Stereochemical and compositional assignments of acrylonitrile/butylacrylate copolymers by two-dimensional NMR spectroscopy

A S Brar & D R Pradhan

Department of Chemistry, Indian Institute of Technology, Delhi, New Delhi 110 016, India

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Acrylonitrile/butylacrylate (A/B) copolymers have been prepared by bulk polymerization using benzoyl peroxide as initiator. 2D-heteronuclear single quantum correlation (HSQC) and total correlated spectroscopy (TOCSY) spectra have been used to resolve the complex $^1$H NMR spectrum and to determine the compositional and configurational sequences of A/B copolymers.

In our earlier publications, we have reported the microstructures of acrylonitrile-alkylmethacrylate,$^{13}$ acrylonitrile-methylacrylate,$^6$ acrylonitrile-ethylacrylate$^5$ and acrylonitrile-butylacrylate$^6$ by $^{13}$C NMR spectroscopy.

Brar et al.$^6$ reported the reactivity ratios using Kelen-Tudos, error in variable methods (EVM)$^{7,8}$ and detailed investigation of $^{13}$C NMR spectra of A/B copolymers. They have reported the microstructural analysis on the basis of carbonyl carbon of butyl acrylate and nitrile carbon of acrylonitrile from $^{13}$C$^1$H HSQC NMR spectrum. Two-dimensional NMR spectroscopy offers a powerful tool for the stereochemical investigation of polymers.$^{9-12}$ In our investigation we have used $^{13}$C$^1$H NMR, HSQC and TOCSY to determine the compositional and configurational sequences of these copolymers. In continuation of our earlier work, we report the compositional and configurational triad sequences of A/B copolymers. We have resolved the complex and overlapping $^1$H NMR spectrum.

Experimental

A series of A/B copolymers of different compositions 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 chloroform/methanol system.

1D ($^1$H, $^{13}$C$^1$H) and 2D (HSQC, TOCSY) NMR spectra of A/B copolymers were recorded at 25°C in CDCl$_3$, on a Bruker 300 MHz DPX spectrometer using different standard pulse sequences. Other related details are given in our earlier papers.$^{13-16}$

Results and discussion

$^{13}$C$^1$H NMR studies

The $^{13}$C$^1$H NMR spectrum of the copolymer A/B ($F_A$=0.47) in CDCl$_3$ is shown in Fig. 1a along with the signal assignments. The spectral region $\delta$ 10.0-70.0 ppm is not complex and can be assigned without ambiguity with the help of C-13 NMR spectrum.$^6$ In the expanded nitrile region (Fig. 1b) the signals around $\delta$ 118.2-118.9, $\delta$ 118.8-119.9 and $\delta$ 119.8-121.1 ppm are assigned to AAA, AAB and BAB triads, on the basis of variation of the intensity of the signals with the copolymer composition. In the carbonyl region (Fig. 1c), the intensities of the signals around $\delta$ 172-173.1, $\delta$ 173.1-174 and $\delta$ 174-174.9 ppm are assigned to ABA, BBA and BBB triads respectively, on the basis of change in the intensity of the signals with the copolymer composition. All the assignments are shown in the Fig. 1a-c.

HSQC NMR studies

The 2D $^{13}$C$^1$H HSQC NMR spectrum of A/B copolymer ($F_A$=0.47) is shown in Fig. 2a. The $\alpha$-CH (methine) carbon signals of A unit show compositional as well as configurational sensitivity. The cross peaks at $\delta$ 26.90/3.00 (1), $\delta$ 27.50/3.02 (2), $\delta$ 28.00/3.07 (3) ppm are assigned to AmAmA, ArAmA and ArArA triads respectively, on the basis of HSQC spectrum of poly(acrylonitrile). The other cross peaks in the A-centered methine region are assigned on the basis of change in intensity with change in copolymer composition. The cross peaks at $\delta$ 27.03/2.78 (4), $\delta$ 28.30/2.82 (5) and $\delta$ 27.70/2.63 (6) ppm are assigned to AmAB, A:AB and BAB respectively.

The $\alpha$-CH carbon signals of B unit show compositional triad sensitivity. The cross peaks at $\delta$ 41.10/2.79 (7), $\delta$ 41.21/2.53 (8) and $\delta$ 41.25/2.32 (9) ppm
Fig. 1—(a) The $^{13}$C($^1$H) NMR spectrum of A/B copolymer ($F_A=0.47$), (b) Expanded nitrile carbon region, (c) Expanded carbonyl carbon region.

