# One- and Two-Dimensional Nuclear Magnetic Resonance Studies on the Compositional Sequence and the Microstructure of Acrylamide/Acrylonitrile Copolymers 

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#### Abstract

Copolymers containing acrylamide $(A)$ and acrylonitrile ( $B$ ) units of different compositions were synthesized by free-radical solution polymerization. The reactivity ratios were estimated by the Kelen Tudos and nonlinear error-in-variable methods. The triad sequence distribution in terms of $A$ - and $B$-centered triads were obtained from ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$-NMR spectroscopy. The complete spectral assignments in terms of compositional and configurational sequences of the overlapping carbon and proton spectra of these copolymers were done using distortionless enhancement by polarization transfer (DEPT), two-dimensional proton-detected heteronuclear correlation (inverse-HETCOR), and total correlated spectroscopy (TOCSY) experiments. The Monte Carlo simulation was used to study the effect of the fractional conversion on the triad fractions. © 1999 John Wiley \& Sons, Inc. J Appl Polym Sci 73: 55-67, 1999


Key words: acrylamide; acrylonitrile; copolymers; microstructure; NMR

## INTRODUCTION

The physical and chemical properties of polymers are influenced fundamentally by their molecularlevel microstructure which involves the character of the monomer distribution in the polymer chain and the stereochemical arrangement of various groups (tacticity). ${ }^{1-3}$ High-resolution nuclear magnetic resonance (NMR) spectroscopy has been particularly effective in the determination of the chain structure of polymers. ${ }^{4}$ One-dimensional (1D) techniques were not always suitable for unequivocal signal assignments; therefore, two-dimensional (2D) NMR, especially homonuclear (COSY, TOCSY) and heteronuclear (HETCOR)

[^0]correlation spectroscopies, has been successfully applied to provide the tacticity assignments and microstructure analysis of various polymer systems. ${ }^{5-7}$

Homo- and copolymers of acrylonitrile are of great interest in many industrial applications, for example, as adhesives, binders, antioxidants, viscosity index improvers, and insecticides. The microstructure of acrylonitrile copolymers has been studied extensively by various workers. ${ }^{8-10}$ Copolymers of acrylamide/acrylonitrile are commercially useful because their fibers show improved dyeability, impart better moisture regain, and possess good suitability characteristics.

In this article, we report the copolymerization mechanism of acrylamide/acrylonitrile ( $A / B$ ) copolymers prepared by solution polymerization. The various compositional/configurational sequences were assigned using inverse HETCOR and DEPT experiments. 2D TOCSY was used for complete assignments of the broad and

Table I Feed Mol Fractions, Percent Conversion, and Copolymer Compositions for Acrylamide/Acrylonitrile Copolymers (A/B)

| Sample No. | Feed Mol Fraction $\left(f_{A}\right)$ | Percent Conversion | $\left(F_{A}\right){ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}-\mathrm{NMR}$ |
| :---: | :---: | :---: | :---: |
| 1 | 0.15 | 5.2 | 0.14 |
| 2 | 0.30 | 4.1 | 0.27 |
| 3 | 0.40 | 3.8 | 0.33 |
| 4 | 0.50 | 5.1 | 0.38 |
| 5 | 0.55 | 6.3 | 0.43 |
| 6 | 0.60 | 5.5 | 0.49 |
| 7 | 0.65 | 3.5 | 0.52 |
| 8 | 0.70 | 5.8 | 0.57 |
| 9 | 0.75 | 6.5 | 0.61 |
| 10 | 0.80 | 5.6 | 0.67 |

overlapping proton spectra of the $A / B$ copolymer system.

## EXPERIMENTAL

Acrylamide (SRL, India) was recrystallized twice from chloroform. N,N-Dimethylformamide (DMF; Merck, Germany) was distilled and dried. Acrylonitrile (CDH, India) was distilled under reduced pressure and stored below $5^{\circ} \mathrm{C}$. A series of acrylamide/acrylonitrile ( $A / B$ ) copolymers containing different mol percents of acrylamide in the feed were prepared by solution polymerization using benzoyl peroxide as the initiator at $65^{\circ} \mathrm{C}$. The percent conversion was kept below $10 \%$ by precipitating the copolymers in methanol. The copolymers were further dissolved in DMSO and reprecipitated in methanol and vacuum-dried.

The ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$-NMR spectra were recorded in DMSO- $d_{6}$ on a Bruker DPX 300 MHz spectrometer operating at 300.13 and 75.5 MHz , respectively. All the 2D experiments were carried out on the Bruker DPX 300 MHz spectrometer. The quantitative ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$-NMR experiments were carried out using the inverse-gated decoupling pulse program with a 12 -s delay time. DEPT measurements were carried in DMSO- $d_{6}$ at $100^{\circ} \mathrm{C}$ using the standard pulse sequence with a $J$ modulation time of 3.7 ms $\left(J_{\mathrm{CH}}=135 \mathrm{~Hz}\right)$ with a 2 -s delay time. A 2D proton-detected ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ heteronuclear chemical shift correlation spectrum was recorded in DMSO $-d_{6}$ at $100^{\circ} \mathrm{C}$ using the standard pulse sequence. A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the 512 $t_{1}$ experiments. The 2D TOCSY experiment ${ }^{11}$
was carried out at $100^{\circ} \mathrm{C}$ in DMSO- $d_{6}$. The mixing times used for these experiments were 4 and 80 ms . All the curve fittings were done using a nonlinear least-square deconvoluting program. In all cases, regression converged to $\chi^{2}<1$.

## RESULTS AND DISCUSSION

## Reactivity Ratio Determination

The composition of acrylamide (A)/acrylonitrile (B) copolymers were determined from quantita-


Figure 1 The 95\% joint confidence intervals for the acrylamide/acrylonitrile comonomer pair.


Figure $2{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$-NMR spectrum of the $A / B$ copolymer ( $F_{A}=0.49$ ) in DMSO- $d_{6}$ at $100^{\circ} \mathrm{C}$.
tive ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$-NMR spectra. Table I shows the comonomer mol fraction in the feed and in the copolymer along with the percentage conversion. The terminal model reactivity ratios of the comonomers were estimated as $r_{A}=0.37 \pm 0.05$ and $r_{B}=1.03 \pm 0.10$ using the Kelen Tudos ${ }^{12}$ (KT) method. These values along with the copoly-
mer composition data were used to calculate the reactivity ratios using the EVM program. ${ }^{13}$ The terminal model reactivity ratios obtained from the EVM program are $r_{A}=0.36$ and $r_{B}=1.01$, respectively. A 95\% joint confidence interval plot for the $A / B$ comonomer pair is shown in Figure 1.


$$
\begin{array}{llllllllllllllllllll}
44 & 43 & 42 & 41 & 40 & 39 & 38 & 37 & 36 & 35 & 34 & 33 & 32 & 31 & 30 & 29 & 28 & 27 & 26 & \mathrm{ppm}
\end{array}
$$

Figure 3 The DEPT-135 spectra of the $A / B$ copolymer ( $F_{A}=0.49$ ) in DMSO- $d_{6}$ at $100^{\circ} \mathrm{C}$.


Figure 4 Expanded DEPT-135 spectra showing the methine carbon signals of the $B$ unit of different copolymer compositions $\left(F_{A}\right)$ : (a) 0.14 ; (b) 0.27 ; (c) 0.38 ; (d) 0.49 ; (e) 0.57 ; (f) 0.67 .

