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George E. Ham[a]
[a] G. E. Ham Associates, Massachusetts

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TRIAD CONCENTRATIONS ($P_{12}P_{23}P_{31}$ AND $P_{13}P_{32}P_{21}$) AS A GUIDE TO MONOMER REACTIVITY IN COPOLYMERS AND TERPOLYMERS

GEORGE E. HAM

G. E. Ham Associates
52 Riverview Drive
Dalton, Massachusetts 01226

ABSTRACT

A simple procedure using triangular coordinates for representing triad concentrations as a function of terpolymer compositions (and monomer proportions) is presented. Equal triad concentrations are represented by concentric closed loops or rings of equal triad concentrations converging to a unique point of highest triad concentration. The technique is illustrated with several common terpolymer systems. Alternation in terpolymer systems is assessed by determination of heterotriad concentrations. These results are compared with alternation in component binary systems. An equation is derived for calculating $P_{12}P_{21}^{\mathrm{MAX}}$, maximum 1,2-dyad concentration (maximum mol fraction alternation) from r_1r_2 product at equimolar copolymer. Alternatively, an equation is proposed for calculating $P_{12}P_{21}^{\mathrm{MAX}}$ from Q-e values. Uses and limitations of r_1r_2 product in assessing alternation in binary copolymers are discussed.

DISCUSSION

Recent papers have summarized the background and current status of attempts to relate heterotriad ($P_{12}P_{23}P_{31}$ and $P_{13}P_{32}P_{21}$) concentrations in free radical

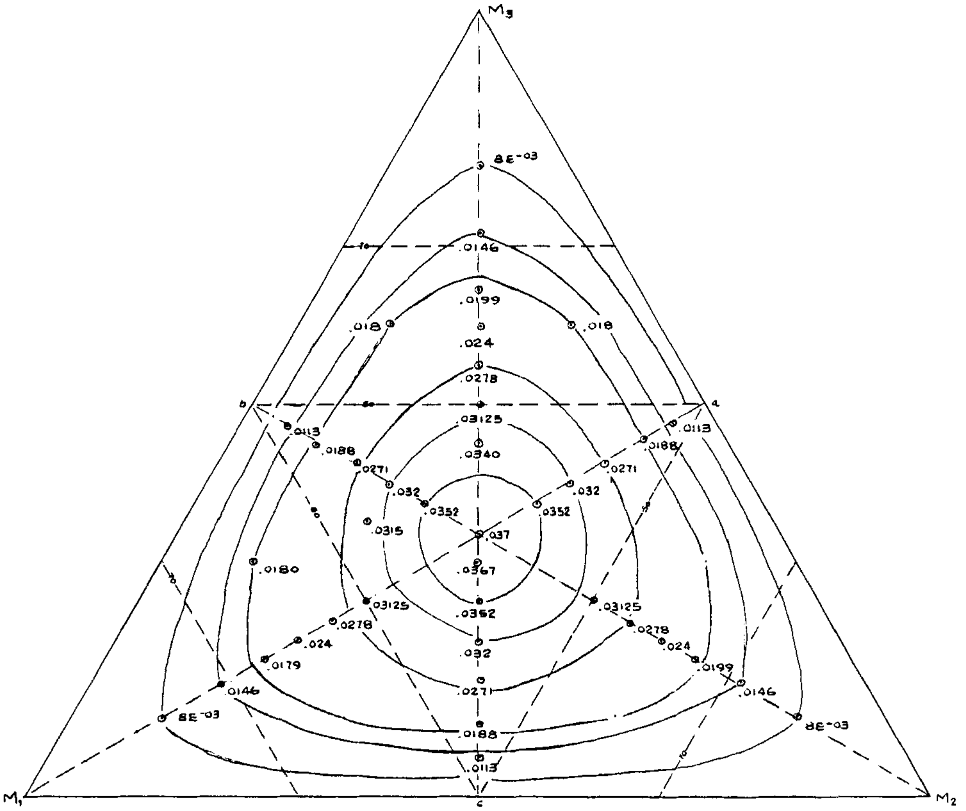

FIG. 1. Random terpolymer vs monomer (and terpolymer) content. Heterotriad content.

terpolymers* to individual monomer reactivity in binary copolymerization and terpolymerization [1-3].

Progress in this field has been hampered by the lack of a convenient method of representing triad concentrations as a function of terpolymer compositions (in turn related to monomer proportions). This paper proposes a simple procedure using triangular coordinates in which closed loops or rings of equal triad concentrations are shown as "isobars" or "isocons" converging to a unique point of highest triad concentration, $\mathcal{P}_e$.