Fig. 2—(a) The 2D-HSQC spectra of A/B copolymers of composition $F_A=0.47$, (b) Expanded α-methylene carbon region of A-monomeric unit, (c) Expanded α-methylene carbon region of B-monomeric unit.
are assigned to ABA, BBA and BBB triads respectively (Fig. 2b & 2c).

**1H and 2D-TOCSY NMR studies**

The proton spectrum along with its complete assignments is shown in Fig. 3 ($F_A=0.47$). Once the $^{13}$C–$^1$H NMR spectrum of the A/B copolymers are assigned completely, the various overlapping resonance signals in $^1$H NMR spectrum may be assigned by one to one correlation between carbon and proton with the help of 2D-HSQC spectrum. In the $^1$H NMR spectrum, the methine protons of acrylonitrile and butyl acrylate are assigned around $\delta$ 2.52-3.20 and $\delta$ 2.28-3.00 ppm respectively. The $\beta$-methylene protons of A-and B-units resonate around $\delta$ 1.40-2.27 ppm. The methine proton signals of acrylonitrile and butyl acrylate show a multiplet, indicating that they are compositionally sensitive. These signals can be assigned with the help of TOCSY spectrum.
At shorter mixing time, there is direct coupling (AM spin type) between the bonded protons whereas at higher mixing time there is relay coupling (AMX spin type) through magnetization transfer. Figures 4a and 5a show the TOCSY spectra of the A/B copolymer (F_A=0.47) in CDCl_3 at two mixing times, 4 and 80 ms. The cross peaks of methyl/methylene protons at δ 3.00/2.12 (1), δ 3.04/1.88 (2), δ 3.08/1.92 (3) ppm are assigned to AmAmA, AmArA and ArArA triad sequences. In the AAB triads, the central methine proton shows three-bond coupling with two types of methylene protons (A and B type) at δ 2.82/2.06 (4), δ 2.83/1.79 (5) and δ 2.88/1.85 (6) ppm, assigned to ArAB+AmAB, AAmB and AArB triads respectively. The cross peak at δ 2.58/1.69 (7) is assigned to BAB triad. Similarly, in the ABA triad region, the methine proton shows three-bond coupling between the methylene protons at δ 2.79/1.92 (8) ppm. The cross peaks at δ 2.52/2.04 (9) (BrBA) and δ 2.68/2.09 (10) (BrBA) ppm are due to the three-bond coupling between the methine proton and the methylene protons of the B types. The other three-bond coupling between the methine proton and the methylene protons of A type is at δ 2.56/1.85 (11) (BBA) ppm. The three-bond coupling between methine and methylene protons at δ 2.33/1.70 (13) ppm is assigned to BBA triad. The cross peak at δ 2.32/1.99 (12) ppm is due to the coupling of the methine proton with the β-methylene protons in the poly(butylacrylate). All these assignments have been made on the basis of the assignments done in the homopolymer, poly(butylacrylate) (Fig. 4b).

The cross peak at δ 3.01/2.89 (19) ppm is a relayed coupling between the methine protons of AAA and AAB triads, which accounts for AAAB tetrad. The methine proton of BAB triad fraction (δ 2.78 ppm) shows a relayed coupling with methine proton of ABA triad fraction (δ 2.68 ppm). This cross peak at δ 2.78/2.68 ppm is assigned to BAB (ABAB) (20) tetrad. Similarly, the cross peak at δ 2.80/2.51 (21) ppm is assigned to AABB tetrad. The methine proton of BBA (ABB) (δ 2.58 ppm) shows a relayed coupling with methine proton of BBB (δ 2.40 ppm), which accounts for BBBA (22) tetrad. The other cross peaks at δ 1.93/1.59 (15), δ 1.60/1.39 (16), δ 1.33/0.95 (17), δ 4.11/1.61 (18), δ 1.59/0.93 (23), δ 4.09/0.92 (24) and δ 4.10/1.38 (25) are due to the coupling in the branched chain of the copolymer. The cross peak at δ 2.02/1.75 (14) is assigned as due to the coupling of β-methylene protons (head-to-tail linkage) of both the monomeric units in the copolymer [Figs 4 (a & b), 5 (a & b)].

The overlapping and broad signals in the carbon and proton NMR spectra of acrylonitrile/butylacrylate copolymers are assigned completely to various compositional and configurational sequences with the
help of HSQC, TOCSY (4 ms and 80 ms) experiments. The methine carbon resonances are assigned to triad compositional and configurational sequences.

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**References**