Ternary Copolymerization: Azeotropy and Pseudoazeotropy

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TERNARY COPOLYMERIZATION: AZEOTROPY AND PSEUDOAZEOTROPY

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ABSTRACT

An analysis of experimental data for ternary copolymerizations has been performed by an optimizing calculation method, resulting in the estimation of the r_{ij} copolymerization constants. The azeotrope calculation results have been compared to those based on the r_{ij} constants found for binary copolymerization. For each set of r_{ij} constants, the possibility of the ternary azeotropy was studied. The formation of quasihomogeneous ternary copolymers was studied subsequent to the determination of the ternary pseudoazeotropy domains occurring at the intersection of the partial pseudoazeotropy domains.

INTRODUCTION

The Alfrey-Goldfinger equation [1] for ternary copolymerization requires the true values of the apparent monomer reactivity ratios (MRR). If ternary homogeneous copolymers are to be obtained, the accuracy of the MRR (r_{ij}) estimation will influence the choice of the monomer feed compositions (M_1, M_2, M_3) to generate the azeotrope copolymer.

Ternary copolymerization azeotropy [2] is much more complex than binary copolymerization azeotropy. A wider variety of azeotropes is noted in the former case if certain conditions are introduced in the ternary copolymerization equations. Thus, there exist lateral azeotropes L_{ij} ($M_i = m_i, M_j = m_j$, $M_k = 0$)

$$M_i = \frac{(1 - r_{ji})}{(2 - r_{ij} - r_{ji})},$$

(1)

$$M_j = 1 - M_i,$$

a unitary azeotrope, U_i ($M_i = m_i$):

$$K_1 M_i^3 + (K_2 + K_3 M_j)M_i^2 + (K_4 + K_5 M_j + K_6 M_j^2)M_i + K_7 + K_8 M_j$$

$$+ K_9 M_j^2 + K_{10} M_j^3 = 0,$$

(2)

binary azeotropes B_{ij} ($M_i/M_j = m_i/m_j$):

$$C_1(M_j/M_i)^2 + [C_2 + C_3(M_k/M_i)] (M_j/M_i) + C_4 + C_5(M_k/M_i)$$

$$+ C_6(M_k/M_i)^2 = 0,$$

(3)

and the ternary azeotrope T ($M_1 = m_1$, $M_2 = m_2$, and $M_3 = m_3$). T stands for the intersection point of all the U_i and B_{ij} curves:

$$Q_1 M_i^4 + Q_2 M_i^3 + Q_3 M_i^2 + Q_4 M_i + Q_5 = 0,$$

(4)

complemented by Eq. (2), where the initial monomer compositions M_i, M_j, and M_k generate m_i, m_j, and m_k copolymer compositions. The K, C, and Q coefficients depend exclusively on the r_{ij}. The Tarasov formulas [3] can also be used in order to determine the T point.

The L_{ij} points stand for binary copolymerization azeotropes which, in their turn, are limiting cases of ternary copolymerization processes. Ternary systems characterized by a T point have at least one L_{ij} point. Only hypothetical systems [4] lack lateral azeotropes.

The existence of the L_{ij} points raises the question of the relationship between the r_{ij} determined from the binary copolymerization and the constants that can be used in the Alfrey-Goldfinger equation.

It is certain that every copolymerization system includes, within the monomer compositions domain $M_i \in [0, 1]$, some roots of Eqs. (2) and (3), irrespective of the accuracy with which the r_{ij} values are calculated. These values determine only the position and not the existence of the unitary or binary azeotropy curves within the domain $M_i \in [0, 1]$.

The situation is quite different with regard to the T point [5], the presence of which within the [0, 1] domain is not certain due to the unreliability of the values recorded for the r_{ij} constants [6]. If values are given for r_{ij} within

the confidence interval [7], the T point may lie outside the domain $M_i \epsilon$ [0, 1]. Thus, a ternary copolymerization system having a ternary azeotrope changes into a system having no ternary azeotrope $(T\phi)$.

