Complete spectral assignments of methacrylonitrile-styrene-methyl methacrylate terpolymers by 2D NMR spectroscopy

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Abstract

Methacrylonitrile-styrene-methyl methacrylate (N/S/M) terpolymers of different monomer concentrations were prepared by bulk polymerization. The terpolymer compositions were determined by quantitative $^{13}$C/$^1$H NMR spectra and compared with those calculated by Goldfinger's equation using comonomer reactivity ratios: $r_{NS} = 0.30$, $r_{SN} = 0.45$; $r_{NM} = 0.91$, $r_{MN} = 0.88$; $r_{SM} = 0.52$, $r_{MS} = 0.47$. The overlapping and complex $^{13}$C/$^1$H and $^1$H NMR spectra of the terpolymers were assigned with the help of distortionless enhancement by polarization transfer and two-dimensional (2D) $^{13}$C/$^1$H heteronuclear single quantum coherence experiments. The various vicinal and geminal couplings between the protons in the polymer chains can be seen in the 2D total correlated spectroscopy experiments.

Keywords: Sequence distribution; Two-dimensional NMR; Methacrylonitrile-styrene-methyl methacrylate terpolymer; Multicomponent

1. Introduction

Number of polymers possess a wide range of mechanical, thermal and other properties. A wide variety of chemical or physical strategies including copolymerization, polymer blends and composites or crosslinking network have been explored to match the individual requirements [1]. Terpolymerization has continued to evoke interest from both academics and industry. However, the properties of a terpolymer depends upon its microstructure [2]. The study of the microstructure of terpolymers requires prior knowledge about comonomer sequences in the copolymer system.

The two-dimensional (2D) NMR spectroscopy [3-6] has been used as the most reliable technique to determine compositional and stereochemical [7, 8] structure of the copolymers. Styrene-methacrylonitrile (S/N) copolymer is already investigated by many workers [9-11]. Brar et al. [12] and other workers [13] have reported the comonomer sequences and cotacticity in the methacrylonitrile/methyl methacrylate (N/M) copolymer. Dhal et al. [14] and other workers [15,16] have reported the spectral assignments of styrene/methyl methacrylate (S/M) copolymer using $^1$H and $^{13}$C/$^1$H NMR spectra.

In this work, we report the complete $^1$H and $^{13}$C/$^1$H NMR spectral assignments of the methacrylonitrile/
styrene/methyl methacrylate (N/S/M) terpolymers. The compositions of the terpolymers were determined from quantitative $^{13}$C-$^1$H NMR spectra and the sequence distribution of the methacrylonitrile/styrene/methyl methacrylate (N/S/M) terpolymer was done with the help of 2D NMR spectroscopy. The $^{13}$C-$^1$H and $^1$H NMR spectra of terpolymer are quite complex and have been assigned with the help of DEPT-135 (distortionless enhancement by polarization transfer) and 2D heteronuclear single quantum coherence (HSQC) NMR spectroscopy. 2D Total correlated spectroscopy (TOCSY) NMR experiments are used to ascertain the various proton-proton couplings in the terpolymer chains.

2. Experimental

2.1. Sample preparation

Methacrylonitrile (E-Merck, Germany), Styrene (Commercial, India) and Methyl methacrylate (E-Merck, Germany) monomers were vacuum distilled under reduced pressure and stored below 5°C. Methacrylonitrile/styrene/methyl methacrylate (N/S/M) terpolymers were prepared by bulk polymerization at 60°C using benzoyl peroxide as initiator. The conversion was kept below 10% by controlling the time of polymerization (,2 h) and precipitating the terpolymers in excess of methanol. The terpolymers were further purified in chloroform/methanol system. The monomer compositions in the terpolymer were determined experimentally by quantitative $^{13}$C-$^1$H NMR spectroscopy. The molecular weight averages were determined by gel permeation chromatography (GPC) using poly(styrene) as a narrow standard. The molecular weight determination was carried out on a Waters GPC instrument attached with a refractive-index detector using a Styragel-HR4 column.

