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ORIGINAL RESEARCH ARTICLE

NMR spectroscopy based configurational and compositional analysis of isobornyl methacrylate—Acrylonitrile copolymers

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ABSTRACT

The authors conducted free radical polymerization using an initiator to synthesize a copolymer of isobornyl methacrylate—Acrylonitrile (I/A). The reactivity ratios of I (r_1) and A (r_2) monomers were determined as $r_1 = 1.63 \pm 0.14$, $r_2 = 0.61 \pm 0.06$ for linear KT (Kelen–Tudos) method and $r_1 = 1.58$, $r_2 = 0.60$ for the EVM (Error-in-Variable Method). We interpreted ^{1}H and ^{13}C{^{1}H} NMR spectra of the I/A copolymers using DEPT-135 and 2D HSQC spectra. The α-CH_3 carbon in the I-unit was identified and confirmed using a 2D HSQC NMR spectrum, up to the level of triad of compositional and configurational sequences. The CH (C_{14}) and β-CH_2 carbon peaks were also identified up to the triad level and higher, respectively. A 2D TOCSY spectrum revealed geminal and vicinal interactions within various CH and β-CH_2 protons. A 2D HMBC NMR spectrum provided a complete assignment of the coupling between nitrile, carbonyl, and quaternary carbons with CH_3 and CH_2 protons.

Keywords: Isobornyl Methacrylate; Compositional Sequence; Configurational Sequence; Copolymer; 2D-NMR; Reactivity Ratio

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1. Introduction

Isobornyl methacrylate (I) copolymers exhibit improved tensile strength, maximum elongation, and operational temperature[1–3], as well as chemical and water resistance, making them useful for adhesives, light-waveguide device films[4], coatings[5] and cosmetics[6]. These are also used as suitable sustainable bio-based replacement of methyl methacrylate in latex pressure sensitive adhesive[7] and in improvement of water resistance and mechanical properties with bio-based polymerization[8]. Different techniques have been used to synthesize copolymers of isobornyl methacrylate, including free radical[3,4,9–11]. Studies have been carried out to understand the behaviour of these copolymers, and sustainably sourced isobornyl methacrylate has been used in the synthesis of copolymers with other monomers. Synthesis of copolymers of Acrylonitrile with isobornyl acrylate and isobornyl methacrylate was accomplished employing AIBN as an initiator in dimethyl formamide (DMF), followed by thermal and dielectric studies on the resulting copolymers[12]. Further, a successful synthesis of copolymers has also been reported using nitroxide mediated polymerization technique[13,14].

Acrylonitrile (A) homo and copolymers are widely used in various industrial applications due to their unique properties and reactivity. Acrylonitrile-styrene copolymers are utilized in various applications such as medical devices, battery casings, automotive components, household items. Many studies have been performed on the copolymerization of acrylonitrile with vinyl monomers, with ^{13}C NMR spectroscopy being used to analyze distribution of monomer sequences. Various researchers have used ^{13}C NMR spectroscopy to determine the microstructure of copolymers of acrylonitrile with alkyl acrylates[15–17].

Various researchers have used 1D and 2D NMR spectroscopy to report on the microstructure of copolymers of acrylonitrile with alkyl acrylates[18–21]. Copolymers of acrylonitrile have also been synthesized by various techniques[22–25] using different starting compositions at different temperatures and pressures.

The microstructure, tacticity, polymerization mechanism, and physico-chemical properties[26–29] of vinyl polymeric materials are closely related to their monomer sequence distribution. Although the spectral pattern of copolymers is complex, 2D NMR experiments[30–32] have become crucial for identifying their microstructure due to the sensitivity of chemical shifts to composition sequence distribution and stereochemical assignments of monomeric units.

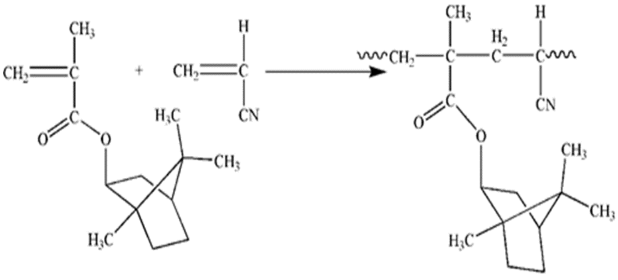
This paper presents the microstructure of I/A copolymers for the first time and determines the reactivity ratios using nonlinear EVM[33] and KT techniques[34]. Complete spectral assignments of ^1H and $^{13}C\{^1H\}$ NMR spectra are also achieved using various techniques such as DEPT, HSQC, TOCSY, and HMBC.

2. Experimental

The I/A copolymers with different mol fractions of I (**Table 1**) were synthesized with high grade chemicals (Aldrich) as described (**Scheme 1**). The polymerization time was controlled to 2 hours, and excess methanol was used to precipitate the copolymers. The obtained crude copolymer was purified using tetrahydrofuran/methanol Aldrich (HPLC grade) and subsequently air-dried. The NMR spectrum of the sample was obtained using a Bruker DPX-300 spectrometer in $CDCl_3$, Aldrich (HPLC grade) at standard pulse sequences. The experiments conducted to obtain the HSQC and HMBC spectra utilized the invigpt and inv4gplplrnd sequences, respectively.

Table 1. Copolymer composition data of isobornyl methacrylate—Acrylonitrile copolymers

S. No.	Infeed (f_I)	Outfeed (F_I)	% Monomer conversion
1	0.20	0.29	13.2
2	0.30	0.41	10.5
3	0.40	0.52	15.4
4	0.50	0.61	12.6
5	0.60	0.72	13.7
6	0.70	0.79	9.8



Scheme 1. Copolymerization of isobornyl methacrylate and acrylonitrile.

3. Determination of reactivity ratio

The proton NMR spectrum (**Figure 1**) was used to ascertain the relative composition of the I/A copolymers, as reported in **Table 1**. The reactivity ratios were found to be $r_1 = 1.63 \pm 0.14$ and $r_2 = 0.61 \pm 0.0$ for KT method and $r_1 = 1.58$, $r_2 = 0.60$ for EVM. It is worth mentioning here that these reactivity ratios have been reported in the literature for the first time by us.

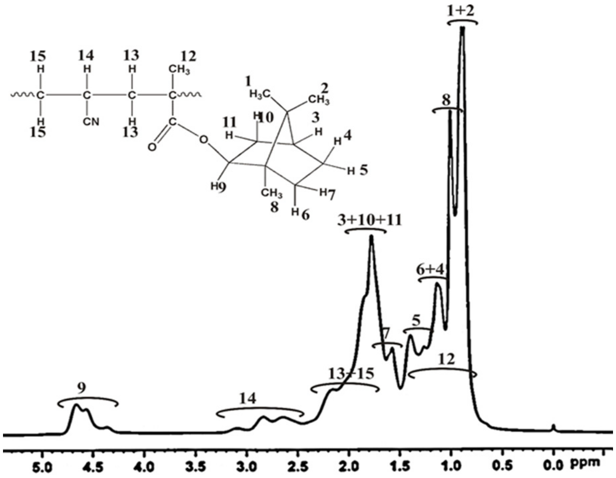


Figure 1. ^1H NMR spectrum of isobornyl methacrylate—Acrylonitrile copolymer ($F_I = 0.61$) in $CDCl_3$ at 25 °C.