The above-mentioned peculiarities have been presented in order to point out that a ternary copolymerization represents a separate case in many respects. Consequently, the use in ternary copolymerization of the r_{ij} constants for binary copolymerization seems to be rather inappropriate [8, 9]. The present paper deals with a discussion of the relationship between binary and ternary copolymerization processes which aims at supplying further details related to the concept of azeotropy in ternary copolymerization.

RESULTS AND DISCUSSIONS

The ternary system put forward by Rudin and coworkers [10], methacrylonitrile (M_1)/styrene (M_2)/α-methylstyrene (M_3), has been reanalyzed. Table 1 shows the values of the MRR estimated from the respective binary copolymerizations and by several methods directly from the ternary copolymerization data [9]. The OPT-6 method starts with the ternary copolymerization data and minimizes an objective deviation function F [9], which is the square root of the sum of the squares of the differences between the experimentally determined copolymer compositions and the corresponding values calculated from a proposed set of r_{ij} constants. If the conversion is kept to low levels (0.1%), F_{co} stands for the minimized function, while if the conversions of each experiment are also taken into account, F_c stands for the function.

The estimation method put forward in the previous paper [9] allows the calculation of the two reactivity ratios for binary copolymerization (OPT-2) or of the six reactivity ratios for ternary copolymerization (OPT-6). The same method can also make use of the conversion data (OPT-2C and OPT-6C method, respectively).

The monomer compositions corresponding to the T point have been calculated according to each set of constants (Table 1). The specific set of r_{ij} for which the respective system had no ternary azeotrope is also noted $(T\phi)$.

The same experimental data for ternary copolymerization [10] lead to different sets of MRR if computed according to different techniques.

Figure 1 shows the unitary azeotrope curves (U_i) for this ternary system. The curves were calculated by Eq. (2), which includes the r_{ij} estimated from the respective binary copolymerizations [11] (see Table 1). The T point occurs at the intersection of the three U_i curves within the $M_i \epsilon$ [0, 1] domain of monomer concentrations. It appears that a homogeneous ternary co-

TABLE 1. Monomer Reactivity Ratios and Monomer Compositions Corresponding to the T Points for the Ternary Copolymerization of Methacrylonitrile (M_1), Styrene (M_2), and α-Methylstyrene (M_3)

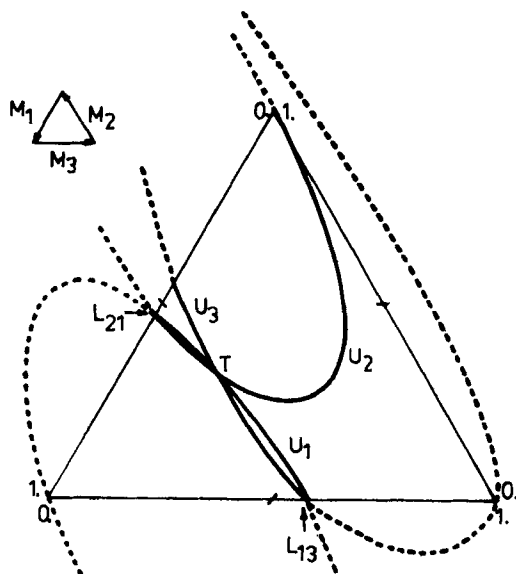| No.	Calculation method	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}	Compositions of the T point, mole fraction		
								M_1	M_2	M_3
1.	Binary copolymerization	0.44	0.37	0.38	0.53	1.12	0.63	0.471	0.317	0.212
2.	Rudin M-1	0.46	0.18	1.15	0.24	0.17	0.34	0.617	0.407	-0.022
3.	Rudin M-2	0.53	0.52	1.13	0.23	0.40	0.85	0.507	0.407	0.086
4.	Rudin M-3	0.55	0.45	1.49	0.23	0.33	0.57	0.534	0.413	0.053
5.	OPT-6	0.492	0.469	0.791	0.266	0.562	0.765	0.513	0.512	-0.025

FIG. 1. The ternary copolymerization methacrylonitrile (M_1)/styrene (M_2)/α-methylstyrene (M_3). The unitary azeotropy curves (U_i) were calculated with the r_{ij} constants for the respective binary copolymerizations.

polymer can be obtained up to 100% conversion. Hence, a more accurate calculation of the T point position is very important.

