Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Chan, Richard K. S. and Meyer, Victor(1967) 'Azeotropes in Ternary Copolymerization', Journal of Macromolecular Science, Part A, 1: 6, 1089 — 1093
To link to this Article: DOI: 10.1080/10601326708053759
URL: http://dx.doi.org/10.1080/10601326708053759

J. MACROMOL. SCI.—CHEM., A1(6), pp. 1089–1093, Oct., 1967

Azeotropes in Ternary Copolymerization

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Summary

A method is outlined for the calculation of azeotropic compositions in ternary copolymerization. The results of these calculations are consistent with those reported by Tarasov et al. (2), and with those calculated by a recent method developed by L. J. Young of the Dow Chemical Company. Our results are further checked with the calculated monomer/copolymer composition during the predicted azeotropic copolymerizations. It was found, in all cases, that the monomer/copolymer composition stays constant, as expected. A method of graphical extrapolation is introduced for estimating the azeotropic composition when some reactivity ratios are inaccurate.

Methods of calculating the composition of ternary azeotropes were reported by Slocombe (*1*) and Tarasov et al. (*2*). A criterion was derived in Ref. 2 for testing the existence of ternary azeotrope for a given set of reactivity ratios. Recently, the results calculated by Tarasov and co-workers (*2*) has been questioned by Ham (*3*). The purpose of this paper is to present a more convenient method for calculating ternary azeotropes. This has been done by a numerical method. The Burroughs 5500 computer time used in the calculation of one azeotrope is only a few seconds. Following is a brief description and results of the method.

The notations used in this paper are the same as those in Ref. *4*: Subscripts i and j range from 1 to 3.

M_j = monomer j

$\sim M_j \cdot$ = free radical j

k_{ij} = specific rate constant

$r_{ij} = \frac{k_{ii}}{k_{ij}}$ = reactivity ratios

$M = M_1 + M_2 + M_3$

$f_j = \frac{M_j}{M}$ = mole fraction of monomer j (1)

$F_j = \frac{dM_j}{dM} = \frac{dM_j}{\Sigma_j dM_j}$ = instantaneous mole fraction of monomer j in the copolymer (2)

Using the steady-state approximation, Alfrey and Goldfinger (*4,5*) derived the ternary copolymerization equations:

$$\begin{aligned} dM_1 : dM_2 : dM_3 = {} & f_1\left[\frac{f_1}{r_{31}r_{21}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{31}r_{23}}\right]\left[f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}}\right] \\ & f_2\left[\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{12}r_{32}} + \frac{f_3}{r_{32}r_{13}}\right]\left[f_2 + \frac{f_1}{r_{21}} + \frac{f_3}{r_{23}}\right] \\ & f_3\left[\frac{f_1}{r_{13}r_{21}} + \frac{f_2}{r_{23}r_{12}} + \frac{f_3}{r_{13}r_{23}}\right]\left[f_3 + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}}\right] \end{aligned} \quad (3)$$

In azeotropic copolymerization, the polymer being formed has the same ratio of monomers as the feed; i.e.,

$$F_j = f_j \quad (4)$$

From the definition of F_j, Eq. (2), together with Eq. (3), F_j can be expressed as a function of f_i and r_{ij}; consequently, Eq. (4) represents a set of nonlinear simultaneous equations of the form

$$f_j = \text{function } (f_i, r_{ij}) \quad (5)$$

Equation (5) can be solved for f_j in terms of r_{ij}'s by a three-dimensional iterative method (*6,7*). Differentiation of Eq. (1) gives

$$df_j/dM = (F_j - f_j)/M \quad (6)$$

If the initial conditions of f_j and M are given, Eq. (6) can be solved by the Runge-Kutta method (*4,5*) to find f_j, as M varies. For azeotropic copolymerization f_j should stay constant during the polymerization process. This provides a good check of the internal consistency of the method of predicting ternary azeotropic composition.

It was found that our results are in agreement with those predicted in Ref. 2, and with those calculated by a recent method de-

veloped by L. J. Young of the Dow Chemical Company. One of the three sets of azeotropic mixtures listed in the table of Ref. 2 (the system of styrene, vinylidene chloride, and diethyl fumarate) was used as initial monomer feed. The results from integrating Eq. (6) indicate that f_j (or F_j) stays constant during the copolymerization, as shown in Fig. 1. The other azeotropic mixtures resulting from our calculations show similar calculated behavior in copolymerization; however, f_j's do not stay constant if the feed composition is different from the azeotropic composition. Figure 2 (f_j vs. r_{23}, all other r_{ij}'s are held constant) shows some other results of our calculation. Careful examination of Fig. 2 reveals that when

$$\begin{aligned} r_{12} &= r_{13} = 0.1 \\ r_{31} &= r_{32} = 0.2 \\ r_{23} &\geq 0.3 \end{aligned} \tag{7}$$

no azeotrope will be expected for $r_{21} = 0.1$ and $r_{21} \geq 1.1$, i.e., their azeotropic compositions are not realistic, the mole fraction of one of the three monomers is either zero or negative. Suppose in a set of reactivity ratios that the conditions above are satisfied. If r_{21} has been experimentally determined to be 1.0, when it should be 1.2 (this is the order of magnitude of the error suffered in most of the determinations of r_{ij}) from Fig. 2 the system with $r_{21} = 1.0$ has