2.2. NMR measurements

All the 1D ($^1$H, $^{13}$C-$^1$H), DEPT-135) and 2D (HSQC, TOCSY) NMR spectra of N/S/M terpolymers were recorded in CDCl3 at 25°C, on a Bruker 300 MHz DPX spectrometer using different standard

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Table 1: Terpolymer compositions of methacrylonitrile-styrene-methyl methacrylate terpolymers (N/S/M)

a: Terpolymer composition using quantitative $^{13}$C-$^1$H NMR spectroscopy; b: terpolymer composition using statistical model using Alfrey-Goldfinger's equations; $\bar{M}_n$ and $\bar{M}_w$: weight average and number average molecular weights; $P$: polydispersity.
pulse sequences [17,18]. The other related details are given in our earlier papers [19,20].

3. Results and discussion

3.1. Terpolymer composition and molecular weights determination

The compositions of the methacrylonitrile/styrene/methyl methacrylate (N/S/M) terpolymers were determined from the quantitative $^1$H NMR spectra and compared those with the compositions calculated from Goldfinger's equation [21] using the reactivity ratios: $r_{NS} = 0.30$, $r_{SN} = 0.45$; $r_{NM} = 0.91$, $r_{MN} = 0.88$; $r_{SM} = 0.52$, $r_{MS} = 0.47$. The average molecular weights of the terpolymers with different compositions are given in Table 1.

3.2. $^{13}$C($^1$H) NMR studies

The complete assignment of the $^{13}$C($^1$H) NMR spectrum of the terpolymer, N/S/M (N = 0.33, S = 0.33, and M = 0.34 mol% in the terpolymer) in CDCl₃ is shown in Fig. 1. The spectral regions $d$ 15.5-30.0 and $d$ 43.2-54.5 ppm are complex and overlapping and can be assigned to aliphatic carbons in the main and branch chains of the terpolymer. The a-methyl carbon resonances of N- and M-units are assigned around $d$ 15.5-30.0 ppm. The spectral region around $d$ 31.7-36.3 ppm is due to quaternary carbon resonances of N-monomeric unit. The a-methine carbon of S-unit resonates at $d$

![Fig. 1. The $^{13}$C($^1$H) NMR spectrum of the methacrylonitrile-styrene-methyl methacrylate terpolymer (N/S/M) (N — 0.33, S — 0.33, and M — 0.34 mol% in the terpolymer) in CDCl₃.](image-url)
35.0-41.0 ppm. The quaternary carbon resonances of the M-unit, the methoxy carbon resonances of the M-unit and b-methylene carbon resonances of N-, S- and M-units of the terpolymer are overlapping. These overlapping carbon resonances can be assigned without ambiguity with the help of DEPT-135 (Fig. 2) experiments. The signals around $\delta$ 43.5-46.0 ppm are assigned to quaternary carbon resonances of M-monomeric unit. In the DEPT-135 experiment, the methyl (N and M-monomeric units), methine (S-monomeric unit) and methoxy (M-unit) carbon signals appear as positive phase, while the methylene carbon signals appear as negative phase, respectively. The methylene carbon resonances of N-, S- and M-units can be assigned around $\delta$ 41.0-55.5 ppm. The signals around $\delta$ 50.5-51.8 ppm can be assigned to methoxy carbon resonances of M-monomeric unit, which is overlapping with the methylene carbon resonances of the terpolymer. The methyl carbon signals of N- and M-units show triad compositional sensitivity. The methine carbon resonances of S-unit also show compositional triad sensitivity.

The nitrile carbon signals resonate around $\delta$ 121.2-124.7 ppm. The signals around $\delta$ 141.2-146.8 ppm are assigned to quaternary carbon in the phenyl group of the S-unit. The signals around $\delta$ 173.5-178.5 ppm are due to carbonyl carbon resonances. All the resonance signals were assigned by comparing with the $^{13}$C{H} NMR spectra of the N/S, S/M and N/M copolymers.

Fig. 3a-f shows the expanded $^{13}$C{H} NMR spectra of the carbonyl carbon resonances of the N/S/M terpolymers along with the poly(methyl methacrylate) (PMMA) and copolymers (S/M and N/M). All the signals can be assigned to M-centered compositional sequences. The assignments to various signals are done with the help of

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Fig. 2. The DEPT-135 spectrum of the methacrylonitrile-styrene-methyl methacrylate terpolymer (N/S/M) (N — 0.33, S — 0.33, and M — 0.34 mol% in the terpolymer) in CDCl$_3$. 

