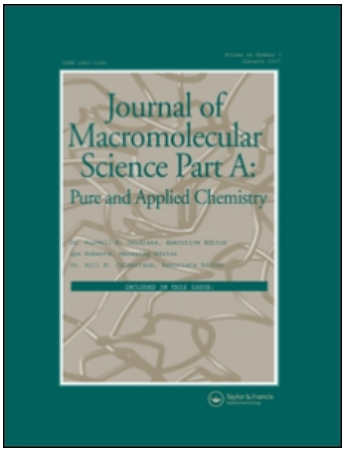


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# Computation of Monomer Feeds and Probability Products for Given Terpolymer Systems

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# Computation of Monomer Feeds and Probability Products for Given Terpolymer Systems

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## Summary

Based on the simplified terpolymer composition equations, a computer program has been written to calculate monomer feeds necessary to produce terpolymers of specified composition. From the computed feed composition for equimolar terpolymers, the probability products, which will be at a maximum under these conditions, were calculated for a number of monomer trios. The results show that considerable interaction occurs among the monomers under conditions of maximum alteration and that effects due to $e$ values rather than $Q$ values of the monomers predominate.

The evolution of general reactivity parameters, $p$, for monomers in copolymerization is discussed in detail in an earlier publication (*1*). The development is believed to be rigorous, relying only upon the assumption of "sequence reversibility," expressed as

$$P_{12}P_{23}P_{31} = P_{13}P_{32}P_{21} = \mathscr{P}$$

It was recognized that $\mathscr{P}$ varies with monomer composition. Comparisons were made accordingly, and $p$ values calculated at equimolar monomer ratios where a simplified equation in reactivity ratios results.

$$\frac{r_{13}}{r_{13} + r_{13}r_{12} + r_{12}} \frac{r_{21}}{r_{21} + r_{21}r_{23} + r_{23}} \frac{r_{32}}{r_{32} + r_{32}r_{31} + r_{31}}$$

$$= \frac{r_{12}}{r_{12} + r_{13}r_{12} + r_{13}} \frac{r_{31}}{r_{31} + r_{31}r_{32} + r_{32}} \frac{r_{23}}{r_{23} + r_{23}r_{21} + r_{21}} = \mathscr{P}$$

That monomer reactivity comparisons should be made at equimolar values of these monomers is axiomatic. However, additional important information regarding monomer reactivities can be generated by comparisons at equimolar terpolymer compositions.* At this point heterogeneous monomer sequences are at a maximum:

$$\sim\!M_1M_2M_3\!\sim$$
$$\sim\!M_1M_3M_2\!\sim$$
$$\sim\!M_2M_1M_3\!\sim$$

Indeed, $\mathscr{P}$ at this point ($\mathscr{P}_e$) is the sum of the probabilities of finding $\sim\!M_1M_2M_3\!\sim$, $\sim\!M_2M_3M_1\!\sim$, and $\sim\!M_2M_1M_3\!\sim$ sequences. Monomer reactivity is therefore being considered under conditions of maximum alteration and $\mathscr{P}_e$ is a measure of alternating tendency in the equimolar terpolymer. By so choosing equimolar polymer composition, we are essentially suppressing the effects due to $Q$, the reactivity of the monomer, and are concerned now only with the interactions of the monomers expressed by their $e$ values.



## MATHEMATICAL MODEL

With the above considerations in mind, the simplified terpolymer composition equations (2,3) were rearranged to yield the two simultaneous equations

$$Ax^2 + Bxy + Cy^2 + Dx + Ey = 0$$
$$Mx^2 + Nxy + Py^2 + Qx + Ry + S = 0$$

where the monomer concentrations $M_1 = x$, $M_2 = y$, and $M_3 = 1 - x - y$. The coefficients $A$ through $S$ have the values shown in Table 1, where $\alpha = m_1/m_2$ and $\beta = m_1/m_3$, and $m_1$, $m_2$, and $m_3$ are the concentrations of the respective monomer units in the terpolymer.

One of the unknowns, $y$, was eliminated from the simultaneous equations by forming their resultant, following, for example, Uspensky (*4*).

