# Complete Assignment of ¹H and ¹³C NMR Spectra of Methacrylonitrile/Methylmethacrylate Copolymers

Ajaib Singh BRAR[†] and Dev Ranjan PRADHAN

*Department of Chemistry, Indian Institute of Technology, Delhi, New Delhi 110016, India*

ABSTRACT:    Methacrylonitrile/methylmethacrylate (A/M) copolymers were prepared by bulk polymerization. The ¹³C DEPT-135 (distortionless enhancement by polarization transfer) spectrum was used to differentiate between the carbon resonance signals of methyl, methoxy, and methylene units in the copolymers (A/M). Comonomer reactivity ratios were determined using Kelen–Tudos and non-linear error in variable methods. 2D heteronuclear single quantum correlation (HSQC) and total correlated spectroscopy (TOCSY) spectra were used to resolve the complex ¹H NMR spectrum.

KEY WORDS    Methacrylonitrile / Methylmethacrylate Copolymer / Monomer Reactivity Ratio / ¹H, ¹³C Nuclear Magnetic Resonancc (NMR) / Distortionless Enhancement by Polarization Transfer 135 (DEPT-135) / Heteronuclear Single Quantum Correlation (HSQC) / Total Correlated Spectroscopy (TOCSY) / Microstructure /

Methacrylonitrile/methylmethacrylate (A/M) copolymers have been the subject of intensive investigation mainly because of its great interest in industrial applications,[1] especially as photoresist materials[2] and in the thermal degradation processes.

Two-dimensional (2D) NMR spectroscopy offers a powerful tool for the stereochemical investigation of polymers.[4—7] In our earlier publications, we have reported the microstructure of acrylonitrile,[8] alkylmethacrylate,[9] alkylacrylate[10] copolymers.

Roman *et al.*[3] reported the reactivity ratios and detailed investigation of C-13 spectra of A/M copolymers. They have reported the microstructural analysis on the basis of carbonyl carbon and quarternary carbon of methacrylonitrile from ¹³C{¹H} NMR spectrum. However, they have not assigned $\beta$-CH$_2$ group, -CN group in ¹³C{¹H} NMR and also ¹H NMR spectra. We have used in our investigation ¹³C{¹H} NMR, heteronuclear single quantum correlation (HSQC) and total correlated spectroscopy (TOCSY) to determine the compositional and configurational sequences of these copolymers. Our assignments of $\alpha$-CH$_3$ carbons of ¹³C{¹H} NMR spectra are different from the earlier workers[3] and these are confirmed from 2D-HSQC spectrum. Further, we have resolved complex and overlapped $\beta$-CH$_2$ resonances in ¹³C{¹H} NMR and also ¹H NMR spectra using 2D HSQC, and TOCSY spectra. The reactivity ratios of the comonomers have been calculated using Kelen–Tudos (KT) and the non-linear error in variable (EVM) methods.[11, 12]

## EXPERIMENTAL

### Sample Preparation

Methacrylonitrile, A (Merck) was purified by ordinary distillation and Methylmethacrylate, M (commercial) was purified by washing three times with 5% NaOH aqueous solution and then several times with distilled water. The monomers were stored below 5°C. Benzoyl peroxide was recrystalized twice from ethanol.

A series of A/M copolymers containing different mol% of methacrylonitrile in feed were prepared by bulk polymerization at 60°C using benzoyl peroxide as initiator. The conversion was kept below 10% by precipitating the copolymers in methanol. The copolymers were further purified using dimethyl sulfoxide (DMSO)/methanol system.

### NMR Measurements

1D {¹H, ¹³C{¹H}, DEPT-135 (distortionless enhancement by polarization transfer)} and 2D {HSQC, TOCSY} NMR spectra of A/M copolymers were recorded at 80°C on 20% (w/v) predeuterated dimethyl sulfoxide (DMSO-$d_6$), with a Bruker 300 MHz DPX spectrometer using different standard pulse sequences and other related details are given in our earlier papers.[13—15]

## RESULTS AND DISCUSSION

### Reactivity Ratios Determination

The compositions of A/M copolymers were determined from quantitative ¹³C{¹H} NMR spectroscopy

---

[†]To whom correspondence should be addressed.

**Table I.** Copolymer composition and molecular weight averages of methacrylonitrile/methylmethacrylate copolymers

| Sample | $f_A$ | $f_M$ | $F_A$ | $F_M$ | $\overline{M}_w$ $\times 10^{-4}$ | $\overline{M}_n$ $\times 10^{-4}$ | $\overline{M}_z$ $\times 10^{-4}$ | $\overline{M}_{z+1}$ $\times 10^{-4}$ | P |
|---|---|---|---|---|---|---|---|---|---|
| AM1 | 0.20 | 0.80 | 0.23 | 0.77 | 4.945 | 2.793 | 8.600 | 13.422 | 1.78 |
| AM2 | 0.30 | 0.70 | 0.32 | 0.68 | 5.371 | 2.721 | 9.934 | 15.550 | 1.97 |
| AM3 | 0.40 | 0.60 | 0.41 | 0.59 | 3.521 | 2.055 | 5.965 | 8.977 | 1.71 |
| AM4 | 0.50 | 0.50 | 0.50 | 0.50 | 2.609 | 1.431 | 4.616 | 7.224 | 1.82 |
| AM5 | 0.60 | 0.40 | 0.59 | 0.41 | 4.066 | 1.787 | 12.607 | 28.042 | 2.28 |
| AM6 | 0.70 | 0.30 | 0.69 | 0.31 | 3.546 | 1.706 | 10.478 | 25.666 | 2.08 |
| AM7 | 0.80 | 0.20 | 0.79 | 0.21 | 2.429 | 1.348 | 6.766 | 22.513 | 1.80 |

