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Graphical Representation of Terpolymerization Systems

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ABSTRACT

As a modification and improvement of Slocombe's and O'Driscoll's terpolymerization patterns, a new graphical representation of terpolymer systems has been proposed. The suggested patterns retain all the information necessary to describe ternary systems, including also those related to their azeotropic behavior. The main advantage of the proposed representation is its similarity to the accustomed binary representation: the sides of the composition triangles depict the behavior of the corresponding binary systems.

INTRODUCTION

Terpolymerization systems have growing practical importance. They are informative from the theoretical point of view too: the reactivity relations derived from binary copolymerization systems can be controlled and improved with the aid of terpolymerization data.

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The treatment of data on terpolymerization systems, on the other hand, is not a simple task, and, what is more, a sufficiently informative graphical representation of ternary systems is not yet known. The cause of the latter becomes clear when we compare the dimensions required for characterization of binary and ternary systems, respectively.

The most direct representation of a binary system [1, 2] is the usual plot of polymer composition (e.g., as mole fraction of monomer unit 1 (m_1) in the copolymer) as a function of the mole fraction of monomer 1 (M_1) in the initial monomer mixture:

$$p_1 = f(m_1) \tag{1}$$

where

$$m_1 = [M_1]/([M_1] + [M_2])$$

$$p_1 = d[M_1]/(d[M_1] + d[M_2])$$

This well known kind of representation is shown in Fig. 1. As an example, we chose the binary system of styrene (M_1) and diethyl

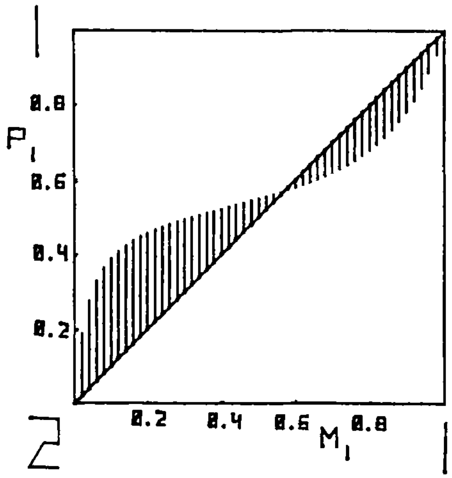

FIG. 1. Composition diagram of the binary system styrene (1)-diethyl fumarate (2). Reactivity ratios $r_{12} = 0.3$, $r_{21} = 0.07$. (Data from Ham [1], Appendix A, ref. 170).

fumarate (M_2). The reactivity ratios were taken from the literature [1]. The diagonal in Fig. 1 represents polymer composition exactly equal to monomer feed (azeotropic copolymerization), i.e., the lines connecting the diagonal with the actual polymer compositions are measures of deviation from azeotropy.

In a terpolymerization system [1-3], the monomer composition can be sufficiently characterized by two parameters, say, m_1 and m_2 ($m_3 = 1 - m_1 - m_2$). Analogously, the characterization of the terpolymer composition also needs two parameters, p_1 and p_2 ($p_3 = 1 - p_1 - p_2$). The representation of this system is clearly a four-dimensional one:

$$(p_1, p_2) = f(m_1, m_2) \tag{2}$$

where

$$m_1 = [M_1]/([M_1] + [M_2] + [M_3]) \tag{2}$$

$$p_1 = d[M_1]/(d[M_1] + d[M_2] + d[M_3])$$

Two-dimensional projection of this, a seemingly straightforward procedure, results in sophisticated and hardly understandable diagrams. Therefore some other way must be chosen. Slocombe [2] proposed a vectorial representation: in a triangular diagram, commonly used for three-component systems, the Slocombe vectors are determined by the monomer composition and the corresponding terpolymer composition, the starting and ending points of the vectors, respectively. The monomer points are usually taken at equal increments of monomer mole fractions, mostly at 0.1 units.

In the usual equilateral triangle the Cartesian coordinates of the monomer point $M(m_1,m_2)$ are given by

$$x_m = 1 - (m_1/2) - m_2$$

$$y_m = (\sqrt{3}/2)\, m_1 \tag{3}$$

presuming that the binary side [2, 3] lies in the x-axis with 2 (i.e., with $m_1 = m_3 = 0$) at the origin. From the terpolymer composition, known experimentally or calculated by the terpolymerization equation [3], the coordinates of the polymer point $P(p_1,p_2)$ in the above equilateral triangle are given analogously by