Solution of the resulting polynomial in $x$ will obviously yield a maximum of four values for $x$, and subsequent substitution of these values in one of the simultaneous equations will give eight values for $y$. Significant sets of solutions of $x$, $y$, and $1 - x - y$, i.e., those for which $0 < x < 1$, $0 < y < 1$, and $x + y < 1$, must then be in-

* These are hypothetical terpolymers, since the comparisons can be derived from calculations based on the three binary reactivity ratios concerned.

**TABLE 1**

Coefficients of Simultaneous Equations in $M_1$ and $M_2$

| Coefficient | Value | Coefficient | Value |
|---|---|---|---|
| $A$ | $\frac{1}{r_{21}} - \frac{1}{r_{21}r_{23}}$ | $M$ | $\frac{\beta}{r_{13}r_{31}} - \frac{\beta}{r_{13}} - \frac{1}{r_{31}r_{13}} + \frac{1}{r_{31}}$ |
| $B$ | $\frac{1-\alpha}{r_{21}r_{12}} + \frac{\alpha}{r_{12}r_{23}} - \frac{1}{r_{21}r_{13}}$ | $N$ | $\frac{\beta}{r_{13}r_{31}} - \frac{1}{r_{13}r_{31}} + \frac{\beta}{r_{13}r_{32}} + \frac{1}{r_{31}r_{12}} - \frac{2\beta}{r_{13}}$ |
| $C$ | $\frac{\alpha}{r_{12}r_{23}} - \frac{\alpha}{r_{12}}$ | $P$ | $\frac{\beta}{r_{13}r_{32}} - \frac{\beta}{r_{13}}$ |
| $D$ | $\frac{1}{r_{21}r_{13}}$ | $Q$ | $\frac{1}{r_{31}r_{13}} - \frac{\beta}{r_{13}r_{31}} + \frac{2\beta}{r_{13}}$ |
| $E$ | $\frac{-\alpha}{r_{12}r_{23}}$ | $R$ | $\frac{2\beta}{r_{13}} - \frac{\beta}{r_{13}r_{32}}$ |
| | | $S$ | $\frac{-\beta}{r_{13}}$ |

troduced into the original terpolymer composition equations to ascertain which values of monomer feed composition will satisfy the given $\alpha$ and $\beta$ values.

For $\alpha = \beta = 1$, the resulting monomer value will, of course, generate equimolar terpolymers.

## RESULTS FOR THE GENERAL CASE

For the general case in which $\alpha$ and $\beta$ have different positive values, the results shown in Table 2 were obtained. These can be compared with those of Table 4 of the paper by Ham (2). The reactivity ratios used in both examples were

$$r_{12}\ 0.52;\ r_{23}\ 1.35;\ r_{31}\ 0.114;\ r_{13}\ 0.41;\ r_{32}\ 0.18;\ r_{21}\ 0.46$$

## RESULTS FOR EQUIMOLAR TERPOLYMERS

Table 3 gives appropriate monomer values for a number of equimolar terpolymers. Values for the reactivity ratios used in the calculations were taken from the paper by Ham (5). Calculation of $\mathscr{P}_e$, the maximum value of $\mathscr{P}$ as a function of monomer composition, yields a measure of maximum alternation tendency in the systems shown. Thus 6.7% of the three member sequences in styrene–acrylonitrile–methyl methacrylate are $\sim\!M_1M_2M_3\!\sim$ or its variations ($\sim\!M_2M_3M_1\!\sim$, $\sim\!M_3M_1M_2\!\sim$) at a maximum. For compari-

son, equal reactivity would lead to a random value of $(1/3)^3 = 0.037$; so it is seen that considerable interaction is occurring.

Examination of a large number (60) of monomer trios, involving trios having zero, one, two, or three crossover systems, allows the

**TABLE 2**

Calculation of Feed for Given Terpolymer

| Monomers | | | | | Calcd. mole fraction of monomer in feed | | |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | $\alpha$ | $\beta$ | $M_1$ | $M_2$ | $M_3$ |
| Styrene | Methyl methacrylate | Acrylonitrile | 1.44 | 1.50 | 0.3620 | 0.3633 | 0.2747 |
| | | | | | 0.3592[a] | 0.3603 | 0.2805 |
| Styrene | Methyl methacrylate | Acrylonitrile | 2.26 | 2.28 | 0.5352 | 0.2607 | 0.2041 |
| | | | | | 0.5323[a] | 0.2651 | 0.2036 |

[a] Original feed compositions from data of Ham (5).