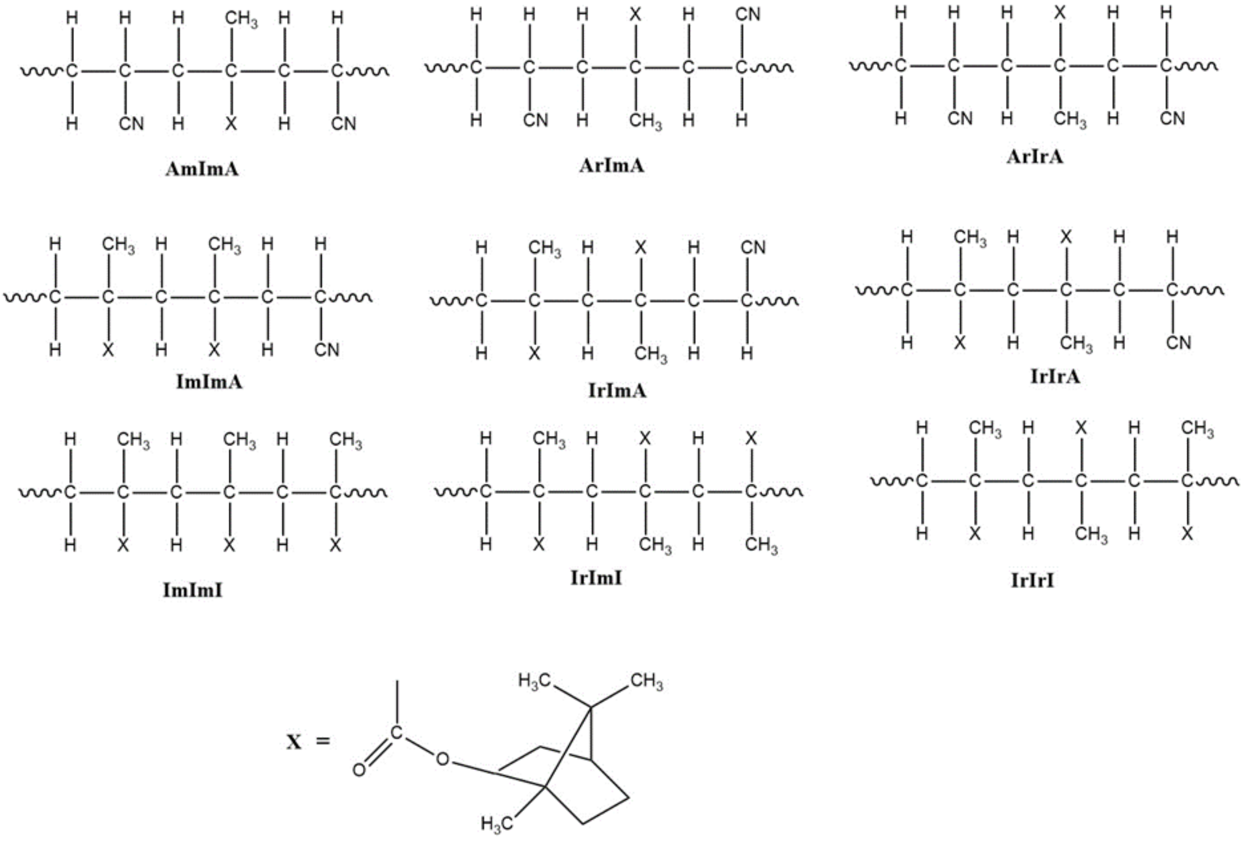
4. Results and discussion

4.1 $^{13}C\{^1H\}$ NMR analysis

Figure 2(a) displays fully designated $^{13}C\{^1H\}$ NMR spectra of I/A copolymer with a feed composition of 0.61 and further verified using 2D HSQC NMR spectrum. The spectrum is intricate and superimposed, but it was successfully resolved using the NMR spectra of homopolymers and the DEPT-135 NMR spectrum (**Figure 3**). The peak at δ 11.8 ppm is due to the CH_3 carbon (C_1), while the region around δ 16.2–22.6 ppm is attributed to the overlapping signals of CH_3 carbons (C_2 and C_8) and α-CH_3 (C_{12}) of the unit I present in I/A copolymer. The α-CH_3 carbon (C_{12}) of I unit shows compositional and configurational triads of AIA, IIA and III and shows splitting in ^{13}C NMR signal as it is present in different magnetic environments, shown in **Scheme 2**. The broad signal in the range δ 16.2–17.4 ppm is designated to IrIrI + IrImI + IrIrA triads, and the signal in the range δ 18.4–18.9 ppm is designated to ImImI + IrImA triads in C_{12}. ImImA and ArIrA triads of C_{12} appear around δ 19.2–20.8 ppm with overlapping of the signals of C_2 and C_8 methyl carbon of the isobornyl ring. The peaks at δ 21.5 ppm and δ 22.6 ppm are assigned respectively to the ArImA triad and AmImA triad of C_{12} as depicted in **Figure 2(b)**.

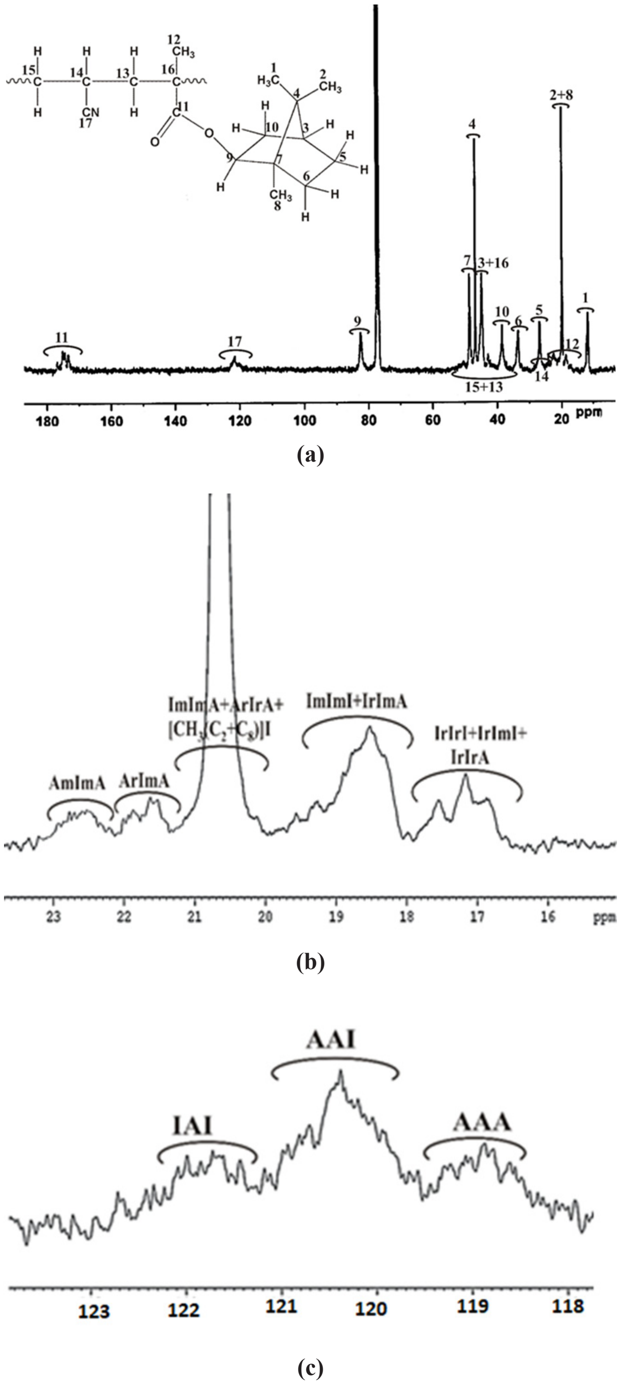
The spectrum shows that the β-CH_2 carbons (C_{13} and C_{15}) of both I and A units show tetrad level sequences and have resonances in the range of δ 34.0–55.0 ppm. The CH carbon (C_{14}) of A unit has a broad range of shift δ 21.7–28.9 ppm. The peaks arising due to the methylene carbons (C_{10}, C_6, and C_5) of the isobornyl ring can be seen at δ 38.40, 33.7 and 27.5 ppm. The peak at δ 45.0 ppm is due to the superimposition of methine carbon (C_3) and quaternary carbon (C_{16}). It may be noted that the peaks which appear at δ 47.57 ppm and 49.33 ppm in 2D HSQC spectrum due to C_4 and C_7 of the unit I are not seen in the DEPT-135 NMR spectrum. Similar behaviour has been reported by Khandelwal *et al.*[35] for isobornyl methacrylate/styrene copolymer also.

