# Organotin Polymers. IX. Copolymerization Parameters of Di-(tri-n-Butyltin) Itaconate with Styrene and Methyl Methacrylate

A. F. SHAABAN, M. M. H. ARIEF, and A. A. MAHMOUD, *Chemistry Department, Faculty of Science, Zagazig University-Benha Branch, Benha, Egypt,* and N. N. MESSIHA, *Laboratory of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt*

## Synopsis

Copolymerization reactions of di-(tri-n-butyltin) itaconate with styrene and methyl methacrylate were carried out in solution at 70°C using 1 mol% azobisisobutyronitrile as a free radical initiator. The copolymer compositions were determined by chemical analysis as well as from $^1$H-NMR data. The monomer reactivity ratios for copolymerizations of di-(tri-n-butyltin) itaconate with styrene and methyl methacrylate have been found to be $r_1 = 0.228$, $r_2 = 0.677$, and $r_1 = 0.220$, $r_2 = 1.635$, respectively. The sequence distribution of the triad fractions were calculated from reactivity ratios and compared with those obtained from $^1$H-NMR data.

## INTRODUCTION

Organotin polymers have been investigated as long-lived, film-forming resinous antifouling coatings with steady leaching of the organotin compounds.[1,2] Since properties of copolymers are related to the sequence distribution of monomer units in copolymer chain, it is of great interest to know the actual reactivity which controls the sequence distribution. Our previous studies have been devoted to binary and ternary copolymerizations of tri-n-butyltin acrylate and methacrylate with various film-forming comonomers.[3-7] Also, the copolymerizations of tri-n-butyltin maleate and triphenyltin methacrylate with some vinyl monomers were investigated.[8-10] The work is now extended to study the copolymerizations of di(tri-n-butyltin) itaconate with styrene and methyl methacrylate.

## EXPERIMENTAL

Tri-n-butyltin oxide was provided by M & T Chemical (Rahway, NJ). Di(tri-n-butyltin) itaconate (T) was prepared by reaction of itaconic acid with tri-n-butyltin oxide according to the method described in our previous work.[11] Styrene (S) and methyl methacrylate (M) (E. Merk, Darmstadt, products) were purified by distillation under reduced pressure and the middle fractions retained for use.

Copolymers from T with S and M were obtained by solution polymerization in toluene (2 mol/L) at 70°C, in the presence of 1 mol% azobisisobutyronitrile (AIBN) based on total monomer, according to the method previously described.[3] The copolymers were purified by reprecipitation from methanol;

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TABLE I
Monomer Reactivity Ratios for Copolymerizations of Di-(tri-$n$-Butyltin) Itaconate
with Styrene and Methyl Methacrylate

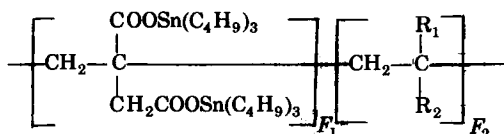| | Fineman–Ross method | | Kelen–Tudos method | | |
|---|---|---|---|---|---|
| $M_1$–$M_2$ | $r_1$ | $r_2$ | $r_1$ | $r_2$ | $\alpha$ |
| T–S[a] | $0.139 \pm 0.058$ | $0.643 \pm 0.039$ | $0.228 \pm 0.044$ | $0.677 \pm 0.045$ | 0.259 |
| T–M[a] | $0.316 \pm 0.100$ | $1.729 \pm 0.129$ | $0.220 \pm 0.076$ | $1.635 \pm 0.080$ | 0.616 |
| T–S[b] | $0.115 \pm 0.042$ | $0.652 \pm 0.029$ | $0.156 \pm 0.035$ | $0.645 \pm 0.022$ | 0.237 |
| T–M[b] | $0.230 \pm 0.098$ | $1.578 \pm 0.100$ | $0.182 \pm 0.083$ | $1.553 \pm 0.054$ | 0.377 |

[a] Calculated on the basis of $^1$H-NMR data.
[b] Calculated on the basis of tin analysis.