**TABLE 3**

Feed Compositions and Probability Products for Several Equimolar Terpolymers

| | | | Mole fraction in feed for equimolar polymer comp. | | | | | |
|---|---|---|---|---|---|---|---|---|
| $M_1$ | $M_2$ | $M_3$ | $M_1$ | $M_2$ | $M_3$ | $P_{12}P_{23}P_{31}$ | $P_{13}P_{32}P_{21}$ | $\mathscr{P}_e$ |
| Styrene | Acrylonitrile | Methyl methacrylate | 0.160 | 0.495 | 0.345 | 0.0636 | 0.0710 | 0.0673 |
| Styrene | Methyl acrylate | Methyl methacrylate | 0.180 | 0.502 | 0.318 | 0.0600 | 0.0452 | 0.0526 |
| Acrylonitrile | Methyl acrylate | Methyl methacrylate | 0.352 | 0.527 | 0.121 | 0.0338 | 0.0568 | 0.0453 |
| Styrene | Acrylonitrile | Methyl acrylate | 0.078 | 0.510 | 0.412 | 0.0328 | 0.0817 | 0.0572 |
| Styrene | Acrylonitrile | Methacrylonitrile | 0.091 | 0.561 | 0.348 | 0.0622 | 0.0512 | 0.0567 |
| Styrene | Methacrylonitrile | Methyl methacrylate | 0.251 | 0.374 | 0.375 | 0.0559 | 0.0701 | 0.0630 |
| Styrene | Methyl methacrylate | Vinyl chloride | 0.048 | 0.040 | 0.911 | 0.0257 | 0.0499 | 0.0378 |
| Methyl methacrylate | Acrylonitrile | Methacrylonitrile | 0.175 | 0.575 | 0.250 | 0.0525 | 0.0495 | 0.0510 |
| Methyl methacrylate | Acrylonitrile | Vinylidene chloride | 0.141 | 0.406 | 0.453 | 0.0378 | 0.0718 | 0.0548 |
| Vinyl chloride | Vinyl acetate | Vinylidene chloride | 0.274 | 0.654 | 0.072 | 0.0403 | 0.0523 | 0.0463 |

conclusion that one, and only one, feed composition will satisfy given $\alpha$ and $\beta$ values.

Finally, it should be noted that maximum alternation occurs in a binary system at a monomer ratio which yields equimolar copolymers. Thus

$$1 = \frac{m_1}{m_2} = \frac{r_1(M_1/M_2) + 1}{r_2/(M_1/M_2) + 1}$$

whence

$$M_1/M_2 = \sqrt{r_2/r_1}$$

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**Zusammenfassung**

Auf der Grundlage einer vereinfachten ternären Polymerenzusammensetzungsgleichung wurde ein Rechenprogramm entwickelt, das die Berechnung der notwendigen Monomerendosierung berechnet um ternäre Polymere gegebener Zusammensetzung herzustellen. Aus den berechneten Dosiermengen für äquimolare ternäre Polymere wurden die wahrscheinlichsten Produkte berechnet, welche sich unter diesen Bedingungen maximieren werden. Die Ergebnisse zeigen, dass beträchtliche Wechselwirkungen zwischen den Monomeren unter den Bedingungen der maximalen Änderung auftreten und dass Einflüsse der *e*-Werte die der *Q* Werte der Monomeren überwiegen.

**Résumé**

Basé sur des équations simplifiées de la composition des terpolymères on a developé un programme pour ordinateur afin de calculer les alimentations en monomère, necessaires pour la production des terpolymères à composition determinée. A partir des compositions computées pour des

terpolymères équimoléculaires, on a calculé pour un certain nombre de trois polymères, les produits probables, qui seront présents en quantité maxima dans ces conditions. Les resultats montrent l'occurrence d'une interaction considérable entre les monomères dans ces conditions d'alternation maxima et la prédominance due aux valeurs d'*e* plutot qu'aux valeurs *Q* des monomères.

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