The fact that the new U_i curves (Fig. 2) intersect outside the $M_i \in [0, 1]$ domain was found by means of the r_{ij} set determined by the OPT-6 method (Table 1), which is much more reliable [9]. Thus, the reinterpretation of the same experimental data has led to the conclusion that the system lacks a ternary azeotrope ($T\phi$).

The above results make it a controversial point whether the ternary azeotrope exists or not. Wittmer [12] noted the presence of 37 ternary systems having a T point, but these systems represent only about 5% of the systems submitted to analysis. On the other hand, many of the T points determined by Wittmer failed to withstand more thorough examination [6].

The data included in the present paper suggest a reduced probability of finding a T point in ternary copolymerizations, but any debate of this matter should focus on the reliability of the r_{ij} values.

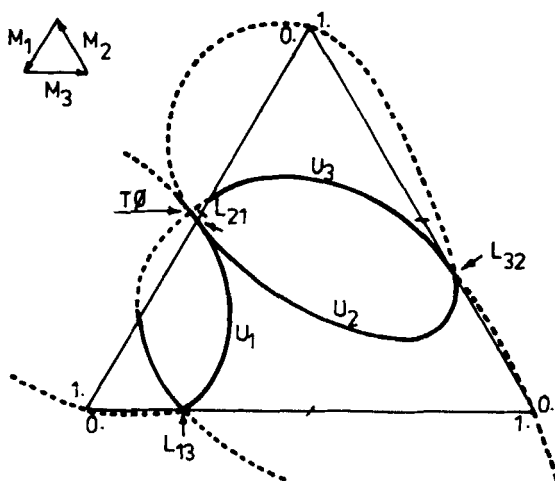In what follows, an analysis of several ternary systems [13-15], including

FIG. 2. The ternary copolymerization methacrylonitrile (M_1)/styrene (M_2)/α-methylstyrene (M_3). The unitary azeotropy curves (U_i) were calculated with the r_{ij} constants determined for the ternary copolymerization by the OPT-6 method.

the acrylonitrile-styrene pair, for which the data from the respective binary copolymerizations [16-18] are also available, is presented.

The F function is a comparison standard [9] for the effectiveness of predicting the experimental data for ternary copolymerization by various sets of r_{ij}. Thus, the superiority of the r_{ij} set determined with the OPT-6C program becomes obvious, since this method makes direct use of the ternary copolymerization data and includes the conversion values. The set determined for binary copolymerizations $(r_{ij})_B$ by the most appropriate method (OPT-2C) [9] proves to be rather inadequate for ternary copolymerization (Table 2). Thus, the $(r_{ij})_T$ determined directly from the ternary copolymerization data should be used for ternary copolymerizations.

The Kelen-Tüdös method is quite satisfactory for binary copolymerization processes. It also leads to an improved checking technique, compared to OPT-2C, for ternary copolymerization processes. However, the Kelen-Tüdös method is less accurate than OPT-6C. At the same time, the use of the conversion values (OPT-6C vs OPT-6, F_c and F_{co}, respectively, Table 2) brings the calculated values closer to the experimentally determined data.

Analysis of the r_{12} and r_{21} constants for the acrylonitrile (M_1)/styrene

TABLE 2. Monomer Reactivity Ratios for Acrylonitrile (M_1)/Styrene (M_2)/M_3 Copolymerizations