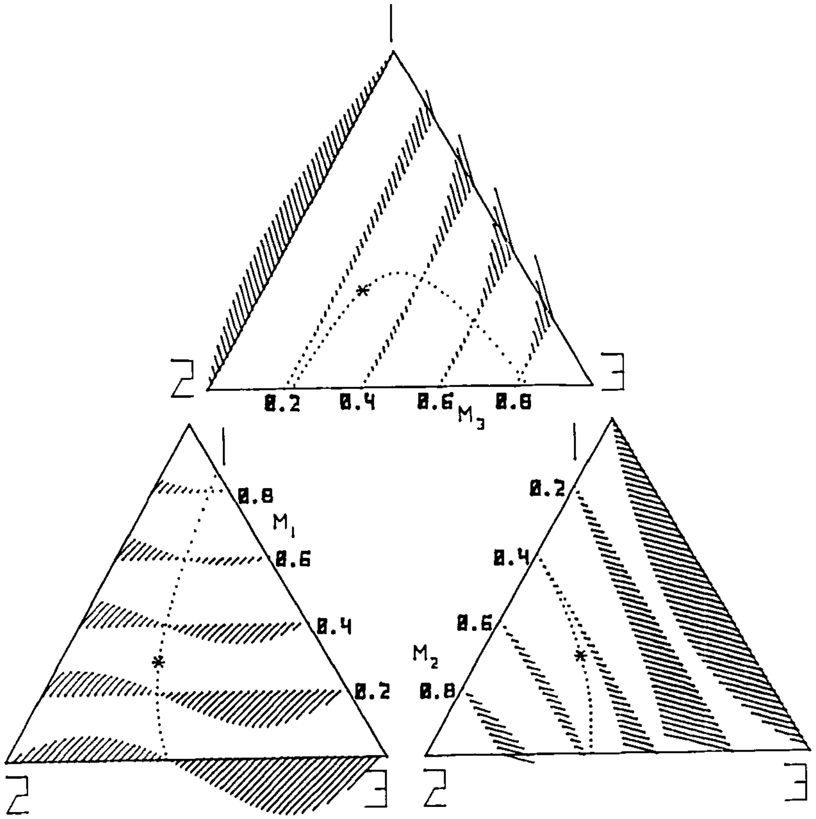

FIG. 2. The proposed representation of the system 1,3-butadiene (1)-styrene (2)-diethyl fumarate (3). Dotted lines denote loci of partial azeotropy. The asterisk shows the composition of the ternary azeotrope. Reactivity ratios $r_{12} = 1.4$, $r_{21} = 0.5$, $r_{23} = 0.3$, $r_{32} = 0.07$, $r_{31} = 0.25$, $r_{13} = 2.13$, are taken from Wittmer et al. [5]. For comparison with the Slocombe version see Fig. 7 of Wittmer [5].

$$x_p = 1 - (p_1/2) - p_2$$

$$y_p = (\sqrt{3}/2)\, p_1 \qquad (4)$$

The vector defined by Slocombe connects these points, i.e., it is a vector starting from M and ending in P.

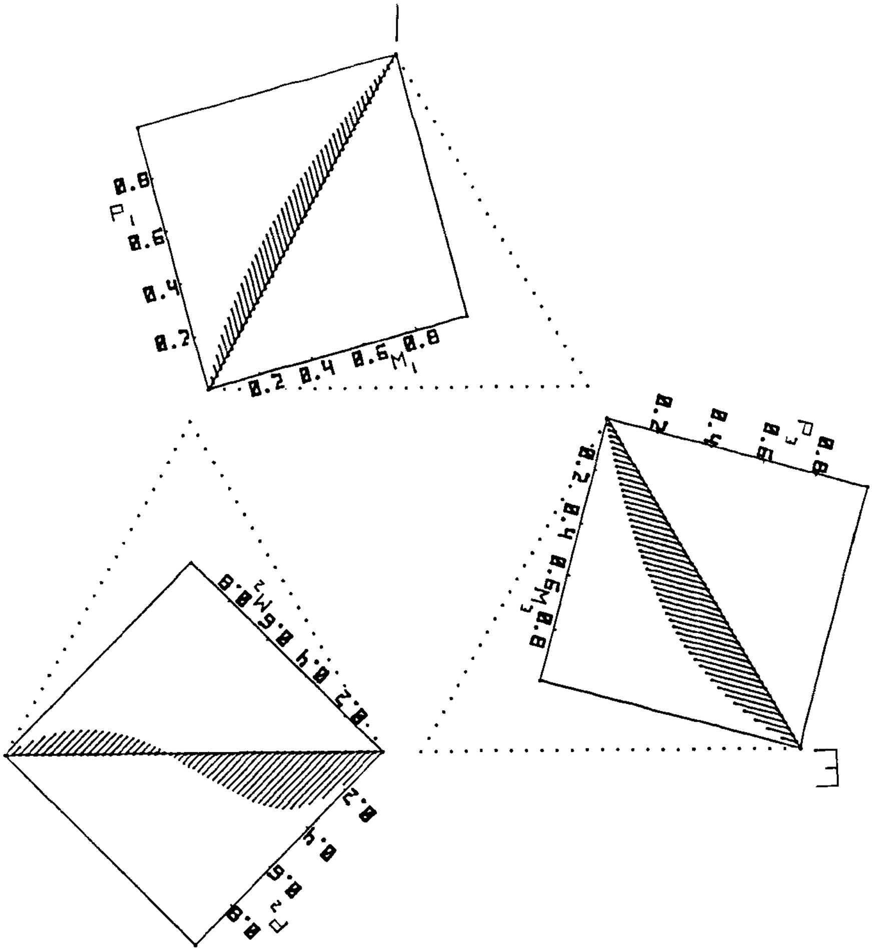

FIG. 3. Relation of the conventional representation of binary systems to the proposed terpolymerization plot (see also Figs. 1 and 2).