The simplest case is represented by Fig. 1 in which three hypothetical monomers of equal reactivity are allowed to generate initial or instantaneous terpolymers with characteristic heterotriad contents. The closed loops denote families of identical heterotriad concentrations as a function of terpolymer composition. The closed loops or rings may be seen as truncated circles with 3-fold symmetry, in which for every point there exists two other points of equivalent position on the same trun-

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*However, conclusions should apply equally to other statistical copolymers, including anionic, cationic, and coordinated catalytic systems.

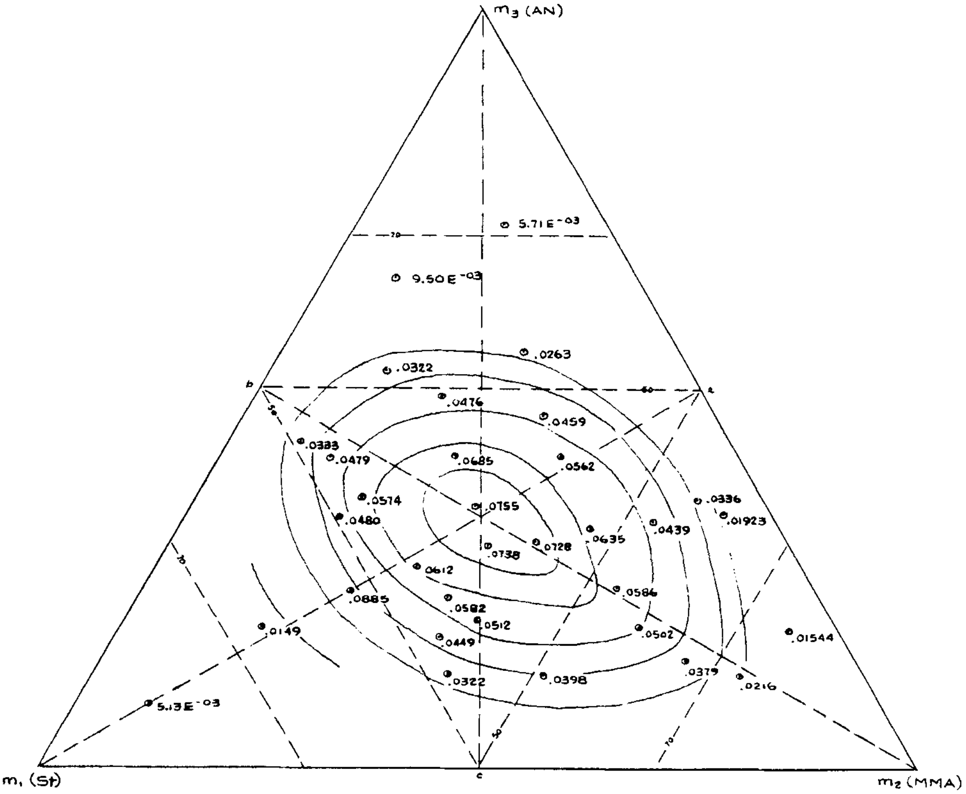

FIG. 2. $M_1M_2M_3$ triad concentrations vs terpolymer compositions. Terpolymer St-MMA-AN:

$r_{12} = 0.5$ $r_{13} = 0.41$ $r_{23} = 1.2$
$r_{21} = 0.5$ $r_{31} = 0.04$ $r_{32} = 0.15$

cated circle. The circles are distorted because of the nature of the triangular coordinates.

Certain characteristic features of the random terpolymer system shown should be pointed out.

1. The maximum concentration of $-M_1M_2M_3-$ triads (equimolar terpolymer) is 0.037.
2. The concentration of $-M_1M_2M_3-$ triads is halved at about 9% m_1, m_2, or m_3, with the other comonomer units varying between about 30.5 and 60.5%.
3. At 3% m_1, m_2, or m_3, $-M_1M_2M_3-$ triad concentration drops sharply to about 7×10^{-3} (other comonomers of about equal concentration).

