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# Copolymerization of Acrylonitrile and Methacrylic Acid. An Assessment of the Copolymerization Mechanism

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ABSTRACT: The free-radical copolymerization of acrylonitrile and methacrylic acid has been investigated in bulk at 60 °C with the aim of elucidating the best model for the polymerization. Quantitative measurements of the copolymerization compositions and diad, triad, and tetrad fractions in the comonomer sequence distribution have been determined by using elemental analysis and $^1$H, $^{13}$C, and $^{13}$C DEPT NMR. This microstructural information was found to be consistent with a terminal polymerization mechanism with $r_M = 3.7$ and $r_A = 0.19$. The penultimate model was not found to provide a statistically significant improvement over the terminal model.

## Introduction

There have been few studies of the mechanism of copolymerization of methacrylic acid (M) and acrylonitrile (A). Alfrey et al.[1] in 1953 studied the copolymerization at 70 °C in aqueous solution at pH 7. They determined the polymer compositions by microanalysis. Greenley[2] analyzed their experimental data in terms of the terminal model and obtained reactivity ratios of $r_M = 0.194$ and $r_A = 0.027$.

Simionescu et al.[3] (1967) investigated the polymerization in solution in ethylene glycol carbonate at 70 °C and reported terminal model reactivity ratios of $r_M = 2.5$ and $r_A = 0.093$. Their data were reevaluated by Greenley,[2] who obtained values of $r_M = 2.39$ and $r_A = 0.092$.

Pichot et al.[4] studied the emulsion copolymerization at 35 °C and obtained the copolymer compositions by analysis of the residual monomer using gas chromatography. They evaluated the reactivity ratios from the analysis of four, low-conversion polymers prepared over the feed composition range 0.98–0.997 mole fraction acrylonitrile; thus, only the value of $r_A$ could be determined with high accuracy. The terminal model reactivity ratios so obtained were $r_M = 2.4$ and $r_A = 0.128$. The study also included an examination of the $^1$H and $^{13}$C NMR spectra of poly(acrylonitrile), poly(methacrylic acid), and copolymers with high acrylonitrile content, in which cotacticity and sequence distribution peaks were assigned. The peak intensities were found to be in good agreement with values calculated from their reactivity ratios.

Makushka et al.[5] studied the copolymerization of acrylonitrile and methacrylic acid in dimethyl sulfoxide (DMSO) at 70 °C and calculated the reactivity ratios for the terminal model. The polymerization was carried out with a total monomer concentration of 3.75 M under a nitrogen atmosphere. They calculated values for the reactivity ratios; $r_M = 0.75$ and $r_A = 0.25$.

Makushka et al.[6] subsequently investigated the copolymerization of methacrylic acid and acrylonitrile over the complete range of feed compositions in DMSO and in mixtures of DMSO and water (mole ratio approximately 1:4). The polymerizations were carried out under nitrogen at 60 °C with monomer conversions in the range 1–7%. The copolymer compositions were determined by nitrogen analysis and $^1$H NMR. The acrylonitrile-centered triad fractions were calculated from the methine resonance in the $^1$H NMR and the methacrylic acid centered triad fractions were calculated from the carbonyl resonance in the $^{13}$C NMR. Penultimate model reactivity ratios were calculated from the triad fractions using the equations derived by Chujo et al.[7] They reported the following values for the reactivity ratios in DMSO: $r_{MM} = 0.65$, $r_{AM} = 0.85$, $r_{AA} = 0.36$, and $r_{MA} = 0.33$ and in DMSO–H$_2$O, they reported $r_{MM} = 0.98$, $r_{AM} = 1.35$, $r_{AA} = 0.23$, and $r_{MA} = 0.20$. The authors suggest that there is a significant penultimate group effect for the methacrylic acid chain end radical in addition to polarity effects due to the nature of the solvent.