The carbon atom of the nitrile group (C_{17}) appears in the NMR spectrum at a shift of δ 118.8–122.0 ppm and exhibits sensitivity up to the triad level as illustrated in **Figure 2(c)**. **Figure 4** displays the superimposed peak of C_{11} of carbonyl carbon group in unit I of different compositions with poly (isobornyl methacrylate) (PiBMA). The chemical shift range of oxymethine carbon (C_9) of the I ring



Scheme 2. The structures of configurational and conformational sequences of AIA, IIA and III triads of I/A copolymer.

is wide and its splitting pattern is well-defined. The various spectral assignments attributed to the signals are shown in **Figure 5**.



(a)

(b)

(c)

Figure 2. (a) $^{13}C\{^1H\}$ NMR spectrum ($F_I = 0.61$); (b) expanded α-methyl region ($F_I = 0.61$); (c) expanded nitrile region ($F_I = 0.41$) of $^{13}C\{^1H\}$ NMR spectrum of isobornyl methacrylate—Acrylonitrile copolymer in $CDCl_3$ at 25 °C.

4.2 HSQC and TOCSY NMR analysis

Since overlapping proton peaks cannot be assigned using 1D spectral analysis, the necessary correlation and required designations can be provided in the 2D HSQC spectrum and can then be corroborated by the 2D TOCSY experiment.

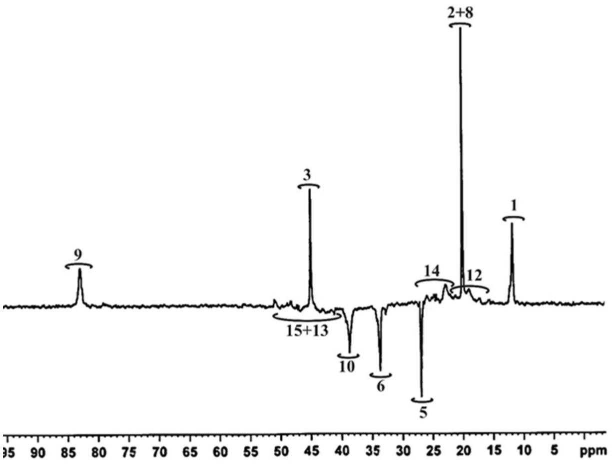


Figure 3. DEPT-135 NMR spectrum of isobornyl methacrylate—Acrylonitrile copolymer ($F_I = 0.61$) in $CDCl_3$ at 25 °C.

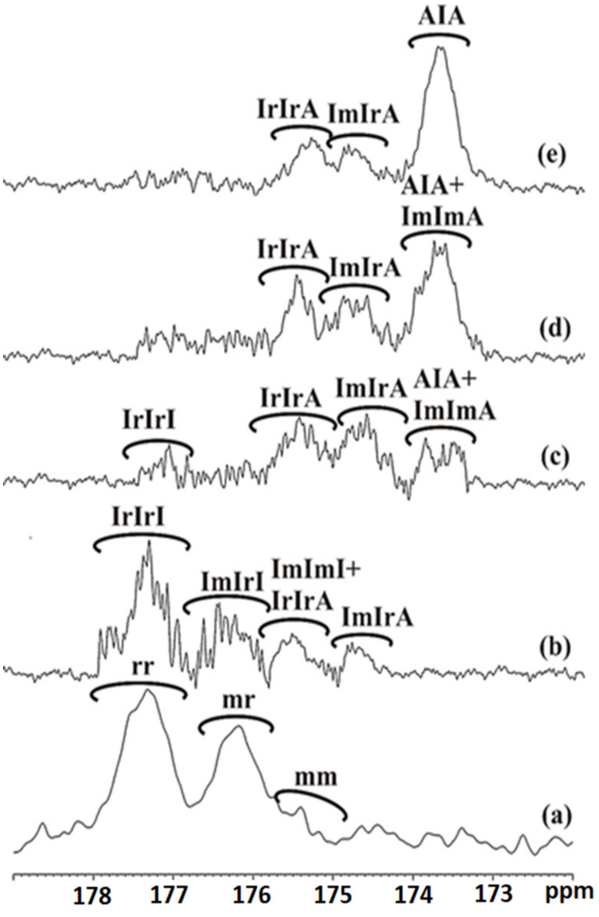


Figure 4. Expanded carbonyl carbon region in $^{13}C\{^1H\}$ NMR spectra of (a) PiBMA and isobornyl methacrylate—Acrylonitrile copolymer with compositions (F_I =): (b) 0.79, (c) 0.61, (d) 0.52, and (e) 0.29 in $CDCl_3$ at 25 °C.

4.3 β-CH_2 carbon region analysis

The CH_2 region in the $^{13}C\{^1H\}$ spectrum appears around δ 55.0–34.1 ppm and the different diads can be assigned based on comparison with homopolymers. The spectral range δ 55.0–51.6 ppm is assigned to II, δ 48.1–41.5 ppm to IA/AI, and δ

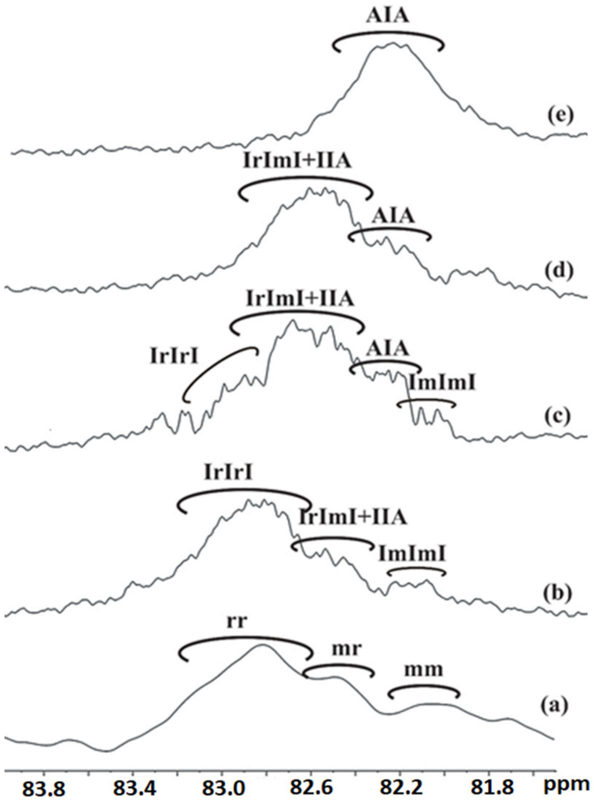


Figure 5. Expanded oxymethine (OCH) region of isobornyl ring in $^{13}C\{^1H\}$NMR spectra of (a) PiBMA and isobornyl methacrylate—Acrylonitrile copolymer with compositions (F_I =): (b) 0.79, (c) 0.52, (d) 0.41, (e) 0.29 in $CDCl_3$ at 25 °C.