## NMR Studies

Figure 2 shows the ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$-NMR spectrum of the $A / B$ copolymer ( $F_{A}=0.49$ ) in DMSO- $d_{6}$ at $100^{\circ} \mathrm{C}$. The carbonyl carbon $( \rangle \mathrm{C}=\mathrm{O})$ and the nitrile carbon (-CN) resonances show multiplets around $\delta 173.8-177.2$ and $119.5-122.4 \mathrm{ppm}$, respectively, indicating their sensitivity toward compositional sequences. Thus, these signals can be used to assess the copolymerization mechanism. The aliphatic carbon region can be assigned using the DEPT-135 system, where the methine carbon sig-
nals have a positive phase and the methylene carbon signals have a negative phase, as shown in Figure 3. The methylene carbon signals of both the $A$ and $B$ units appear around $\delta 32.5-36.5 \mathrm{ppm}$. The signals around $\delta 40.8-42.8$ and $26.5-28.3$ ppm are assigned to the methine carbon resonances of the $A$ and $B$ units, respectively. These signals show both configurational and compositional sensitivity. The methine carbon resonance signals can be divided into three envelopes which do not change with the copolymer composition


Figure 5 Expanded DEPT-135 spectra showing the methine carbon signals of the $A$ unit of different copolymer compositions $\left(F_{A}\right)$ : (a) 0.14 ; (b) 0.27 ; (c) 0.38 ; (d) 0.49 ; (e) 0.57 ; (f) 0.67 .
and are assigned to configurational sequences, such as $m m, m r(r m)$, and $r r$ triads, on the basis of the assignments done in the respective homopolymer spectra. ${ }^{14,15}$ Figure $4(a-f)$ shows the methine carbon signals of the $B$ unit of six different compositions. The three broad envelopes of signals are assigned to $m m$ ( $\delta 26.70-27.20 \mathrm{ppm})$, $m r$ ( $\delta 27.21-27.82 \mathrm{ppm}$ ), and $r r$ ( $\delta 27.83-28.30 \mathrm{ppm}$ ), respectively, as assigned in the polyacrylonitrile ${ }^{15}$ spectra. Within these configurational sequences, compositional triad fractions can be assigned on the basis of the change in the intensity of the signals with the copolymer composition. Thus, the
signals at $\delta 27.15,27.05$, and 26.87 ppm are assigned to $B m B m B, B m B m A$, and $A m B m A$, respectively. In the $m r$ region, the three signals which change in intensity with the copolymer composition are assigned to the BmBrB ( $\delta 27.64$ $\mathrm{ppm}), B m B r A+B r B m A(\delta 27.53 \mathrm{ppm})$, and $\mathrm{Am}-$ $\operatorname{BrA}(\delta 27.42 \mathrm{ppm})$ triad configurational sequences. Similarly, the signals around $\delta 28.0-28.30$ and at 27.87 ppm are assigned to the $B r B r A+B r B r B$ and $A r B r A$ triad fractions, respectively. The methine carbon signals of the $A$ unit are similarly assigned as shown in Figure $5(\mathrm{a}-\mathrm{f})$. The signals around $\delta 40.8-41.5,41.6-42.0$,


Figure 6 The inverse-HETCOR spectrum showing the methine and methylene region of acrylamide/acrylonitrile (A/B) copolymer (a) $\mathrm{F}_{\mathrm{A}}=0.27$, (b) 0.49 , (c) 0.67 in DMSO- $\mathrm{d}_{6}$ at $100^{\circ} \mathrm{C}$.


Figure 6 (Continued from the previous page)
and $42.0-42.8 \mathrm{ppm}$ are assigned to the $\mathrm{mm}, \mathrm{mr}$, and $r r$ configurational triad fractions, respectively, as the intensity of the signals do not change with the copolymer compositions. The compositional
triad sequences within these configurational regions overlap considerably. The various compositional and configurational sequences in the methylene carbon region $\left(\mathrm{CH}_{2}\right)(\delta 33.0-36.1 \mathrm{ppm})$ could


Figure $7{ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of the $A / B$ copolymer $\left(F_{A}=0.49\right)$ in DMSO- $d_{6}$ at $100^{\circ} \mathrm{C}$.


Figure 8 Expanded 2D-TOCSY spectrum ( 4 ms ) of the $A / B$ copolymer ( $F_{A}=0.49$ ) in DMSO- $d_{6}$ at $100^{\circ} \mathrm{C}$.
not be assigned due to considerable overlap of the signals.