M_3	Calculation method	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}	$F_{co} \times 10^3$	$F_c \times 10^3$
2,4,6-Tribromophenyl methacrylate	KT (binary copolymerization)	0.16	0.3	0.2	0.98	0.2	0.27	17.73	17.41
	OPT-2 (binary copolymerization)	0.149	0.332	–	–	–	–	–	–
	OPT-6	0.142	0.208	0.196	0.873	0.132	0.214	13.63	13.68
	OPT-6C	0.141	0.200	0.194	0.872	0.127	0.199	–	13.60
Pentabromophenyl acrylate	KT (binary copolymerization)	0.16	0.3	0.87	1.62	0.09	0.26	27.05	27.17
	OPT-2 (binary copolymerization)	0.149	0.332	0.819	1.806	0.089	0.258	34.63	35.09
	OPT-6	0.208	0.305	0.890	1.871	0.123	0.278	15.76	15.41
	OPT-6C	0.201	0.332	0.904	1.874	0.129	0.252	–	14.93
2,3-Dibromopropyl acrylate	KT (binary copolymerization)	0.16	0.3	0.87	0.75	0.41	0.22	19.57	19.44
	OPT-2 (binary copolymerization)	0.149	0.331	0.836	0.738	0.429	0.240	21.92	21.75
	OPT-6	0.154	0.290	0.838	0.750	0.433	0.177	16.64	16.62
	OPT-6C	0.146	0.277	0.825	0.735	0.435	0.180	–	16.50

(M_2) pair shows that the $(r_{ij})_B$ are rather different from those determined directly from the ternary copolymerization data. This proves that the effect of the penultimate units is a particular feature of ternary copolymerization processes. In other words, there must be a particular set of $(r_{ij})_T$ for each ternary copolymerization system which must be determined from the data for the respective ternary copolymerization. This was confirmed by the characterization (through the OPT-6 and OPT-6C methods) of other ternary copolymerization systems [19, 20], including acrylonitrile/styrene (Table 3).

The new values noted for r_{12} and r_{21} support the above remark: a unique point in binary copolymerization processes (i.e., the azeotropy point for the acrylonitrile/styrene copolymerization), which becomes the L_{21} point in ternary copolymerization, changes from 51.8 to 66.1 mol% styrene according to the patterns shown in Tables 2 and 3. Each ternary system has a $(r_{ij})_T$ set and an L_{21} point of its own. The inappropriate use of the r_{ij} constant sets leads to significant deviations of the U_i curves and to errors in the determination of the T point (Figs. 1 and 2).

Under such circumstances, particular attention has to be paid to the choice of the r_{ij} constants used for the azeotrope calculation and, subsequently, to the selection of methods for the estimation of the r_{ij}. The use of the $(r_{ij})_B$ values must represent a preliminary stage in the analysis of a ternary copolymerization. The Alfrey-Goldfinger equation requires the use of the $(r_{ij})_T$ value. The simple terminal kinetic model seems to be a poor approach to the copolymerization processes.

Even if the $(r_{ij})_T$ values estimated by the OPT-6C method are used, the azeotropy point calculated by Eqs. (2) and (4) represents the monomer composition most likely to generate a homogeneous copolymer. Thus, it is not the ternary azeotropy point which must be noted, but a whole domain of monomer compositions for which the ternary copolymers shows a degree of homogeneity within certain limits.

As regards the definition of the degree of homogeneity, the conversion should also be mentioned because copolymer generation at high conversions is concerned. Thus, a conversion of 95% and a compositional deviation of 5% [21] between the copolymer generated at low conversions (m_i^0) and those obtained at a conversion of 95% (m_i^{95}) was chosen. The calculation of m_i^{95} was performed by integration of the ternary copolymerization equation with the Runge-Kutta method of the 3rd degree. The calculation program was designed to perform the selection of the domain of monomer compositions (ternary pseudoazeotropy deomains, T-PAD) that generate copolymer within certain limits of homogeneity:

$$\Delta_i = |m_i^0 - m_i^{95}| \leqslant 5\%.$$

TABLE 3. Reactivity Ratios for the Acrylonitrile (M_1)/Styrene (M_2)/M_3 Ternary Copolymerization