$f_A$ and $f_M$ are the mol fractions of A and M comonomers, respectively, in feed. $F_A$ and $F_M$ are the mol fractions of A and M comonomers, respectively, in the copolymer. $\overline{M}_w$, $\overline{M}_n$, $\overline{M}_z$, and $\overline{M}_{z+1}$ are the weight average, number average, Z-average and (Z+1)- average molecular weights of the copolymers, respectively. P: Polydispersity.
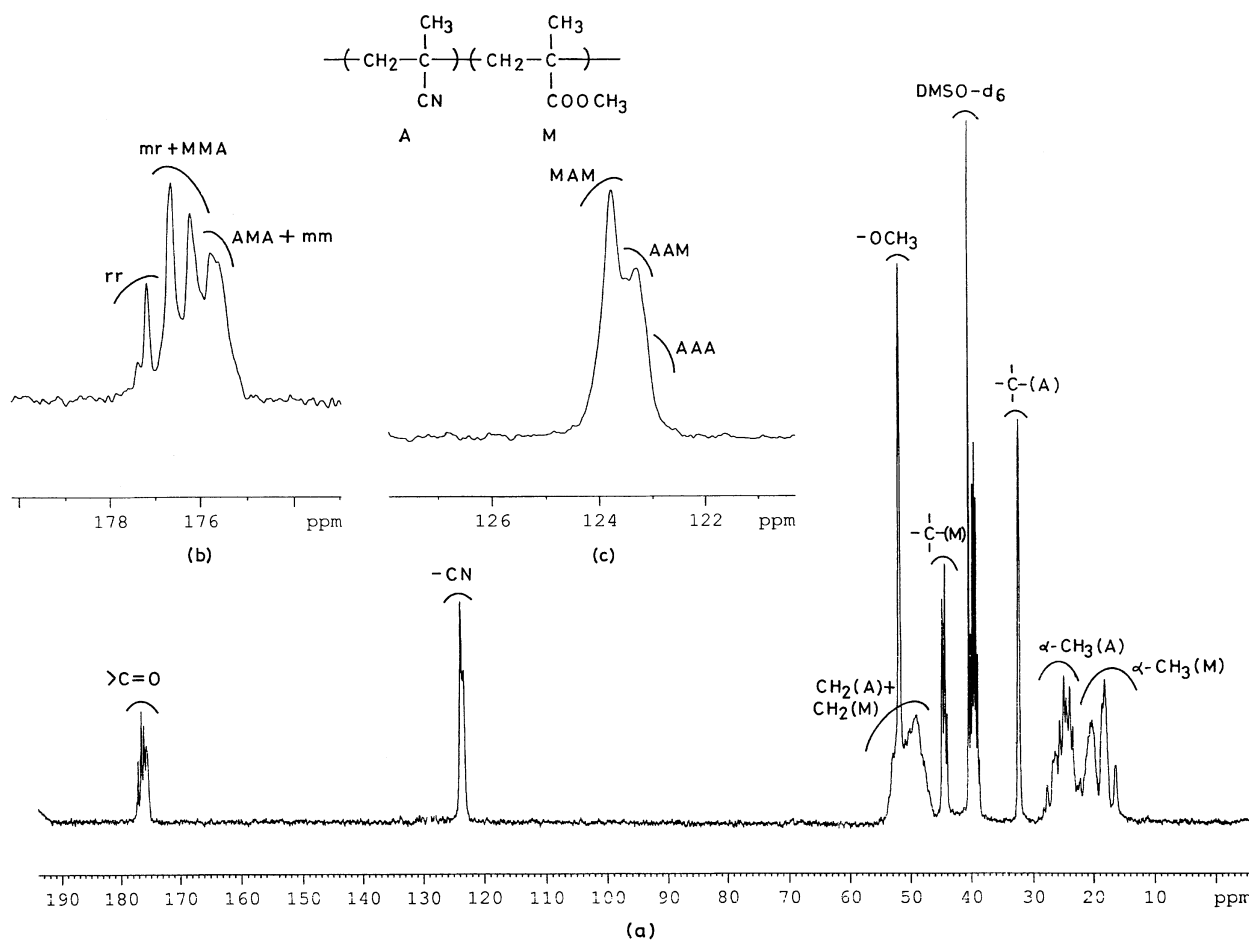


**Figure 1.** (a)The $^{13}C\{^1H\}$ NMR spectrum of A/M copolymer ($F_A = 0.50$), (b) Expanded carbonyl carbon region, (c) Expanded nitrile carbon region.

using standard pulse program with the repetition time 10 s. Table I shows the comonomer mole fractions in the feed and in the copolymer. The copolymer composition data were used to calculate the terminal model reactivity ratios according to the Kelen–Tudos (KT) method. These reactivity ratio values along with the copolymer composition data were used to calculate the reactivity ratio from the error in variable (EVM) program. The values of reactivity ratios obtained from Kelen–Tudos (KT)[11] and non linear error in variable

method (EVM)[12] are $r_A = 0.91 \pm 0.09$, $r_M = 0.88 \pm 0.11$, and $r_A = 0.85$, $r_M = 0.83$ respectively. These values are in good agreement with the reported values in the literature.[3] The molecular weight averages were determined by GPC are given in Table I.