Once the ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$-NMR spectrum of the copolymer is completely assigned, the complex and overlapping ${ }^{1} \mathrm{H}$-NMR spectrum can be assigned using the inverse HETCOR experiment. Figure 6(a-c) shows the ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ proton-detected heteronuclear correlation spectrum of the $A / B$ copolymers of three different compositions ( $F_{A}=0.27,0.49$, and $0.67)$. The methine proton signals of both $A$ and $B$ units are assigned to compositional triad sequences using one-to-one correlation between the carbon and the corresponding protons in the inverse HETCOR spectra. In the ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum, the methine proton signals of the $A$ unit resonance around $\delta 2.0-2.6 \mathrm{ppm}$, whereas the $B$ unit resonance around $\delta 2.4-3.2 \mathrm{ppm}$. The methine proton signals of both the $A$ and $B$ units were assigned to the various compositional triad sequences on the basis of the variation of the intensity of the signals with the copolymer composition, as seen in the inverse HETCOR spectra [Fig. 6(a-c)]. Thus, the signals around $\delta 2.0-2.2$,
$\delta 2.2-2.4, \delta 2.4-2.6, \delta 2.6-2.87$, and $\delta 2.87-3.2 \mathrm{ppm}$ were assigned to the $A A A, A A B, B A B+A B A$, $B B A$, and $B B B$ triads, respectively, in the ${ }^{1} \mathrm{H}-$ NMR spectrum of the $A / B$ copolymer system (Fig. 7). The methylene proton signals of both the $A$ and $B$ units resonance around $\delta 1.2-2.0 \mathrm{ppm}$ and cannot be resolved due to considerable overlap of the signals.

The various $\mathrm{CH} / \mathrm{CH}_{2}$ proton couplings in the triad fractions can be assigned using the DQFCOSY spectrum. However, in the DQFCOSY spectrum, all the cross peaks were not seen clearly due to overlapping and cancellation of negative and positive signals. These cross peaks can be clearly seen in the low-mixing-time TOCSY spectrum. The direct couplings between the bonded protons (AM spin type) can be seen in short-mixing-time ( 4 ms ) TOCSY, whereas at a longer mixing time ( 80 ms ), one can see the relay couplings (AMX spin type) through magnetization transfer. Figure 8 shows the expanded TOCSY ( $4-\mathrm{ms}$ ) spectrum of the $A / B$ copolymer ( $F_{A}=0.49$ ). The three $A$-centered triad fractions further show configurational sensitivity.


Figure 9 Expanded 2D-TOCSY spectrum $(80 \mathrm{~ms})$ of the $A / B$ copolymer $\left(F_{A}=0.49\right)$ in DMSO- $d_{6}$ at $100^{\circ} \mathrm{C}$.

The methine proton ( $\delta 2.15 \mathrm{ppm}$ ) in the $A m A m A$ triad fraction shows two three bond coupling with the nonequivalent protons at $\delta 1.37$ and 1.69 ppm , respectively. Thus, the cross peak at $\delta 2.15 / 1.37$ and $\delta 2.15 / 1.69 \mathrm{ppm}$ (peak no. 1 ) is assigned to the $A m A m A$ triad fraction. The geminal coupling between the two nonequivalent methylene protons are seen at $\delta 1.37 / 1.69 \mathrm{ppm}$ (2). Similarly, the cross peaks at $\delta 2.11 / 1.49$ (3) and $\delta 2.06 / 1.46$ (4) ppm are assigned to the $A m A r A$ and $A r A r A$ triad fractions, respectively. In the $A A B$ triad region, the methine proton at $\delta 2.34 \mathrm{ppm}$ is assigned to the $A m A B$ triad fraction and shows two cross peaks at $\delta 2.34 / 1.41$ and $2.34 / 1.73 \mathrm{ppm}$ (5), which are due to three-bond coupling between the methine proton and two different types of methylene protons, that is, the methylene protons of the $A A$ and $A B$ dyads. Similarly, the methine proton at $\delta 2.27 \mathrm{ppm}$ is assigned to the $A r A B$ triad fraction which also shows two cross peaks to different types of methylene protons [ $\delta 2.27 / 1.54$ and 2.27/ 1.80 ppm (6)]. Furthermore, in the $A m A B$ triad, the methylene protons in the $A m A$ dyad are nonequivalent and show geminal coupling at $\delta 1.41 /$
1.73 ppm (7). Similarly, the three cross peaks at 82.46/1.68 (2.46/1.85) (8), 2.50/1.76 (9), and 2.52/ 1.84 ppm (10) are due to the $m m, m r$, and $r r$ configurational sequences in the $B A B$ triad fraction. The geminal coupling of the nonequivalent methylene protons in the $B m A m B$ triad fraction is assigned to $\delta 1.68 / 1.85 \mathrm{ppm}$ (11).