| M_3	Calculation method	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}	$F_{co} \times 10^3$	$F_c \times 10^3$
Ciannamolazide	OPT-6	0.004	0.266	0.499	0.421	1.013	0.008	26.5	26.45
	OPT-6C	0.007	0.283	0.568	0.262	1.415	0.004	—	22.21
Methyl α-cyanocinnamate	OPT-6	0.073	0.358	20.15	0.389	0.669	0.009	25.96	24.96
	OPT-6C	0.084	0.371	21.47	0.549	0.630	0.008	—	24.83
Ethyl α-cyanocinnamate	OPT-6	0.059	0.526	14.87	0.472	1.536	0.698	37.18	38.85
	OPT-6C	0.059	0.517	13.96	0.507	1.546	0.273	—	36.41
n-Butyl α-cyanocinnamate	OPT-6	0.002	0.366	12.43	0.748	0.600	0.008	16.27	15.82
	OPT-6C	0.001	0.363	13.11	0.792	0.554	0.008	—	15.20
n-Hexyl α-cyanocinnamate	OPT-6	0.073	0.415	16.26	0.308	0.887	0.009	16.31	16.08
	OPT-6C	0.070	0.426	16.10	0.304	0.880	0.009	—	15.50
Cyclohexyl α-cyanocinnamate	OPT-6	0.100	0.487	24.79	0.672	0.658	0.011	59.87	59.51
	OPT-6C	0.095	0.500	24.70	0.680	0.645	0.001	—	59.06
Benzyl α-cyanocinnamate	OPT-6	0.052	0.403	15.42	0.673	0.644	0.023	17.89	16.53
	OPT-6C	0.058	0.397	15.49	0.665	0.651	0.007	—	15.73
2-Ethylhexyl α-cyanocinnamate	OPT-6	0.058	0.318	12.83	0.602	0.543	0.008	23.91	23.79
	OPT-6C	0.080	0.330	12.65	0.620	0.555	0.009	—	23.72
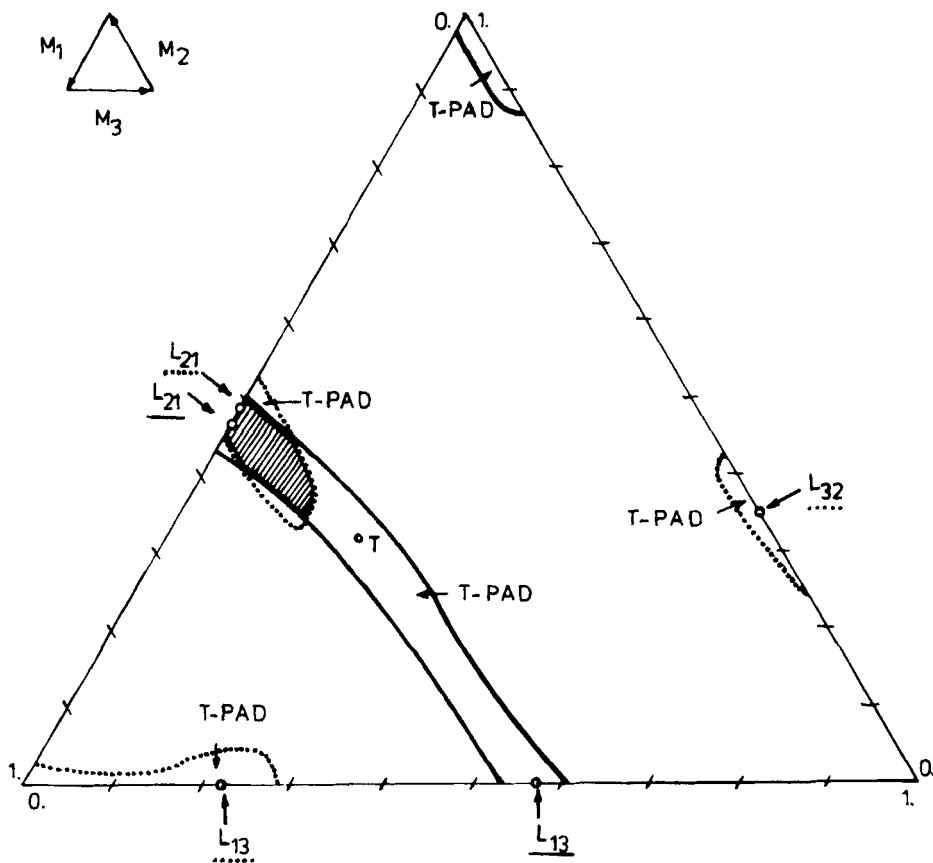
FIG. 3. The ternary copolymerization methacrylonitrile (M_1)/styrene (M_2)/α-methylstyrene (M_3): the ternary pseudoazeotropy domains (T-PAD). $\Delta_i \leqslant 0.05$ mole fraction; (——) domains for $(r_{ij})_B$, ($\cdot \cdot \cdot \cdot$) domains for $(r_{ij})_T$.