The aim of the present work has been to analyze the bulk copolymerization of methacrylic acid and acrylonitrile by using experimentally determined copolymer compositions, determined by nitrogen analysis and $^{13}$C NMR, and sequence distributions determined by $^1$H and $^{13}$C NMR, including the use of DEPT multipulse sequencing. Reactivity ratios have been calculated for the terminal and penultimate models using techniques that we have described previously.[8,9]

## Experimental Section

Methacrylic acid and acrylonitrile were passed through chromatographic columns to remove the inhibitor. A poly(styrene sulfonate) packing was used for methacrylic acid to remove hydroquinone and the methyl ester, and a neutral alumina column was used for acrylonitrile. The initiator, benzoyl peroxide, was recrystallized from chloroform by addition of methanol. The required amounts of initiator ($1.9 \times 10^{-3}$ M) were accurately weighed into the ampules, and the monomers were added by accurate volumetric techniques. The monomer mixtures were then thoroughly freeze–thaw degassed, and the ampules were sealed under vacuum. The polymerizations were carried out at 60 °C to conversions of 0.6–7.5% (average = 2.9%). The polymer was precipitated by addition to a 10-fold excess of acidified methanol or water (for high acrylonitrile content polymers), acidified distilled water (in the midrange), and acidified acetone (for high methacrylic acid content polymers). The copolymers were then reprecipitated from DMSO or pyridine into the above nonsolvents in the ranges indicated. The purified polymers were then dried in vacuo at room temperature for 12 h.

## Characterization

The compositions of the copolymers were determined from (i) nitrogen analysis by the micro-Kjedahl technique and (ii) from the relative intensities of the carbonyl (M units) and nitrile (A units) resonances in the $^{13}$C NMR

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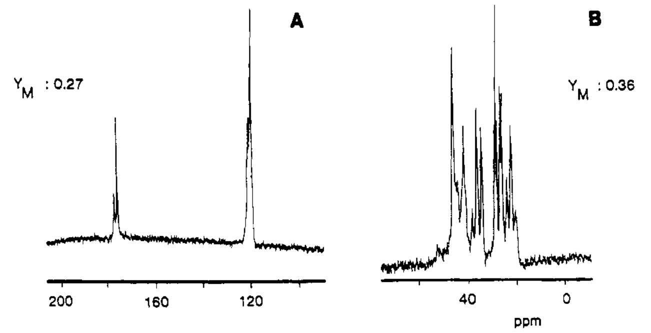

**Figure 1.** $^{13}C$ NMR spectra of poly(acrylonitrile-*co*-methacrylic acid) showing (A) the CO and CN region (solvent = DMSO-$d_6$) and (B) the CH region (solvent = pyridine-$d_5$).

spectra. $^{13}C$ NMR spectra were obtained using quantitative conditions: a 90° pulse angle, 15-s pulse delay, and inverse-gated decoupling to suppress NOE. From inversion-recovery experiments (60 and 80 °C), 15 s was shown to be longer than $5T_1$, for the slowest relaxing carbon atom, the quaternary resonance. These spectra were obtained on a Brüker CXP 300 NMR spectrometer (300 MHz for $^1H$ and 75.46 MHz for $^{13}C$) and/or a JEOL GX 400 NMR spectrometer (400 MHz for $^1H$ and 100 MHz for $^{13}C$) under a variety of conditions: room temperature and 60 and 80 °C, with methanol-*d*, acetone-$d_6$, DMSO-$d_6$, or pyridine-$d_5$ as solvents. Sample tubes of 10 mm o.d. were used, and the concentration of the solutions was, generally, in the range 8–10 w/v %.

The triad sequence distribution information was similarly extracted from the $^{13}C$ NMR spectra, concentrating upon the nitrile and carbonyl regions. Triad sequence distributions were also calculated from the methine resonance in the $^1H$ NMR spectra. These spectra were obtained with ≅4 w/v % solutions at 60 and 100 °C using a 45° pulse angle and pulse delays of 1.4, 10, 15, and 30 s.