*$^{13}C\{^1H\}$NMR Studies*

The $^{13}C\{^1H\}$NMR spectrum of the copolymer A/M ($F_A = 0.50$) in DMSO-$d_6$ is shown in Figure 1a along
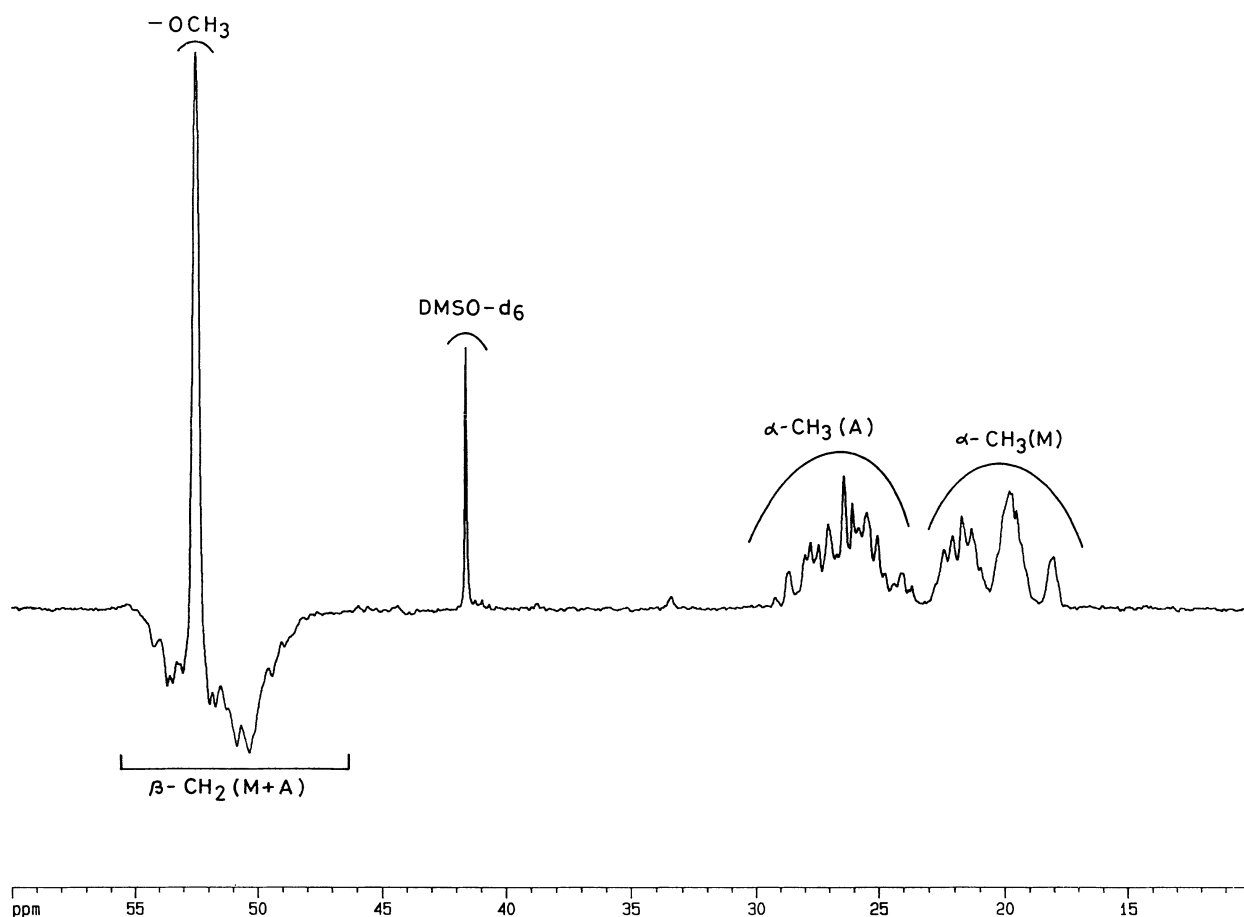
**Figure 2.** The DEPT-135 spectrum of A/M copolymer ($F_A = 0.50$) in DMSO-$d_6$.

with signal assignments. The spectral region $\delta$ 15.0–60.0 ppm is complex and overlapped and can be assigned to aliphatic carbons in the main and side chain of copolymers. The overlapped carbon resonances of $\alpha$-methyl group of A- and M- monomeric units, –OCH$_3$, $\beta$-methylene carbon can be assigned without ambiguity with the help of DEPT-135 experiments (Figure 2), where methylene and methyl carbon signals appear as negative and positive phase, respectively. The signals around $\delta$ 16.0–32.0 ppm are due to $\alpha$-CH$_3$ carbon resonances of both methacrylonitrile and methylmethacrylate units in copolymer. The $\beta$-methylene carbon of both methacrylonitrile and methylmethacrylate unit resonates around $\delta$ 45.1–57.0 ppm. The –OCH$_3$ carbon signals appear at $\delta$ 52.5 ppm. The quaternary carbon signals of methacrylonitrile and methylmethacrylate are assigned at $\delta$ 32.2 and $\delta$ 44.2 ppm respectively. The carbonyl and nitrile carbon resonances are assigned around $\delta$ 174.5–178.0 ppm and $\delta$ 122.3–124.6 ppm respectively.

The expanded $^{13}$C{$^1$H} NMR spectrum of the nitrile group carbon resonance of A/M copolymers is shown in Figure 1c. In this region, the signals around $\delta$ 122.3–122.95, $\delta$ 122.95–123.5, and $\delta$ 123.5–124.6 ppm are assigned to AAA, AAM, and MAM

compositional triads sequences respectively, by comparing with poly(methacrylonitrile) $^{13}$C{$^1$H} NMR spectrum. The expanded carbonyl region in copolymer is shown in Figure 1b. The three broad signals around $\delta$ 174.5–175.75, $\delta$ 175.75–176.7, and $\delta$ 176.7–178.0 ppm are assigned to mm, rm, and rr configurational sequences by comparing them with $^{13}$C{$^1$H} NMR spectrum of poly(methylmethacrylate). These three broad envelopes show variation in intensity with copolymer composition, which shows that resonance signals around $\delta$ 174.5–176.7 ppm are not pure configurational rather overlapped with compositional sequences. The signals around $\delta$ 174.75–175.75 ppm shows increase in intensity with increase in A- content in copolymer, while signals around $\delta$ 176.7–178.0 ppm shows decrease in intensity with increase in A- content in A/M copolymer. This shows that signals around $\delta$ 174.5–175.75 ppm have predominant concentration of AMA copolymer compositional sequences in copolymer, while signals around $\delta$ 176.7–178.0 ppm are due to MrMrM configurational sequences only. The signals around $\delta$ 175.75–176.7 ppm are assigned collectively to MrMmM and MMA triad sequences.

The $\alpha$-CH$_3$ region of $^{13}$C{$^1$H} NMR spectrum is complex and overlapped. The multiplets in
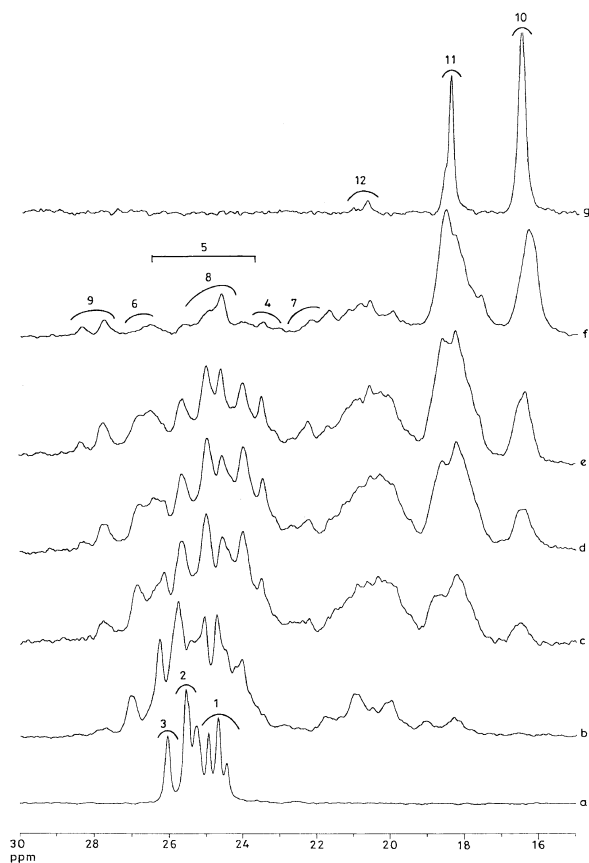
**Figure 3.** Expanded $^{13}$C{$^1$H} NMR spectrum showing $\alpha$-methyl carbon signals in (a) poly(methacrylonitrile), copolymer with composition $F_A$: (b) 0.79, (c) 0.59, (d) 0.50 (e) 0.41, (f) 0.23, and (g) poly(methylmethacrylate).