Similarly, the $B$-centered triad fractions were assigned to various configurational sequences using the TOCSY spectrum [Fig. 8(a)]. The $B B B$ triad fraction shows only one cross peak at $\delta 2.98 /$ 1.94 ppm (12). In the $B B A$ triad fraction, the central methine proton will show three-bond coupling to two different types of methylene protons, that is, $\left(\mathrm{CH}_{2}\right)_{A}$ and $\left(\mathrm{CH}_{2}\right)_{B}$ types. Therefore, the cross peaks at $\delta 2.81 / 1.87$ (2.81/1.67) (13), 2.74/ 1.85 (2.74/1.69) (14), and 2.69/1.63 (2.69/1.77) ppm (15) can be assigned to $B m B m A, B m B r A$, and $B r B r A$. In the $B m B m A$ triad fraction, the methylene protons in the $B m B$ dyad show geminal coupling at $\delta 1.87 / 1.67 \mathrm{ppm}(16)$, due to the presence of nonequivalent methylene protons. Similarly, the cross peaks at $\delta 2.55 / 1.59$ (17), 2.48/ 1.59 (18), and $2.44 / 1.52 \mathrm{ppm}$ (19) are assigned to

Table II TOCSY ${ }^{1} \mathbf{H}-{ }^{1} H$ Shift Correlation with Assignments

| Peak No. | Type of Proton (ppm) | Coupled to (ppm) | Assignments |
| :---: | :---: | :---: | :---: |
| 1 | $\mathrm{CH}(2.15)$ | CH2 (1.37 and 1.69) | $A m A m A$ |
| 2 | $\mathrm{CH}_{2}$ (1.37) | $\mathrm{CH}_{2}$ (1.69) | $A m A m A$ (geminal) |
| 3 | $\mathrm{CH}(2.11)$ | $\mathrm{CH}_{2}$ (1.49) | AmArA |
| 4 | CH(2.06) | $\mathrm{CH}_{2}$ (1.46) | ArArA |
| 5 | CH(2.34) | $\mathrm{CH}_{2}$ (1.41 and 1.73) | $A m A B$ |
| 6 | CH(2.27) | $\mathrm{CH}_{2}$ (1.54 and 1.80) | ArAB |
| 7 | $\mathrm{CH}_{2}$ (1.41) | $\mathrm{CH}_{2}$ (1.73) | $A m A B$ (geminal) |
| 8 | CH(2.46) | $\mathrm{CH}_{2}$ (1.68 and 1.85) | $B m A m B$ |
| 9 | $\mathrm{CH}(2.50)$ | $\mathrm{CH}_{2}$ (1.76) | BmArB |
| 10 | CH(2.52) | $\mathrm{CH}_{2}$ (1.84) | BrArB |
| 11 | $\mathrm{CH}_{2}(1.68)$ | $\mathrm{CH}_{2}$ (1.85) | $B m A m B$ (geminal) |
| 12 | CH(2.98) | $\mathrm{CH}_{2}$ (1.94) | BBB |
| 13 | CH(2.81) | $\mathrm{CH}_{2}$ (1.87 and 1.67) | BmBmA |
| 14 | CH(2.74) | $\mathrm{CH}_{2}(1.85$ and 1.69) | $B m B r A(B r B m A) ~$ |
| 15 | CH(2.69) | $\mathrm{CH}_{2}$ (1.63 and 1.77) | BrBrA |
| 16 | $\mathrm{CH}_{2}(1.67)$ | $\mathrm{CH}_{2}$ (1.87) | $B m B m A$ (geminal) |
| 17 | CH(2.55) | $\mathrm{CH}_{2}(1.59)$ | AmBmA |
| 18 | $\mathrm{CH}(2.48)$ | $\mathrm{CH}_{2}$ (1.59) | $A m B r A$ |
| 19 | CH(2.44) | $\mathrm{CH}_{2}$ (1.52) | ArBrA |
| 20 | CH(2.50) | CH (2.74) | BBAB |
| 21 | CH(2.42) | CH (2.57) | $B A B A$ |
| 22 | CH(2.28) | CH (2.48) | $A B A A B+B A B A A$ |
| 23 | CH(2.34) | CH (2.69) | $B B A A$ |
| 24 | CH(2.13) | CH (2.27) | $B A A A$ |