It is clear that the Slocombe vectors retain all the information given by m_1, m_2, p_1, and p_2. Unfortunately, however, in the limiting binary cases, i.e., if the mole fraction of one of the components in the monomer mixture is equal to zero, all the vectors lie in the corresponding side of the composition triangle, not showing the behavior of these two-component partial systems, especially not in the accustomed manner as shown in Fig. 1.

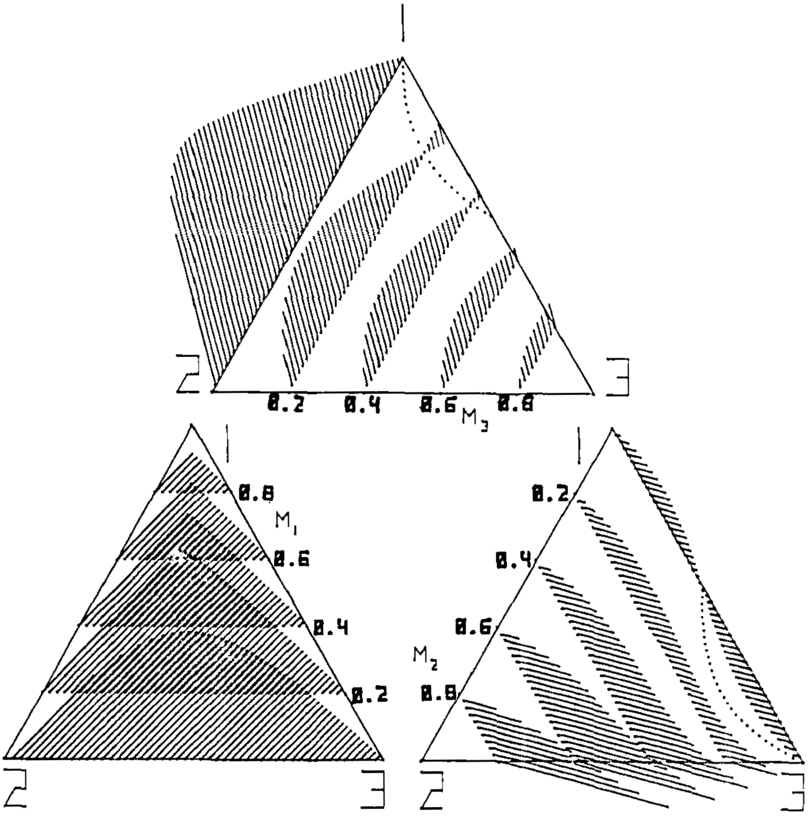

FIG. 4. System styrene (1)-vinyl acetate (2)-methyl methacrylate (3). Reactivity ratios $r_{12} = 55$, $r_{21} = 0.01$, $r_{23} = 0.015$, $r_{32} = 20$, $r_{31} = 0.46$, $r_{13} = 0.52$ are taken from Ham [1], Appendix A, refs. 170 and 195.

Another solution of the problem has been proposed by O'Driscoll [4], who constructs triangular contour maps, one for each of the three components. Contour lines in these triangles represent constant mole fractions of the corresponding components in the terpolymer.

The patterns of O'Driscoll have the advantage of giving information separately on the individual polymer components but also they are uninformative in respect of the composing binary systems.