38.9–33.9 ppm to AA diads. Additional splitting of diads is seen suggesting more complex combinations and arrangements. To identify the intricate CH_2 region, 2D HSQC (**Figure 6**) and TOCSY spectra (**Figure 7**) of copolymers were employed with various I/A ratios. Two cross peaks along with a single cross-correlation peak can be seen in the HSQC and TOCSY spectra respectively due to the coupling of tetrads with CH_2 meso protons Ha and Hb, demonstrating that the latter supports and distinguishes between the racemic and meso protons assigned in the HSQC spectrum.

Figure 6 displays the β-CH_2 region, and **Table 2** provides the corresponding assignments of peak positions from No. 1 to No. 30. Cross peaks No. 1–9 in the HSQC spectrum of copolymers with higher A content are attributed to AA-centered diads. The assignment of cross peaks to different tetrads can be found in **Table 2**.

The meso protons of both ImA and IrA centred tetrads display two coupling peaks due to coupling with the CH_2 carbon. The IA/AI-centered tetrads are represented by cross peaks No. 10–21 in **Figure 6** and their intensity increases with an increase in I content. The coupling between meso protons of IAmII tetrad and the geminal protons of IImII tetrad results in the cross-correlation peak No. 60 and peak No. 58 respectively in the 2D TOCSY spectrum (**Table 3**).

4.4 CH carbon region analysis

By comparing HSQC spectrum of copolymers with different A-unit compositions, it was found that the methine carbon region in $^{13}C\{^1H\}$ NMR spectra was well-separated and showed pentad-level sensitivity to composition and configuration (**Figure 8**). The identification of different triads and pentads in the copolymers is achieved by comparing them with the HSQC (2D) spectrum of polyacrylonitrile (PAN). **Table 4** depicts the details of the coupling peaks assignments due to various triads and pentads.

2D TOCSY studies confirmed the assignments and 1, 3–bond interactions between CH_2 of AA and AI/IA-centered tetrads and CH protons of A-unit were also identified (as shown in **Figure 7**). The HSQC (2D) spectrum shows the CH proton in A-unit appearing around δ 2.13–3.14 ppm in the 1H NMR spectrum. The cross-correlation peaks observed in the spectra are used to assign the couplings between the CH proton and CH_2 protons of various compositional and configurational sequences and are summarized in **Table 3**.

4.5 α-CH_3 carbon region analysis

The α-CH_3 carbon in $^{13}C\{^1H\}$ spectra, as depicted in **Figure 2(b)**, is intricate because of the presence of overlapping signals from different compositional and configurational sequences, as well as the residual signals of CH_3 carbons from the isobornyl ring. To resolve this, 2D HSQC spectra of various compositions have been used. **Figure 9** displays the expanded α-CH_3 region of HSQC spectrum for the I/A copolymer and identifies the various triads due to presence of α-CH_3 carbon. In different magnetic environments (**Scheme 2**), the α-CH_3 of I-unit shows compositional and configurational sensitivity. The cross peak at δ 16.0/0.85 ppm is assigned to the IrIrI triad of I/A copolymer. The cross peaks at δ 17.1/0.98, 18.3/1.16 and 17.6/1.02 ppm are assigned to IrImI, ImImI and IrIrA triads of I/A copolymers, respectively, while IrImA, ImImA and ArIrA triads of α-CH_3 region are assigned at δ

Table 2. Assignments of β-methylene carbon resonances of isobornyl methacrylate—Acrylonitrile copolymers from 2D HSQC spectra

Cross peak No.	**Cross peak assignment**	**Peak position (^{1}H/^{13}C ppm)**
1.	AAmAA (Ha)	1.99/34.1
2.	AArAA	2.12/34.2
3.	AAmAA (Hb)	2.19/33.9
4.	IAmAA (Ha)	1.88/35.8
5.	IArAA	1.99/36.1
6.	IAmAA (Hb)	2.11/36.1
7.	IAmAI (Ha)	1.95/38.9
8.	IArAI	2.06/38.9
9.	IAmAI (Hb)	2.18/38.9
10.	AAmIA (Ha)	1.55/41.5
11.	AArIA (Ha)	1.71/41.8
12.	AArIA (Hb)	1.98/41.6
13.	AAmIA (Hb)	2.15/41.8
14.	AImAI/IImAA (Ha)	1.43/43.1
15.	AIrAI/IIrAA (Ha)	1.55/42.9
16.	AIrAI/IIrAA (Hb)	1.78/43.0
17.	AImAI/IImAA (Hb)	1.96/43.2
18.	IAmII (Ha)	1.61/43.61
19.	IArII (Ha)	1.75/48.1
20.	IArII (Hb)	1.98/47.5
21.	IAmII (Hb)	2.07/47.3
22.	AImIA (Ha)	1.71/51.8
23.	AIrIA	1.82/51.7
24.	AImIA (Hb)	1.96/51.6
25.	AImII (Ha)	1.89/53.0
26.	AIrII	1.91/52.9
27.	AImII (Hb)	2.08/52.9
28.	IImII (Ha)	1.89/55.0
29.	IIrII	1.97/55.0
30.	IImII (Hb)	2.05/55.0

Table 3. ^{1}H-^{1}H cross correlations between non-equivalent geminal protons in isobornyl methacrylate—Acrylonitrile copolymers observed from 2D TOCSY spectra

Correlation peak No.	**Coupled protons**		**Peak position ^{1}H/^{1}H; δ: ppm**
	Proton I	**Proton II**	
44.	CH of AmAmA	CH$_2$ of AAmAI (Ha)	3.10/1.85
45.	CH of AmArA	CH$_2$ of AAmAA (Ha)	3.10/2.02
46.	CH of ArArA	CH$_2$ of AArAA	3.10/2.14
47.	CH of ArArI	CH$_2$ of AIrAI/AArII (Hb)	2.84/1.79
48.	CH of ArArI	CH$_2$ of AArIA (Hb)	2.84/1.98
49.	CH of AArAmIA	CH$_2$ of IAmAI (Hb)	2.84/2.15
50.	CH of AArAmIA	CH$_2$ of IImAA/AImAI (Ha)	2.84/1.40
51.	CH of ImAmI	CH$_2$ of IAmII (Hb)	2.69/2.10
52.	CH of ImAmI	CH$_2$ of AImAI/AAmII (Hb)	2.69/1.93
53.	CH of ImAmI	CH$_2$ of IAmII (Ha)	2.70/1.62
54.	CH of ImAmI	CH$_2$ of AImAI/AAmII (Ha)	2.68/1.40
55.	CH of IArAmIA	CH$_2$ of IAmAI (Hb)	2.50/2.19
56.	CH of IImArII	CH$_2$ of IArII (Ha)	2.15/1.73
57.	CH of IImArII	α-CH$_3$ of AmImA	2.15/1.32
58.	CH$_2$ of IImII (Ha)	CH$_2$ of IImII (Hb)	1.90/2.02

