from their commercial sources, were nevertheless purified by distillation. The constants were as follows: vinyl acetate (from Carbide and Carbon Chemicals), b.p. 72–73°C., n_D^{20} 1.3953; N-vinyl pyrrolidone (Antara), b.p. 51–52°C. at ca. 4 mm. Hg, n_D^{20} 1.5127; dioctyl fumarate (Rubber Corp. of America and our own laboratories), b.p. 191–194°C., at 3–4 mm. Hg, n_D^{20} 1.4574. The VAc was stored in the dark with 15 ppm of hydroquinone added, until used. The NVP was stored in the dark over a pellet of sodium hydroxide. The Fum, which was prepared from branched chain, C_8 "oxo" alcohol, was found to be stable at ordinary temperatures without special precautions. As solvents during polymerization, n-heptane (Phillips 99) or reagent-grade benzene was used and the initiator was $tert$-butyl perbenzoate (Wallace and Tiernan, Lucidol Div.). Other solvents and reagents were either purified by standard methods or used as obtained.

Procedure

For both the co- and terpolymerizations the monomers and solvent were weighed into a 100- or 250-ml. Pyrex glass tube. Initiator, $tert$-butyl perbenzoate, was added in an amount calculated to give a reasonable rate of reaction. A thermometer was placed in the tube and the tube closed with a vented cap. The reactants were de-aerated by alternate applications of nitrogen and vacuum, and then sealed under a slight pressure of nitrogen. (Loss due to volatilization was less than 1%.) The polymerizations were carried out in a constant-temperature oil bath held at 76 ± 1°C. and the reactions proceeded in a homogeneous phase. All copolymerizations were run in duplicate.

In the copolymerization of VAc-NVP the conversion of monomer was kept below 5 mole-%. The conversion level was determined from the weight of recovered polymer. In the Fum-NVP copolymerizations the degree of conversion ranged from 2–13%. In the case of Fum-NVP and

VAc-Fum-NVP, conversion was followed by polarographic analyses for unreacted Fum, accurate to about 2 parts in 100. Neither VAc nor NVP interferes in such a determination.

At the end of a polymerization run a sample was taken for conversion analysis and the remaining solution, with hydroquinone added, poured into a solvent which would precipitate the polymer. The isolated polymers were purified by multiple precipitations or dialysis against heptane through a gum rubber membrane.[13] (The VAc-NVP copolymers were precipitated from benzene with hexane while Fum-NVP copolymers and VAc-Fum-NVP terpolymers were precipitated from hexane with methanol.) All polymers were dried as films for 24–48 hr. in a vacuum oven at 60°C.

Nitrogen analysis by a modified Kjeldahl method was used to determine the NVP content in all the polymers. A correction factor of 1.10 was applied to all nitrogen analyses (see section entitled "Results"). In the case of terpolymers, carbon and hydrogen analyses were used to determine the VAc-Fum ratio, after subtracting the contribution to C and H due to NVP. Repeat analyses were made in all cases.

CALCULATIONS

Reactivity ratios for the VAc-NVP and Fum-NVP systems were calculated from the initial feed composition–initial copolymer composition relationship by the Fineman-Ross method.[14] These reactivity ratios, along with the literature values for VAc-Fum[10] were used to calculate terpolymer compositions.

For the three-component VAc-Fum-NVP system, the initial terpolymer composition and the change in composition with conversion were calculated by two methods. The first method involved programing the differential terpolymer composition equations on a digital computer in the following form:

$$dM_1:dM_2:dM_3 =$$

$$M_1 [M_1 r_{23} r_{32} + M_2 r_{31} r_{23} + M_3 r_{32} r_{21}] \quad [M_1 r_{12} r_{13} + M_2 r_{13} + M_3 r_{12}]:$$

$$M_2 [M_1 r_{32} r_{13} + M_2 r_{13} r_{31} + M_3 r_{12} r_{31}] \quad [M_2 r_{21} r_{23} + M_1 r_{23} + M_3 r_{21}]: \qquad (1)$$

$$M_3 [M_1 r_{12} r_{23} + M_2 r_{13} r_{21} + M_3 r_{12} r_{21}] \quad [M_3 r_{31} r_{32} + M_1 r_{32} + M_2 r_{31}]$$

where dM_1, dM_2, dM_3 are the incremental moles of VAc, Fum, and NVP respectively, appearing in the terpolymer; M_1, M_2, M_3 are the moles of VAc, Fum, and NVP respectively, in the feed; $r_{xy} = k_{xx}/k_{xy}$, appropriate reactivity ratios; and k_{xy} is the second-order rate constant in the addition of radical x to monomer y.