washed, dried, and weighed. Overall conversions were limited to less than 10% in every case. The $^1$H-NMR spectra (in $CDCl_3$ as a solvent and using TMS as zero reference) were obtained at room temperature with a Varian EM-390 Spectrometer operating at 90 MHz. Copolymers were analyzed for tin by the method of Gilman and Rosenberg.[12]

## RESULTS AND DISCUSSION

The copolymer composition of each copolymer sample was determined from tin analysis. The monomer reactivity ratios of systems studied were determined from the feed composition copolymer composition relationship according to Fineman–Ross[13] and Kelen–Tudos[14] methods (Table I). Also, the copolymerization parameters were determined from $^1$H-NMR spectroscopy (Figs. 1 and 2). Thus, the structure of the copolymer systems studied (T–S and T–M) can be written as:

$$\left[ \begin{array}{c} COOSn(C_4H_9)_3 \\ | \\ -CH_2-C- \\ | \\ CH_2COOSn(C_4H_9)_3 \end{array} \right]_{F_1} \left[ \begin{array}{c} R_1 \\ | \\ CH_2-C- \\ | \\ R_2 \end{array} \right]_{F_2}$$

for styrene containing polymer, $R_1 = H$ and $R_2 = C_6H_5$ and for methyl methacrylate containing copolymer, $R_1 = CH_3$ and $R_2 = COOCH_3$.

The distribution of protons is an important factor to distinguish the units in the copolymer chain. Figure 1 shows typical $^1$H-NMR spectra for a series of copolymer samples for the T–S system. Two signals appear distinctly at $\delta$ 7.1 and 6.50 due to the phenyl protons in all copolymer samples. All the aliphatic protons of S and T units are overlapping and appear at 2.0–0.88 $\delta$. The integral trace corresponding to the $-CH_2-CH-$ protons of the styrene units (calculated on the basis of the peak area of the aromatic protons) was subtracted from the integrated traces corresponding to all aliphatic protons, and the copolymer composition of each sample was calculated according to
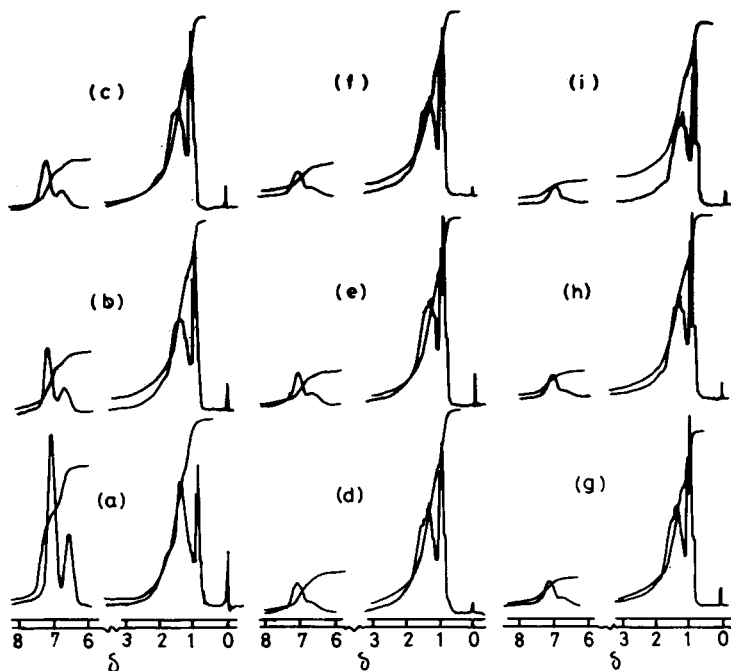
$$b = \frac{(I_a - I_s) \times 5}{I_p \times 58} \tag{1}$$