Table 3. (*Continued*)

Correlation peak No.	Coupled protons		Peak position $^1H/^1H$; δ: ppm
	Proton I	Proton II	
59.	CH_2 of AArIA (Ha)	α-CH_3 of ImIrA	1.70/1.24
60.	CH_2 of IAmII (Hb)	CH_2 of IAmII (Ha)	2.03/1.61
61.	CH_2 of $[(H_7)e]I$	CH_2 of $[(H_6)a]I$	1.70/1.11
62.	CH_2 of AIrAI/IIrAA (Ha)	α-CH_3 of ArIrA	1.52/1.09
63.	CH_2 of AImIA (Ha)	α-CH_3 of ImImA	1.71/1.31
64.	CH_2 of AAmIA (Ha)	α-CH_3 of ImImA	1.53/1.34
65.	CH of ArArA	CH of ArArI	3.10/2.88

Table 4. Assignments of methine carbon resonances of isobornyl methacrylate—Acrylonitrile copolymers from 2D HSQC spectra

Cross peak No.	Cross peak assignment	Peak position ($^{13}C/^1H$; δ: ppm)
31.	ArArA	28.9/3.14
32.	ArAmA	27.6/3.11
33.	AmAmA	26.4/3.05
34.	ArArI	26.5/2.84
35.	AArAmIA	24.9/2.84
36.	IArAmIA	25.0/2.56
37.	IArAmII	25.0/2.17
38.	AmAmI	24.0/2.79
39.	IrArI	23.2/2.58
40.	AImArIA	22.4/2.63
41.	IImArIA	22.6/2.17
42.	IImArII	22.6/2.13
43.	ImAmI	21.7/2.6

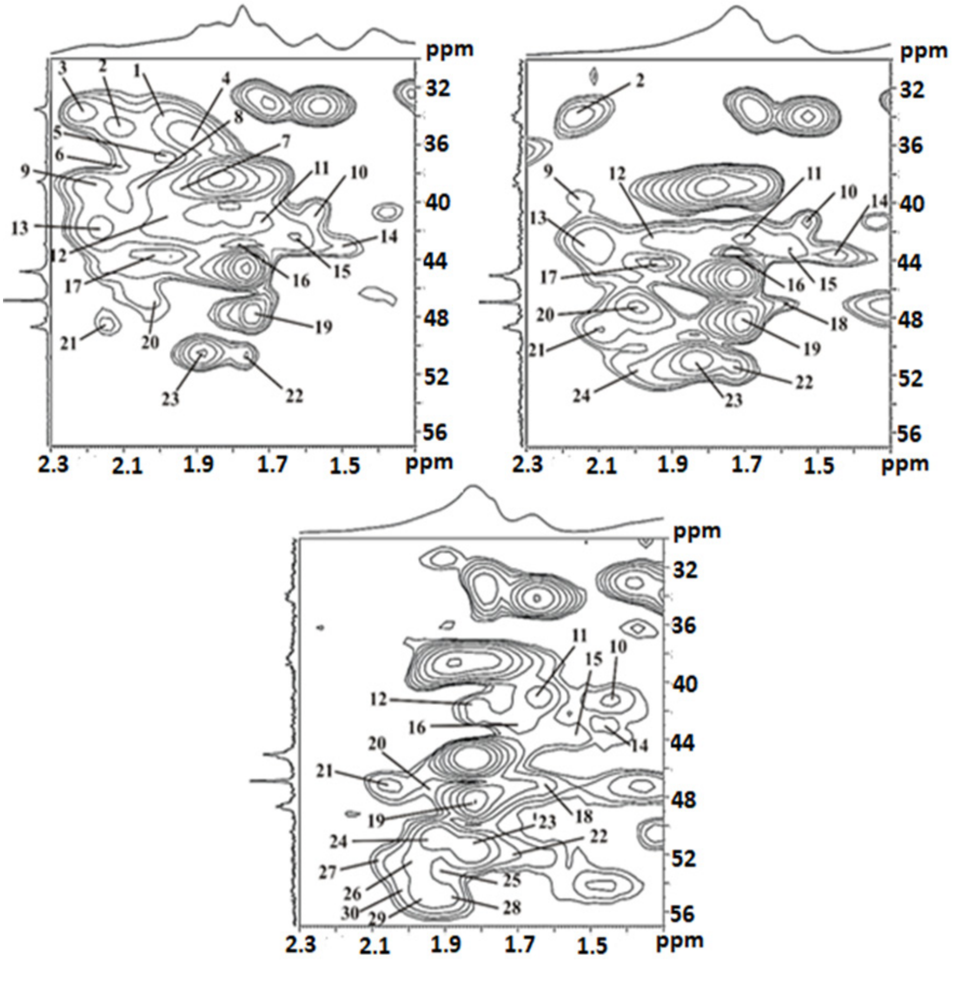


Figure 6. Expanded β-methylene carbon regions of 2D HSQC spectra of isobornyl methacrylate—Acrylonitrile copolymers with composition (F_1 =): (a) 0.29, (b) 0.52 and (c) 0.79 in $CDCl_3$ at 25 °C.

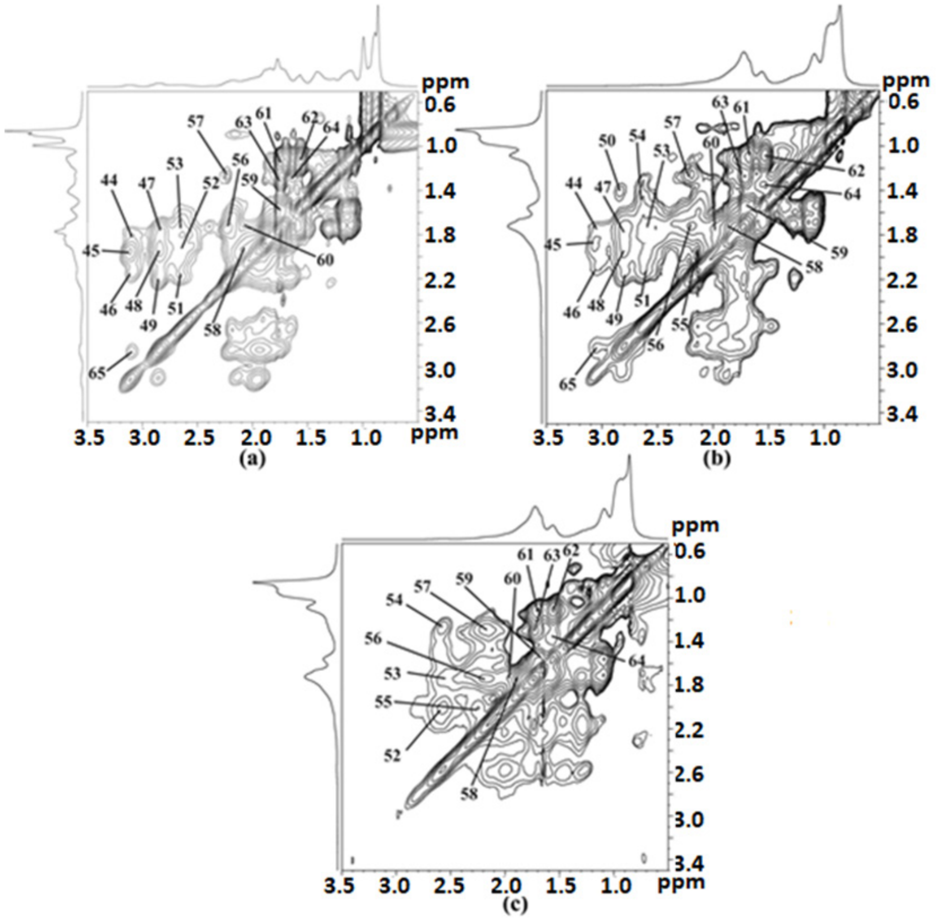


Figure 7. Expanded 2D TOCSY spectra of isobornyl methacrylate—Acrylonitrile copolymers with composition (F_I =): (a) 0.29, (b) 0.52 and (c) 0.79 in $CDCl_3$ at 25 °C.