the $\alpha$-CH$_3$ carbons of poly(methacrylonitrile) and poly(methylmethacrylate) are assigned to configurational sequences and are not overlapped with each other. The spectra of copolymers show signals of homopolymers along with some new signals are shown in Figure 3. All the signals could be assigned to A- and M- centered compositional as well as configurational sequences. The assignments to various signals are done with the help of the spectra of individual homopolymers and by observing change in intensity of signals with the change in composition of copolymers. There are two broad A- and M- centered envelops in the $\alpha$-CH$_3$ region. The A- centered envelope ranges from $\delta$ 22.1–28.8 ppm and M- centered envelope ranges from $\delta$ 15.0–22.1 ppm.

In the M- centered $\alpha$-CH$_3$ region, the signals around $\delta$ 16.7 (10), $\delta$ 18.65 (11), and $\delta$ 20.99 (12) ppm are assigned to MrMrM, MmMrM, and MmMmM respectively, by comparing with the $^{13}$C{$^1$H} NMR spectrum of poly(methylmethacrylate). The other M- centered triad sequences of copolymers show very complex and overlapped pattern and hence are difficult to assign from $^{13}$C{$^1$H} NMR spectrum only.

In the A-centered $\alpha$-CH$_3$ region, the signals at $\delta$
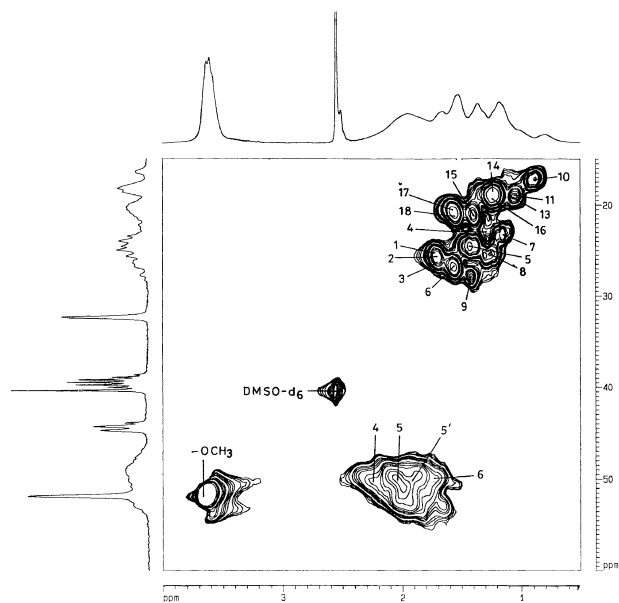


**Figure 4.** The 2D-HSQC spectra of A/M copolymers of composition $F_A = 0.50$.

23.80–25.40 (1) ppm, $\delta$ 25.40–26.10 (2) ppm, and $\delta$ 26.10–27.0 (3) ppm are assigned to ArArA, ArAmA, and AmAmA respectively, by comparing with the $^{13}$C{$^1$H} NMR spectrum of poly(methacrylonitrile). The various $\alpha$-CH$_3$ signals around $\delta$ 22.8–23.70 (4), $\delta$ 26.6–27.30 (6) ppm, which first shows increase and then decrease in intensity with decrease in A-content are assigned to ArArM and AmAmM respectively. The triad sequence ArAmM at $\delta$ 23.70–26.60 (5) ppm is difficult to assign due to overlapping with the configurational sequences of poly(methacrylonitrile). The signals at $\delta$ 22.1–23.0 (7), $\delta$ 24.2–25.60 (8), $\delta$ 27.30–28.70 (9) ppm which show increase in intensity with increase in M-content in copolymer are assigned to MrArM, MrAmM, and MmAmM respectively. All these assignments are shown in Table II.

*2D-HSQC Spectra Studies*

The 2D $^{13}$C-$^1$H HSQC NMR spectrum of A/M copolymer ($F_A = 0.50$) is shown in Figure 4. The $\alpha$-CH$_3$ group in both monomeric units shows compositional as well as configurational sensitivity. The cross peaks at $\delta$ 25.3/1.75 (1), $\delta$ 26.0/1.71 (2), and $\delta$ 26.9/ 1.70 (3) ppm are assigned to ArArA, ArAmA, and AmAmA triads respectively, on the basis of the assignments done in HSQC spectrum of poly(methacrylonitrile). The other cross peaks in A-centered $\alpha$-CH$_3$ region are assigned on the basis of change in intensity with change in copolymer composition. The cross peaks at $\delta$ 23.0/1.29 (4), $\delta$ 24.5/1.38 (5), and $\delta$ 26.7/1.52 (6) ppm are assigned to ArArM, ArAmM, and AmAmM respectively, while the cross peaks at $\delta$ 23.0/1.11 (7), $\delta$ 25.5/1.20 (8), and $\delta$ 28.0/1.39
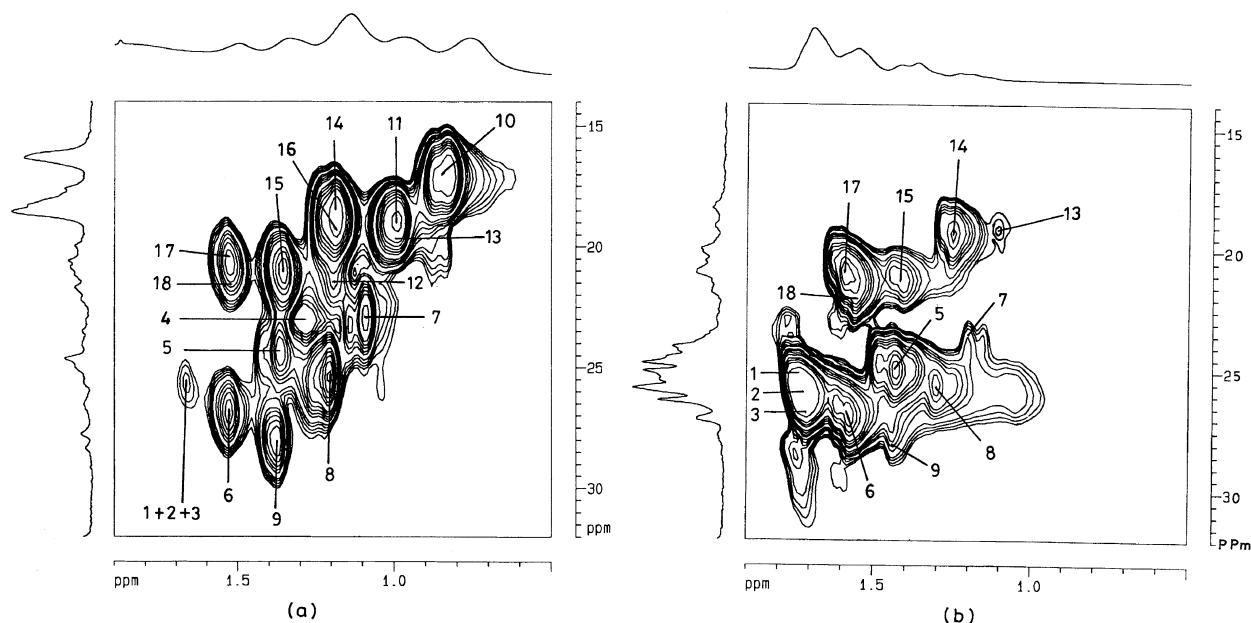
**Figure 5.** The expanded $\alpha$-methyl region in 2D-HSQC spectrum of A/M copolymers of composition $F_A$: (a) 0.23 and (b) 0.79.