The DEPT experiments were run by using the standard pulse sequence,[10] with $J_{CH} \cong 130$ Hz, and a pulse delay of 2 s. These samples were prepared to ≅10 w/v % in pyridine-$d_5$ and run at a temperature of 80 °C.

## Results

A detailed discussion of the $^1H$ and $^{13}C$ NMR spectra of these copolymers has been reported in a separate paper,[11] where the complex structure of the peaks in the aliphatic, nitrile, and carbonyl regions of the $^{13}C$ NMR spectra has been assigned. Typical $^{13}C$ NMR spectra of these copolymers are shown in Figure 1.

The experimentally determined copolymer compositions are given in Table I together with the comonomer feed compositions and the corresponding conversions. The $^{13}C$ NMR results, calculated from the relative intensities of the peaks in the carbonyl and nitrile regions, showed good agreement with the compositions determined from elemental analysis (% N).

The resolution of the major resonances in the carbonyl region and the nitrile region of the $^{13}C$ NMR, 173–181 and 118–124 ppm, respectively, allow spectrometer integration of the relative intensities and hence the calculation of the methacrylic acid centered and acrylonitrile-centered triad fractions, respectively. These are detailed in Table I.

The acrylonitrile-centered triad fractions can also be obtained from the DEPT subspectrum of the methine region of the $^{13}C$ NMR spectrum, 20–30 ppm. The acrylonitrile-centered triad fractions can also be obtained from the methine region of the $^1H$ spectra of these copolymers (see Figure 2). The agreement between the various methods for calculation of the acrylonitrile-centered triad fractions is excellent.

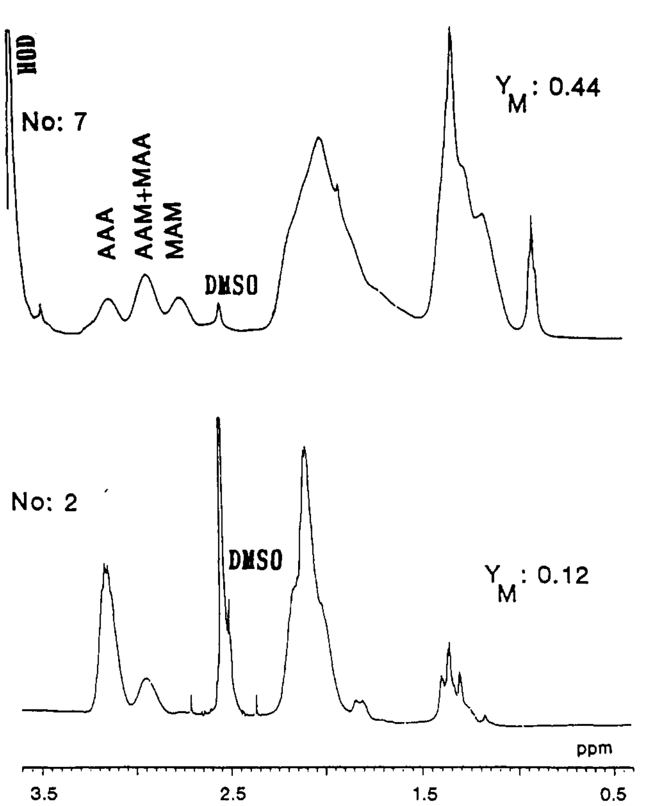

**Figure 2.** $^1H$ NMR spectra indicating the changes in the methine region, 2.5–3.2 ppm (reference DMSO-$d_6$, 2.49 ppm) with increasing methacrylic acid in the copolymer.