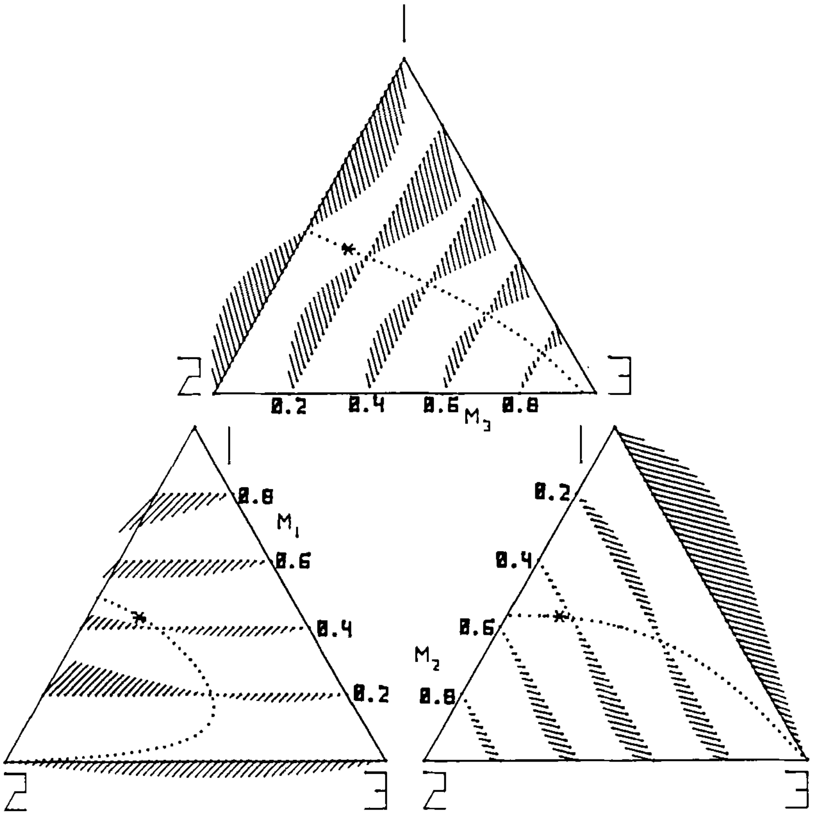

FIG. 5. System vinyl isocyanate (1)-acrylonitrile (2)-methyl acrylate (3). Reactivity ratios $r_{12} = 0.16$, $r_{21} = 0.19$, $r_{23} = 1.26$; $r_{32} = 0.67$, $r_{31} = 1.38$, $r_{13} = 0.14$ are taken from Ham [1], Appendix A, refs. 24 and 137.

THE PROPOSED REPRESENTATION

The deficiencies of the above representations can be overcome by their combination and improvement. On the one hand, we propose to maintain the separate triangles of O'Driscoll for each of the monomers but without drawing the contour lines. Instead of this, on the other hand, we propose, as a modification of Slocombe's idea, to draw the individual components of the deviation vectors instead of their resultant, i.e., instead of the Slocombe vectors. Another

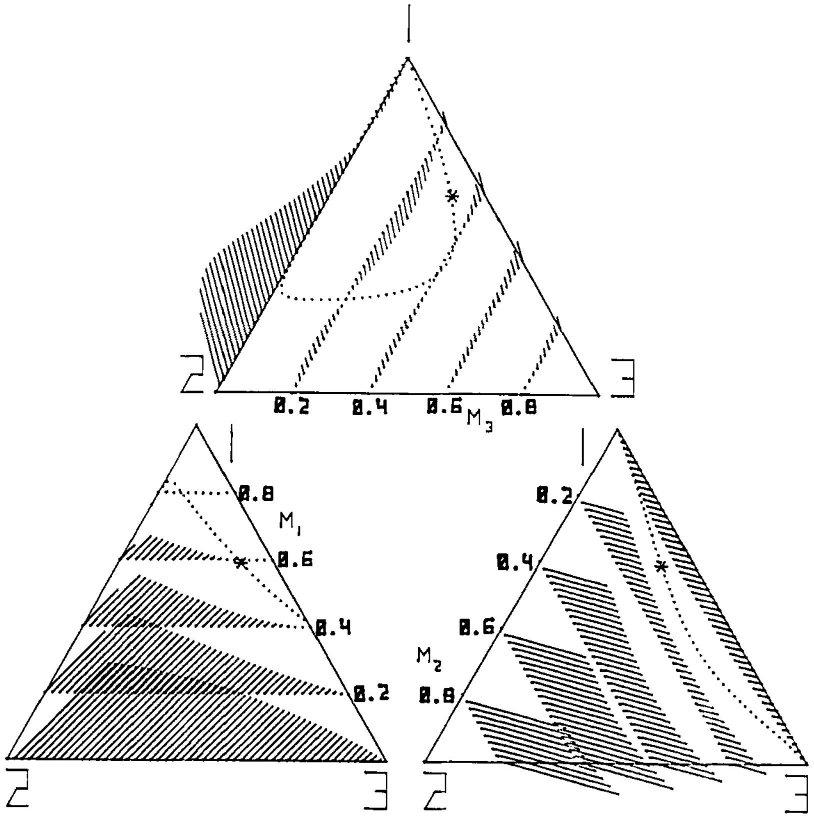

FIG. 6. System acrylonitrile (1)-ethyl vinyl ether (2)-methyl acrylate (3). Reactivity ratios $r_{12} = 0.7$, $r_{21} = 0.03$, $r_{23} = 0.0001$, $r_{32} = 3.3$, $r_{31} = 0.84$, $r_{13} = 1.5$ are taken from Wittmer [5].

alteration accomplished by us relates to the direction and length of the vectors to be drawn: in order to achieve full resemblance to the usual binary diagrams we propose to direct the vectors at an angle of 45° to the corresponding side of the triangle and to divide their length by $\sqrt{2}$.