**Table II.** The compositional and configurational assignments of $\alpha$-CH$_3$ carbon resonance signals of $^{13}$C$\{^1$H$\}$ NMR spectra of A/M copolymers

| S.No. | Chemical Shift($\delta$), ppm | Assignment |
|---|---|---|
| 1 | 23.80-25.40 | ArArA |
| 2 | 25.40-26.10 | ArAmA |
| 3 | 26.10-27.00 | AmAmA |
| 4 | 22.80-23.70 | ArArM |
| 5 | 23.70-26.60 | ArAmM[a] |
| 6 | 26.60-27.30 | AmAmM |
| 7 | 22.10-23.00 | MrArM |
| 8 | 24.20-25.60 | MrAmM |
| 9 | 27.30-28.50 | MmAmM |
| 10 | 16.70 | MrMrM |
| 11 | 18.65 | MrMmM |
| 12 | 20.99 | MmMmM |

[a]Assignment is difficult due to overlapping with homopolymer configurational sequences.

(9) ppm which increases in intensity with decrease in A- content are assigned to MrArM, MrAmM, and MmAmM respectively.

The $\alpha$-CH$_3$ group of M- unit is further assigned to compositional and configurational sequences. The cross peaks region at $\delta$ 16.8/0.88 (10), $\delta$ 18.9/1.12 (11), and $\delta$ 21.2/1.19 (12) ppm are assigned to MrMrM, MrMmM, and MmMmM triads respectively, on the basis of the assignments done in HSQC spectrum of poly(methylmethacrylate). The other cross-peaks in M-centered $\alpha$-CH$_3$ region are assigned on the basis of change in intensity of signals with change in copolymer composition. The cross-peaks at $\delta$ 19.9/1.01 (13), $\delta$ 18.4/1.20 (14), and $\delta$ 21.2/1.38 (15) ppm are assigned to MrMrA, MrMmA, and MmMmA respectively, while the intensity of cross peaks at $\delta$ 19.5/1.19

(16), $\delta$ 20.5/1.52 (17), and $\delta$ 21.5/1.51 (18) ppm increase with increase in A- content in copolymer are assigned to ArMrA, ArMmA, and AmMmA respectively. The cross peak intensities in 2D-HSQC spectra of the copolymers show that triad sequences with greater A-content shows more preference for mm configuration as compared to triad sequences with greater M-content. The assignments 1, 2, 3, and 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18 are done according to Figure 5a ($F_A$ = 0.23), and Figure 5b ($F_A$ = 0.79) respectively. All these assignments are shown in Figure 4 ($F_A$ = 0.50), Figure 5a ($F_A$ = 0.23), and Figure 5b ($F_A$ = 0.79). In the spectral assignment done by *Roman et al.*,[3] in the M-centered $\alpha$-CH$_3$ region, the chemical shift difference between corresponding configurational AMM and AMA sequences is greater than that between corresponding configurational MMM and AMM sequences. Similarly, in the A- centered $\alpha$-CH$_3$ region, the chemical shift difference between corresponding configurational MAA and MAM sequences is greater than that between corresponding configurational AAA and MAA sequences. With the help of 2D-HSQC we could assign the various triad sequences without ambiguity and it is observed that the chemical shift difference between corresponding A- and M- centered configurational sequences follows a regular trend. The various $\alpha$-CH$_3$ assignments done on the basis of 2D- HSQC NMR assignments are shown in Table III.

