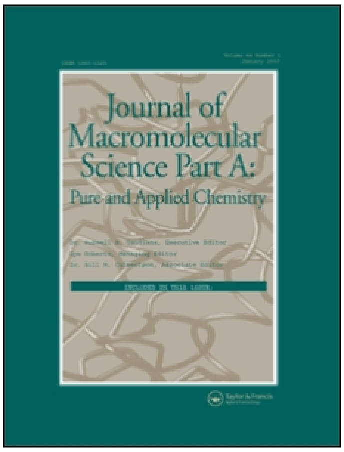

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TERPOLYMER RELATIONSHIPS AND AZEOTROPES

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ABSTRACT

In a 1983 paper in this *Journal* (*A19,* 693), Ham questioned the existence of ternary azeotropes. A recent paper by Quella [*Makromol. Chem., 190,* 1445 (1989)] has criticized the earlier thesis, in part on the basis that Ham's "indications have certainly not encouraged the search for ternary azeotropes," and on the basis of "further experimental results from other authors." This paper responds to Quella, further develops evidence against ternary azeotropes, and, in addition, discusses pertinent terpolymer interactions in terms of terpolymerization probabilities and in terms of general monomer reactivities.

INTRODUCTION

Interest in monomer-polymer relationships in terpolymers and terpolymer azeotropes as well as the associated binary systems (M_1/M_2, M_2/M_3, M_3/M_1) dates from the forties. The commercial interest in such materials—actual and potential—has always been a powerful driving force in such studies. In addition, theoretical interest in the field has always been substantial because of the intriguing questions raised about the constraints of monomer reactivity in such groups and the implications of sequence reversibility in terpolymers in devising simplified approaches to compositional equations, as well as to monomer reactivity.

Experience over the last 45 years has led to the delineation and sharpening of certain partially answered questions (generalizations?) about terpolymers, associated copolymers, and monomer reactivity. Some of these are as follows:

1. Does terpolymer azeotropy, in fact, exist?
2. Why is the heterosequence frequency ($-M_1 M_2 M_3 M_1-$, for example) in all terpolymers of high *Q*, high *e* monomers similar and of the same order as that expected for random addition ($P_{12}P_{23}P_{31} \approx 0.037$ for that derived from equal monomer proportions)?
3. Why is the heterosequence frequency ($-M_1 M_2 M_3 M_1-$, for example) in all terpolymers containing one high *Q* monomer and two low *Q* monomers similar and of about 1/6 the frequency expected for random addition (~ 0.006 at equal monomer proportions)?
4. Why is the heterosequence frequency ($-M_1 M_2 M_3 M_1-$, for example) in all terpolymers containing two high *Q* monomers and one low *Q* monomer similar and about 1/6 that expected for random addition (at equal monomer proportions)?
5. Why do Examples 3 and 4 yield similar results?
6. Why do combinations of three low *Q* monomers yield the same results as combinations of three high *Q*, high *e* monomers (Example 2)?
7. What is the significance of the increase in concentration of heterosequences in certain terpolymers (styrene-acrylonitrile-methyl methacrylate, for example)? Can it be validly used as a basis of determining general monomer reactivity of individual monomers in lieu of the *Q*-*e* scheme?
8. Is terpolymer sequence reversibility ($-M_1-M_2-M_3-M_1-$, for example) leading to $P_{12}P_{23}P_{31} = P_{13}P_{32}P_{21}$ absolute? If not, is there any special significance to the ratio $P_{12}P_{23}P_{31}/P_{13}P_{32}P_{21}$ or the dependent ratio (at equal monomer proportions)

$$r_{13}r_{32}r_{21}/r_{12}r_{23}r_{31}?$$

9. Are binary reactivity ratios better determined in terpolymer systems for use in terpolymer or in binary systems? *or* Do binary reactivity ratios, particularly those allowing for penultimate unit effects determined in binary systems, adequately describe terpolymer systems?