the $A m B m A, A m B r A$, and $A r B r A$ triad fractions, respectively.

Figure 9 shows the $80-\mathrm{ms} 2 \mathrm{D}$ TOCSY spectra of the $A / B$ copolymer $\left(F_{A}=0.49\right)$ in DMSO- $d_{6}$. The central methine proton of the $B A B$ triad fraction ( $\delta 2.50 \mathrm{ppm}$ ) shows a four-bond relayed coupling with the methine proton of the $B B A$ triad fraction ( $\delta 2.74 \mathrm{ppm}$ ); thus, the cross peak at $\delta 2.50 / 2.74$ ppm (20) is assigned to the $B B A B$ tetrad. The cross peak at $2.42 / 2.57 \mathrm{ppm}$ (21) is the relayed coupling between the central methine protons of the $B A B$ and $A B A$ triad fractions, thus accounting for the $B A B A$ tetrad. Similarly, the cross peak at $\delta 2.28 / 2.48 \mathrm{ppm}$ (22) is assigned to $A B A A B$ $+B A B A A$ pentad sequences, due to relayed coupling between the methine proton of BAA ( $\delta 2.28$ $\mathrm{ppm})$ and the $A B A+B A B(\delta 2.48 \mathrm{ppm})$ triad fractions. The methine proton at $\delta 2.34 \mathrm{ppm}$ (BAA) shows a relayed coupling with the methine proton at $\delta 2.69 \mathrm{ppm}(B B A)$. Thus, the cross peak at $\delta 2.34 / 2.69 \mathrm{ppm}(23)$ is assigned to the BBAA tetrad sequence. Similarly, the cross peak at $\delta 2.13 /$ 2.27 (24) is the relayed coupling between the central methine protons of the $A A A$ and $B A A$ triad, thus accounting for the BAAA tetrad. All the $\mathrm{CH} /$ $\mathrm{CH}_{2}$ couplings are given in Table II.

The carbonyl $( \rangle \mathrm{C}=\mathrm{O})$ and the nitrile ( -CN ) carbon resonances show multiplets, indicating
that they are sensitive toward the compositional sequences and can be used to assess the copolymerization mechanism. The expanded ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}-$ NMR spectrum of the carbonyl and the nitrile carbon resonances of the $A / B$ copolymer ( $F_{A}$ $=0.49)$ is shown in Figure 2. The signals around $\delta 176.2-177.2, \quad \delta 175.3-176.2$, and $\delta 173.8-175.3$ ppm are assigned to $A A A, A A B(B A A)$, and $B A B$, respectively, on the basis of variation in the intensity of the signals with copolymer composition. Similarly, the nitrile carbon resonance also shows triad sensitivity and the resonance signals around $\delta 119.5-120.6, \delta 120.6-121.2$, and $\delta 121.2-$ 122.4 ppm were assigned to the $B B B, B B A(A B B)$, and $A B A$ triad fractions, respectively. The concentration of various $A$ - and $B$-centered triad fractions were calculated from the relative areas of the resonance signals. Assuming the AlfreyMayo (first-order Markov) model to be valid at any moment of the low-conversion copolymers, the triad fractions can be calculated using the terminal model reactivity ratios, $r_{A}=0.36$ and $r_{B}$ $=1.01$. Table III shows the $A$ - and $B$-centered triad fractions calculated from the Alfrey-Mayo model using Harwood's program ${ }^{16}$ and the experimentally (NMR) determined triad fractions. There is a good agreement between the calculated and the experimentally (NMR) determined triad