The $\beta$-CH$_2$ region is sensitive to dyad, tetrad etc. due to its symmetry. This region is divided into broad MM, MA, and AA dyads on the basis of change in intensity of signals with change in copolymer composition. These three dyads are assigned around $\delta$ 48.5–50.5,
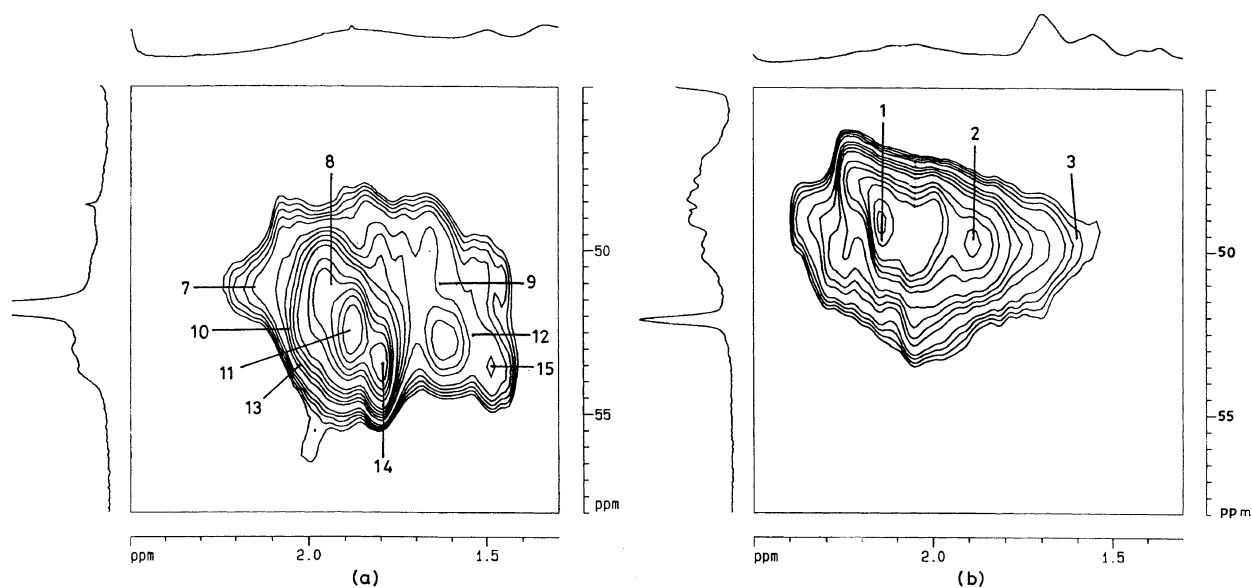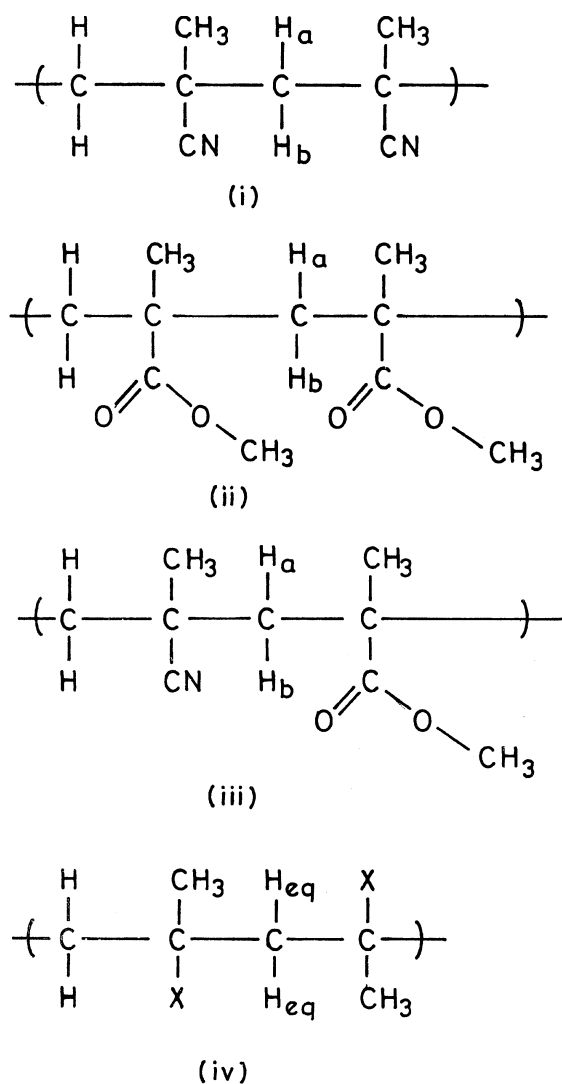
**Figure 6.** The expanded $\beta$-methylene region in 2D-HSQC spectrum of A/M copolymers of composition $F_A$: (a) 0.23 and (b) 0.79.
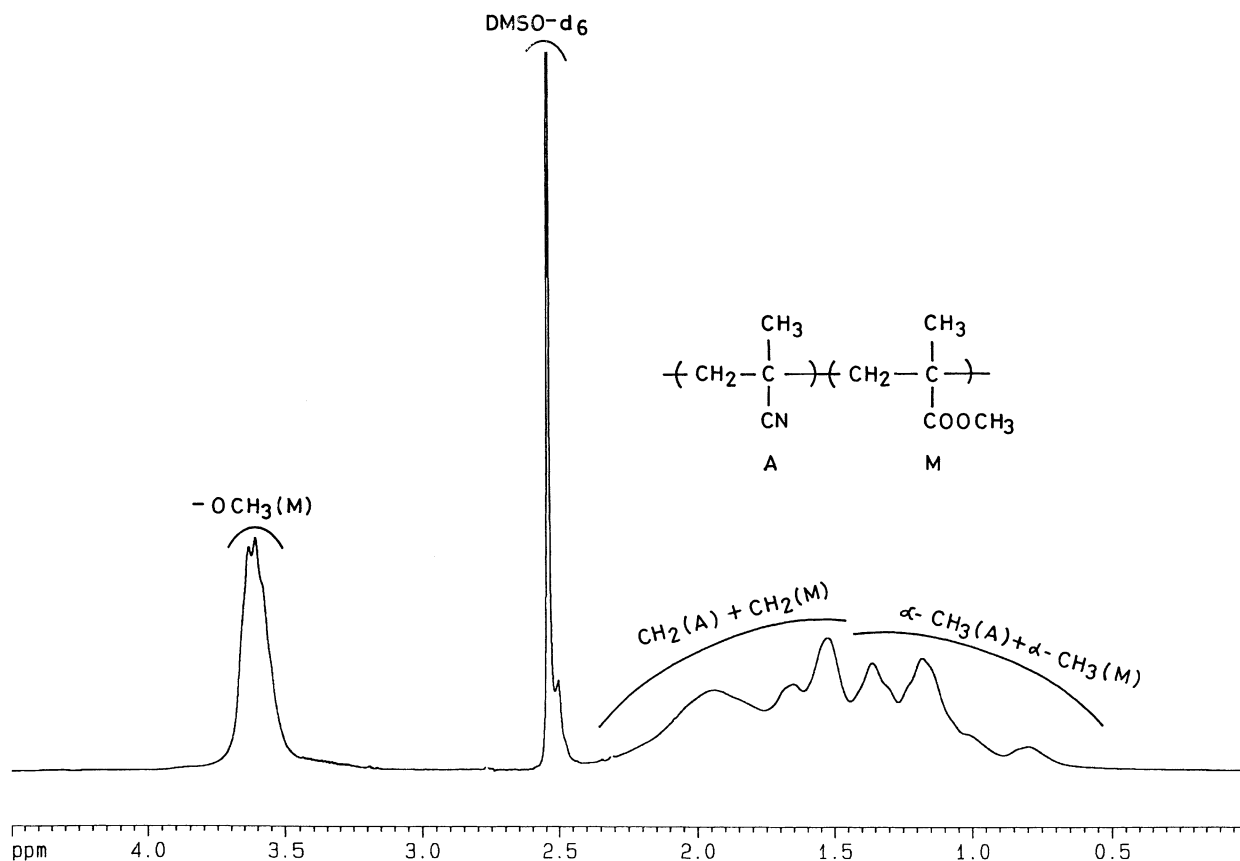
**Table III.** The Compositional and Configurational assignments of $\alpha$-CH$_3$ carbon signals of the A/M Copolymers from 2D-HSQC NMR spectrum