10. What is the best way to assess reactivity ratios unique to terpolymer systems: k^{122}/k^{123}, k^{121}/k^{123} or k^{322}/k^{321}, k^{323}/k^{321} or k^{133}/k^{132}, k^{131}/k^{132} or k^{233}/k^{231}, k^{232}/k^{231} or k^{311}/k^{312}, k^{313}/k^{312} or k^{211}/k^{213}, k^{212}/k^{213}?
11. Alternating tendency in terpolymers appears to be best assessed by determining values of $P_{12}P_{23}P_{31}$ and/or $P_{13}P_{32}P_{21}$. Values of more than $(1/3)^3 = 0.0370$ (for equimolar monomer mixtures) indicate a tendency toward alternation. Higher values indicate increasing alternation, with a theoretical limiting value of 1 for perfect alternation. Values of less than 0.037 would, of course, indicate a tendency toward blockiness.

    Why do wide variations in initial monomer content lead to relatively little change in the values of $P_{12}P_{23}P_{31}$ or $P_{13}P_{32}P_{21}$, the sum of the probabilities of finding $\sim M_1 M_2 M_3 \sim$, $\sim M_2 M_3 M_1 \sim$, and $\sim M_2 M_1 M_3 \sim$ sequences.

Maximum alternation results from selecting monomer proportions that generate equimolar terpolymers. Presumably, effects due to resonance stabilization (*Q*) are suppressed and those due to polarity (*e*) are emphasized under these circumstances. Can polarity (*e*) or some other measure of monomer reactivity be better assessed under these circumstances?

DISCUSSION

Given the overview outlined above, we may now discuss the specific questions presented above in more detail.

1. Does terpolymer azeotropy, in fact, exist? Since Tarasov's landmark paper [3] on the calculation of terpolymer azeotropes, it has been taken as a given that terpolymer azeotropes exist and could be unequivocally calculated from a knowledge of the six binary reactivity ratios concerned. Ham's 1967 paper [1] called into question the applicability of Tarasov's calculations and, indeed, showed that for the large class of monomers which obey the *Q*-*e* scheme, terpolymer azeotropy was impossible.* It was further questioned whether terpolymer azeotropy exists at all.

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*This statement was undoubtedly conservative. By now, the preponderance of known monomers has been studied in copolymerization, and *Q* and *e* values have been calculated from experimentally determined reactivity ratios with at

Thus, for monomers i and j obeying the Q-e scheme:

$$r_{ij} = Q_i Q_j \exp[-e_i(e_i - e_j)] \tag{1a}$$

$$r_{ji} = Q_j Q_i \exp[-e_j(e_j - e_i)] \tag{1b}$$

It follows that for systems of three monomers, for which all binary reactivity ratios are known,

$$r_{12}r_{23}r_{31} = r_{13}r_{32}r_{21} \tag{2}$$

However, Tarasov's equations *only* hold if

$$r_{12}r_{23}r_{31} \neq r_{13}r_{32}r_{21} \tag{3}$$

Moreover, Ham showed that when Eq. (2) holds, simplified terpolymer composition equations may be calculated. From these it was shown that terpolymer azeotropy was impossible [1, 2].

Notwithstanding the above, several papers have appeared, claiming the existence of terpolymer azeotropes [3-6]. Certain of these claims [3, 4] have been questioned in a new paper [7] and comments offered on the others [5, 6].

Quella [8] recently questioned my assertions about terpolymer azeotropes. His paper will be answered at length elsewhere [20]. However, Quella cites Tomescu's [9] "experimental proof" of a ternary azeotrope of acrylonitrile-butyl acrylate-vinylidene chloride by using reactivity ratios of $r_{12} = 1.003$, $r_{21} = 1.005$, $r_{13} = 0.91$, $r_{31} = 0.37$, $r_{23} = 0.83$, $r_{32} = 0.85$. The reported Tomescu azeotrope occurred at $M_1 = 84.48$, $M_2 = 13.83$, $M_3 = 1.72\%$ molar and led to an initial copolymer of $m_1 = 84.48$, $m_2 = 13.65$, $m_3 = 1.87\%$ molar—arguably not an exact azeotrope.