Fig. 1.   $^1$H-NMR spectra of T–S copolymer samples: (a) 0.05 ( $f_1$ mol fraction of $M_1$ in feed); (b) 0.15; (c) 0.20; (d) 0.25; (e) 0.30; (f) 0.33; (g) 0.40; (h) 0.45; (i) 0.50.
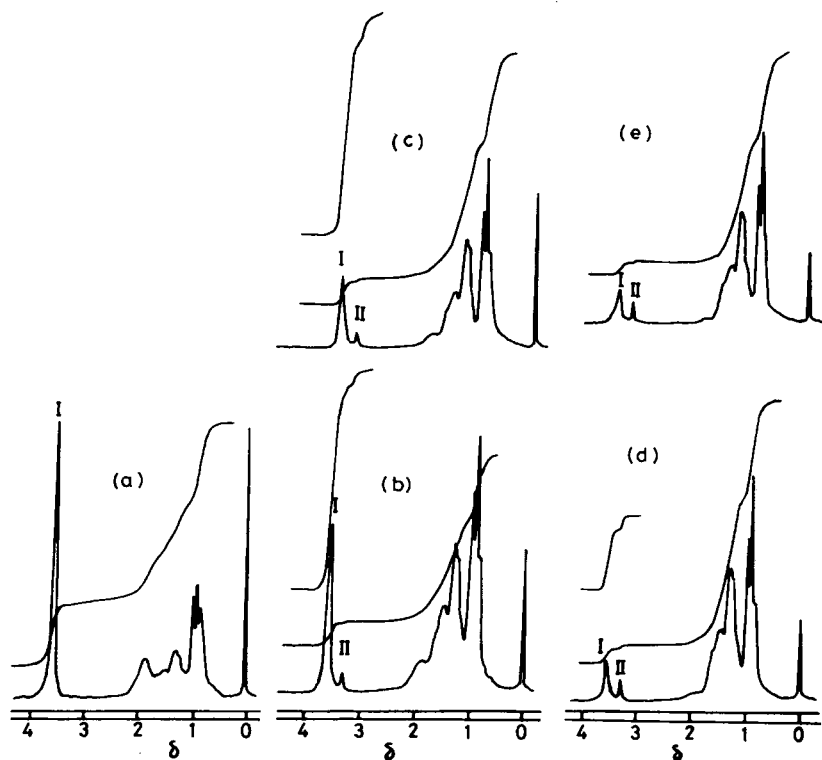


Fig. 2.   $^1$H-NMR spectra of T–M copolymer samples: (a) 0.10 ( $f_1$ mol fraction of $M_1$ in feed); (b) 0.25; (c) 0.34; (d) 0.45; (e) 0.50.
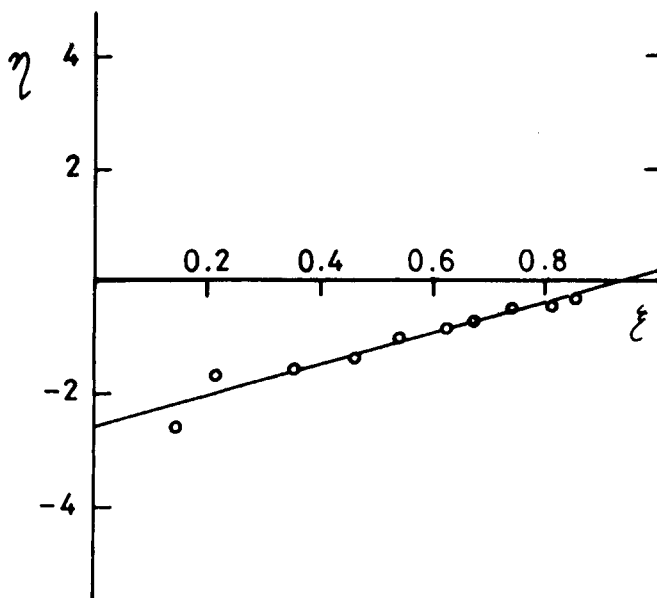
Fig. 3. Kelen–Tüdős plot for copolymerization reaction of T–S based on $^1$H-NMR spectra data. $\xi = a^2/(\alpha b + a^2)$ and $\eta = a(b - 1)/(\alpha b + a^2)$, where $a$ = feed composition, $b$ = copolymer composition and $\alpha = a_{min} \cdot a_{max}/(b_{min} \cdot b_{max})^{1/2}$.