Figure 3 shows the T-PAD for the system put forward by Rudin and co-workers [10] and for which the unitary azeotropy curves have been calculated (Figs. 1 and 2), if sets of r_{ij} Numbers 1 and 5 (Table 1) are used.

The intersection of the domain set by the $(r_{ij})_B$ with T-PAD by the $(r_{ij})_T$ represents the overall compositions within the range of Δ_i for both variants. Such compositions lead to maximum probability for the generation of a quasi-homogeneous copolymer.

The T point determined by the $(r_{ij})_B$ is located within the T-PAD determined by these constants, but it is absent from the intersection with the domain calculated by the $(r_{ij})_T$.

Under certain circumstances, initially noted by Slocombe [22], homogeneous ternary copolymers seem to be generated by the monomer compositions occurring near a line which links together two lateral azeotropes from within the compositions triangle. Since the T-PAD do not always join two triangle sides (Fig. 3), it is necessary to draw the unitary pseudoazeotropy domains (U_i-PAD) [23] for which the conditions imposed by the Δ_i value refers to a single monomer.

Figure 4 shows the U_i-PAD for the system shown in Figure 3. The same sets of $(r_{ij})_B$ and $(r_{ij})_T$, respectively, were used. Not even in this case does the T point, calculated by $(r_{ij})_B$, occur within the intersection of the U_i-PAD.

Starting from the above-mentioned data, it has been proved once again that the position of the T point determined from the respective binary copolymerization data is not reliable enough to lead to a homogeneous ternary copolymer ($\Delta_i = 0$).

The unitary pseudoazeotropy domain supports Slocombe's hypothesis for the M_1 monomer (i.e., acrylonitrile), but this is not so for the ternary system shown in Fig. 4. The tie line which links L_{21} to L_{13} (calculated with the $(r_{ij})_T$) does not lie within the unitary pseudoazeotropy domain.

Most of the ternary systems have no T point [6, 12], and this is why the analysis of such a system becomes interesting for the drawing of the pseudoazeotropy domains.

Figure 5 describes the acrylonitrile (M_1)/styrene (M_2)/pentabromophenyl acrylate (M_3) system [14] (Table 2). The U_i curves were drawn according to the $(r_{ij})_B$ and $(r_{ij})_T$ constants. Although the general characteristics of curves of this type are the same, significant changes in the position of the intersection points of the U_i curves with the triangle sides are noted if the set of r_{ij} constants is changed.

In the absence of the T point, one can still draw the pseudoazeotropy domain, the presence of which has been noted by Janovic and coworkers [14].

The T-PAD is represented (Fig. 6) as the intersection of the U_i-PAD. The calculation reveals the existence of four regions determined by the $(r_{ij})_T$ constants (the OPT-6C method) for $\Delta_i \leqslant 5\%$. The cross-hatched region, experimentally found by Janovic [15], appears in Fig. 6, but other interesting regions were revealed by analysis of the entire domain of monomer concentrations.