It should also be pointed out that in the above example, acrylonitrile and butyl acrylate are treated as having almost identical reactivities ($r_{12} = 1.003$, $r_{21} = 1.005$). In that case, the "terpolymer azeotrope" may be regarded as a "pseudobinary azeotrope" with randomly dispersed acrylonitrile and butyl acrylate units (in proportion to acrylonitrile-butyl

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least two other monomers possessing known Q and e values. The reports of Q and e values may be taken as *prima facie* evidence that the investigators believe the monomers obey the Q,e scheme.

acrylate–vinylidene chloride composition outside vinylidene chloride regions). Thus, the reported terpolymer azeotrope must be regarded as of a very special sort. This example calls to mind the Ring [5] terpolymer azeotrope of methyl methacrylate–glycidyl methacrylate–styrene in which $r_{12} \simeq r_{21} \simeq 1$. Similar comments can be made about that system.

Quella further asserts that "(Ham's) indications have certainly not encouraged the search for ternary azeotropes."

I must respond that my purpose was merely to comment on the prospects for finding such azeotropes, and was not intended to discourage work in the field. In fact, I suggested that the search for partial or "near" azeotropes would be a more fertile area for study [1].

2. Why is the heterosequence frequency ($-M_1\,M_2\,M_3\,M_1-$, for example,) in all terpolymers of high Q, high e monomers similar and of the same order as that expected for random addition ($P_{12}P_{23}P_{31} \simeq 0.037$ for that derived from equal monomer proportions)?

This thesis and supporting data and calculations were detailed in two papers [10, 11]. Frank Mayo gave an exhaustive criticism of the thesis [12], questioning the universality of the conclusions drawn; however, O'Driscoll [13], in turn, "criticized" the criticism, pointing out that errors in reported values of reactivity ratios did not rule out the possible validity of the thesis. Indeed, Mayo's selected data supported my thesis, according to O'Driscoll.

In the intervening years no telling refutation of the arguments originally presented has appeared. Simplified compositional equations for terpolymer and higher multipolymer calculations grew out of the thesis [14] and predict very satisfactorily terpolymer and multipolymer compositions realized.

Sequence reversibility also has in its favor the possibility of unequivocal assessment of terpolymer sequences (by calculation or analysis), without having to define them as directional or vector quantities (for example, $M_1M_2M_3M_1$ and $M_1M_2M_3M_1$) arising from how the sequences were originally formed. The advantage is obvious.

3. The subject of ternary combinations of one high Q monomer and two low Q monomers and the effect on values of $P_{12}P_{23}P_{31}$ and $P_{13}P_{32}P_{21}$ has been treated [15]. The results have significance not only for terpolymerization but also for assessing the interdependence of the component binary systems and implications for assessing general reactivity of individual monomers. It has been noted that

$$P_{12}P_{23}P_{31} \simeq P_{13}P_{32}P_{21} \simeq 0.006 \qquad (4)$$

compared to a value of $(1/3)^3 \simeq 0.037$ for strictly random addition of equimolar monomers (approximately observed for three high Q monomers).

4. The related subject of ternary combinations of two high Q monomers and one low Q monomer was also treated [15], with results similar to those obtained in 3 above.

It was further suggested that a monomer reactivity parameter p reflecting the lower reactivity of unconjugated monomers might be calculated from the relation

$$p_1 p_2 p_3 = P_{12}P_{23}P_{31} \simeq P_{13}P_{32}P_{21} \simeq 0.006 \qquad (5)$$

when p_1 = reactivity of unconjugated monomer 1
p_2 = reactivity of conjugated monomer 2
p_3 = reactivity of conjugated monomer 3

The suggestion has elicited little response in the literature except for the early papers by O'Driscoll and Mayo noted previously.

5. Examples 3 and 4 give equivalent results ($\mathbf{P} \simeq 0.006$), presumably because they represent equivalent bridging conditions between three conjugated monomers ($\mathbf{P} \simeq 0.0037$) and three unconjugated monomers ($\mathbf{P} \simeq 0.037$).