| Peak No. | $^{13}$C/ppm | $^1$H/ppm | Assignments |
|---|---|---|---|
| 1 | 25.3 | 1.75 | ArArA |
| 2 | 26.0 | 1.71 | ArAmA |
| 3 | 26.9 | 1.70 | AmAmA |
| 4 | 23.0 | 1.29 | ArArM |
| 5 | 24.5 | 1.38 | ArAmM |
| 6 | 26.7 | 1.52 | AmAmM |
| 7 | 23.0 | 1.11 | MrArM |
| 8 | 25.5 | 1.20 | MrAmM |
| 9 | 28.0 | 1.39 | MmAmM |
| 10 | 16.8 | 0.88 | MrMrM |
| 11 | 18.9 | 1.12 | MrMmM |
| 12 | 21.2 | 1.19 | MmMmM |
| 13 | 19.9 | 1.01 | MrMrA |
| 14 | 18.4 | 1.20 | MrMmA |
| 15 | 21.2 | 1.38 | MmMmA |
| 16 | 19.5 | 1.19 | ArMrA |
| 17 | 20.5 | 1.52 | ArMmA |
| 18 | 21.5 | 1.51 | AmMmA |



**Figure 7.** The nonequivalent protons in meso (i) AA, (ii) MM, (iii) AM dyads, and equivalent protons in (iv) racemic dyads (where, X = –CN or – COOCH$_3$ or both) of the A/M copolymer.

$\delta$ 50.5–51.5, $\delta$ 51.5–54.0 ppm respectively. The MM and MA dyads show further splitting into three cross peaks along proton axis due to stereochemical configurations. The meso- configuration gives two peaks due to the two methylene protons lying in different environment and racemic gives one cross peak lying in between two cross peaks corresponding to meso configurations. The two cross peaks at $\delta$ 49.5/2.13 (1) and $\delta$ 49.5/1.64 (3) ppm (Figure 6b) in MM dyad (Figure 7 ii) are due to meso configuration and that at $\delta$ 49.5/1.88 (2) ppm (Figure 6b) in MM dyad is due to racemic configuration. Similarly, the cross peaks at $\delta$ 50.5/2.26 (4) and $\delta$ 50.3/1.70 (6) ppm (Figure 4) in AM dyad (Fig-

**Figure 8.** The $^1$H NMR spectrum of A/M copolymer ($F_A = 0.50$) in DMSO-$d_6$.

ure 7 iii) are due to meso configuration and that at $\delta$ 50.5/2.01 (5) ppm and $\delta$ 50.4/1.94 (5′) (Figure 4) in AM dyad is due to racemic configuration. The AA dyad region ($\delta$ 51.5–54.0 ppm) of $\beta$-CH$_2$ shows further splitting, which is assigned to configurational sequences as done in poly(methacrylonitrile) as reported by Matsuzaki *et al.*[16] The signals around $\delta$ 1.42–1.75, $\delta$ 1.75–1.93, and $\delta$ 1.93–2.16 ppm along proton axis are assigned to meso (proton 'a'), racemic and meso (proton 'b') centered AA (Figure 7 i and 7 iv) configurational sequences. Further splitting along carbon axis within these three regions are assigned to higher configurational sequences. The cross peaks at $\delta$ 52.0/2.16 (7) and $\delta$ 52.0/1.93 (8) ppm are assigned to mmm in proton 'a' and 'b' respectively. The cross peaks at $\delta$ 52.6/2.06 (10) and $\delta$ 52.6/1.88 (11) ppm are assigned to mmr in proton 'a' and 'b' respectively. Similarly, the cross peaks at $\delta$ 53.5/2.02 (13) and $\delta$ 53.5/1.79 (14) are assigned to rmr in proton 'a' and 'b' respectively. The cross peaks at $\delta$ 52.0/1.68 (9), $\delta$ 52.6/1.56 (12), and $\delta$ 53.5/1.51 (15) ppm lie in between two meso configurational sequence along proton axis are assigned to mrm, mrr, and rrr configurational sequences, respectively. The assignments 7, 8, 9, 10, 11, 12, 13, 14, and 15 are shown in Figure 6a. The remaining peaks may be due to higher configurational/compositional sequences and difficult to assign. The various $\beta$-CH$_2$ assignments

**Table IV.** The Compositional and Configurational assignments of $\beta$-CH$_2$ carbon signals of the A/M Copolymers from 2D-HSQC spectrum

| Sl. No. | $^{13}$C/ppm | $^1$H/ppm | Assignments |
|---|---|---|---|
| 1 | 49.5 | 2.13 | MmM |
| 2 | 49.5 | 1.88 | MrM |
| 3 | 49.5 | 1.64 | MmM |
| 4 | 50.5 | 2.26 | AmM |
| 5 | 50.5 | 2.01 | ArM |
| 5′ | 50.4 | 1.94 | ArM |
| 6 | 50.3 | 1.70 | AmM |
| 7 | 52.0 | 2.16 | AmAmAmA |
| 8 | 52.0 | 1.93 | AmArAmA |
| 9 | 52.0 | 1.68 | AmAmAmA |
| 10 | 52.6 | 2.06 | AmAmArA |
| 11 | 52.6 | 1.88 | AmArArA |
| 12 | 52.6 | 1.56 | AmAmArA |
| 13 | 53.5 | 2.02 | ArAmArA |
| 14 | 53.5 | 1.79 | ArArArA |
| 15 | 53.5 | 1.51 | ArAmArA |

are done on the basis of 2D-HSQC NMR assignments are shown in Table IV.