Figure 2 shows a similar plot of $-M_1M_2M_3-$ triad concentrations calculated for an actual terpolymer styrene-methyl methacrylate-acrylonitrile [St-MMA-AN] ($r_{12} = 0.5$, $r_{21} = 0.5$, $r_{13} = 0.41$, $r_{31} = 0.04$, $r_{23} = 1.2$, $r_{32} = 0.15$). In this case,

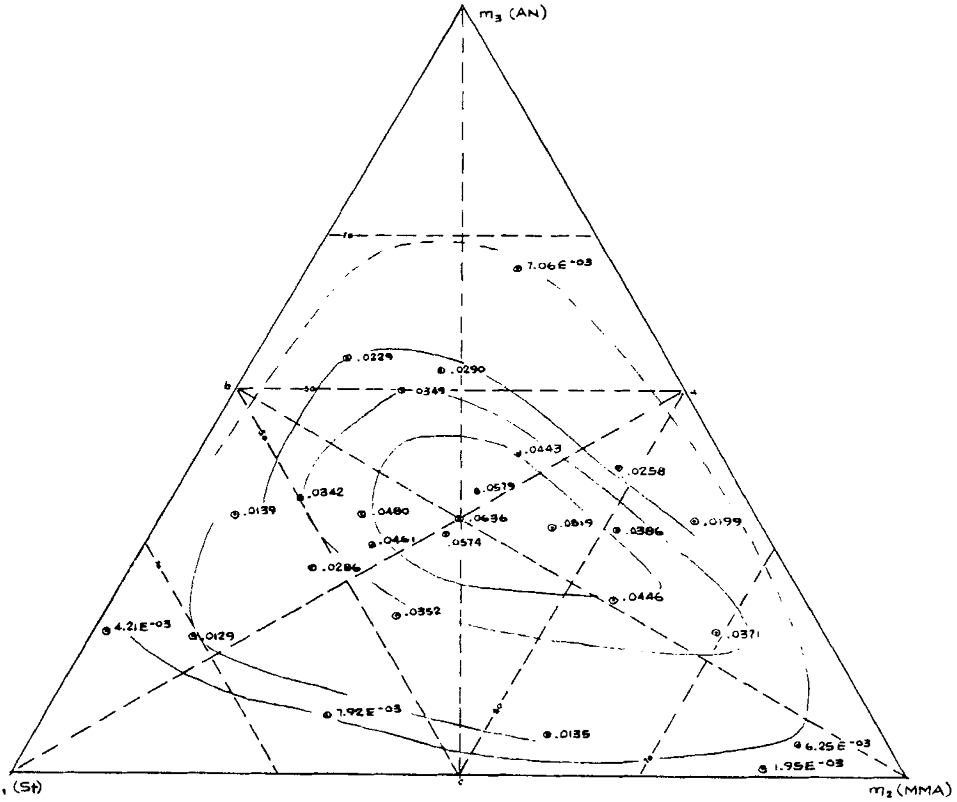

FIG. 3. $M_1M_2M_3$ triad concentrations vs terpolymer compositions. Terpolymer St-MMA-AN vs terpolymer composition:

$r_{12} = 0.52$ $r_{13} = 0.30$ $r_{23} = 1.35$
$r_{21} = 0.46$ $r_{31} = 0.04$ $r_{32} = 0.18$

however, $-M_1M_2M_3-$ triad concentration attains a maximum of about 0.076 at $\frac{1}{3}m_1$, $\frac{1}{3}m_2$, $\frac{1}{3}m_3$, more than twice the level for the random case.

The concentration of $-M_1M_2M_3-$ triads is not reduced by at least one-half until m_1 is reduced to about 10% *or* m_2 is reduced to about 12% *or* m_3 to about 11%. However, $-M_1M_2M_3-$ concentration is not reduced to less than 0.0185 until about 4% m_1, about 40% m_2, or about 3% m_3.

As noted above, this level is reached in random terpolymers at over twice the concentration of m_1, m_2, and m_3, individually.

Finally, the "isobars" or "isocons" in this terpolymer delineate elongated ellipses with no precise symmetry. However, there appears to be an approximate line of symmetry connecting the 100% m_2 point with the 50% m_1-50% m_3 point.

Figure 3 shows similar calculations of styrene-methyl methacrylate-acrylonitrile with slightly different reactivity ratios ($r_{12} = 0.52$, $r_{21} = 0.46$, $r_{13} = 0.30$, $r_{31} = 0.04$, $r_{23} = 1.35$, and $r_{32} = 0.18$). Now, a maximum of .0636 $-M_1M_2M_3-$ triads results at $\frac{1}{3}m_1$, $\frac{1}{3}m_2$, $\frac{1}{3}m_3$. Alternation ($-M_1M_2M_3-$ triad concentrations) still continues at a high level throughout much of the range of terpolymer concentrations, but not at as high a level as in the previous case.