These alterations have been made because in our proposed representation the sides of the triangle take over the role of the diagonal of the corresponding binary diagrams. As it can be seen from Fig. 1, the deviation vectors incline at 45 degrees to the diagonal. On the other hand, if in such a binary diagram the diagonal is of unit length,

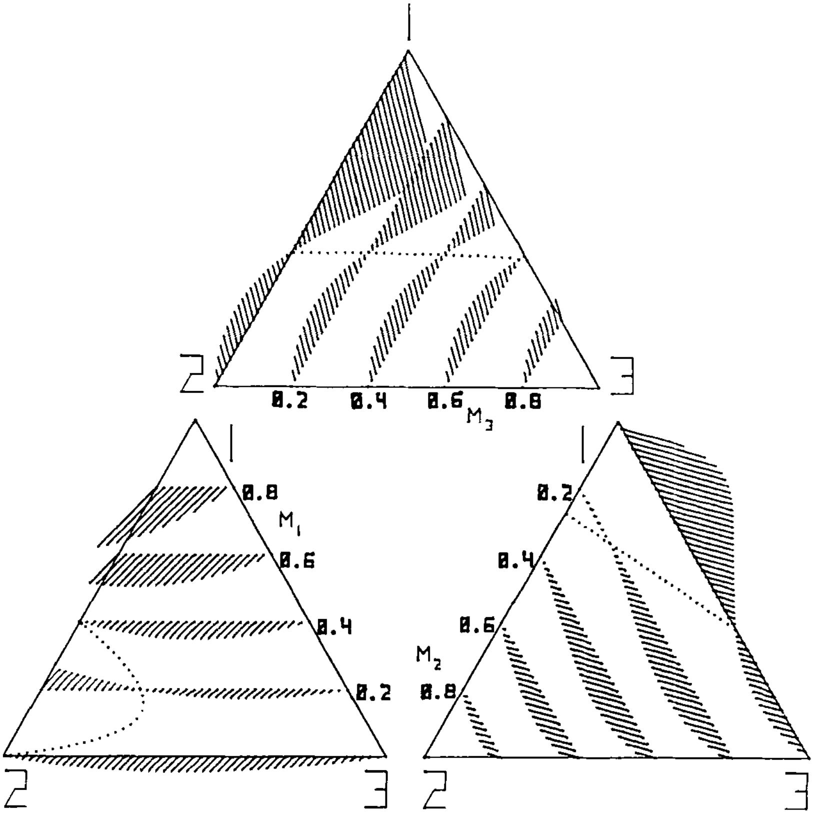

FIG. 7. System acrylonitrile (1)-1,3-butadiene (2)-styrene (3). Reactivity ratios $r_{12} = 0.02$, $r_{21} = 0.35$, $r_{23} = 1.39$, $r_{32} = 0.78$, $r_{31} = 0.41$, $r_{13} = 0.04$ are taken from Ring [6], where a Slocombe diagram of the system is also given (Fig. 2).

the sides and the deviation vectors parallel to them are measured in $1/\sqrt{2}$ units. This way, we draw deviation vectors, the length of which are, as follows:

$$\begin{aligned} D_1 &= (p_1 - m_1)/\sqrt{2} \\ D_2 &= (p_2 - m_2)/\sqrt{2} \qquad (5) \\ D_3 &= (p_3 - m_3)/\sqrt{2} \end{aligned}$$

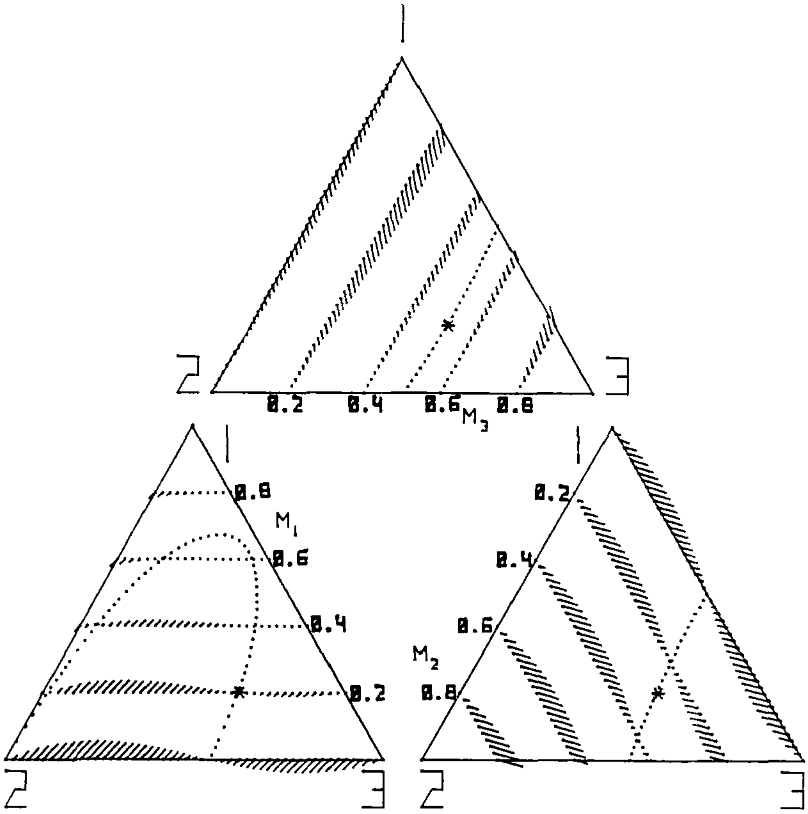

FIG. 8. System methyl methacrylate (1)-glycidyl methacrylate (2)-styrene (3). Reactivity ratios $r_{12} = 0.8$, $r_{21} = 1.05$, $r_{23} = 0.44$, $r_{32} = 0.53$, $r_{31} = 0.5$, $r_{13} = 0.5$ are taken from Ring [6], where the Slocombe diagram of this system is also given (Fig. 3).