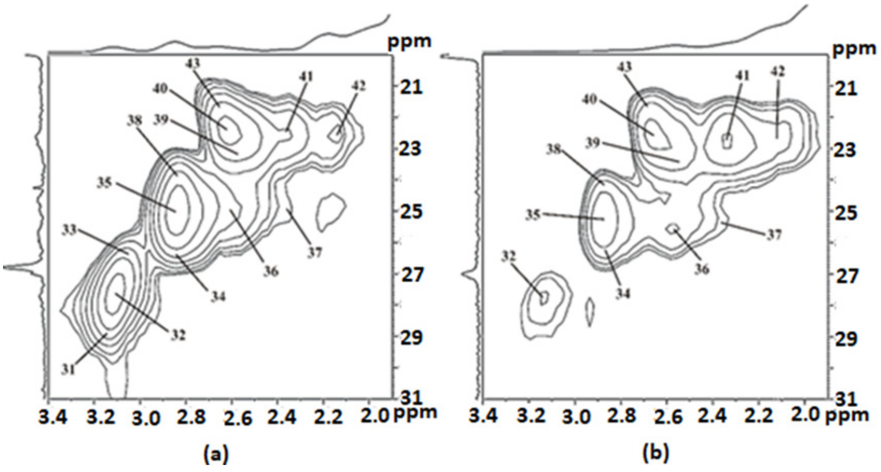


Figure 8. Expanded methine carbon regions of 2D HSQC spectra of isobornyl methacrylate—Acrylonitrile copolymers with composition (F_I =): (a) 0.29 and (b) 0.52 in $CDCl_3$ at 25 °C.

18.9/1.20, 20.8/1.34 and 19.2/1.07 ppm, respectively. The cross peaks at δ 21.6/1.21, and 22.8/1.34 ppm correspond to ArImA, and AmImA triads, respectively. Furthermore, the α-CH_3 protons show cross-correlation with β-CH_2 protons in the TOCSY (2D) spectrum and the resulting peak positions are listed in **Table 3**.

4.6 HMBC (2D) analysis

In order to analyze the sensitivity of these carbon resonances to composition and configuration, HMBC (2D) spectrum of copolymer with outfeed values (a) 0.29, (b) 0.52 and (c) 0.79 were observed and are shown in **Figure 10** and **Figure 11**. **Table 5** presents a comprehensive list of all the assignments made for the CO carbon region and the CN carbon

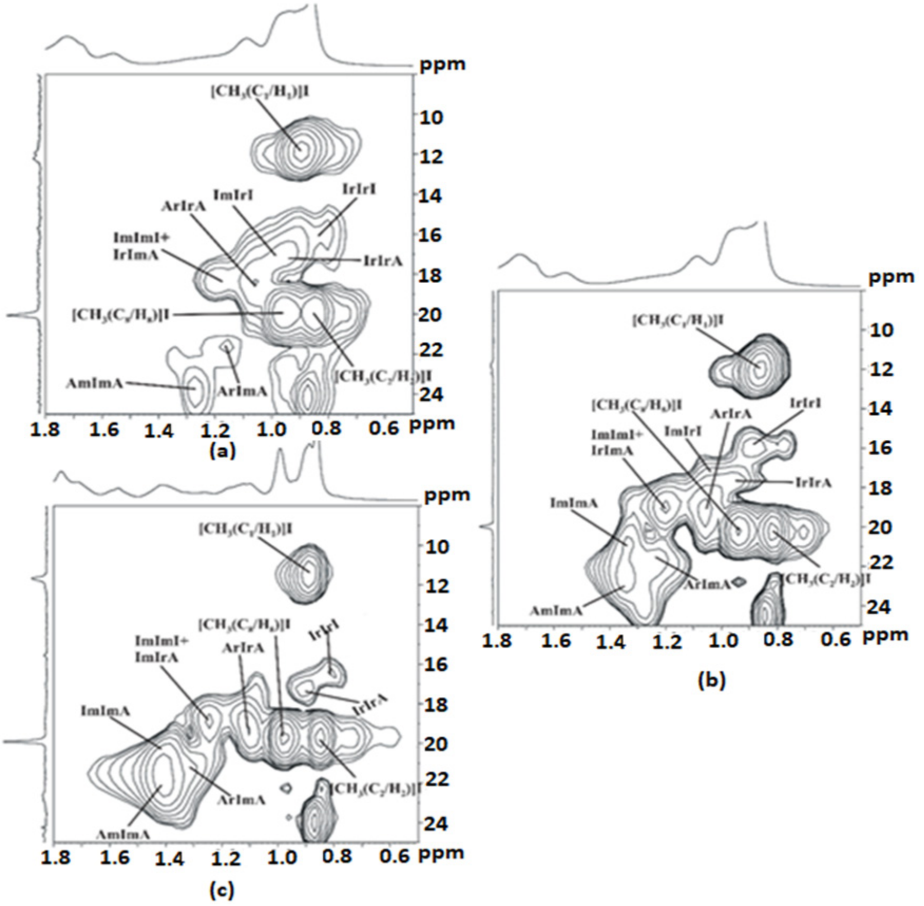


Figure 9. Expanded α-methyl carbon regions of 2D HSQC spectra of isobornyl methacrylate—Acrylonitrile copolymers with composition (F_I =): (a) 0.29, (b) 0.52 and (c) 0.79 in $CDCl_3$ at 25 °C.

Table 5. 2D HMBC assignments of carbonyl and nitrile carbons of isobornyl methacrylate—Acrylonitrile copolymer

Cross peak No.	Peak position ($^{13}C/^{1}H$; δ: ppm)	Type of carbon	Coupled to proton
66.	177.3/0.92	CO(IrIrI)	α-$CH_3(H_{12})$ (IrIrI)
67.	176.2/1.01	CO(IrImI)	α-$CH_3(H_{12})$ (IrImI)
68.	175.2/1.15	CO(IrIrA)	α-$CH_3(H_{12})$ (IrIrA)
69.	174.6/1.05	CO(IrImA)	α-$CH_3(H_{12})$ (IrImA)
70.	175.1/1.13	CO(ImImI)	α-$CH_3(H_{12})$ (ImImI)
71.	173.8/1.08	CO(AIA)	α-$CH_3(H_{12})$ (ArIrA)
72.	173.2/1.25	CO(AIA)	α-$CH_3(H_{12})$ (AmIrA)
73.	173.4/1.35	CO(AIA)	α-$CH_3(H_{12})$ (AmImA)
74.	121.4/1.35	CN(IAI)	α-$CH_3(H_{12})$ I
75.	120.3/1.46	CN(AAI)	β-CH_2 (AImAI/IImAA) (Ha)
76.	120.3/1.52	CN(AAI)	β-CH_2 (AIrAI/IIrAA) (Ha)
77.	120.3/1.56	CN(AAI)	β-CH_2 (AAmIA) (Ha)