The program was set up so that conversion was based on M_2 (in this case, Fum). The feed compositions of interest and the six reactivity ratios were supplied for each case and the computer performed a stepwise numerical integration at increments of 0.1% of Fum converted. Reducing the increment to 0.05% produced no increase in accuracy. At a given feed com-

position the following data were printed out in tabular form for each per centage of Fum converted: (1) the instantaneous feed composition, (2) the instantaneous composition of the polymer being formed, (3) the average polymer conposition, and (4) the per cent conversion of the other two monomers. From these data detailed diagrams of the change in terpolymer composition with feed conversion were drawn. Since it is based on the most general form of the terpolymer equation, the computer program is able to define any co- or terpolymer system in a like manner.

A second, more limited, method can be used to calculate terpolymer composition for the VAc-Fum-NVP system with certain feed compositions. Because of the relative size of the reactivity ratios, many of the sums in eq. (1) contain terms which are less than 5% of the total and may be dropped, as an approximation. This leads to a simplified form which gives good agreement with the results from the full equation. The modification is applicable to the present system, however, only when the ratio of reactants is such that the mole fraction of NVP is small compared with VAc and Fum. The differential equations take a degenerate form which has been discussed by Walling and Briggs.[3]

$$dM_1 : dM_2 : dM_3 = \left[\frac{M_1}{r_{21}} \right] : \left[M_2 + \frac{M_1}{r_{21}} + \frac{M_3}{r_{23}} \right] : \left[\frac{M_3}{r_{23}} \right] \qquad (2)$$

As the equation indicates, the important reactivity ratios are r_{21} and r_{23} for this particular system. This means that the important factor is the choice the fumarate radical makes between the VAc and NVP monomers.

The change in terpolymer composition with conversion could be well approximated by analytical integration of the parts of eq. (2). Two equations result.

$$M_1 = M_1{}^\circ \left[\frac{M_3}{M_3{}^\circ} \right]^R \qquad (3)$$

where $M_1{}^\circ$, $M_3{}^\circ$ are the moles of monomer in initial feed, M_1, M_3 are the moles of monomer in feed after partial conversion, and R is the ratio of r values, r_{23}/r_{21}.

Having selected a degree of conversion for M_1 and determined the corresponding conversion of M_3, the conversion of M_2 at that point can be determined by eq. (4).

$$M_3{}^{-r_{23}} \left[M_2 - \frac{RM_1}{R - r_{23}} - \frac{M_3}{1 - r_{23}} \right] = C \qquad (4)$$

where C is a constant which is evaluated by first solving the equation with $M_1{}^\circ$, $M_2{}^\circ$, and $M_3{}^\circ$.

Starting with a given feed and using eq. (3) and (4), the course of conversion of any two monomers, as the third is consumed, could be determined, subject to the stated restrictions.

RESULTS

Copolymerizations

After preliminary experiments for determining approximate conversion rates, the copolymerizations were carried out in pairs to low levels of conversion with each of the selected feed ratios. The resultant copolymers were analyzed at least twice by a Kjeldahl procedure, and nitrogen values for copolymers from a given feed were averaged. The recovery of nitrogen from poly(N-vinyl pyrrolidone) was found to be about 10% below the theoretical. This observation led us to apply a correction factor of 1.10 to all nitrogen analyses, in common with previous authors who have encountered the same shortcoming with the Kjeldahl analysis.[12] The correction factor was further justified on the basis that it eliminated a negative reactivity ratio r_{32} and it improved the consistency of the elemental analyses on the terpolymers.

The results which were obtained from VAc-NVP copolymerization are shown in Table I; those from Fum-NVP, in Table II. The data are plotted by the method of Fineman and Ross[14] in Figure 1. The four reactivity ratios which result are given in Table III, along with the two others

TABLE I

Copolymerization of Vinyl Acetate (M_1) and N-vinyl Pyrrolidone (M_3)[a]

Feed,[b] moles			Copolymer	
Vinyl acetate	N-vinyl pyrrolidone	Time, hr.	Corrected Nitrogen, %[c]	Mole ratio VAc/NVP
0.60	0.20	0.75	7.14	0.987
0.20	0.30	0.75	9.85	0.361
0.20	0.40	1.0	10.82	0.212

[a] Charge made up to 100 ml. with benzene; 0.01–0.015 mole/l. *tert*-butyl perbenzoate initiator; 75–76°C.