where $b$ = molar ratio of T and S in copolymer sample (T/S), $I_a$ = sum of the integrated traces corresponding to all aliphatic protons, $I_s$ = integrated traces of —$CH_2$—$CH$— protons in S units, and $I_p$ = integrated trace of phenyl protons in S units. Also, the $^1$H-NMR spectra of copolymer samples for the T–M system (Fig. 2) show two signals at $\delta$ 3.6 and 3.3 (peaks I and II, respectively) due to the methoxy protons of M units. All other protons of T and M units (due to $CH_3$— and —$CH_2$— groups) are overlap and appear at $\delta$ 2.1–0.8. The copolymer composition of T–M copolymer samples were determined from

$$b = \frac{(I_r - I_0) \times 3}{I_m \times 58} \tag{2}$$

where $b$ = molar ratio of T and M in copolymer sample (T/M), $I_r$ = sum of integrated traces corresponding to all aliphatic protons, $I_0$ = sum of integrated traces corresponding to $\alpha$-methyl and methylene protons in M unit. Table I illustrates the monomer reactivity ratios ($r_1$ and $r_2$) for the two systems studied based on the $^1$H-NMR spectral data as well as the tin analyses. The values of $r_1$ and $r_2$ calculated from $^1$H-NMR spectroscopy are almost identical to those obtained from tin analysis. Figures 3–5 show the Kelen–Tudos plots for the two systems based on both $^1$H-NMR and tin analysis. From Table I it is clear that the reactivity ratios ($r_1$ and $r_2$) for the T–S system are both less than unity, and this system should possess azeotropic composition. The composition curve for this system (T–S), illustrated in Figure 6, cross the line representing $F_1 = f_1$ at 0.30 mole fraction. This point of intersection corresponds to the azeotropic composition yielding homogenous copolymer regard-
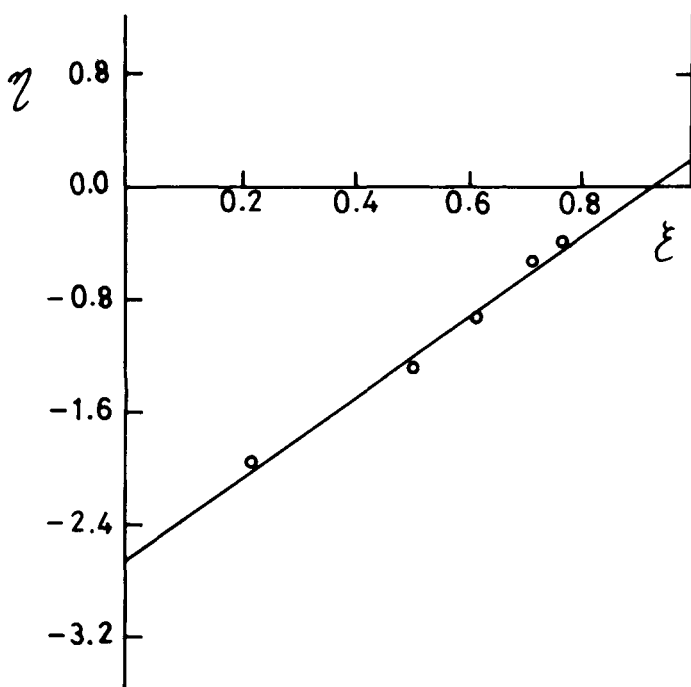
Fig. 4.   Kelen–Tüdős plot for copolymerization of T–M based on ^{1}H-NMR spectra data.

less of conversion. However, the monomer reactivity ratios of the T–M system show no azeotropic composition. The value of $r_1$ compared to $r_2$ in the copolymerization of T with M indicates the preferential addition of M to the growing macroradical. From this it is evident that the T–M copolymer chain consists of longer sequences of methyl methacrylate units interrupted by di(tri-$n$-butyltin) itaconate units. The ^{1}H-NMR spectra of T–M copolymer samples (Fig. 2) show two methoxy resonances which are readily observed at 3.6 and 3.3 $\delta$ (peaks I and II, respectively). The upfield signal ($\delta$ 3.3) is apparently due to the T-containing triad (TMT) since its area decreases with increasing M in feed ratios. The downfield signal ($\delta$ 3.6) may be due to the MMM triad fractions since its relative area increases at high methyl methacrylate feed ratios.