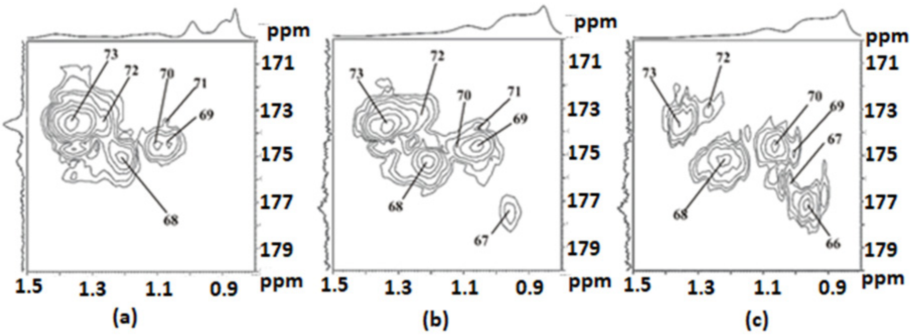


Figure 10. Expanded 2D HMBC spectra of isobornyl methacrylate—Acrylonitrile copolymers of carbonyl carbon region with composition (F_I =): (a) 0.29, (b) 0.52 and (c) 0.79 in $CDCl_3$ at 25 °C.

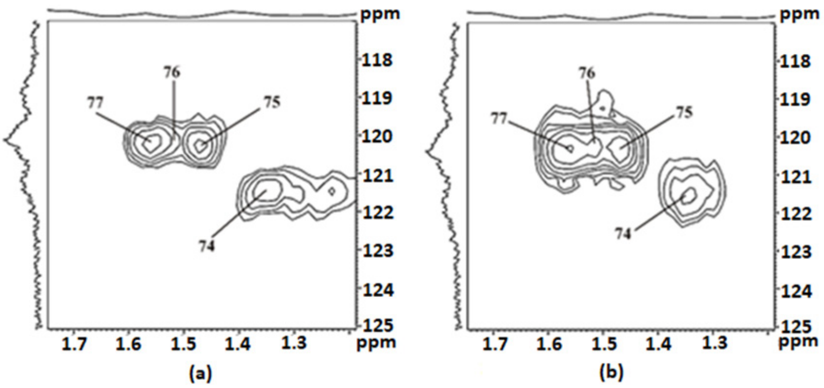


Figure 11. Expanded 2D HMBC spectra of isobornyl methacrylate—Acrylonitrile copolymers of nitrile region with composition (F_I =): (a) 0.29 and (b) 0.52 in $CDCl_3$ at 25 °C.

region along with the various couplings involved. The coupling peaks 75, 76, and 77 correspond to AAI triad of CN interacting with AImAI/IImAA, AIrAI/IIrAA and AAmIA tetrads of β-CH_2 protons.

4.7 ^{1}H NMR studies

The I/A copolymer's ^{1}H NMR spectrum depicted in **Figure 1** has been interpreted by comparing it to the proton NMR spectrum of PAN and PiBMA and with HSQC and TOCSY. The proton peaks around δ 4.5–4.8 ppm and around δ 2.13–3.14 ppm correspond to the OCH (H_9) proton and CH (H_{14}) proton of the A unit respectively. The CH_2 protons viz. H_5, H_7 in equatorial positions along with (H_4 and H_6) in axial positions of the isobornyl ring of unit I have been designated, respectively, to signals at δ 1.52–1.72 ppm and δ 0.92–1.11 ppm. The peaks observed at δ 1.44–2.21 ppm and δ 1.64–1.92 ppm are attributed to the H_{13}, H_{15} protons of the β-CH_2 group in the copolymer I/A and H_3, H_{10}, and H_{11} protons of the I ring, respectively. Furthermore, an overlap of peaks has been observed in unit I, at δ 0.85–1.35 ppm and δ 0.88 and δ 0.95 ppm between the α-CH_3 protons (H_{12}), and H_1, H_2, H_8 CH_3 protons of I ring respectively.

5. Conclusions

A copolymer of isobornyl methacrylate and acrylonitrile (I/A) was synthesized using AIBN as an initiator. Reactivity ratios $r_1 = 1.63 \pm 0.14$, $r_2 = 0.61 \pm 0.06$ for KT method and $r_1 = 1.58$, $r_2 = 0.60$ for EVM were found. DEPT-135 and HSQC (2D) spectra were used to understand the intricate and superimposed ^{1}H and $^{13}C\{^1H\}$ NMR spectra of the I/A copolymers. The α-methyl carbon and CH carbon in the unit I were designated up to the level of triads, while the β-CH_2 carbon was designated up to the tetrad level. The TOCSY spectrum (2D) showed geminal and vicinal interactions amongst various CH and the β-CH_2 protons. The HMBC spectra were used to completely assign the far-range order interactions amongst carbonyl, nitrile and quaternary carbons and CH_2, CH_3 protons. The information obtained from this study is important for the design and synthesis of copolymers with desired properties for various applications. Further studies can be conducted to investigate the properties of copolymers with different microstructures and compositions.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

1. Hadjichristidis N, Mays J, Ferry W, *et al*. Properties and chain flexibility of poly (dl-isobornyl methacrylate). Journal of Polymer Science Part B: Polymer Physics 1984; 22(10): 1745–1751. doi: 10.1002/pol.1984.180221004.
2. Matsumoto A, Mizuta K, Otsu T. Synthesis and thermal properties of poly(cycloalkyl meth-

acrylate)s bearing bridged- and fused-ring structures. Journal of Polymer Science Part A: Polymer Chemistry 1993; 31: 2531–2539. doi: 10.1002/pola.1993.080311014.