[b] Duplicate preparations at each feed ratio.

[c] Average of two pairs of duplicate analyses on each preparation.

TABLE II

Copolymerization of Dioctyl Fumarate (M_2) and N-Vinyl Pyrrolidone (M_3)[a]

Feed,[b] moles			Copolymer	
Dioctyl fumarate	N-vinyl pyrrolidone	Time, hr.	Corrected N, %[c]	Mole ratio Fum/NVP
0.20	0.10	1.0	2.94	1.075
0.15	0.15	0.50	3.09	1.005
0.10	0.20	0.75	3.20	0.960
0.075	0.30	0.50	3.26	0.936

[a] Charge made up to 150 ml. with Phillips 99 n-heptane and absolute ethanol; 0.006–0.010 mole/l. *tert*-butyl perbenzoate initiator; 75–76°C.

[b] Duplicate preparations at each feed ratio.
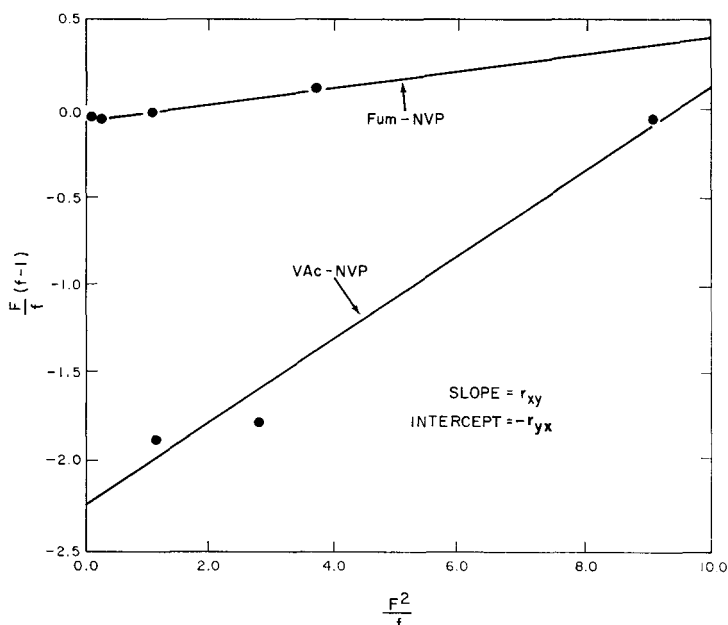
[c] Average of two pairs of duplicate analyses.

Fig. 1. Copolymerization of N-vinyl pyrrolidone (M_3) with vinyl acetate (M_1) and dioctyl fumarate (M_2). Fineman-Ross plot: $(F/f)(f-1) = r_{xy}(F^2/f) - r_{yx}$, where $F = M_x/M_y$ in the feed and $f = m_x/m_y$ in the copolymer.

TABLE III
Reactivity Ratios for the VAc (M_1)/Fum (M_2)/NVP (M_3) System[a]

$r_{12} = 0.011 \pm 0.001$	$r_{23} = 0.041 \pm 0.007$	$r_{13} = 0.237 \pm 0.037$
$r_{21} = 0.444 \pm 0.003$	$r_{32} = 0.030 \pm 0.033$	$r_{31} = 2.28 \pm 0.19$

[a] Ratios r_{12} and r_{21} were taken from Lewis and Mayo.[10]

required. The best values were obtained by the method of least squares, and the associated standard deviations by regression analysis. The reactivity ratios for the VAc-NVP system, r_{13} and r_{31}, are less accurate than the other pair in Figure 1, but fortunately the inaccurate pair has only a small influence on the terpolymerization result, as indicated earlier.