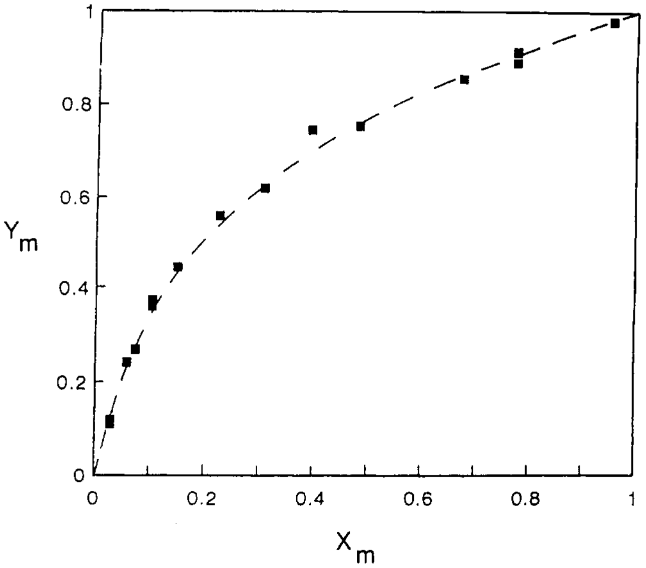

**Figure 3.** Terminal model fit using NLLS analysis of the copolymer composition data obtained using $^{13}$ NMR: (■) experimental points, (– –) terminal model fit to the data. $X_M$ = mole fraction MAA in the feed. $Y_M$ = mole fraction MAA in the polymer.

The DEPT subspectra of the methylene region of the $^{13}C$ NMR spectra, 33–57 ppm, consist of resonances that can be assigned to the diad and tetrad sequences in the copolymers. However, some overlap occurs between a few of the tetrad resonances, in particular, the AMMA and the MAMM resonances, which leads to some uncertainty in the values for the MM and AM diad fractions.

## Discussion

**Evaluation of Reactivity Ratios.** Reactivity ratios based upon best fits of the composition and triad fraction

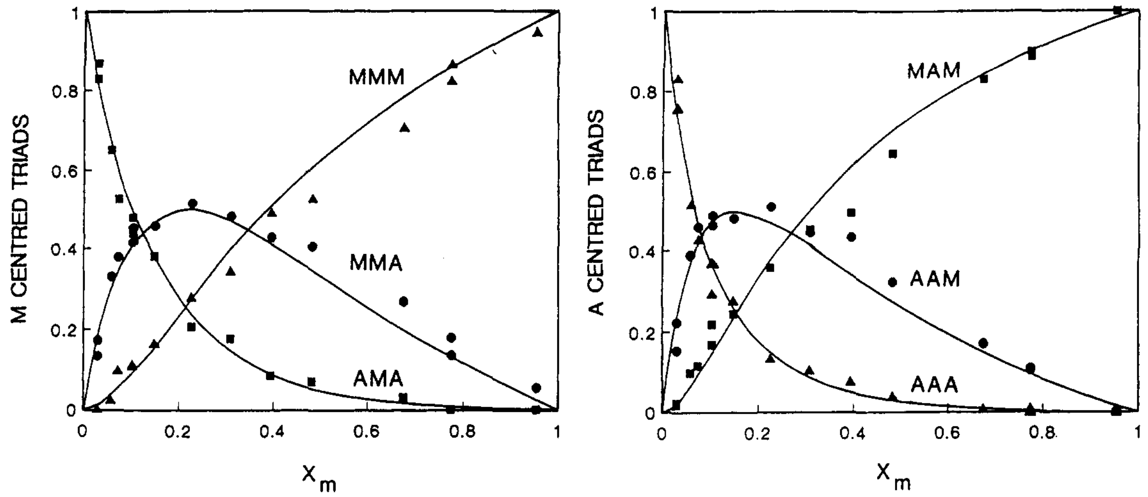

**Figure 4.** Terminal model fit (using NLLS analysis) to the M-centered and A-centered triad fractions. Calculated curve (—).