Table III Triad Compositions Calculated from NMR Spectra and Alfrey-Mayo Model in Acrylamide/ Acrylonitrile (A/B) Copolymer

| Sample No. | Feed Mol Fraction of $A$ | Triads | Triad Concentration ${ }^{\text {a }}$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$-NMR | Alfrey-Mayo |
| 1 | 0.30 | $A A A$ | 0.00 | 0.02 |
|  |  | $A A B$ | 0.25 | 0.23 |
|  |  | $B A B$ | 0.75 | 0.75 |
|  |  | $B B B$ | 0.49 | 0.49 |
|  |  | $B B A$ | 0.42 | 0.42 |
|  |  | $A B A$ | 0.09 | 0.09 |
| 2 | 0.40 | $A A A$ | 0.05 | 0.04 |
|  |  | $A A B$ | 0.32 | 0.31 |
|  |  | $B A B$ | 0.63 | 0.65 |
|  |  | $B B B$ | 0.34 | 0.36 |
|  |  | $B B A$ | 0.51 | 0.48 |
|  |  | $A B A$ | 0.15 | 0.16 |
| 3 | 0.50 | $A A A$ | 0.06 | 0.07 |
|  |  | $A A B$ | 0.38 | 0.39 |
|  |  | $B A B$ | 0.56 | 0.54 |
|  |  | $B B B$ | 0.26 | 0.25 |
|  |  | $B B A$ | 0.51 | 0.50 |
|  |  | $A B A$ | 0.23 | 0.25 |
| 4 | 0.55 | $A A A$ | 0.11 | 0.09 |
|  |  | $A A B$ | 0.42 | 0.42 |
|  |  | $B A B$ | 0.47 | 0.48 |
|  |  | $B B B$ | 0.22 | 0.20 |
|  |  | $B B A$ | 0.47 | 0.49 |
|  |  | $A B A$ | 0.31 | 0.30 |
| 5 | 0.60 | $A A A$ | 0.14 | 0.12 |
|  |  | $A A B$ | 0.46 | 0.46 |
|  |  | $B A B$ | 0.40 | 0.42 |
|  |  | $B B B$ | 0.14 | 0.16 |
|  |  | $B B A$ | 0.49 | 0.48 |
|  |  | $A B A$ | 0.36 | 0.36 |
| 6 | 0.65 | $A A A$ | 0.17 | 0.16 |
|  |  | $A A B$ | 0.47 | 0.48 |
|  |  | $B A B$ | 0.36 | 0.36 |
|  |  | $B B B$ | 0.11 | 0.12 |
|  |  | $B B A$ | 0.45 | 0.46 |
|  |  | $A B A$ | 0.44 | 0.42 |
| 7 | 0.70 |  |  | 0.21 |
|  |  | $A A B$ | 0.49 | 0.50 |
|  |  | $B A B$ | 0.30 | 0.29 |
|  |  | $B B B$ | 0.09 | 0.09 |
|  |  | $B B A$ | 0.44 | 0.42 |
|  |  | $A B A$ | 0.47 | 0.49 |
| 8 | 0.75 | $A A A$ | 0.27 | 0.27 |
|  |  | $A A B$ | 0.50 | 0.50 |
|  |  | $B A B$ | 0.23 | 0.23 |
|  |  | $B B B$ | 0.05 | 0.06 |
|  |  | $B B A$ | 0.38 | 0.38 |
|  |  | $A B A$ | 0.57 | 0.56 |
| 9 | 0.80 | $A A A$ | 0.33 | 0.35 |
|  |  | $A A B$ | 0.52 | 0.48 |
|  |  | $B A B$ | 0.15 | 0.17 |
|  |  | $B B B$ | 0.04 | 0.04 |
|  |  | $B B A$ | 0.30 | 0.32 |
|  |  | $A B A$ | 0.66 | 0.64 |