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the spectrum of homopolymer (PMMA) and by observing change in the intensity of signals with the change in composition of copolymers and terpolymers. The signals around δ 175.7-176.3(1), 8 176.5-177.3(2) and δ 177.3-178.4(3) ppm are assigned to MmMmM, MmMrM and MrMrM triads with the help of the 13C{1H} NMR spectrum of poly(methyl methacrylate) (Fig. 3a). There are three broad envelops in the carbonyl carbon region around δ 175.8-176.5(4) and δ 176.5-177.4(5) ppm are assigned to NMN and MmMrM • NMM triads in the methacrylonitrile/methyl methacrylate (N/M) copolymer (Fig. 3b). Similarly, the signals around δ 174.2-176.1(7) and 8 176.1-177.5(6) ppm are assigned to SMS and MMS triads in the styrene/methyl methacrylate (S/M) copolymer, by comparing the carbonyl carbon resonance signals of poly(methyl methacrylate)

Fig. 3. The expanded 13C{1H} NMR spectra of the carbonyl carbon region of: (a) PMMA; (b) N/M copolymer (0.41:0.59); terpolymer (N, S, and M = mol% in the terpolymer) (c) 0.27:0.13:0.60, (d) 0.33:0.33:0.34, (e) 0.51:0.36:0.13; and (f) S/M copolymer (0.43:0.57) in CDCl3.
(Fig. 3f). The signals around δ 174.4-177.3 ppm are overlapping, complex and difficult to assign (Fig. 3d).

Fig. 4a-f shows the expanded $^{13}$C{¹H} NMR spectra of the quaternary carbon resonances of S-unit in the N/S/M terpolymers along with the poly(-styrene) and copolymers (S/M and N/S). The quaternary region of the S-unit of $^{13}$C{¹H} NMR spectrum show multiplets and can be assigned to compositional sequences. There are some new signals of terpolymers along with the signals of poly(styrene) (PS) and copolymers (S/M and N/S). All the signals can be assigned to S-centered compositional sequences. The assignments to various signals are done with the help of the spectrum of the poly(styrene) and by observing the change in intensity of the signals with the change in composition of copolymers and terpolymers. The signals

![Graphical representation](image_url)

Fig. 4. The expanded $^{13}$C{¹H} NMR spectra of the quaternary carbon region of: (a) PS; (b) S/M copolymer (0.43:0.57); terpolymer (N, S, and M = mol% in the terpolymer) (c) 0.25:0.54:0.21, (d) 0.33:0.33:0.34, (e) 0.51:0.36:0.34; and (f) N/S copolymer (0.39:0.61) in CDCl₃.
around δ 144.5-145.5(1), δ 145.5-145.8(2) and δ 145.8-146.5(3) ppm are assigned to SrSrS, SmSrS and SmSmS triads with the help of the $^{13}$C{1H} NMR spectrum of poly(styrene) (Fig. 4a). The spectral regions of the quaternary carbon region around δ 142.2-143.9(4) and δ 143.9-145.0(5) ppm are assigned to MSM and MSS triads in the styrene/methyl methacrylate copolymer (Fig. 4b). Similarly, the signals around δ 142.5-143.7(7) and δ 143.7-144.9(6) ppm are assigned to NSN and NSS triads in the methacrylonitrile/styrene (N/S) copolymer, by comparing the quaternary carbon resonance signals of poly(styrene) (Fig. 4f). The signals around δ 142.0-146.2 ppm of the N/S/M terpolymer are overlapping, complex and difficult to assign (Fig. 4d).

