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Microstructure determination of poly(acrylonitrile-co-methyl methacrylate-co-methyl acrylate) terpolymers by 2D HMBC

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ABSTRACT

A compositional and configurational sequence analysis from two-dimensional heteronuclear multiple bond correlation (HMBC) spectra of acrylonitrile/methyl methacrylate/methyl acrylate (A/B/M) terpolymer is being reported here. The methylene and methine carbon resonances assigned from 2D HSQC spectra were established by analyzing two and three bond order couplings with methyl, methylene and methine protons. α-Methyl carbon resonance of B-unit and methine carbon resonances of A- and M-unit were assigned up to triad compositional and configurational sequences while methylene carbon resonances were assigned up to tetrad compositional and configurational sequences. The assignments of carbonyl carbon resonances based on analysis of three bond couplings with methyl and methylene protons are reported. Quaternary carbon resonance of B-unit was assigned completely with the help of two bond order couplings with methyl and methylene protons. Both carbonyl and quaternary carbon resonances were found to be sensitive up to triad compositional and configurational sequences. Complete spectral assignment of quaternary and carbonyl carbon resonances showing the critical contribution of 2D HMBC spectra is indirect analysis of carbon resonances.

1. Introduction

Two-dimensional NMR spectroscopy tenders a powerful tool for the stereochemical investigation of polymers to resolve and assign the resonances in these complicated patterns [1–2]. Long-range heteroatom couplings (e.g. carbon-proton) from heteronuclear multiple bond correlation (HMBC) spectra have proven to be highly informative in the microstructure analysis of polymers [3–7]. Rinaldi and coworkers studied the stereosequence of various triads in different copolymers and terpolymers by various 2D NMR techniques [8–11]. Brar et al. have reported the microstructure of various terpolymers and copolymers by 2D NMR [12–15]. Both carbonyl and quaternary carbons do not show any coupling in 2D HSQC spectrum therefore, the compositional and configurational sensitivity of these carbon resonances have been investigated using 2D HMBC technique. Carbonyl carbon resonances show two–three bond couplings with α-methyl, methine and methylene regions of A/B/M terpolymers in 2D HMBC spectrum which were assigned with the help of 2D HSQC and TOCSY spectral analysis. Assignments of quaternary carbon of B-unit have been done from 2D HMBC spectral analysis. In our earlier publication [16], stereosequence analysis of acrylonitrile/methyl methacrylate/methyl acrylate (A/B/M) terpolymer synthesized by ATRP was carried out using 2D HSQC and TOCSY along with 1D [^{1}H, ^{13}C{^{1}H} and DEPT] NMR techniques. In continuation of our earlier study, in this article, complete configurational and compositional assignments of carbonyl and quaternary carbon resonances of acrylonitrile/methyl methacrylate/methyl acrylate (A/B/M) terpolymers have been reported by investigating two and three bond order ^{13}C/^{1}H couplings from HMBC spectra.

2. Experimental

A series of acrylonitrile/methyl methacrylate/methyl acrylate (A/B/M) terpolymers were synthesized by atom transfer radical polymerization method as described in earlier publication [16]. Various 1D and 2D NMR spectra were recorded at 25 °C on Bruker DPX-300 NMR spectrometer in about 10% polymer solutions using $CDCl_3$ as a solvent in 5.0 mm NMR tube. The detail of recording the spectra is given elsewhere [17].

3. Results and discussion

The expanded overlapped carbonyl carbon resonances of B- and M-unit in acrylonitrile/methyl methacrylate/methyl acrylate (A/B/M) terpolymer along with spectra of poly (methyl methacrylate) and poly (methyl acrylate) is shown in Fig. 1. Assignment of