The theoretical fractions of the three triad types MMM, MMT, and TMT (corresponding to $f_{222}$, $f_{221}$, and $f_{212}$ triad fractions, respectively) in the copolymer chain of T–M copolymer, can be calculated from eqs. (3)–(7) on the basis of the terminal-copolymerization model[14] as follows:

$$P_{22} = \left(1 + m_1/r_2 m_2\right)^{-1} \tag{3}$$

$$f_{222} = P_{22}^2 \tag{4}$$

$$P_{21} = \left(1 + r_2 m_2/m_1\right)^{-1} \tag{5}$$

$$f_{121} = P_{21}^2 \tag{6}$$
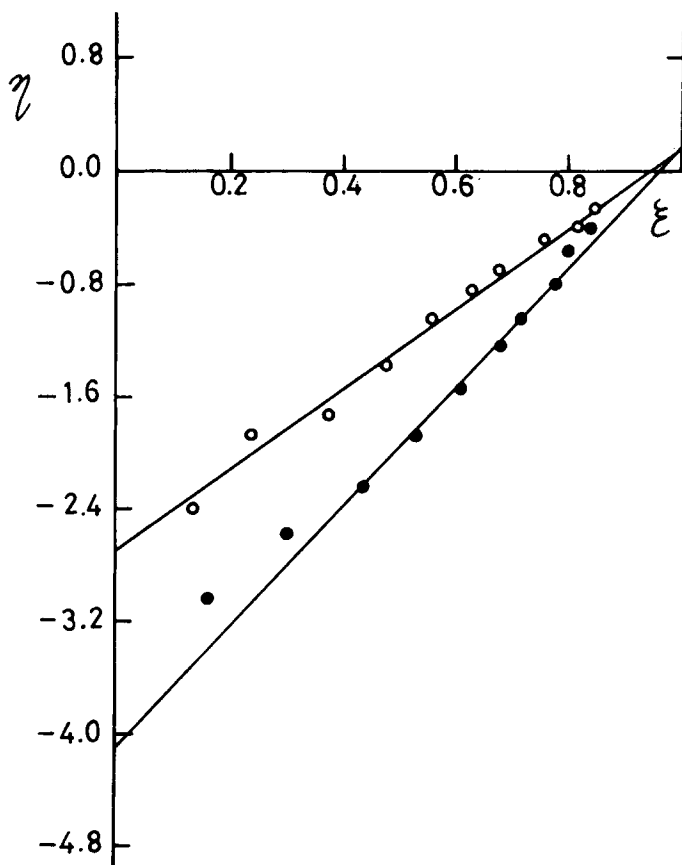
$$f_{221} = 2 P_{21}(1 - P_{21}) \tag{7}$$

Fig. 5. Kelen–Tüdős plots for copolymerization of (○) T–S and (●) T–M, based on tin analysis.
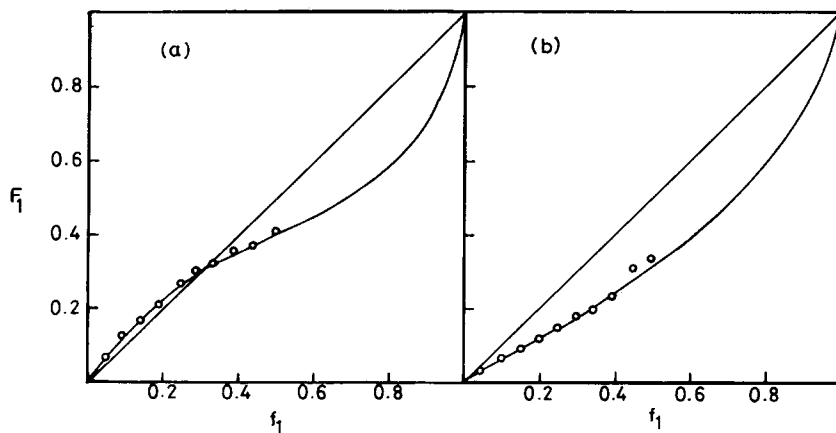