Determination of Heterotriad Concentration

According to Tosi [4], alternation in binary copolymers is fully described by the r_1r_2 binary reactivity ratio product and copolymer composition. However, in terpolymerization the level of alternation or heterotriad concentration ($P_{12}P_{23}P_{31}$ and $P_{13}P_{32}P_{21}$) must include components related to monomer feed proportion.

$$P_{12}P_{23}P_{31} = \left(\frac{M_2r_{13}}{M_2r_{13} + \mathrm{M}_1r_{12}r_{13} + \mathrm{M}_3r_{12}}\right) \times \left(\frac{M_3r_{21}}{M_3r_{21} + \mathrm{M}_2r_{23}r_{21} + \mathrm{M}_1r_{23}}\right) \times \left(\frac{M_1r_{32}}{M_1r_{32} + \mathrm{M}_3r_{31}r_{32} + \mathrm{M}_2r_{31}}\right) \tag{1}$$

$$P_{13}P_{32}P_{21} = \left(\frac{M_3r_{12}}{M_3r_{12} + \mathrm{M}_1r_{13}r_{12} + \mathrm{M}_2r_{13}}\right) \times \left(\frac{M_2r_{31}}{M_2r_{31} + \mathrm{M}_3r_{31}r_{32} + \mathrm{M}_1r_{32}}\right) \times \left(\frac{M_1r_{23}}{M_1r_{23} + \mathrm{M}_2r_{21}r_{23} + \mathrm{M}_3r_{21}}\right) \tag{2}$$

It has been proposed that $P_{12}P_{23}P_{31} \simeq P_{13}P_{32}P_{21}$ in terpolymerizations. Such an equality leads to simplified terpolymer equations. Simplified higher order multicomponent polymerizations arise from similar assumptions. Furthermore, the prospect of simplified measures of general monomer reactivity in copolymerization is offered. In addition, such a simplification is in harmony with the *Q-e* concept [5].

It is herewith proposed, for the first time, that even if $P_{12}P_{23}P_{31}$ is not precisely equal to $P_{13}P_{32}P_{21}$, the above simplifications and their advantages can still be obtained by the use of an average value of the two in calculations.

In the case at hand, it should be noted that the ratio of $P_{12}P_{23}P_{31}/P_{13}P_{32}P_{21}$ will be precisely equal to $r_{13}r_{32}r_{21}/r_{12}r_{23}r_{31}$.

Thus, Fig. 2 represents a plot of $P_{12}P_{23}P_{31}$ for the indicated terpolymerization. There would, of course, exist a companion plot for $P_{13}P_{32}P_{21}$ as a function of monomer composition, in which the resulting closed loops and maximum would be displaced by a small but constant amount.

Similarly, for Fig. 3 there exists a companion plot in which every point is displaced by a constant value.

It will be appreciated that triangular coordinates may be used to show the relationship between heterotriad concentration and monomer feed composition. Figure 4 shows such a plot for styrene-methyl methacrylate-acrylonitrile. Although the mathematical relationship between heterotriad concentration and feed composition is simpler, the triangular plot is not as readily interpreted as Figs. 1-3. This difficulty is due to the predominant effect of terpolymer composition/monomer feed relationships over heterotriad/terpolymer composition relationships.