Terpolymerizations

The 16 terpolymers which were prepared were analyzed for carbon, hydrogen, and nitrogen. Oxygen content was obtained by difference, for a check on the consistency of composition as indicated by the C and H determinations. The results of the analyses of terpolymers from two feed compositions at different levels of conversion are shown in Table IV. Based on the data, the NVP, VAc, and Fum contents of each polymer were derived. The results of these calculations are shown by the experimental points in Figures 2 and 3. Terpolymer compositions computed on the basis

TABLE IV
Terpolymer Composition

| Fumarate converted, %	Corrected nitrogen, wt.-%	Carbon, wt.-%	Hydrogen, wt.-%	Oxygen,[a] wt.-%
A. Charge: VAc/Fum/NVP; mole ratio = 1.00/1.00/1.08; wt. ratio = 1.00/3.97/1.40				
21	2.88	68.50	10.08	18.54
25	2.73	68.61	10.07	18.59
35	2.75	69.59	10.01	18.65
52	2.61	69.20	10.08	18.11
68	2.63	68.93	10.02	18.42
82	2.90	68.82	10.03	18.25
89	2.77	68.74	10.12	18.37
97	2.86	68.72	10.11	18.31
B. Charge: VAc/Fum/NVP; mole ratio = 1.00/1.00/0.20; wt. ratio = 1.00/3.90/0.26				
7	1.95	68.33	10.18	19.54
13	1.90	68.96	10.05	19.09
21	1.67	68.63	10.23	19.47
30	1.66	68.60	10.08	19.66
39	1.60	68.57	10.10	19.73
53	1.40	68.76	10.23	19.61
89	0.79	68.46	10.11	20.64
95	0.75	68.51	10.04	20.70

[a] By difference.
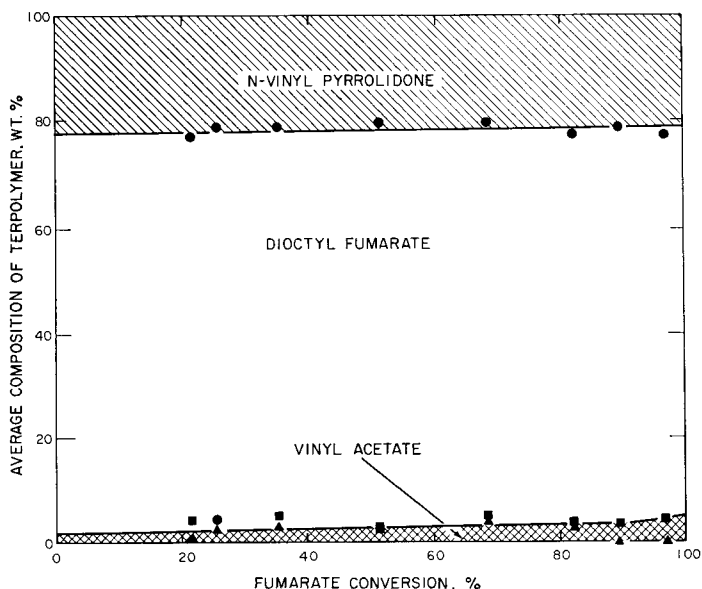
Fig. 2. Terpolymer composition as a function of reactant conversion. Feed: VAc/Fum/NVP; mole ratio = 1.00/1.00/1.08; wt. ratio = 1.00/3.96/1.40. Based on experimental analysis for (●) nitrogen, (■) carbon, (▲) hydrogen; line predicted from integration of eq. (1).
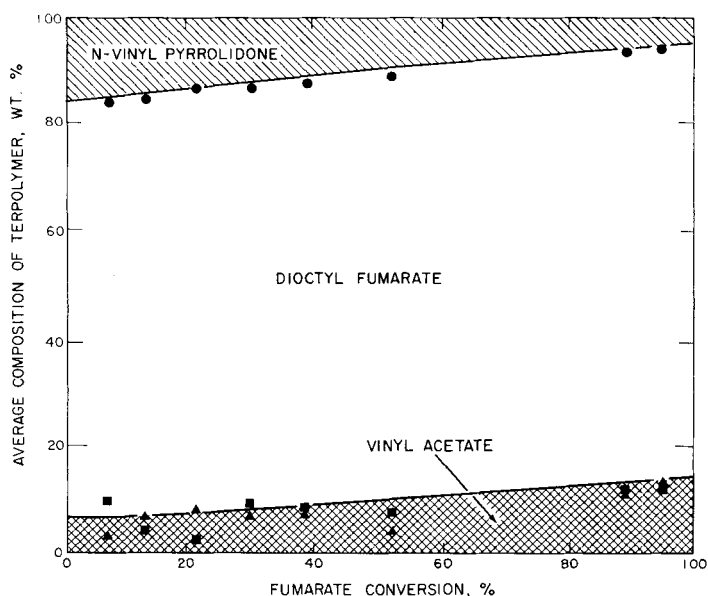
Fig. 3. Terpolymer composition as a function of reactant conversion. Feed: VAc/Fum/NVP; mole ratio = 1.00/1.00/0.20; wt. ratio = 1.00/3.90/0.26. Based on experimental analysis for (●) nitrogen, (■) carbon, (▲) hydrogen; line predicted from integration of eq. (1).