With the transformations proposed above, the monomer points M, i.e., the starting points of the vectors, remain unchanged, but the ending points will have the following Cartesian coordinates:

For component 1 in the terpolymer (upper triangle):

$$\begin{aligned} x &= x_m - D_1 \cos 75^\circ \\ y &= y_m + D_1 \sin 75^\circ \end{aligned} \tag{6}$$

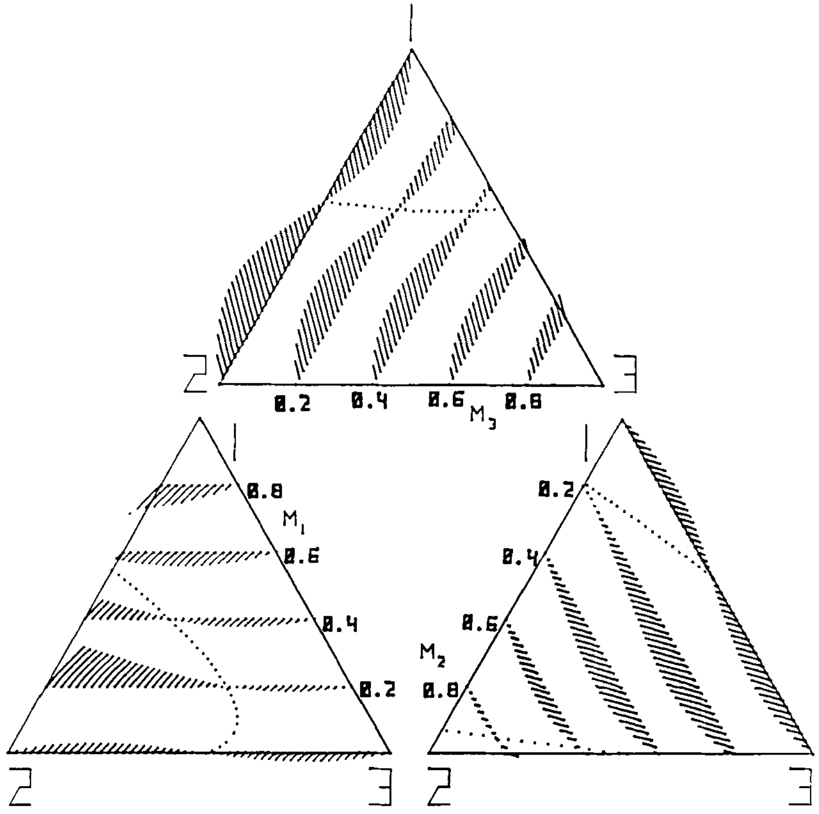

FIG. 9. System styrene (1)-methacrylonitrile (2)-methyl methacrylate (3). Reactivity ratios $r_{12} = 0.3$, $r_{21} = 0.16$, $r_{23} = 0.65$, $r_{32} \approx 0.67$, $r_{31} = 0.46$, $r_{13} = 0.52$ are taken from Ham [1], Appendix A, refs. 170 and 171.

For component 2 (lower left triangle):

$$x = x_m - D_2 \cos 45^\circ$$
$$y = y_m - D_2 \sin 45^\circ \qquad (7)$$

For component 3 (lower right triangle):