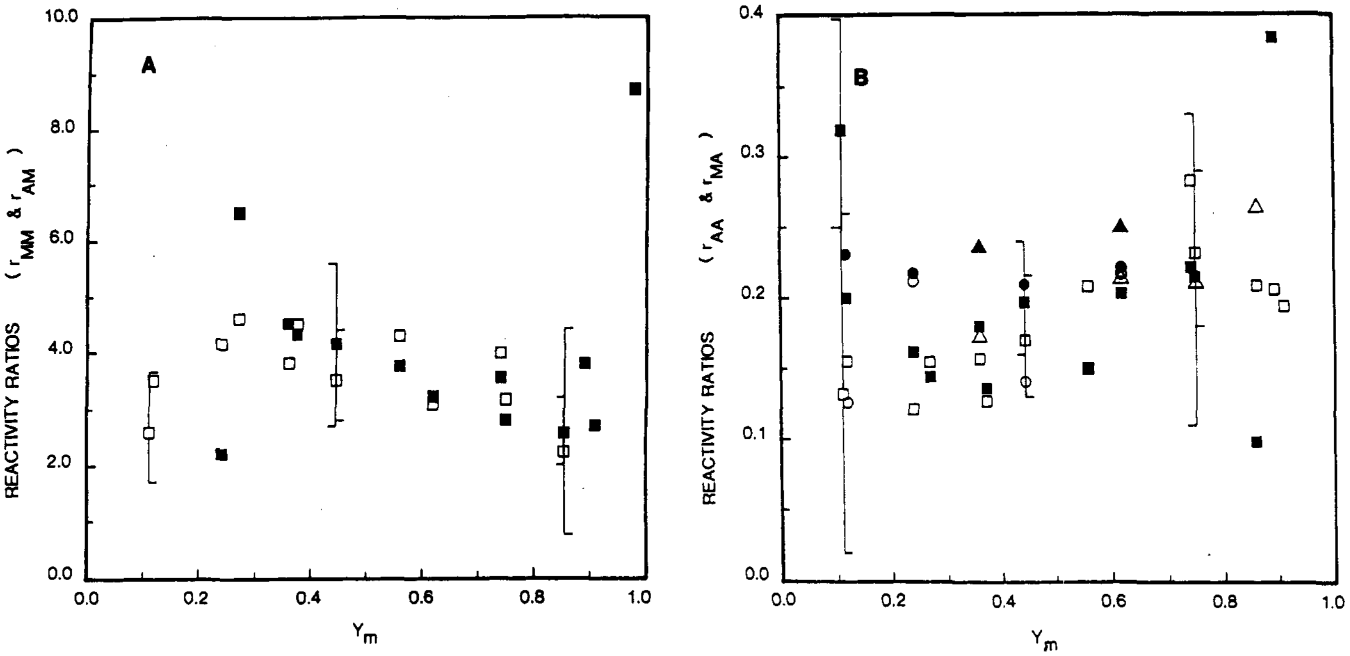

**Figure 5.** Penultimate model reactivity ratios evaluated using Chujo's equations. (A) (■) $r_{MM}$, (□) $r_{AM}$. (B) (■) $r_{AA}$, nitrile region; (●) $r_{AA}$, methine region in $^1$H NMR; (▲) $r_{AA}$, methine region in $^{13}$C NMR; (□) $r_{MA}$, nitrile region; (○) $r_{MA}$, methine region in $^1$H NMR; (△) $r_{MA}$, methine region in $^{13}$C NMR. Examples of the changes in the magnitude of the errors over the composition range are indicated.