of oxygen content are not shown because they are almost identical with the compositions derived from the carbon content.

By the insertion of the six reactivity ratios and one of the chosen feed compositions into eq. (1), a prediction of the average terpolymer composition was obtained at each level of conversion. This was done most easily on digital computer, but hand calculations, eqs. (3) and (4) being used for the feed with low NVP content, yielded similar results (Table V). The predicted changes in average composition as a function of reactant conversion are shown by the smooth curves in Figures 2 and 3.

TABLE V
Change in Average Composition with Conversion[a]

Fumarate conversion, %	Terpolymer composition, wt.-%					
	Numerical integration[b]			Analytical integration		
	VAc	Fum	NVP	VAc	Fum	NVP
25	7.3	79.5	13.2	7.1	79.8	13.1
50	9.7	80.4	9.9	9.4	80.7	9.9
75	11.8	81.1	7.1	11.6	81.3	7.1

[a] Charge: VAc/Fum/NVP; mole ratio = 1.00/1.00/0.20; wt. ratio = 1.00/3.90/0.26.
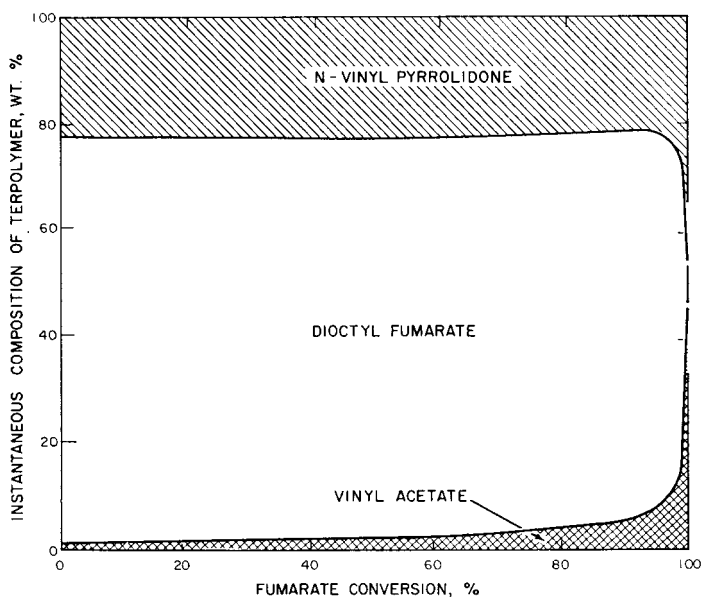[b] By computer.

Fig. 4. Calculated instantaneous terpolymer composition as a function of reactant conversion. Feed: VAc/Fum/NVP; mole ratio = 1.00/1.00/1.08; wt. ratio = 1.00/3.97/1.40.
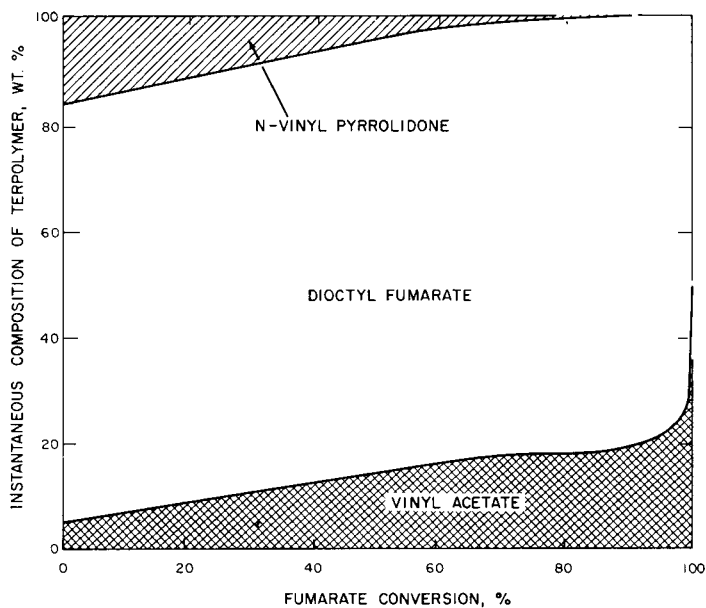