### $^1$H and 2D-TOCSY Spectra Studies

The proton spectrum along with complete assignments is shown in Figure 8 ($F_A = 0.50$). Once $^{13}$C{$^1$H} NMR spectrum is assigned completely, the various
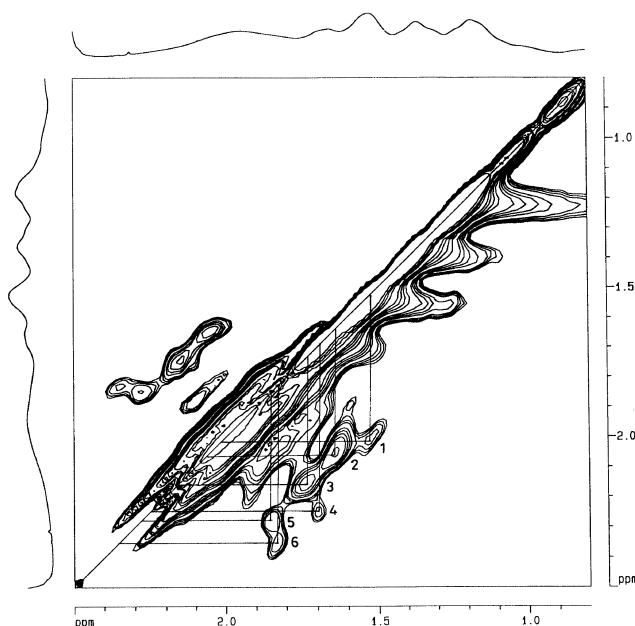
**Figure 9.** The 2D-TOCSY spectrum of A/M copolymer ($F_A = 0.50$) in DMSO-$d_6$.

**Table V.** TOCSY $^1$H–$^1$H shift correlations

| S. No. | Assignments | Coupled to proton | $^1$H/ppm |
|---|---|---|---|
| | geminal coupling | ppm | |
| 1 | MM | CH$_2$ (2.02) | CH$_2$ (1.53) |
| 2 | MM | CH$_2$ (2.07) | CH$_2$ (1.65) |
| 3 | AM | CH$_2$ (2.18) | CH$_2$ (1.73) |
| 4 | AM | CH$_2$ (2.24) | CH$_2$ (1.70) |
| 5 | AA | CH$_2$ (2.28) | CH$_2$ (1.86) |
| 6 | AA | CH$_2$ (2.36) | CH$_2$ (1.83) |

overlapped resonance signals in $^1$H NMR spectrum are assigned by one to one correlation between carbon and proton with the help of 2D-HSQC spectrum. In order to understand the connectivity and to confirm the various couplings in the copolymer chain, the TOCSY spectrum was recorded. It is easier to pinpoint and identify the couplings within the $\beta$-CH$_2$ group. In a racemic dyad, the two protons are considered to be equivalent. Hence, all the cross-peaks within the $\beta$-CH$_2$ group are assigned to coupling between the non-equivalent protons in meso dyads (shown in Figure 9). The couplings between the protons of $\beta$-CH$_2$ in A/M copolymer can be clearly seen in TOCSY spectrum of low mixing time (4 ms) as shown in Figure 9 ($F_A = 0.50$). The cross peaks at $\delta$ 2.02/1.53 (1) and $\delta$ 2.07/1.65 (2) ppm are due to coupling of inequivalent protons of $\beta$-CH$_2$ in MM dyad. Similarly, the cross peaks at $\delta$ 2.18/1.73 (3) and $\delta$ 2.24/1.70 (4) ppm are due to coupling of inequivalent protons of $\beta$-CH$_2$ in AM dyad and the cross peaks at $\delta$ 2.28/1.86 (5) and $\delta$ 2.36/1.83 (6) ppm are due to coupling of inequivalent protons of $\beta$-CH$_2$ in AA dyad. All these assignments are shown in Table V.

## CONCLUSIONS

The terminal model reactivity ratios were determined from KT and EVM methods, which were in good agreement with the literature.[3] The complex and overlapped $^1$H and $^{13}$C{$^1$H} NMR spectra were resolved without ambiguity with the help of DEPT-135, 2D(HSQC, TOCSY) NMR spectroscopic techniques. The homonuclear 2D(TOCSY) spectrum suggested various structural arrangements of the polymer chain. The $\alpha$-methyl and methylene carbon resonances were assigned upto triad and tetrad compositional and configurational sequences with the help of 2D-HSQC spectrum. The cyanide group is assigned to triad compositional sequences, while carbonyl group is assigned to triad compositional and configurational sequences.

## REFERENCES

1. H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, "Encyclopedia of Polymer Science and Engineering", Wiley Interscience, New York, N.Y., 1985, vol. 1, pp 461.
2. B. C. Ho, W. K. Chin, and Y. D. Lee, *J. Appl. Polym. Sci.,* **42**, 99 (1991).
3. J. S. Roman, B. Vanquez, M. Valero, and G. M. Guzman, *Macromolecules,* **24**, 6089 (1991).
4. L. Dong, D. J. T. Hill, J. H. O'Donnell, and A. K. Whittaker, *Macromolecules,* **27**, 1830 (1994).
5. A. Bulai, M. L. Jimeno, and J. S. Roman, *Macromolecules,* **28**, 7363 (1995).
6. M. Suchoparek and J. Spevacek, *Macromolecules,* **26**, 102 (1993).
7. T. Asakura, N. Nakayama, M. Demura, and A. Asano, *Macromolecules,* **25**, 4876 (1992).
8. A. S. Brar, K. Dutta, and G. S. Kapur, *Macromolecules,* **28**, 8735 (1995).
9. G. S. Kapur and A. S. Brar, *Polymer,* **32**, 1112 (1991).
10. A. S. Brar and Sunita, *J. Polym. Sci., Part A*: *Polym. Chem.,* **30**, 2549 (1992).
11. T. Kelen and F. Tudos, *J. Macromol. Sci., Chem.,* **A9**, 1 (1975).
12. M. Dube, R. A. Sanyel, A. Penlidis, K. F. O' Driscoll, and P. M. Reilly, *J. Polym. Sci., Polym. Chem. Ed.,* **29**, 703 (1991).
13. A. S. Brar and K. Dutta, *Macromol. Chem. Phys.,* **199**, 2005 (1998).
14. A. S. Brar, K. Dutta, and G. S. Kapur, *Macromolecules,* **28**, 8735 (1995).
15. K. Dutta and A. S. Brar, *J. Polym. Sci., Polym. Chem.,* **28**, 3922 (1999).
16. K. Matsuzaki, T. Uryu, and T. Asakura, "NMR Spectroscopy and stereoregularity of polymers", Japan Scientific Societies Press, Tokyo, 1996. vol. 1, p 57.