$$x = x_m + D_3 \cos 15^\circ$$
$$y = y_m - D_3 \sin 15^\circ \qquad (8)$$

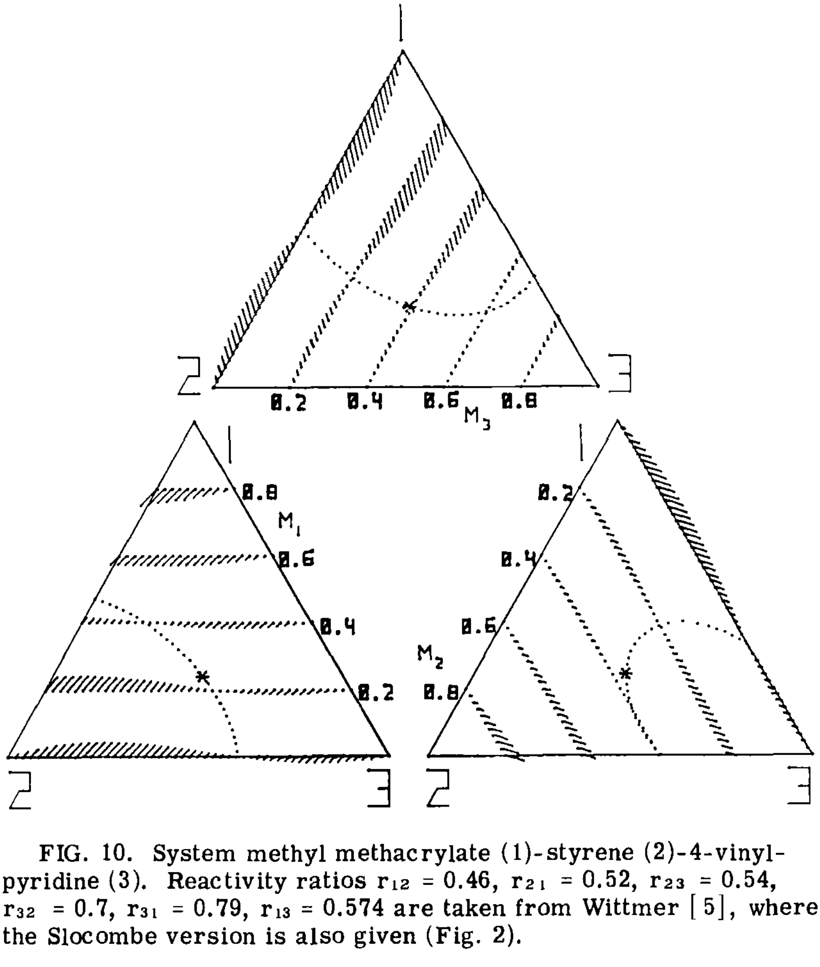

FIG. 10. System methyl methacrylate (1)-styrene (2)-4-vinylpyridine (3). Reactivity ratios r_{12} = 0.46, r_{21} = 0.52, r_{23} = 0.54, r_{32} = 0.7, r_{31} = 0.79, r_{13} = 0.574 are taken from Wittmer [5], where the Slocombe version is also given (Fig. 2).

where x_m and y_m are the coordinates of the monomer point M according to Eq. (3).

A ternary system consisting of 1,3-butadiene as monomer 1, styrene as monomer 2, and diethyl fumarate as monomer 3 is represented with the application of the above transformations in Fig. 2. (Reactivity ratios for the monomer pairs have been taken from Wittmer et al. [5]). The starting points of the deviation vectors are unambiguously indicated as a result of the regular arrangement (in this and later figures the monomer points are taken at 0.2 and 0.02 increments of monomer mole fractions, respectively). We will return later to the explanation of the additional dotted curves shown in Fig. 2.

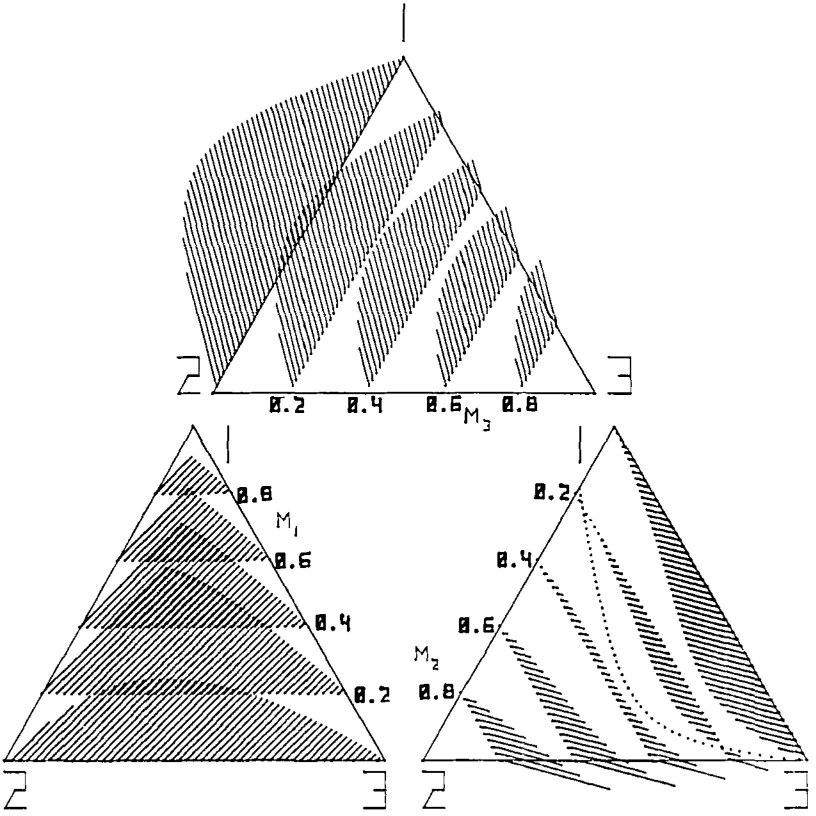

FIG. 11. System methyl methacrylate (1)-vinyl acetate (2)-acrylonitrile (3). Reactivity ratios $r_{12} = 20$, $r_{21} = 0.015$, $r_{23} = 0.061$, $r_{32} = 4.05$, $r_{31} = 0.15$, $r_{13} = 1.20$ are taken from Ham [1], Appendix A, refs. 169 and 195.

As it is apparent from Fig. 2, the suggested modification provides the same picture for the limiting binary cases as is usual in the copolymerization literature. For example, side (3,2) of the lower left triangle corresponds exactly to the diagonal of the usual binary representation shown in Fig. 1. For the sake of better visualization, in Fig. 3 we constructed a combined diagram showing the binary parts of the ternary system of Fig. 2.