Fig. 5. Calculated instantaneous terpolymer composition as a function of reactant conversion. Feed: VAc/Fum/NVP: mole ratio = 1.00/1.00/0.20; wt. ratio = 1.00/3.90/0.26.

As a terpolymerization progresses, the feed changes in composition and the composition of the terpolymer being formed from one instant to the next will change.   A prediction can be made, of the change in instantaneous terpolymer composition with conversion, by means of the computer.   (The change in average composition is, of course, a reflection of the changes in instantaneous composition.)   It is not possible, however, to obtain direct experimental verification of the calculations, except for the initial stages of reaction.   The predicted instantaneous composition of the terpolymers formed during terpolymerization of the selected feeds is shown in Figures 4 and 5.   As shown in the latter figure, a batch polymerization can yield a wide spectrum of polymer compositions and this will have a direct effect on physical properties.

DISCUSSION

The reactivity ratios for VAc-NVP obtained in the present study differ considerably from those of Hayashi and Smets,[11] but are reasonably close to those of Bork and Coleman[12] (see Table VI).

TABLE VI
Reactivity Ratios

	Ref. 11	Ref. 12	This work
r_{13}	0.38	0.205 ± 0.015	0.237 ± 0.037
r_{31}	0.44	3.300 ± 0.150	2.280 ± 0.19

Bork and Coleman[12] noted that the recovery of nitrogen from poly(N-vinyl pyrrolidone), effected by a modification of the Kjeldahl procedure, was incomplete.   A correction factor (1.09) was applied which was of the same magnitude as the one in the present work (1.10).   In the course of our study, it was found that Dumas analysis is somewhat more efficient than the Kjeldahl, but the reproducibility of the results is not as good.

Since it is difficult to obtain very small r values with great accuracy, the error associated with the ratios for Fum-NVP (r_{23}, r_{32}) is quite reasonable. The value of r_{23} is particularly critical in the VAc-Fum-NVP system since the terpolymer composition depends most heavily on the ratio of small numbers, r_{23}/r_{21}, as indicated by eqs. (3) and (4).   It was found, however, that the maximum calculated error in the two r values would cause little difference in the predicted terpolymer composition.

The close fit of the terpolymer composition data from theory and experiment for two feed compositions provides further evidence of the validity of the general terpolymer composition (eq. (1)).   The fact that agreement is obtained across the entire range of conversion demonstrates that the general equation may be used to predict terpolymer composition as a function of conversion.   For the VAc-Fum-NVP system, with feed compositions which are low in NVP content, a simplified terpolymer equation may be in-

tegrated and used to predict the average terpolymer composition at any desired level of reactant conversion.

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References

1. Mayo, F. R., and C. Walling, *Chem. Revs.*, **46**, 225 (1950).
2. Alfrey, T., Jr., and G. Goldfinger, *J. Chem. Phys.*, **12**, 322 (1944).
3. Walling, C., and E. R. Briggs, *J. Am. Chem. Soc.*, **67**, 1774 (1945).
4. Alfrey, T., Jr., and G. Goldfinger, *J. Chem. Phys.*, **14**, 115 (1946).
5. Walling, C., D. Seymour, and K. B. Wolfstirn, *J. Am. Chem. Soc.*, **70**, 1544 (1948).
6. Chapin, E. C., G. E. Ham, and R. G. Fordyce, *J. Am. Chem. Soc.*, **70**, 538 (1948).
7. Fordyce, R. G., E. C. Chapin, and G. E. Ham, *J. Am. Chem. Soc.*, **70**, 2489 (1948).
8. Aggawal, S. L., and F. A. Long, *J. Polymer Sci.*, **11**, 127 (1953).
9. Skeist, I., *J. Am. Chem. Soc.*, **68**, 1781 (1946).
10. Lewis, F. M., and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1533 (1948).
11. Hayashi, K., and G. Smets, *J. Polymer Sci.*, **27**, 275 (1958).
12. Bork, J. F., and L. E. Coleman, *J. Polymer Sci.*, **43**, 413 (1960).
13. Hill, M. W., and M. W. Munsell, paper presented at 138th Meeting of the American Chemical Society, New York, Sept. 1960.
14. Fineman, M., and S. D. Ross, *J. Polymer Sci.*, **5**, 259 (1950).