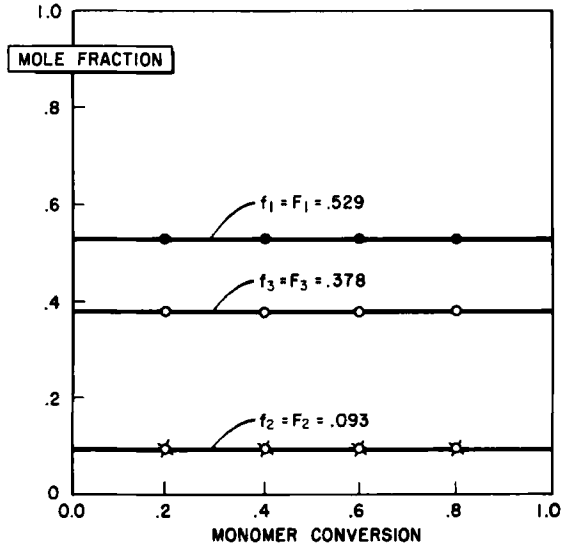

FIG. 1. Copolymerization behavior of styrene, vinylidene chloride, and diethyl fumarate.

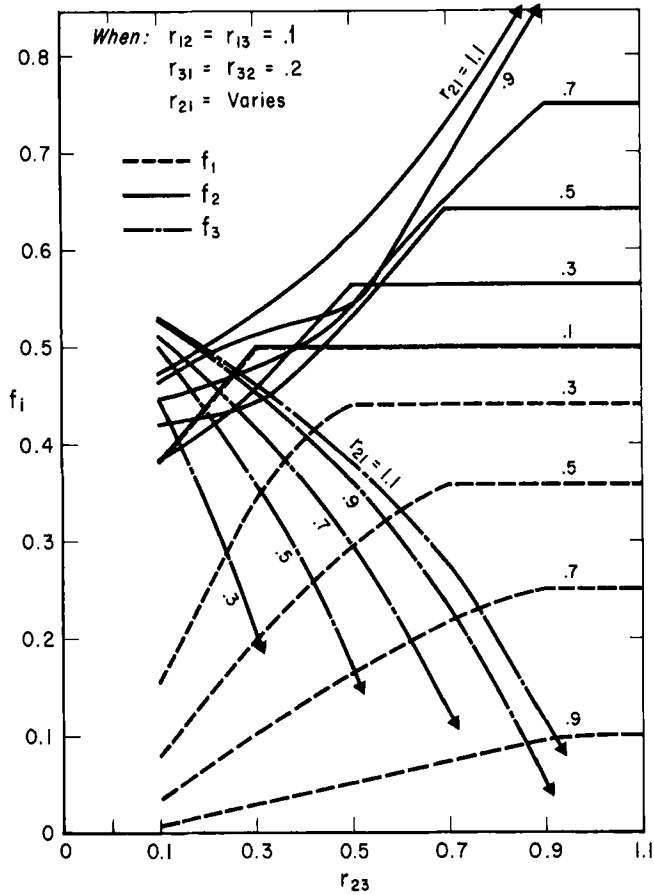

FIG. 2. f_i versus r_{23}.

an azeotrope, while the system with $r_{21} = 1.2$ (the real case) does not. Therefore, it is very likely that inaccurate reactivity ratios can introduce erroneous conclusions about the existence/nonexistence of ternary azeotrope. Plots similar to Fig. 2 can help indicate that possibility, and hopefully clarify the situation.

Acknowledgments

We wish to thank Mr. R. Foy and Dr. L. J. Young of the Dow Chemical Company for their assistance and helpful discussions in this work.

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Zusammenfassung

Eine Methode zur Berechnung von azeotropen Gemischen in ternären Kopolymerisaten wird angegeben. Die Ergebnisse dieser Berechnungen stimmen mit jenen von Tarasov et al. (2) überein, als auch mit jenen nach einer kürzlich entwickelten Methode von L. J. Young, Dow Chemical Company, berechneten. Unsere Ergebnisse stimmen ferner auch mit den berechneten Monomer/Copolymer Zusammensetzungen während der vorausgesagten azeotropen Kopolymerisation überein. In allen Fällen wurde gefunden, dass die Monomer/Polymer Zusammensetzung wie erwartet konstant bleibt. Ferner wird eine graphische Extrapolationsmethode eingeführt, die es gestattet, die azeotrope Zusammensetzung abzuschätzen wenn einige der Reaktivitätsverhältnisse ungenau sind.

Résumé

On présente une méthode de calcul de la composition azéotrope dans des copolymérisation ternaires. Les résultats de ces calculs sont en accord avec ceux de Tarasov et al. (2) et avec les résultats calculés à l'aide d'une nouvelle méthode developée par L. J. Young de Dow Chemical Company. On a également verifié nos résultats avec la composition calculée en monomère/copolymère au cours de la copolymérisation azéotrope prévue. On a trouvé que dans tous les cas la composition monomère/copolymère reste constante comme on s'y attendait. On introduit une méthode d'extrapolation graphique pour l'évaluation de la composition azéotrope quand les rapports de réactivité ne sont pas exacts.

Received by editor December 15, 1966
Submitted for publication August 22, 1967