If the acrylonitrile/styrene/pentabromophenyl acrylate system is considered, only two lateral azeotropes having monomer compositions within the $M_i \in [0, 1]$ domain are generated, i.e., L_{21} and L_{32}. Both these azeotropes contain styrene. In such a case the tie line of the lateral azeotropes
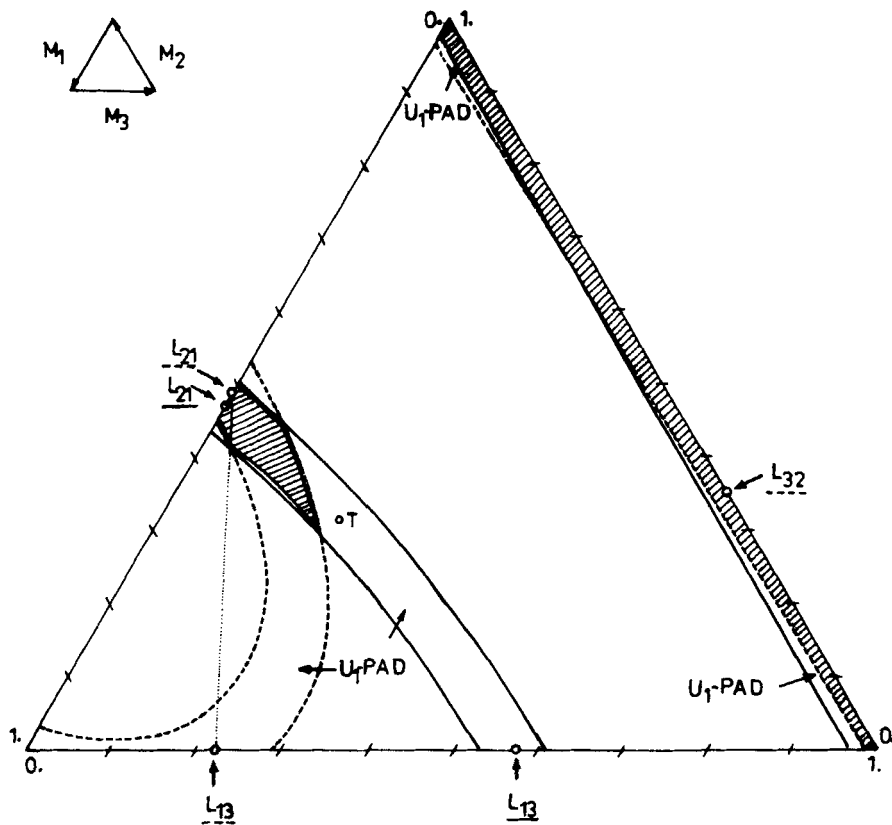
FIG. 4. The ternary copolymerization methacrylonitrile (M_1)/styrene (M_2)/α-methylstyrene (M_3): the unitary pseudoazeotropy domains $(U_1$-PAD). $\Delta_i \leqslant 0.05$ mole fraction; (——) domains for $(r_{ij})_B$, (– – – –) domains for $(r_{ij})_T$.

will provide the generation of homogeneous copolymer if the compatibility conditions are dictated exclusively by the concentration of a single monomer: the monomer shared by the two lateral azeotropes $(U_2$-PAD).

CONCLUSIONS

The Alfrey-Goldfinger equation and the equations derived from it require the utilization of the r_{ij} constants determined from ternary copolymerization
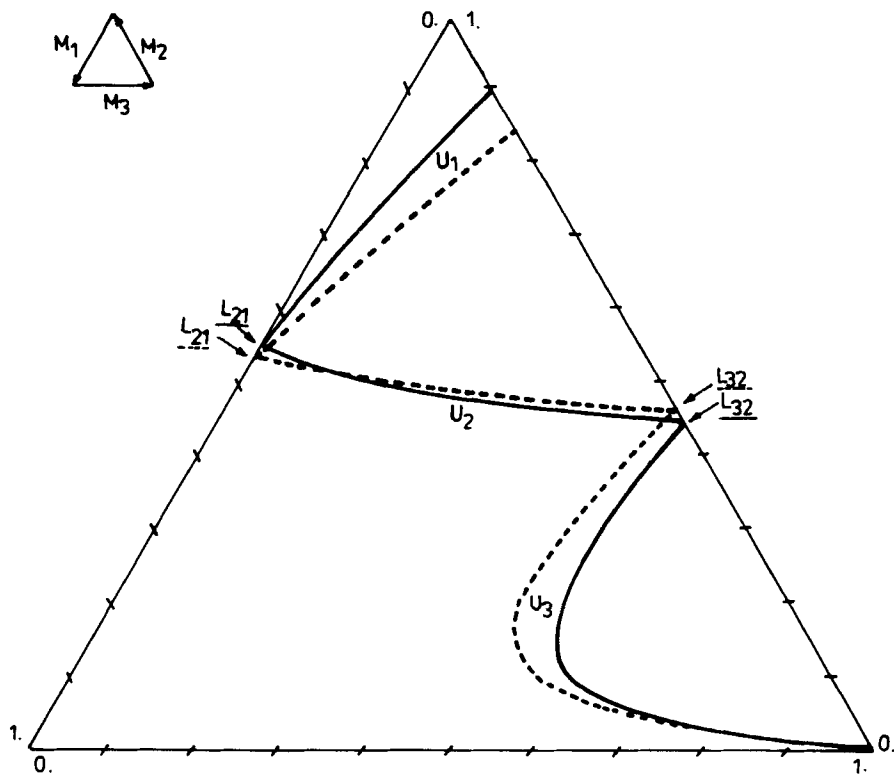
FIG. 5. The ternary copolymerization acrylonitrile (M_1)/styrene (M_2)/-
pentabromophenyl acrylate (M_3): the unitary azeotropy curves. (——) U_i
curves calculated with $(r_{ij})_B$, (– – – –) U_i curves calculated with $(r_{ij})_T$.