[^1]

Figure 10 Variation of $A$ - and $B$-centered triad fractions plotted as a function of the fractional conversion for different feed mol fractions: $(*) f_{A}=0.30 ;(\nabla) f_{A}=0.40 ;(\mathbf{\Lambda}) f_{A}$ $=0.50 ;(\square) f_{A}=0.55 ;(\times) f_{A}=0.60 ;(\bullet) f_{A}=0.65 ;(\triangle) f_{A}=0.70 ;(\bigcirc) f_{A}=0.80$.
fractions as seen from the correlation coefficient value of $R=0.99$.

The conditional probabilities, ${ }^{1} P_{A / B}$ and $P_{B / A}$, were calculated from the triad concentrations. The value of $P_{B / A}$ decreases linearly from 0.88 to 0.41 and $P_{A / B}$ increases from 0.30 to 0.81 with increase in the acrylamide content in the copolymer. From the slopes of the respective plots of $1 /\left[P_{B / A}-1\right]$ versus $f_{A} / f_{B}$ and $1 /\left[P_{A / B}-1\right]$ versus $f_{B} / f_{A}$, the values of $r_{A}$ and $r_{B}$ were calculated as 0.36 and 0.99 , respectively.

## MONTE CARLO (MC) SIMULATION STUDIES

The MC simulation method can be used in conjunction with NMR to determine the triad fractions at different fractional conversions. The detailed methodology of the MC simulation was given elsewhere. ${ }^{17}$ Figure 10 shows the variation of the $A$ - and $B$-centered triad concentrations as a function of the fractional conversion for different feed mol fractions. The AAA triad concentration increases with the fractional con-
version, but at lower values of $f_{A}$, the increase is only at higher conversion. This is because the monomer with a higher reactivity ratio, that is, acrylonitrile ( $B$ ), will be consumed initially and blocks of $A A A$ will be formed only at higher conversion. The $A A B$ triad fraction first increases, goes through a maximum, and then decreases with the fraction conversion. The maximum shifts to a higher conversion as $f_{A}$ decreases. The $B A B$ triad fraction shows the opposite trend to that shown by the $A A A$ triad fraction.

Since acrylonitrile ( $B$ ) has a higher reactivity ratio, the $B B B$ triad fraction is thus formed initially, and its concentration decreases as the fractional conversion increases. For low values of $f_{A}$, that is, $f_{A}=0.3$ and 0.4 , the $B B A$ triad fraction first increases, passes through a maximum,and then decreases with conversion. At higher values of $f_{A}\left(f_{A}>0.4\right)$, a constant decrease in the $B B A$ triad fraction with the fractional conversion is observed. The $A B A$ triad fraction shows an opposite trend to that shown by the $B B B$ triad fraction.

## CONCLUSIONS

The reactivity ratios of the $A / B$ copolymer system are $r_{A}=0.36$ and $r_{B}=1.01$. The overlapping and broad signals in the carbon and proton spectra were assigned completely to various compositional and configurational sequences using in-verse-HETCOR and TOCSY experiments. The methine carbon resonances of both the $A$ and $B$ units were assigned to configurational and compostional triad sequences. The copolymerization mechanism of the $A / B$ copolymers were found to follow the first-order Markov model.

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[^1]:    ${ }^{\text {a }} A$ - and $B$-centered triad fractions add up to unity.