Synopsis

The equations describing the relationships between polymer composition and feed composition in a three-monomer polymerization have been experimentally verified at high monomer conversions for the first time. In this paper, a three-component system involving vinyl acetate–octyl fumarate–N-vinyl pyrrolidone was analyzed. The six reactivity ratios, or relative reaction rate constants, were either taken from previous literature or determined from two-component systems. The differential terpolymerization equations could be integrated analytically in special cases, owing to the negligibility of some of the terms, but a more precise technique was to integrate numerically with a digital computer. Two feed compositions were polymerized to various levels of fumarate conversion covering the entire range. The extent of conversion was determined polarographically. Average terpolymer compositions, determined by elemental analysis, checked with values predicted by the mathematical model well within experimental error. The calculations also showed that the instantaneous terpolymer composition can vary considerably during a batch polymerization and give rise to a spectrum of polymer properties.

Résumé

Les équations qui décrivent les relations entre la composition du polymère et la composition de départ dans une copolymérisation, comprenant 3 monomères, ont été vérifiées expérimentalement et en premier lieu aux degrés de conversion élevés. On a analysé, dans cette publication, un système à trois composants contenant l'acétate de vinyle, le fumarate d'octyle-n et la vinyl-pyrrolidone. Les six rapports de réactivité, ou les constantes de vitesse relatives, ont été, soit trouvés dans la littérature, soit déterminés à partir de systèmes à deux composants. Les équations différentielles de la terpolymérisation pourront être intégrées analytiquement dans des cas particuliers à condition de négliger certains termes; une technique plus précise cependant consiste à intégrer numériquement en utilisant une machine à calculer. Deux compositions de départ ont été polymérisées à différents degrés de conversion en fumarate, couvrant ainsi toute la gamme des degrés de conversion; celui-ci a été déterminé par polarographie. Les com-

positions moyennes du terpolymère déterminées par analyse élémentaire, correspondent aux valeurs prévues à partir du modèle mathématique bien endéans les erreurs expérimentales admissibles. Les calculs ont également montré que la composition instantanée du terpolymère, peut varier considérablement pendant une polymérisation en masse pour donner lieu à un spectre de propriété de polymères.

Zusammenfassung

Die Gleichungen, welche die Beziehung zwischen der Polymerzusammensetzung und dem Monomeransatz bei der Copolymerisation von drei Monomeren angeben, wurden zum ersten Mal bei hohen Monomerumsätzen experimentell verifiziert. In der vorliegenden Mitteilung wird ein ternäres System, bestehend aus Vinylacetat, Octylfumarat und N-Vinylpyrrolidon untersucht. Die sechs benötigten Reaktivitätsverhältnisse, oder relativen Geschwindigkeitskonstanten, wurden entweder der Literatur entnommen oder an den binären Systemen bestimmt. Die Differentialgleichungen für die Terpolymerisation konnten in speziellen Fällen auf Grund der Vernachlässigbarkeit gewisser Terme analytisch integriert werden, jedoch erwies sich die numerische Integration mittels eines Digitalcomputers als das genauere Verfahren. Zwei Monomeransätze wurden zu verschiedenen, den ganzen Bereich umfassenden Fumaratumsätzen polymerisiert. Der Umsatz wurde polarographisch bestimmt. Die durch Elementaranalyse bestimmte mittlere Zusammensetzung der Terpolymeren stimmte mit den für das mathematische Modell berechneten Werten innerhalb der Versuchsfehler gut überein. Die Berechnungen zeigten auch, dass die jeweilige Zusammensetzung des Terpolymeren sich während der Polymerisation eines Ansatzes beträchtlich ändern und Anlass zur Entstehung eines Spektrums von Polymereigenschaften geben kann.