Fig. 6. Composition curves for copolymerization reactions of: (a) T–S; (b) T–M; (—) calculated values; (○) experimental values, where $f_1$ = mol fraction of $M_1$ in feed and $F_1$ = mol fraction of $M_1$ in copolymer.
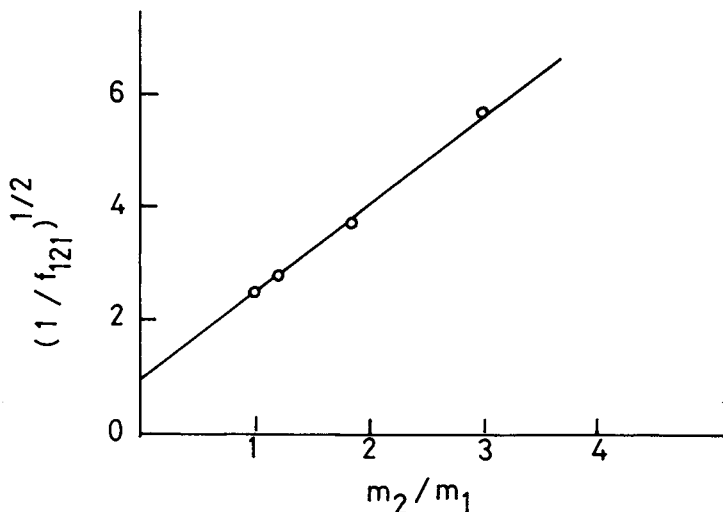
Fig. 7. Plot of $(1/f_{121})^{1/2}$ vs. $m_2/m_1$ according to eq. (8), assuming peak II correspond to TMT triad.

where $P_{22}$ is the conditional probability of adjacent $M_2$ units and $P_{21}$ is the conditional probability of finding an $M_1$ unit adjacent to an $M_2$ unit in the copolymer chain, and $m_1$ and $m_2$ are mole fractions of the two monomers in the feed.

It has also been shown[15] that eqs. (5) and (6) can be combined and rearranged to give eq. (8), which allows $r_2$ to be determined by $^1$H-NMR spectroscopy from $f_{121}$ triad fractions calculated on the basis of the relative integral trace of peak II:

$$(1/f_{121})^{1/2} = 1 + r_2 m_2/m_1 \qquad (8)$$

Application of eq. (8) gave the plot shown in Figure 7, assuming that peak II at $\delta$ 3.3 is due exclusively to the TMT triad. The slope of the experimental line of Figure 7 gives $r_2 = 1.55$, which is identical with that obtained from copolymer composition measurements illustrated in Table I ($r_2 = 1.635$).