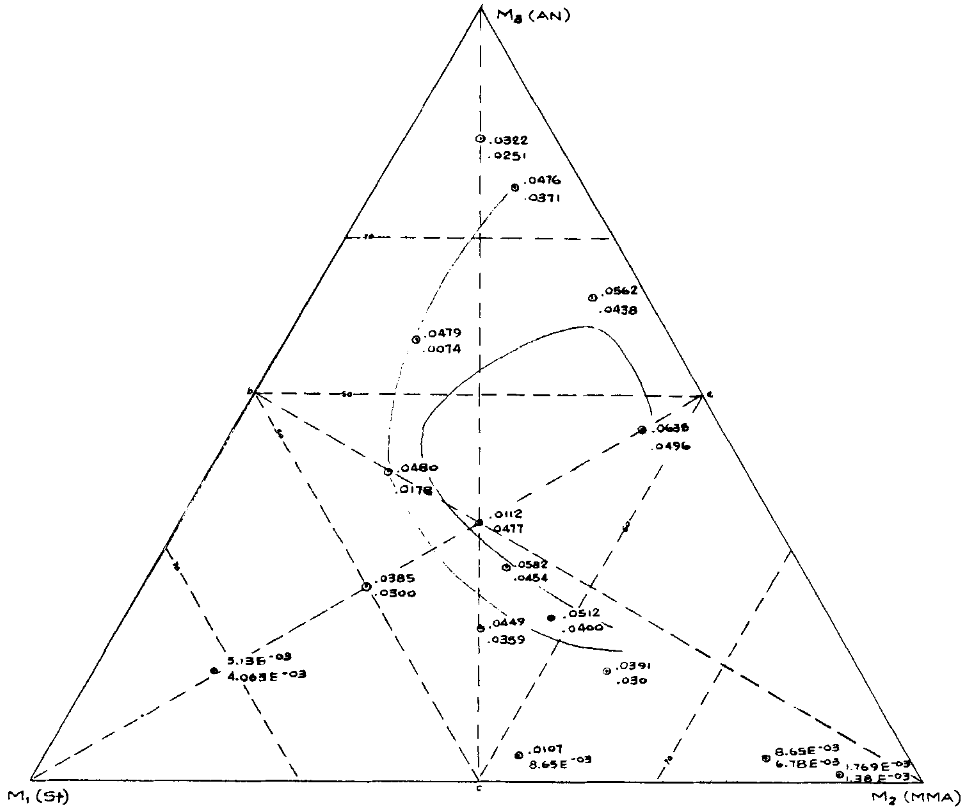

FIG. 4. $P_{12}P_{23}P_{31}$ and $P_{13}P_{32}P_{21}$ vs feed composition. St-MMA-AN.

Figure 5 shows the relationship between heterotriad concentrations and terpolymer composition for styrene-methyl methacrylate-vinyl chloride [St-MMA-VCl]. However, these results are based on $P_{12}P_{23}P_{31}$. A maximum heterotriad concentration of about 0.0286 occurs at about $m_1 = 0.2991$, $m_2 = 0.3248$, $m_3 = 0.3761$.* However, heterotriads calculated from $P_{13}P_{32}P_{21}$ are significantly higher. Thus, a maximum heterotriad concentration of about 0.05327 resulted at the same terpolymer composition. The ratio $P_{12}P_{23}P_{31}/P_{13}P_{32}P_{21} = r_{13}r_{32}r_{21}/r_{12}r_{23}r_{31} = 0.5361$.

Thus, all heterotriad calculations based on $P_{12}P_{23}P_{31}$ will differ from those based on $P_{13}P_{32}P_{21}$ by a constant factor. This problem has been previously noted for combinations of two high and one low Q monomers. Interpretation of these results is difficult and inconclusive. Thus, results based on $P_{12}P_{23}P_{31}$ alone suggest blockiness, and those based on $P_{13}P_{32}P_{21}$ suggest a high level of alternation. It is tempting to take the mean of the two maxima (0.0409), suggesting slight alternation for the overall terpolymer system.†

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*Theoretically, maximum heterotriad concentration should occur at equimolar terpolymer.

†These values should not be confused with much lower values obtained at equimolar monomer ratios.