3.3. 2D NMR studies

3.3.1. HSQC studies

The methyl regions of N- and M-units in 1D ($^{1}$H and $^{13}$C{1H}) NMR spectra of the terpolymers are quite complex and overlapped. This region can be assigned with the help of HSQC NMR spectra. The $^{13}$C-$^{1}$H HSQC NMR spectra of three different compositions of the N/S/M terpolymer are shown in Fig. 5a (N = 0.51, S = 0.36, and M = 0.13 mol% in the terpolymer), Fig. 5b (N = 0.27, S = 0.13, and M = 0.60 mol% in the terpolymer) and Fig. 6 (N = 0.33, S = 0.33, and M = 0.34 mol% in the terpolymer), respectively. In the N/S copolymers, the S-unit adjacent to the N-centered triad leads to the shielding of methyl carbon of the N-unit (SNS, NNS, NNN, in the increasing order of chemical shifts). Similarly, in the N/M copolymers, addition of the methyl methacrylate unit (M-) adjacent to the N-centered triad leads to the shielding of the methyl carbon (MNM, NMN, NNN, in the increasing order of chemical shifts). The CH$_{3}$ group in the N-monomeric unit of the terpolymer shows compositional sensitivity. The assignments of the methyl carbon resonances of the N-monomeric unit in the terpolymer are done on the basis of the change in intensity of the signals with change in the composition of the terpolymers and by comparing the methyl carbon resonances in the HSQC spectra of the methacrylonitrile-styrene (N/S) and methacrylonitrile-methyl methacrylate (N/M) copolymers. The cross peaks at δ 24.8-25.3/1.50-1.55(1), δ 25.3-26.4/1.46-1.50(2) and δ 26.4-27.0/1.40-
1.46(3) are assigned to NmNnN, NmNnN and NmNmN triads, respectively, on the basis of the assignment done in the HSQC spectrum of poly(methacrylonitrile), while the other crosspeaks at $d_{24.5-26.0/1.15(4)}$ and $d_{24.3-25.8/0.80-0.98(5)}$ ppm are assigned to NNS and SNS triads, respectively (Fig. 5a). Similarly, the crosspeaks at $d_{26.5-28.5/1.22-1.38(6)}$ and $d_{23.5-24.5/1.02-1.20(7)}$ ppm are assigned to NNM and MNN triads, respectively (Fig. 5b). The crosspeak at $d_{22.5-24.0/0.82-0.95(8)}$ ppm is due to MNS triad.

The methyl carbon resonances of the M-monomeric unit in the terpolymer also show compositional and configurational triad sensitivity. All the assignments of the methyl group of M-monomeric unit are done on the basis of the change in intensity of the signals with change in the composition of the terpolymers and by comparing the methyl carbon resonances in the HSQC spectra of the styrene-methyl methacrylate (S/M) and methacrylonitrile-methyl methacrylate (N/M) copolymers. In the S/M copolymers, the S-unit adjacent to the M-centered triad leads to the shielding of both methoxy and carbonyl carbons (SMMM, SMM, MMS, SMS, in the increasing order of chemical shifts), at the same time methyl carbon (M-unit) follows the similar arrangement in the triads distribution (SMMM, SMM, MMS, SMS). In the N/M copolymers, addition of the methacrylonitrile unit adjacent to the M-centered triad leads to the shielding of the carbonyl carbon (NMNN, NMMN, MMM, in the increasing order of chemical shifts), at the same time deshielding of the methyl carbons of M-centered triads. So, it follows the reverse trend for the methyl carbons of

Fig. 6. The 2D HSQC spectrum of the N/S/M terpolymer (N = 0.33, S = 0.33, M = 0.34 mol% in the terpolymer) in CDCl₃.
Fig. 7. The expanded b-methylene regions of 2D HSQC spectra of the N/S/M terpolymers with compositions (N, S, M—mol% in the terpolymer) (a) 0.51, 0.36, 0.13 and (b) 0.27, 0.13, 0.60.

Fig. 8. The proton NMR spectrum of the N/S/M terpolymer (N = 0.33, S = 0.33, and M = 0.34 mol% in the terpolymer).
M-centered triads (MMM, NMM, NMN). The cross peaks at $d_{16.5/0.82(9)}$, $d_{18.5/0.99(10)}$ and $d_{20.5/1.17(11)}$ are assigned to MrMrM, MmMrM and MmMmM triads, on the basis of the assignment done in the HSQC spectrum of poly(methyl methacrylate), while the other cross peaks at $d_{18.0/0.65(12)}$ and $d_{21.5-23.0/0.60-0.82(13)}$ ppm are assigned to MMS and SMS triads (Figs. 5b and 6). Similarly, the cross peak at $d_{21.0/1.10(14)}$ is assigned to NMS triad. The cross peaks at $d_{18.0/1.20(15)}$ and $d_{20.5/1.40(16)}$ ppm are due to MMN and NMN triads. All these assignments are shown in Figs. 5(a, b) and 6.