6. Individual combination of three conjugated monomers and three unconjugated monomers give similar results with respect to values of $P_{12}P_{23}P_{31}$ and $P_{13}P_{32}P_{21}$ [15]. In a very general way the conclusions may be drawn that conjugated monomers as a group exhibit similar reactivity and interact in an internally consistent manner, that unconjugated monomers as a group exhibit similar reactivity and interact in an internally consistent manner, and that the reactivity of unconjugated monomers is approximately 1/10 that of conjugated monomers. The constraints of interreactivity within each group lead to similar values of ($\mathbf{P} \simeq 0.037$).

7. Attempts have been made to relate the observed increase in heterosequences ($M_1M_2M_3M_1$, for example) in terpolymers to a general reactivity parameter characteristic of individual monomers [15]. Since terpolymer behavior can be characterized and predicted by the component binary reactivity ratios, actual terpolymer experiments are not usually required. Thus it appears that

$$p_1 p_2 p_3 = P_{12}P_{23}P_{31} \simeq P_{13}P_{32}P_{21} = \mathbf{P} \qquad (6)$$

where p_1, p_2, p_3 are characteristic reactivity parameters for individual monomers; P_{12}, P_{23}, P_{31}, P_{13}, P_{32}, P_{21} are the probabilities associated with the addition of individual monomers in the presence of the other two monomers (these may be calculated from reactivity ratios and monomer feed composition) and **P** is an experimentally determined constant.

For convenience, **P** is usually determined at equimolar ratios of monomers. Thus, values larger than $0.037[(1/3)^3]$ are taken as evidence of alternating behavior. The tendency toward alternation is correspondingly a function of heterosequence concentration and is related to $P_{12}P_{23}P_{31}$ and $P_{13}P_{32}P_{21}$ at equimolar monomer concentrations.

It is readily shown that p_1, p_2, p_3 can be determined from a knowledge of all binary reactivity ratios in any group of four monomers [15].

8. Frank Mayo has questioned the principle of sequence reversibility in terpolymerization (see #2 above; also Ref. 12). However, he suggests that the dependent relationship $r_{12}r_{23}r_{31} = r_{13}r_{32}r_{21}$, if not correct, may offer valuable insights recast in the form

$$r_{12}r_{23}r_{31}/r_{13}r_{32}r_{21} = H \tag{7}$$

H in the case of wholly conjugated monomers approaches 1, but in systems including unconjugated monomers, such as vinylidene chloride, using his data selections, departure from unity was regarded as significant (note, however, Ref. 13). My interpretation, however, is that these results may be due to incorrect reactivity ratios, arising from difficulty in assessing very high or very low values or from too low molecular weight copolymers which have not attained statistical equilibrium of composition.

9. The question has been raised as to whether binary reactivity ratios might be better determined in terpolymer systems for use in terpolymer or in binary systems [8, 10]. My original suggestion of this possibility in 1963 was greeted with skepticism by Mayo [12]. However, recent results by Hagiopol et al. [16] seem to confirm the likelihood of advantages through terpolymer determination.

Much of the difficulty in accounting for terpolymer results may lie in the fact that penultimate unit effects may play an important role. Even when they are taken into account in the binary reactivity ratios, the terpolymer results may still not be completely accounted for due to the heterogeneous additions [17].

$\sim M_2M_1 + M_3 \rightarrow \sim M_2M_1M_3$
$\sim M_3M_1 + M_2 \rightarrow \sim M_3M_1M_2$
$\sim M_1M_2 + M_3 \rightarrow \sim M_1M_2M_3$
$\sim M_3M_2 + M_1 \rightarrow \sim M_3M_2M_1$
$\sim M_1M_3 + M_2 \rightarrow \sim M_1M_3M_2$
$\sim M_2M_3 + M_1 \rightarrow \sim M_2M_3M_1$

Thus, six propagation possibilities out of a total of 27 in terpolymerization with penultimate unit effects involve heterogeneous additions not encountered in binary copolymerization and, accordingly, are not accessible by binary reactivity ratios alone—hence, the fallacy in using only binary reactivity ratios in terpolymerization assessments. That such assessment succeeds at all is due to the fact that the most important effects can usually be assessed by use of the binary reactivity ratios [17].