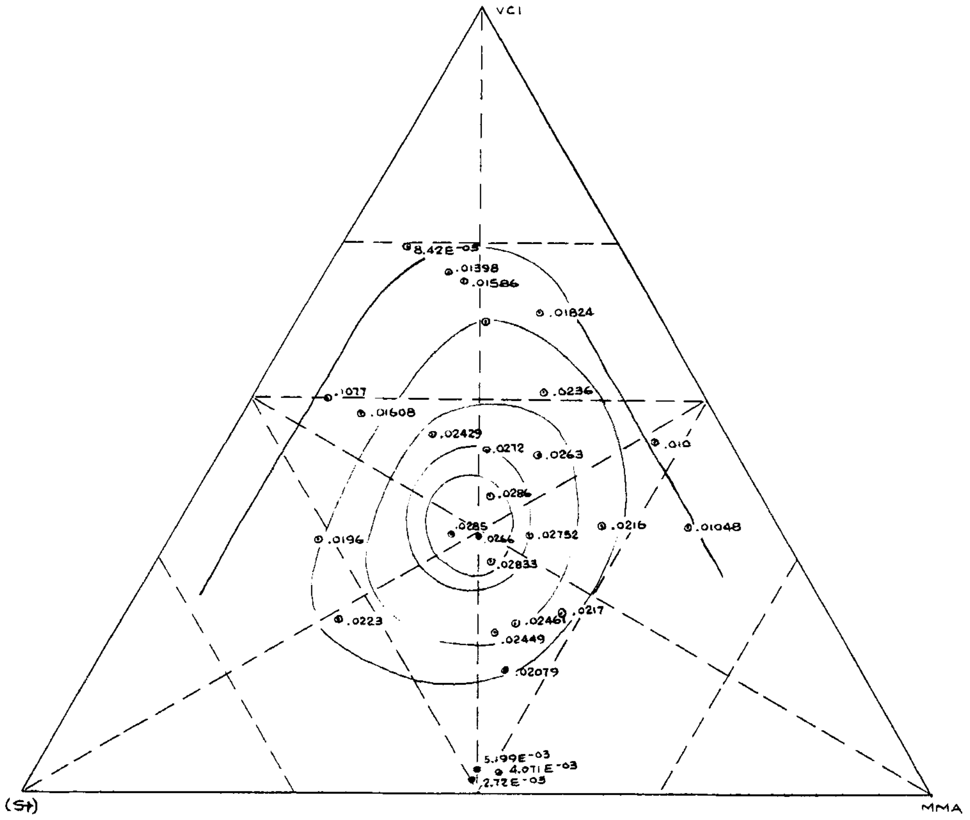

FIG. 5. Heterotriad content vs terpolymer composition ($P_{12}P_{23}P_{31}$). Terpolymer St-MMA-VCl:

$r_{12} = 0.52$ $r_{13} = 3.5$ $r_{23} = 1.5$
$r_{21} = 0.46$ $r_{31} = 0.077$ $r_{32} = 0.02$

Styrene-Methyl Methacrylate-Vinylidene Chloride

$r_{12} = 0.52$ $r_{23} = 2.53$ $r_{13} = 2.0$
$r_{21} = 0.46$ $r_{32} = 0.24$ $r_{31} = 0.14$

$$r_{12}r_{23}r_{31} \simeq r_{13}r_{32}r_{21}$$

$$0.52 \cdot 2.53 \cdot 0.14 \simeq 2.0 \cdot 0.24 \cdot 0.46$$

$$0.1842 \simeq 0.2208$$

By trial and error it was found that $P_{13}P_{32}P_{21}$ reached a maximum of 0.06165 and $P_{12}P_{23}P_{31}$ a maximum of 0.05142 at equimolar proportions of monomer components in terpolymer. Taking an average value of 0.05654, it is evident that a high level of alternation occurs in the terpolymer.

For comparison, Table 3 from Reference 3 is reproduced here.

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

The P_e values previously obtained from a computer program are identical with or similar to the maximum values reported here for $—M_1M_2M_3—$ or $—M_1M_3M_2—$ sequences at equimolar proportions of m_1, m_2, and m_3 in terpolymer.* It should be borne in mind that these heterotriad-based values are not directly applicable to monomer reactivity, since no direct use of monomer concentration is made (except for calculating sequence distribution). However, they may be a means of comparing *packing efficiencies* of various equimolar terpolymers.

It is noted, however, that high alternation is encouraged by a judicious spread of e values [6, 7]. Note that styrene ($e = -0.80$) acrylonitrile ($e \simeq 1.23$), and methyl methacrylate ($e \simeq 0.40$), are associated with a P_e value of 0.0673. For comparison, note that acrylonitrile ($e \simeq 1.23$), methyl acrylate ($e \simeq 0.64$), and methyl methacrylate ($e \simeq 0.40$) are associated with a P_e value of 0.0453. In the former case, there is a total Δe spread of 2.03 units; in the latter case the spread is only 0.83 units.

For determining monomer reactivity in terpolymerization (and ultimately in copolymerization generally), it is appropriate to use Eqs. (1) and (2) to calculate $—M_1M_2M_3—$ and $—M_1M_3M_2—$ triad concentrations at equimolar monomer concentrations. Thus, the equations are considerably simplified and, for systems of three

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*This is particularly noteworthy since the computer program is based on simplified terpolymer equations and the heterotriad calculations are not.

conjugated monomers and three unconjugated monomers, in particular, useful terpolymer ranges result. For combinations of two conjugated and one unconjugated or one conjugated and two unconjugated monomers, the resulting triad concentrations will be considerably reduced under these circumstances, reflecting the reduced reactivity of the unconjugated monomers—one of the conditions we wish to assess.

Furthermore, for systems of three conjugated or three unconjugated monomers, the heterotriad concentration at equimolar *monomer* proportions ($\mathcal{P}$) is relatively insensitive to structural variations, allowing the use of $\mathcal{P} = 0.037$ (the random case) for a rough assessment of monomer reactivity. More complete studies have shown that $\mathcal{P}$ ranges in value from about 0.037 to 0.07 for these types of monomer combinations, allowing more precise calculation of individual monomer reactivity parameters using the relationship $p_1p_2p_3 = \mathcal{P}$.