Along the proton axis, the methine proton of the styrene unit can be assigned by comparing the HSQC spectra of N/S and S/M copolymers and on the basis of the variation in the intensity of the signals with the change in the composition of terpolymers. The cross peaks at $d_{40.7/1.88-2.20(17)}$ and $d_{39.4/2.20-2.40(18)}$ ppm are assigned to MSS and NSS triads, while the cross peaks at $d_{39.2/2.51-2.85(19)}$ and $d_{38.5/2.86-3.17(20)}$ ppm are due to MSM and NSN triads (Fig. 6).

The b-CH$_2$ carbons show dyad compositional sensitivity, which appear at different chemical shifts. The methylene regions can be divided into broad SS, NS, NN, MS, NM and MM dyads on the basis of change in intensity of signals with change in terpolymer composition and by comparing the three different N/S, S/M and N/M copolymers and the homopolymer. Due to overlapping of the methylene carbon signals, there are few assignments (Fig. 7a and b) observed in the methylene carbon region. The cross peaks region around $d_{45.5-47.5/1.2-2.12(21)}$, $d_{47.5-51.5/1.25-2.20(22)}$ and $d_{51.5-55.0/1.15-2.15(23)}$ ppm are assigned to SS b NS, NN b MS and NM b MM dyads, respectively.

Fig. 9. The 2D TOCSY spectrum of the N/S/M terpolymer (N = 0.33, S = 0.33, M = 0.34 mol% in the terpolymer) at low mixing time (4 ms).
3.3.2. \(^1\)H and TOCSY studies

Fig. 8 (N = 0.33, S = 0.33, and M = 0.34 mol\% in the terpolymer) shows the proton spectrum of the terpolymer (N/S/M) along with signal assignments. After assigning the \(^{13}\)C\{\(^1\)H\} NMR spectrum completely, the various overlapping resonance signals in \(^1\)H NMR spectrum are assigned by one to one correlation between carbon and proton with the help of 2D HSQC NMR spectrum. In order to understand the connectivity and to confirm the various couplings in the copolymer chain, the TOCSY spectrum (at low mixing time, 4 ms) was recorded in CDCl\(_3\) as shown in Fig. 9.

The vicinal coupling between the methine proton of the NSN triad and the methylene protons of NS dyad gives the crosspeak at \(d\,2.90/2.12(1)\) ppm. In the MSM triad region, the central methine proton of MSM triad shows three bond coupling with the methylene protons of MS dyad at \(d\,2.75/1.78(2)\) ppm. Similarly, the coupling between the methine proton of NSS triad and methylene protons of NS dyad gives the crosspeak region around \(d\,2.35/2.06(3)\) ppm. The crosspeaks at \(d\,2.18-2.22/1.68(4)\) \(d\,2.12/1.55(5)\) and \(d\,2.05/1.42(6)\) ppm are due to geminal coupling of NN, NM and MM dyads, respectively. The assignments 4, 5, and 6 are done on the basis of change in intensity of signals with the copolymer compositions and by comparing the assignments done in the TOCSY spectrum (4 ms) of the methacrylonitrile/methylmethacrylate copolymer. The vicinal coupling between the methine proton of the MSS triad and the methylene protons of SS dyad gives the crosspeak at \(d\,1.90-2.02/1.49-1.62(7)\) ppm. All the assignments are shown in Fig. 9.

4. Conclusions

The sequence distribution of the methacrylonitrile-styrene-methyl methacrylate terpolymers is analyzed by \(^{13}\)C\{\(^1\)H\} NMR and 2D NMR experiments. The compositions of the N/S/M terpolymers obtained from quantitative \(^{13}\)C\{\(^1\)H\} NMR is in good agreement with those calculated by Goldfinger's equation. The methyl and methine carbon resonances are assigned to triad compositional sequences, whereas the methylene carbon resonances are assigned to dyad compositional sequences with the help of 2D HSQC spectra. The homonuclear 2D (\(^1\)H-\(^1\)H) TOCSY NMR spectrum suggested the various structural arrangements of the polymer chains.

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