3. Jozaghkar MR, Ziaee F, Azar AS. Investigation of poly(α-methyl styrene) tacticity synthesized by photo-polymerization. Polymer Bulletin 2021; 78: 5303–5314. doi: 10.1007/s00289-021-03823-6.
4. Qu J, Cheng J, Wang Z, *et al*. Synthesis, thermal and optical properties of crosslinked poly (isobornyl methacrylate-co-butyl acrylate) copolymer films. Optical Materials 2014; 36(4): 804–808. doi: 10.1016/j.optmat.2013.11.030.
5. Koleske JV. Paint and coating testing manual: Fourteenth edition of the Gardner-Sward handbook. Philadelphia: Astm; 1995.
6. Farcet C (inventor). L'Oréal (assignee). Novel block (Co)polymers composition containing them, method of treatment and method of preparation. US Patent. 20080181859A1. 2008 Jul 31.
7. Fang C, Zhu X, Cao Y, *et al*. Toward replacement of methyl methacrylate by sustainable bio-based isobornyl methacrylate in latex pressure sensitive adhesive. International Journal of Adhesion and Adhesives 2020; 100: 102623. doi: 10.1016/j.ijadhadh.2020.102623.
8. Xu J, Zhai Z, Yan X, *et al*. Improvement of water resistance and mechanical properties of fast-growing poplar with bio-based isobornyl methacrylate monomer. BioResources 2020; 15(2): 2356–2370. doi: 10.15376/biores.15.2.2356-2370.
9. Pirman T, Ocepek M, Likozar M. Radical polymerization of acrylates, methacrylates, and styrene: Biobased approaches, mechanism, kinetics, secondary reactions, and modeling. Industrial & Engineering Chemistry Research 2021; 60(26): 9347–9367. doi: 10.1021/acs.iecr.1c01649.
10. Ko KY, Hwang SH. Monomer composition effects on thermal properties of transparent poly(methyl methacrylate-co-isobornyl methacrylate-co-cyclohexyl maleimide) terpolymers. Journal of Industrial and Engineering Chemistry 2018; 59: 50–55. doi: 10.1016/j.jiec.2017.10.004.
11. Khandelwal D, Hooda S, Brar AS, *et al*. Poly(isobornyl methacrylate-co-methyl acrylate): Synthesis and stereo sequence distribution analysis by NMR spectroscopy. Journal of Polymer Science Part A: Polymer Chemistry 2012; 50(16): 3350–3362. doi: 10.1002/pola.26122.
12. Sridevi S, Rao PR. Thermal and dielectric studies of acrylonitrile with isobornyl acrylate and methacrylate copolymers. Oriental Journal of Chemistry 2008; 24(1): 157–162.
13. Hajiali F, Métafiot A, Benitez Ek L, *et al*. Nitroxide mediated polymerization of sustainably sourced isobornyl methacrylate and tridecyl methacrylate with acrylonitrile co-monomer. Journal of Polymer Science Part A: Polymer Chemistry 2018; 56: 2422–2436. doi: 10.1002/pola.29216.
14. Metafiot A, Gagnon L, Pruvost S, *et al*. β-Myrcene/isobornyl methacrylate SG1 nitroxide-mediated controlled radical polymerization: Synthesis and characterization of gradient, diblock and triblock copolymers. RSC Advances 2019; 9: 3377–3395. doi: 10.1039/C8RA09192G.
15. Bajaj P, Paliwal DK, Gupta AK. Acrylonitrile—Acrylic acids copolymers. I. Synthesis and characterization. Journal of Applied Polymer Science 1993; 49(5): 823–833. doi: 10.1002/app.1993.070490508.
16. Borbley JD, Hill DJT, Lang AP, *et al*. Copolymerization of acrylonitrile and methacrylic acid. An assessment of the copolymerization mechanism. Macromolecules 1991; 24(9): 2208–2211. doi: 10.1021/ma00009a012.
17. Dhar A, Singh U, Koiry BP, *et al*. Investigation of microstructure in poly(methyl methacrylate) prepared via ambient temperature ARGET-ATRP: A combined approach of 1D and 2D NMR spectroscopy. Journal of Polymer Research 2020; 27: 174. doi: 10.1007/s10965-020-02153-x.
18. Brar AS, Kaur J. 2D NMR studies of acrylonitrile-methyl acrylate copolymers. European Polymer Journal 2005; 41(10): 2278–2289. doi: 10.1016/j.eurpolymj.2005.05.003.
19. Hooda S, Goyal AK, Brar AS. Microstructure determination of poly(acrylonitrile-co-methyl methacrylate-co-methyl acrylate) terpolymers by 2D HMBC. Journal of Molecular Structure 2005; 920(1–3): 424–429. doi: 10.1016/j.molstruc.2008.11.042.
20. Brar AS, Saini T. Atom transfer radical copolymerization of acrylonitrile/n-butyl acrylate: Microstructure determination by two-dimensional nuclear magnetic resonance spectroscopy. Journal of Polymer Science Part A: Polymer Chemistry 2005; 43(13): 2810–2825. doi: 10.1016/j.molstruc.2008.11.042.
21. Brar AS, Sunita. Compositional sequence determination of acrylonitrile-butyl acrylate copolymers by ^{13}C n.m.r. spectroscopy. Polymer 1993; 34(16): 3391–3396. doi: 10.1016/0032-3861(93)90466-N.
22. Wang A, Bao Y, Weng Z, *et al*. Synthesis and characterization of a novel polymer electrolyte based on acrylonitrile/*N*-[4-(aminosulfonyl)phenyl]acrylamide copolymers. Chinese Journal of Polymer

Science 2010; 28: 129–135. doi: 10.1007/s10118-010-9057-2.

23. Huang Z, Chen J, Zhang L, *et al*. ICAR ATRP of acrylonitrile under ambient and high pressure. Polymers 2016; 8(3): 59. doi: 10.3390/polym8030059.
24. Ji Y, Catazaro J, Jiang Q, *et al*. Characterization of styrene—Vinyl alcohol copolymers by CP-MAS NMR spectroscopy. Macromolecules 2022; 55(16): 7032–7038. doi: 10.1021/acs.macromol.2c01009.
25. Budnikov SY, Smirnov AA, Vorozhtsov DL, *et al*. Copolymers of isobornyl acrylate with methylmethacrylate or acrylonitrile and its optical properties. Journal of Polymer Research 2020; 27: 59. doi: 10.1007/s10965-019-1904-4.
26. Ziegler MJ, Matyjaszewski K. Atom transfer radical copolymerization of methyl methacrylate and n-butyl acrylate. Macromolecules 2001; 34(3): 415–424. doi: 10.1021/ma001182k.
27. Matyjaszewski K, Ziegler MJ, Arehart SV, *et al*. Gradient copolymers by atom transfer radical copolymerization. Journal of Physical Organic Chemistry 2000; 13: 775–786. doi: 10.1002/1099-1395(200012)13:12<775:AID-POC314>3.0.CO;2-D.
28. Chen EYX. Stereospecific polymerization of methacrylates by metallocene and related catalysts. Journal of Polymer Science Part A: Polymer Chemistry 2004; 42(14): 3395–3403. doi: 10.1002/pola.20184.
29. Bovey FA. Chain structure and conformation of macromolecules. 1st ed. New York: Academic Press; 1982.
30. Matsuzaki K, Uryu T, Asakura T. NMR spectroscopy and stereoregularity of polymers. Tokyo: Japan Scientific Societies Press; 1996.
31. Long YY, Lv J, Li BX, *et al*. Speedy quantitative microstructure determination of Poly(ethylene-co-1-hexene) at triads by ^{1}H–^{13}C two-dimensional NMR. Polymer 2021; 229: 123993. doi: 10.1016/j.polymer.2021.123993.
32. Escher FFN, Galland GB. ^{13}Carbon nuclear magnetic resonance of ethylene-propylene-1-hexene terpolymers. Journal of Polymer Science Part A: Polymer Chemistry 2004; 42: 2474–2482. doi: 10.1002/pola.20097.
33. Dube M, Sanayei PA, Penlidis A, *et al*. A microcomputer program for estimation of copolymerization reactivity ratios. Journal of Polymer Science Part A: Polymer Chemistry 1991; 29(5): 703–708. doi: 10.1002/pola.1991.080290512.
34. Kelen T, Tudos F. Analysis of the linear methods for determining copolymerization reactivity ratios. I. A new improved linear graphic method. Journal of Macromolecular Science: Part A–Chemistry 1975; 9(1): 1–27. doi: 10.1080/00222337508068644.
35. Khandelwal D, Hooda S, Brar AS, *et al*. Microstructure determination of isobornyl methacrylate—Styrene copolymer by NMR spectroscopy. Journal of Polymer Research 2014; 21: 377. doi: 0.1007/s10965-014-0377-8.