**Table I**
**Experimentally Determined Copolymer Compositions and Triad Fractions Determined by $^{13}$C NMR**

| | | | | A-centered triads | | | M-centered triads | | |
|---|---|---|---|---|---|---|---|---|---|
| polymer | $X_M$ | convn, wt % | $Y_M$ | AAA | AAM | MAM | AMA | MMA | MMM |
| 1 | 0.029 | 1.1 | 0.118 | 0.757 | 0.222 | 0.021 | 0.828 | 0.172 | 0.000 |
| 2 | 0.029 | 7.4 | 0.110 | 0.831 | 0.153 | 0.017 | 0.868 | 0.132 | 0.000 |
| 3 | 0.057 | 2.1 | 0.241 | 0.516 | 0.387 | 0.097 | 0.650 | 0.328 | 0.022 |
| 4 | 0.072 | 0.6 | 0.268 | 0.426 | 0.459 | 0.115 | 0.527 | 0.377 | 0.095 |
| 5 | 0.102 | 1.7 | 0.372 | 0.292 | 0.489 | 0.219 | 0.438 | 0.452 | 0.110 |
| 6 | 0.102 | 5.5 | 0.360 | 0.368 | 0.464 | 0.168 | 0.479 | 0.415 | 0.106 |
| 7 | 0.147 | 3.2 | 0.444 | 0.275 | 0.481 | 0.244 | 0.380 | 0.458 | 0.163 |
| 8 | 0.225 | 0.5 | 0.560 | 0.132 | 0.511 | 0.357 | 0.207 | 0.515 | 0.278 |
| 9 | 0.307 | 3.0 | 0.618 | 0.102 | 0.445 | 0.452 | 0.177 | 0.482 | 0.341 |
| 10 | 0.393 | 1.3 | 0.743 | 0.074 | 0.432 | 0.495 | 0.083 | 0.427 | 0.490 |
| 11 | 0.482 | 1.6 | 0.752 | 0.037 | 0.320 | 0.643 | 0.069 | 0.404 | 0.526 |
| 12 | 0.674 | 4.5 | 0.855 | 0.004 | 0.168 | 0.828 | 0.029 | 0.267 | 0.704 |
| 13 | 0.774 | 2.4 | 0.919 | 0.000 | 0.102 | 0.898 | 0.000 | 0.178 | 0.822 |
| 14 | 0.774 | 5.5 | 0.892 | 0.006 | 0.107 | 0.887 | 0.000 | 0.134 | 0.866 |
| 15 | 0.954 | 2.6 | 0.980 | 0.000 | 0.000 | 1.000 | 0.000 | 0.053 | 0.947 |

data to the terminal and penultimate models have been evaluated by using the mathematical techniques that we have described previously.[8,9,12,13] Terminal and penultimate model reactivity ratios have also been calculated from the triad fraction data by using the equations developed by Chujo et al.[7]

**Terminal Model.** The composition data obtained by $^{13}$C NMR have been analyzed in terms of the terminal model. The estimates of the reactivity ratios $r_M$ and $r_A$ are shown in Table II. The nonlinear least-squares fit to

**Table II**
**Terminal Model Reactivity Ratios Calculated from the Copolymer Compositions and Triad Fractions**

| parameter | compositions | triads |
|---|---|---|
| $r_M$ | 3.14 | 3.70 |
| $r_A$ | 0.163 | 0.185 |
| pieces of data | 15 | 90 |
| $s_y$[a] | 0.019 | 0.037 |
| estimated error[b] | 0.015 | 0.04 |

[a] Standard error in the composition or triad fraction calculated from the NLLS curve fit. [b] Experimental error estimated from repeated measurements.