Similarly, combinations of two conjugated and one unconjugated monomer allow calculation of reactivity parameters for the individual unconjugated monomers, using the same equation.

An associated phenomenon related to *equimolar terpolymers* should be reemphasized. As shown in the various ternary diagrams of combinations of three conjugated monomers, there is a persistence at high levels of $—M_1M_2M_3—$ and $—M_1M_3M_2—$ triads—well beyond levels anticipated for monomers of equal reactivity (Fig. 1). This is convincing proof of alternation persisting into terpolymer systems in spite of constraints from electron-repulsion effects necessarily arising from limitations on the Δe values of individual binary monomer combinations.

Maximum Alternation in Binary Copolymers

Maximum alternation in binary copolymers may be calculated as follows:

$P_{12}P_{21}$ = mol fraction of 1,2-dyads in copolymer*

Maximum alternation occurs in a binary system at a monomer ratio which yields equimolar copolymers. Thus,

$$1 = \frac{m_1}{m_2} = \frac{r_1(M_1/M_2 + 1)}{r_2/(M_1/M_2) + 1} \tag{3}$$

whence

$$M_1/M_2 = \sqrt{r_2/r_1} \tag{4}$$

$$P_{12} = \frac{1}{1 + r_1x} \tag{5}$$

$$P_{21} = \frac{x}{r_2 + x} \tag{6}$$

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*P_{12} = the probability of M_2 adding to M_1 in 2-component systems, *except* that P_{12} = the probability of M_2 adding to M_1 in the presence of M_3 (3-component systems).

$$P_{12}P_{21} = \frac{x}{(1 + r_1x)(r_2 + x)}$$

$$= \frac{x}{r_2 + r_1r_2x + x + r_1x^2} \tag{7}$$

Since maximum alternation occurs at $x = \sqrt{r_2/r_1}$, it follows that

$$P_{12}P_{21}^{\text{MAX}} = \frac{1}{2\sqrt{r_1r_2} + r_1r_2 + 1} = \frac{1}{(\sqrt{r_1r_2} + 1)^2} \tag{8}$$

Comparison of maximum alternation in terpolymers with that of component binary copolymers is illustrative:

M_1	M_2	M_3	$P_{12}P_{23}P_{31}$	$P_{13}P_{32}P_{31}$	P_e
St	AN	MMA	0.0636	0.0710	0.0673

Binary	$P_{12}P_{21}^{\text{MAX}}$
St-AN	0.7859
St-MMA	0.451
AN-MMA	0.449

In the case of St-AN-MMA alternation as measured by P_e, 0.0673 is almost twice as high as for the random case (0.037). However, maximum alternation $P_{12}P_{21}^{\text{MAX}}$ in the component binary copolymer cases exceeds 0.44 in every case, varying from a high of 0.7859 for St ($e = -0.8$)-AN ($e = 1.23$) to 0.451 for St ($e = -0.8$)-MMA ($e = 0.40$) to 0.449 for AN ($e = 1.23$)-MMA ($e = 0.40$). Tabulating:

	Δe	Maximum alternation $P_{12}P_{21}^{\text{MAX}}$
St-AN	2.03	0.7859
St-MMA	1.20	0.451
AN-MMA	0.83	0.449

From Eqs. (1) and (3) [6], it is readily seen that

$$r_1r_2 = \exp\{-e_1^2 + 2e_1e_2 - e_2^2\} \tag{9}$$

$$= \exp\{-(e_1 - e_2)^2\} \tag{10}$$

$$P_{12}P_{12}^{\text{MAX}} = \frac{1}{2\sqrt{r_1r_2} + r_1r_2 + 1}$$

$$= \frac{1}{2/\exp(e_1 - e_2) + \exp\{-(e_1 - e_2)^2\} + 1} \tag{11}$$

Calculating maximum alternation backward for Δ*e*'s for St-AN-MMA:

	Δe	Calculated from Δ*e*'s: $P_{12}P_{21}^{\mathrm{MAX}}$	r_1r_2
St-AN	2.03	0.782	0.0164
St-MMA	1.20	0.544	0.239
AN-MMA	0.83	0.421	0.243

Agreement is good for St-AN, in the right direction for St-MMA, and moderately good for AN-MMA. Since r_1r_2 is seen as an inverse measure of alternation, a proper trend is noted.