Another factor of some importance is the practical fact that certain binary combinations of monomers may copolymerize only with difficulty, or not at all, at certain monomer ratios. The addition of a third monomer may result in terpolymerization and the possibility of assessing reactivity ratios [17], hence my early suggestion [10].

10. What is the best way to assess reactivity ratios unique to terpolymer systems (such as k^{122}/k^{123})? Model experiments such as those pioneered by Prementine and Tirrell [18] for binary systems might be instructive. Terpolymerization experiments in the middle range (m_1, m_2, m_3 = 0.25-0.40m) should yield the desired information for determining heterogeneous reactivity ratios.

11. Why do relatively wide variations in initial monomer content lead to relatively little change in the values of $P_{12}P_{23}P_{31}$ or $P_{13}P_{32}P_{21}$? These effects are yet to be quantified in a precise and general way. However, it does appear that terpolymer probability products are relatively insensitive to such changes. In a general way it appears that an increase in the rate of initiation of such sequences leads to an increase in rate of their termination. Thus, the sequences involved are

① $\sim M_1M_2M_3M_1\sim$ ② $\sim M_1M_3M_2M_1\sim$
③ $\sim M_2M_3M_1M_2\sim$ ④ $\sim M_2M_1M_3M_2\sim$
⑤ $\sim M_3M_1M_2M_3\sim$ ⑥ $\sim M_3M_2M_1M_3\sim$

Sequences of ① and ② presumably are favored at higher levels of M_1, ③ and ④ at higher levels of M_2 and ⑤ and ⑥ at higher levels of M_3. Of course, these are the same conditions that suppress heterogeneous addition. Such effects should tend to suppress changes in $P_{12}P_{23}P_{31}$ or $P_{13}P_{32}P_{21}$ as a function of composition. Some drift *does* occur. This could occur in a manner consistent with "sequence reversibility" or "equality of reversed sequences," if concentration of sequences ① and ②, ③ and ④, and ⑤ and ⑥ are equal. Of course, relative concentrations of individual pairs could and probably do vary.

Notwithstanding the above, alternation and heterosequence concentration will be maximized at equimolar concentrations of monomer components in terpolymers. Furthermore, certain monomers such as methyl methacrylate and styrene contribute more highly to alternation (and heterosequence concentration) in terpolymers than others. Therein lies a basis for assessing general monomer reactivity distinct from the *Q*–*e* scheme. Thus, one distinctive parameter may be assigned in this treatment [15] for each monomer.

Alternatively, monomer concentrations required to produce equimolar terpolymers are calculated [19] for four sets of interconnecting terpolymers. For example, terpolymers based on styrene, methyl methacrylate, acrylonitrile, and vinylidene chloride may be assessed in this way. The corresponding probability products $P_{12}P_{23}P_{31}$ and $P_{13}P_{32}P_{21}$ are then calculated from

$$\left(\frac{\mathrm{B}r_{13}}{\mathrm{B}r_{13} + \mathrm{A}r_{12}r_{13} + \mathrm{C}r_{12}}\right)\left(\frac{\mathrm{C}r_{21}}{\mathrm{C}r_{21} + \mathrm{B}r_{23}\mathrm{r}_{21} + \mathrm{A}r_{23}}\right)\left(\frac{\mathrm{A}r_{32}}{\mathrm{A}r_{32} + \mathrm{C}r_{31}r_{32} + \mathrm{B}r_{31}}\right)$$

$$\simeq \left(\frac{\mathrm{C}r_{12}}{\mathrm{C}r_{12} + \mathrm{A}r_{13}r_{12} + \mathrm{B}r_{13}}\right)\left(\frac{\mathrm{B}r_{31}}{\mathrm{B}r_{31} + \mathrm{C}r_{31}r_{32} + \mathrm{A}r_{32}}\right)\left(\frac{\mathrm{A}r_{23}}{\mathrm{A}r_{23} + \mathrm{B}r_{21}r_{23} + \mathrm{C}r_{21}}\right)$$

Individual general reactivity parameters may then be assessed from the relationship [15]

$$p_1p_2p_3 = P_{12}P_{23}P_{31} \simeq P_{13}P_{32}P_{21}$$

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