data. The OPT-6C method allows the estimation of r_{ij} values which agree
best with a given volume of experimental data. These constants represent
values of maximum probability.

The occurrence of a ternary azeotrope is highly improbable. The use of
r_{ij} constants with a certain degree of unreliability cannot accurately deter-
mine the position of the ternary azeotropy point. It is preferable to draw a
pseudoazeotropy domain within which the monomer compositions will lead
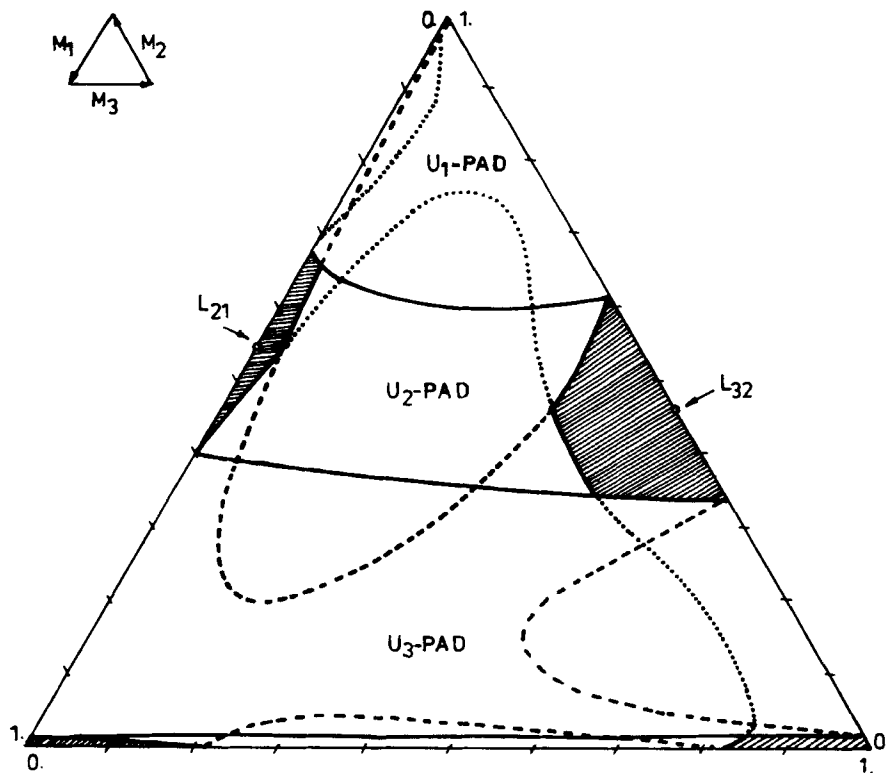to quasi-homogeneous ternary copolymers within given limits.

FIG. 6. The ternary copolymerization acrylonitrile (M_1)/styrene (M_2)/- pentabromophenyl acrylate (M_3): the ternary pseudoazeotropy domains are cross-hatched. $\Delta_i \leqslant 0.05$ mole fraction with the $(r_{ij})_T$ determined by the OPT-6C method.

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