Also, eqs. (3) and (4) can be combined and arranged to give

$$(1/f_{222})^{1/2} = 1 + \frac{1}{r_2} \frac{m_1}{m_2} \qquad (9)$$

from eq. (9), $(1/f_{222})^{1/2}$ can be plotted against the feed ratio $(m_1/m_2)$ to give a line of slope $r_2^{-1}$ as illustrated in Figure 8. The reactivity ratio obtained by this procedure ($r_2 = 0.106$) is too small and differs from that obtained by classical copolymer-composition measurements ($r_2 = 1.635$, Table I). Therefore, the triad peak assignment (MMM) suggested for peak I in the $^1$H-NMR spectra of T-M copolymer might be incorrect. Uebel and Dinan[16] studied the structure and tacticity in $p$-$t$-butylstyrene–methyl methacrylate copolymers by $^1$H-NMR and proposed a new set of peak-triad assignments that reconciles this difficulty and gives good agreement between triad fractions measured by $^1$H-NMR and those calculated from theory. They concluded that the methoxy
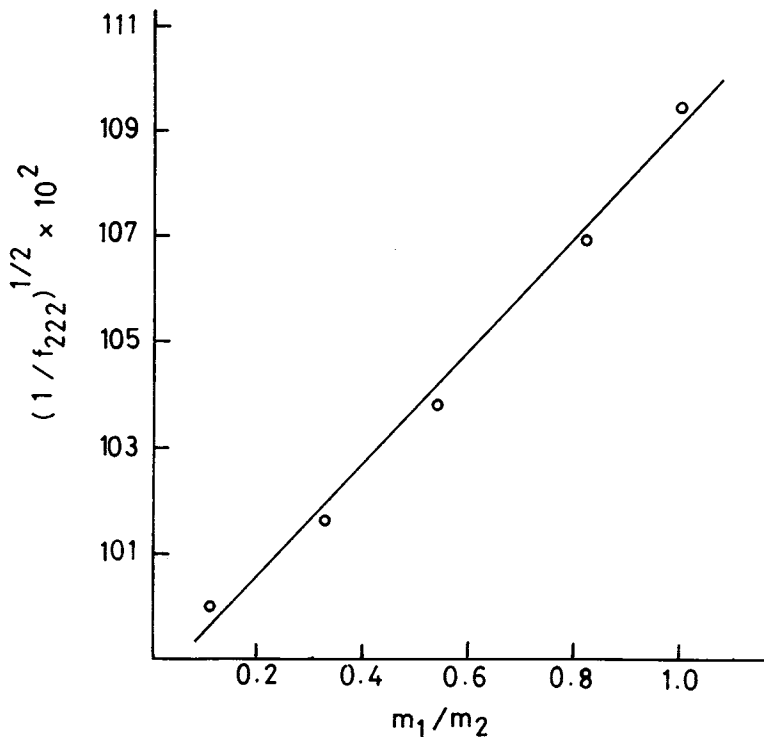
Fig. 8. Plot of $(1/f_{222})^{1/2}$ vs. $m_1/m_2$ according to eq. (9), assuming peak I correspond to MMM triad.

signal at $\delta$ 3.6 represent more than one triad type and the quantitative measure of the two components can be calculated from the following relationship:

$$\Delta = f_I - f_{MMM} \tag{10}$$

where $f_I$ is the normalized fraction of the total methoxy area due to peak I and $f_{MMM}$ is the normalized fraction of MMM triad ($f_{222}$) calculated from eqs. (3) and (4) with $r_2$ value obtained from copolymer composition data ($r_2 = 1.635$).

Assignment of the component $\Delta$ to a specific triad composition was facilitated by comparison of the theoretical triad fractions ($f_{MMM}$, $f_{MMT}$, and $f_{TMT}$) calculated from eqs. (3)–(7), with experimentally observed peak fractions. The theoretical and experimental triad distributions agreed well when $\Delta$ was assumed to be an MMT triad. This finding is in agreement with that observed by Uebel and Dinan.[16] Table II shows that the values of the experimental triad fractions ($f_{MMM}$, $f_{MMT}$, and $f_{TMT}$) are almost identical with that calculated theoretically from eqs. (3)–(7). Therefore, it may be concluded that the triads (MMM + MMT) and TMT are assignments to peaks I and II, respectively.

TABLE II
Theoretical and Experimental Triad Fractions
with Δ Assumed to be MMT

| $f_2$ | $f_{222} + f_{221}$ | | $f_{121}$ | |
|---|---|---|---|---|
| | Experimental | Theoretical | Experimental | Theoretical |
| 0.50 | 0.8333 | 0.8636 | 0.1667 | 0.1364 |
| 0.55 | 0.8750 | 0.8861 | 0.1250 | 0.1140 |
| 0.65 | 0.9280 | 0.9411 | 0.0720 | 0.0589 |
| 0.75 | 0.9688 | 0.9713 | 0.0312 | 0.0287 |
| 0.90 | 1.0000 | 0.9951 | 0.0000 | 0.0040 |

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