Similar comparisons are made with St-AN-MAN:

M_1	M_2	M_3	$P_{12}P_{23}P_{31}$	$P_{13}P_{32}P_{21}$	P_e (from simplified equation)
St	AN	MAN	0.0622	0.0512	0.0567

Binary	From r_1r_2: $P_{12}P_{21}^{\mathrm{MAX}}$
St-AN	0.786
St-MAN	0.579
AN-MAN	0.270

Calculating maximum alternation $P_{12}P_{21}^{\mathrm{MAX}}$ backward from Δ*e*'s:

	Δe	Calculated from Δ*e*'s: $P_{12}P_{21}^{\mathrm{MAX}}$	r_1r_2
St-AN	2.03	0.782	0.0164
St-MAN	1.48	0.638	0.0988
AN-MAN	0.37	0.307	0.858

Agreement is moderately good between $P_{12}P_{21}^{\mathrm{MAX}}$ calculated from reactivity ratios and that calculated from *e* polarity values.

In the case of St-AN-MAN alternation as measured by P_e, 0.0567 is well above that of the random case (0.037). However, $P_{12}P_{21}^{\mathrm{MAX}}$ in the component binary copolymer cases exceeds 0.57 in two of three cases (large Δ*e*'s) and 0.25 in the case of AN-MAN where $\Delta e = 0.37$. A $P_{12}P_{21}^{\mathrm{MAX}}$ of 0.25 in a binary copolymer represents the random case.

The significant point is illustrated for terpolymers—that high alternation (at levels of over 0.10 mol fraction of individual monomer component in terpolymer, for example) is prevented by polarity constraints. If a high Δ*e* is obtained with two of the three-component binary systems, there will necessarily result a smaller Δ*e* for the third binary system, resulting in reduced alternation (frequently approaching the random case). In addition, there is a much greater opportunity for shuffling of components as triads are built up, so that heterotriads are reduced.

It is also significant that the average sequence length in terpolymers is generally smaller than in corresponding copolymers, a factor contributing to reduced heterotriad content [8].

APPENDIX

r_1r_2 as a Measure of Alternation

$P_{12}P_{21}$, the mol fraction of 1,2-dyads in a binary copolymer, is a precise measurement of alternation. As shown in Eq. (7):

$$P_{12}P_{21} = \frac{x}{r_2 + r_1r_2x + x + r_1x^2} \tag{7}$$

It was shown that

$$P_{12}P_{21}^{\mathrm{MAX}} = \frac{1}{2\sqrt{r_1r_2} + r_1r_2 + 1} \tag{8}$$

Thus, $P_{12}P_{21}^{\mathrm{MAX}}$ is an inverse function of r_1r_2. More generally, Eq. (7) shows that $P_{12}P_{21}$ is an inverse function of r_1 and r_2. Furthermore, it is a function of the mol ratio of monomers M_1/M_2.

To illustrate $P_{12}P_{21}^{\mathrm{MAX}}$ in the case of random equimolar copolymer ($r_1r_2 = 1$) equals 0.25. $P_{12}P_{21} = 2/9$ at $x = M_1/M_2 = 2$ and at $M_1/M_2 = 0.5$. At $r_1 = 2$ and $r_2 = 0.5$, equimolar copolymer $P_{12}P_{21}^{\mathrm{MAX}} = 0.25$. At $r_1 = 2$ and $r_2 = 0.5$ and $x = 2$,

$$P_{12}P_{21} = \frac{2}{0.5 + 2 + 2 + 2\cdot 2^2} = \frac{2}{12.5} = 0.16$$

At $r_1 = 2$ and $r_2 = 0.5$ and $x = 0.5$, $P_{12}P_{21} = 0.25$. At $r_1 = 2$ and $r_2 = 0.5$ and $x = 0.1$, $P_{12}P_{21} = 0.139$.

Another relationship of interest may be derived. At $x = 1$, Eq. (7) becomes:

$$P_{12}P_{21} = \frac{1}{r_2 + r_1r_2 + 1 + r_1} \tag{9}$$

To illustrate, at $r_1r_2 = 1$; $r_1 = 2$; $r_2 = 0.5$:

$$P_{12}P_{21} = \frac{1}{0.5 + 1 + 1 + 2} = 0.222$$

At $r_1r_2 = 1$; $r_1 = 0.5$; $r_2 = 2$:

$$P_{12}P_{21} = \frac{1}{2 + 1 + 1 + .5} = 0.222$$

In the random case ($r_1r_2 = 1$), $P_{12}P_{21}$ at $M_1/M_2 = 1$ becomes simply

$$\frac{1}{r_1 + r_2 + 2} \tag{10}$$

Since in this case $r_1 = 1/r_2$, $1/(r_1 + r_2 + 2)$ becomes effectively 1/4.

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