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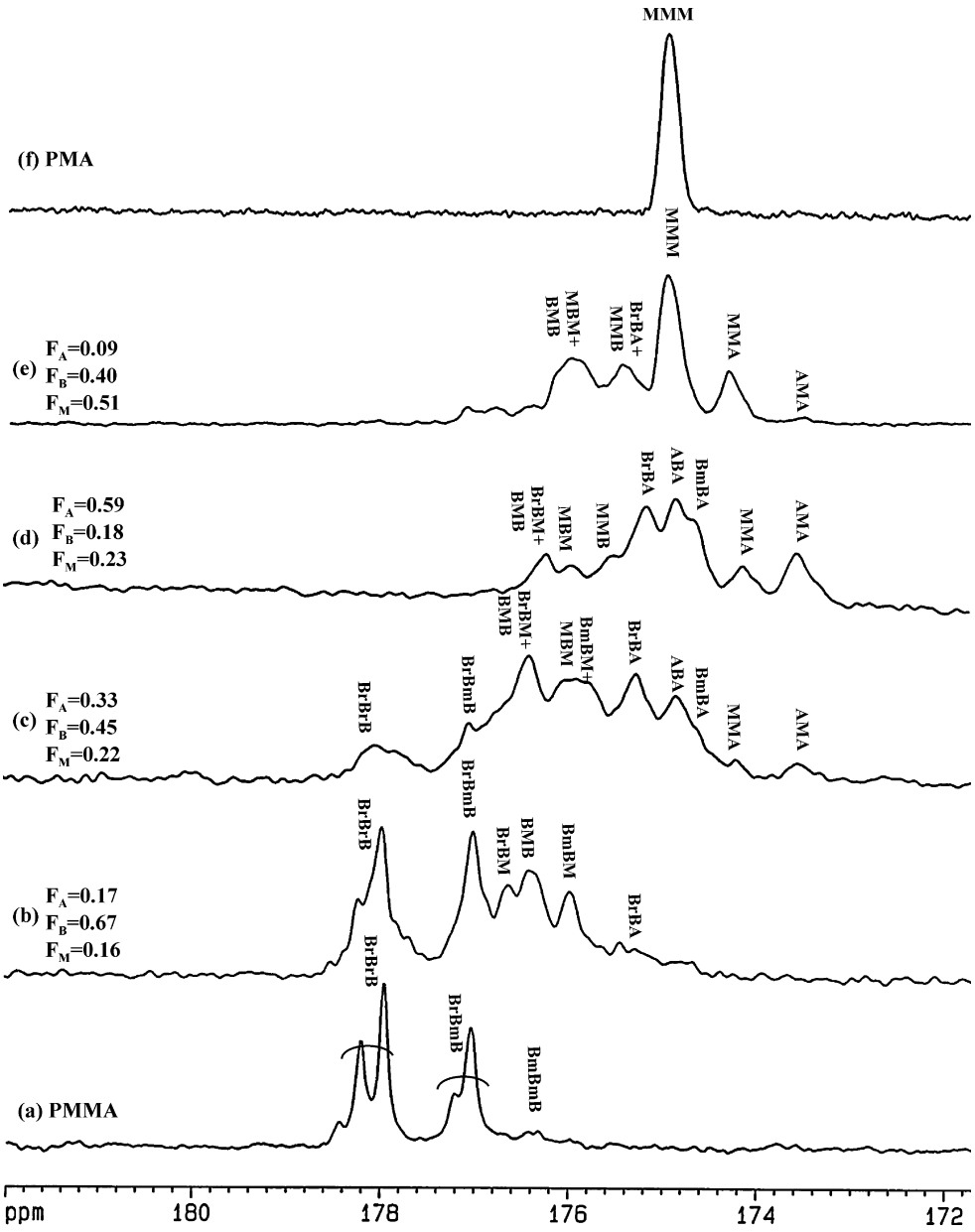

Fig. 1. The expanded carbonyl carbon region of B- and M-unit in $^{13}C\{^1H\}$ NMR spectrum of (a) PMMA, A/B/M terpolymers with compositions, (b) $F_A = 0.17$, $F_B = 0.67$, $F_M = 0.16$, (c) $F_A = 0.33$, $F_B = 0.45$, $F_M = 0.22$, (d) $F_A = 0.59$, $F_B = 0.18$, $F_M = 0.23$ and (e) $F_A = 0.09$, $F_B = 0.40$, $F_M = 0.51$ and (f) PMA in $CDCl_3$ at 25 °C.

carbonyl carbon resonances of terpolymers is a complicated and speculative procedure.

In A/M copolymer [18], carbonyl carbon resonance region was assigned to triad compositional sequences, on the basis of variation in intensity of signals with copolymer composition while in case of M/B [12] and A/B [19] copolymers, resonance signals were assigned to triad compositional and configurational sequences. On similar basis, various triads in carbonyl carbon region of A/B/M terpolymers were assigned tentatively through 1D NMR by comparing $^{13}C\{^1H\}$ NMR spectra of terpolymers having different compositions with that of corresponding copolymers and homopolymers. On comparison with spectrum of poly(methyl methacrylate), the signals at δ 178.10 and δ 177.20 ppm were assigned to BrBrB and BrBmB triads, respectively. The new additional signals at δ 176.50, δ 176.45, δ 176.00 and δ 175.40 ppm as shown in Fig. 1b were assigned to BrBM, BMB, BmBM and BrBA + MMB triad sequences, respectively. In Fig. 1c and d, both signals at δ 176.50 and δ 176.45 ppm merge together while the broadness of signal at δ 176.00 ppm increases so it was assigned to the overlap of BmBM and MBM triads. The resonance signal at δ 174.80 ppm was assigned to the overlap of BmBA, ABA and MMM triads while the resonance signals at δ 174.60 and δ 173.90 ppm were assigned to MMA and AMA triads, respectively.

3.1. 2D HMBC studies

2D HMBC spectral analysis of acrylonitrile/methyl methacrylate/methyl acrylate (A/B/M) terpolymer has been discussed to cross-examine the assignments from 2D HQSC and TOCSY spectral analysis. Both carbonyl and quaternary carbons do not show any coupling in 2D HSQC spectra. To investigate the compositional and configurational sensitivity of these carbon resonances, 2D HMBC spectra of different terpolymer compositions were recorded, wherein we can see 1,3 bond order couplings of carbonyl and qua-