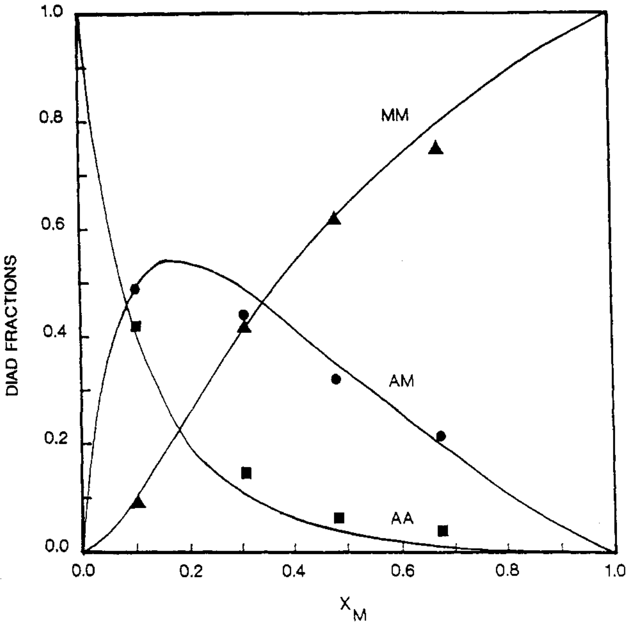

**Figure 6.** Diad fractions calculated from the methylene region, using the DEPT experiment: (■) AA diad, (●) AM diad, (▲) MM diad, (—) predicted diad fractions.

the data obtained from $^{13}C$ NMR (at 25 and 60 °C) is demonstrated in Figure 3. This plot demonstrates that the terminal model provides a very good representation of the experimental composition data.

Analysis of the combined methacrylic acid centered and acrylonitrile-centered triad fraction in terms of the terminal model yielded the reactivity ratios given in Table II. The nonlinear least-squares (NLLS) fit to the sequence distributions across the feed composition range is illustrated in Figure 4. The agreement between the experimental values and the values predicted by the model is excellent for each of the six triad fractions.

The reactivity ratios calculated from the NLLS fit to the triads are in excellent agreement with those calculated from Chujo's equations as weighted averages. The weightings of the individual values of the reactivity ratios calculated from Chujo's relationships were based upon the estimates of the experimental error obtained from integration of the triad peaks in the $^{13}C$ NMR spectra. It is also evident from Table II that the reactivity ratios calculated from both the compositions and the triad fractions yield values that are entirely consistent.

**Penultimate Model.** The reactivity ratios for the penultimate model have been generated from the composition and triad sequence data. An examination of the standard errors, $s_y$, in the fitted data, indicates that there is no significant improvement in the fit of the penultimate model over that for the terminal model. This is true for both the composition and triad sequence data.

The mathematical analysis of the composition data also revealed that there were multiple broad minima on the hypersurface and that several of these had very similar "sums for the squared deviations" ($SS(\hat{\theta})$). By contrast, the penultimate model reactivity ratios based upon the triad fractions were much more clearly defined. The standard error in the triad fractions based upon the fit to the terminal model was 0.038, compared with a value of 0.031 based upon the fit to the penultimate model. These values are compared with external estimates, calculated from repeated experiments, of ≅0.04. The penultimate reactivity ratios can also be calculated from the individual copolymer triad sequence fractions by using Chujo's equations (as indicated in Figure 5). The figures show no evidence of any penultimate unit effect, within experimental error, confirming the observations made using the NLLS analysis of the composition data. It is evident from Figure 5 that within experimental error $r_{AA} = r_{MA}$ and $r_{MM} = r_{AM}$.

**Diad Fractions.** As a test of the accuracy in assigning the terminal model to this system, we have used the terminal model reactivity ratios (calculated from the NLLS fit to the triad sequence fractions) to predict the diad sequence fractions (see Figure 6). The predicted diad fractions are indicated by the drawn curves and can be seen to be in excellent agreement with the diad fractions derived from the methylene subspectra.

## Conclusions

It is evident from the results of fitting the models to the compositions and the triad fractions (using NLLS analysis and Chujo's equations) that the terminal model provides as good a fit to the data as does the penultimate model. It is also evident that the values of the terminal reactivity ratios generated from fitting either the triad sequence fractions or the compositions are in excellent agreement, and therefore this model provides a good description of the copolymerization of methacrylic acid and acrylonitrile in bulk at 60 °C. Moreover, as we have found previously,[12] the reactivity ratios evaluated from the triad fractions provide more accurate values than those evaluated from the composition data. The reactivity ratios derived from the triad fractions have been used to predict the diad sequence fractions, which have been found to be in excellent agreement with those determined experimentally.

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