In the case of "true azeotropy" all the monomer mole fractions are equal to the corresponding mole fractions in the polymer, i.e., each of the deviation vectors disappear. If only one of the mole fractions agrees in the monomer mixture and in the polymer (i.e., on the

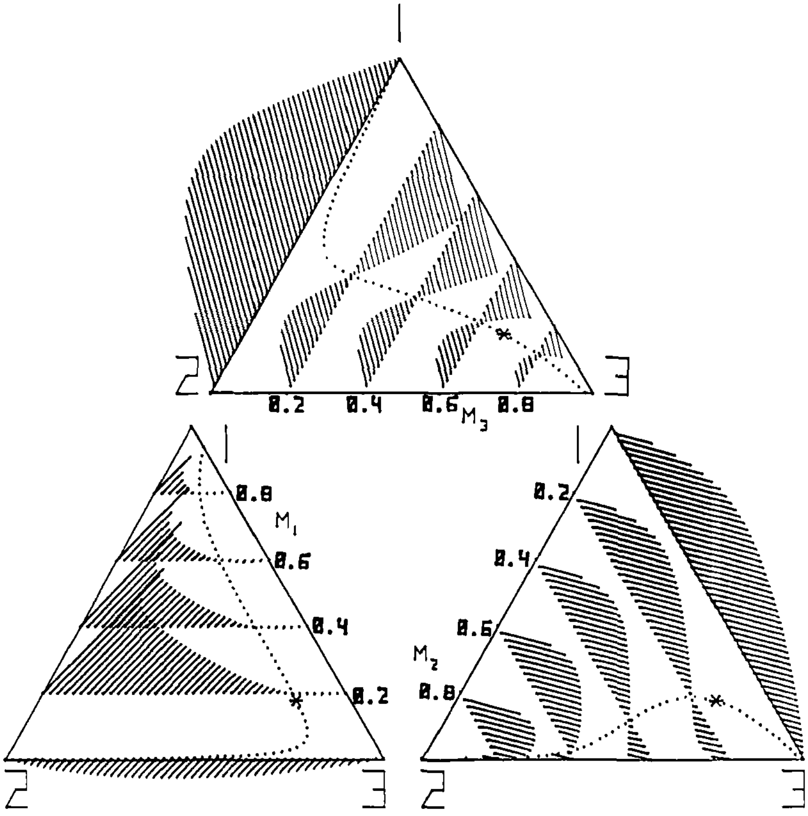

FIG. 12. System 2-vinylpyridine (1)-acrylonitrile (2)-butyl acrylate (3). Reactivity ratios $r_{12} = 21.9$, $r_{21} = 0.05$, $r_{23} = 1.52$, $r_{32} = 0.75$, $r_{31} = 2.51$, $r_{13} = 0.097$ are taken from Ham [1], Appendix A, refs. 141, 160, and 294.

sides of the diagram and in the points corresponding to a "partial azeotropy"), only the corresponding deviation vector disappears. For example, the line connecting the points where $p_2 = m_2$ represents the partial azeotropic line for monomer 2 and is depicted as a dotted curve in the lower left triangle of Fig. 2. In terpolymerization systems, the lines of partial azeotropy (and their occasional intersection point, the ternary azeotrope) have primary importance. Therefore, we suggest, as a further modification of the Slocombe-O'Driscoll-diagram, the indication of the partial azeotropy lines in the same figure. In Fig. 2 and in the later figures these are the dotted lines which give additional information and very useful assistance when planning terpolymerization experiments. The location of the ternary azeotrope is shown by an asterisk. (The computer program for calculating and plotting such figures, written in BASIC for HP 9830, is available on request).

Figures 4-12 give some terpolymerization systems in the suggested representation. These diagrams all correspond to ternary systems composed from real binary components. Figure 4 shows a system in which one of the monomer pairs (methyl methacrylate-styrene) has a binary azeotrope but the ternary system does not. Figures 5 and 6, together with Fig. 2, present systems also having only one limiting binary azeotrope and yet a ternary too. In the case of Figs. 7 and 8, two of the monomer pairs have a binary azeotrope but only the system depicted in Fig. 8 also has a ternary. (It is remarkable that a minimal deviation in the r values–in this case, the use of the customary $r_{31} = 0.52$ and $r_{13} = 0.46$ values for the styrene-methyl methacrylate pair–may result in disappearance of the ternary azeotrope.) Similarly, the systems presented in Figs. 9 and 10 have three limiting binary azeotropes but only that in Fig. 10 has also a ternary.

Figure 11 shows the system methyl methacrylate-vinyl acetate-acrylonitrile in which none of the monomer pairs has an azeotrope, and neither has the ternary system. In the search of Wittmer [5] no such systems were found with a ternary azeotrope. Ring [7] was able to demonstrate the theoretical possibility of a true azeotrope in ternary systems having no binary azeotropes. As an example, in Fig. 12 we show the system 2-vinylpyridine-acrylonitrile-butyl acrylate which possesses this feature.

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