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CONFIGURATIONAL STRUCTURE INVESTIGATION OF POLYISOBORNYL METHACRYLATE (PiBMA) USING NUCLEAR MAGNETIC RESONANCE TECHNIQUES

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Abstract

A 2D NMR analysis was performed to examine the microstructure of Polyisobornyl Methacrylate (PiBMA) which was synthesized using Atom Transfer Radical Polymerization (ATRP) with a copper(I) bromide catalyst and PMDETA - N,N,N',N',N''-pentamethyldiethylenetriamine ligand, as well as a methyl-2-bromopropionate (MBP) initiator. The complex ^{1}H NMR spectra were resolved, and the stereo-sequences of PiBMA were established up to the diad level for β-CH_2 carbons and up to the triad level for α-CH_3 (C_{12}) and carbonyl (C_{11}) carbons using 2D HSQC as well as TOCSY NMR experiments. The 2D HMBC NMR spectra completely resolved the quaternary carbons in the $^{13}C\{^{1}H\}$ *viz*. the carbon observed, proton broadband decoupled NMR spectrum. The analysis revealed that the tacticity of PiBMA, estimated for the C_{11} carbon peaks, was arbitrary, with rr = 53%, mr = 42% and mm = 4%, which was similar to that of PiBMA prepared using AIBN as an initiator through free radical polymerisation.

***Keywords**:* PIBMA, Isobornyl methacrylate, ATRP, Stereo-sequence, NMR, Configuration.

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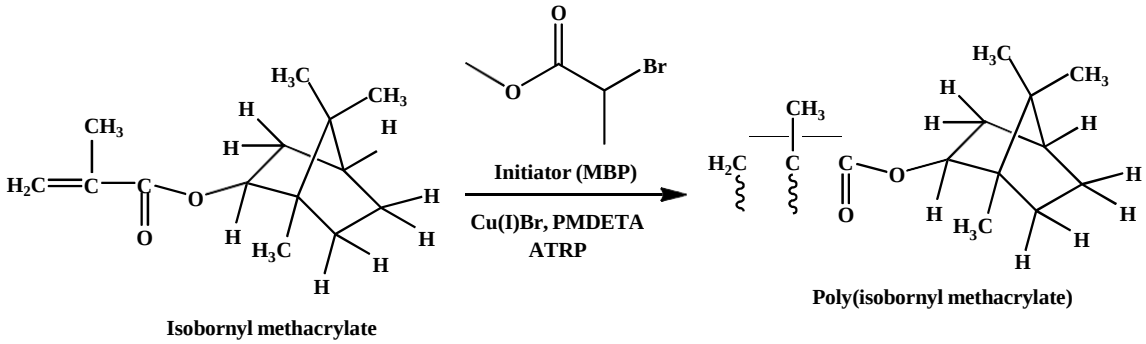
1. INTRODUCTION

Polyisobornyl Methacrylate (PiBMA) is a recently developed clear macromolecule resin that has multifunctional uses in optical materials due to its superior tensile resilience, maximum extension, and upper Operating temperature [1]. PiBMA is a rigid material obtained by polymerising the monomer, which possesses a high glass transition point (T_g) [2,3]. It is also chemically and water-resistant, making it useful in the adhesives and coatings industries [4], as well as in cosmetics [5]. Various methods of controlled radical polymerization have been used to produce PiBMA, including free radical [6], anionic [1], and Atom Transfer Radical Polymerisation (ATRP) [7-11]. NMR spectroscopy is commonly used to determine the microstructure of polymers [12-25]. In our work, we report the stereo-sequences of PiBMA using 1D and 2D NMR spectroscopy for the first time. The microstructure of PiBMA was confirmed using 2D HSQC, TOCSY, and HMBC spectra in conjunction with one dimensional proton-decoupled ^{13}C NMR spectroscopy [26-29].

2. EXPERIMENTAL

An experimental procedure was conducted, which involved the synthesis and purification of Isobornyl methacrylate (iBMA) using various chemicals and solvents purchased from Aldrich. The iBMA underwent a process of refinement using fractional distillation under low pressure. It was then put in a reaction vessel along with PMDETA (N,N,N',N'',N''-Pentamethyldiethylenetri-amine) ligand, copper(I) bromide and methyl 2-bromopropionate ($C_4H_7BrO_2$) in 100:1:1:1 ratio for the synthesis of PiBMA through ATRP method (**Scheme-I**). In order to remove oxygen, N_2 was purged in the reaction vessel for 15 min and the material was kept in an oil bath (60 °C) for an hour and then cooled. After adding CH_3OH to terminate the reaction, the dilute solution of the polymer was purified by removing the copper catalyst with a column of neutral alumina. This was followed by multiple rounds of dissolution and precipitation in THF and CH_3OH to further purify the polymer. PiBMA was also prepared by free radical polymerization using azobisisobutyronitrile (AIBN) as the initiator and purified in the same way. The chemical structures were analyzed using 1D and 2D NMR spectra, which were obtained using a Bruker DPX-300 spectrometer and recorded in $CDCl_3$.



Scheme-I: Polymerization of isobornyl methacrylate by atom transfer radical polymerization

3. RESULTS AND DISCUSSION

3.1. Proton-decoupled ^{13}C NMR spectroscopy

The proton-decoupled ^{13}C NMR spectrum [30-35] of PiBMA at 300 K is shown in Fig. 1a.

According to documented shifts for ^{13}C nuclei, the various resonance signals attributed to CH_3 and CH carbons depicted by Positive Phase, and CH_2 carbons depicted by Negative Phase have been designated in the DEPT-135 spectra (Fig. 2). The peaks at δ 47.05, 49.03, and 39.21 due to Quaternary carbons C_4, C_7, and C_{14} are absent from the DEPT-135 spectra.

The peak at δ 19.90 is due to resonance of C_2 and C_8 CH_3 carbon whereas C_1 is responsible for the resonance peak at δ12.11. The backbone CH_3 carbon (C_{12}) resonates between δ 15.2 and 18.7 and is ascribed to the triads namely rr, mr/rm, and mm triads and further ascertained by the HSQC NMR spectra. Resonance peaks are observed at δ 45.05 and 82.25 due to CH carbons (C_3 and C_9). It is also observed that the peak due to C_9 is getting deshielded as a result of the influence of the oxygen atom. The assignment of the resonances at δ 27.15, 34.33, and 38.32 for the CH_2 carbon (C_5), (C_6) and (C_{10}) is based on the shielding or deshielding effect. The multiplet attributed to backbone CH_2 carbon (C_{13}) ranges from δ 53.3-56.5.

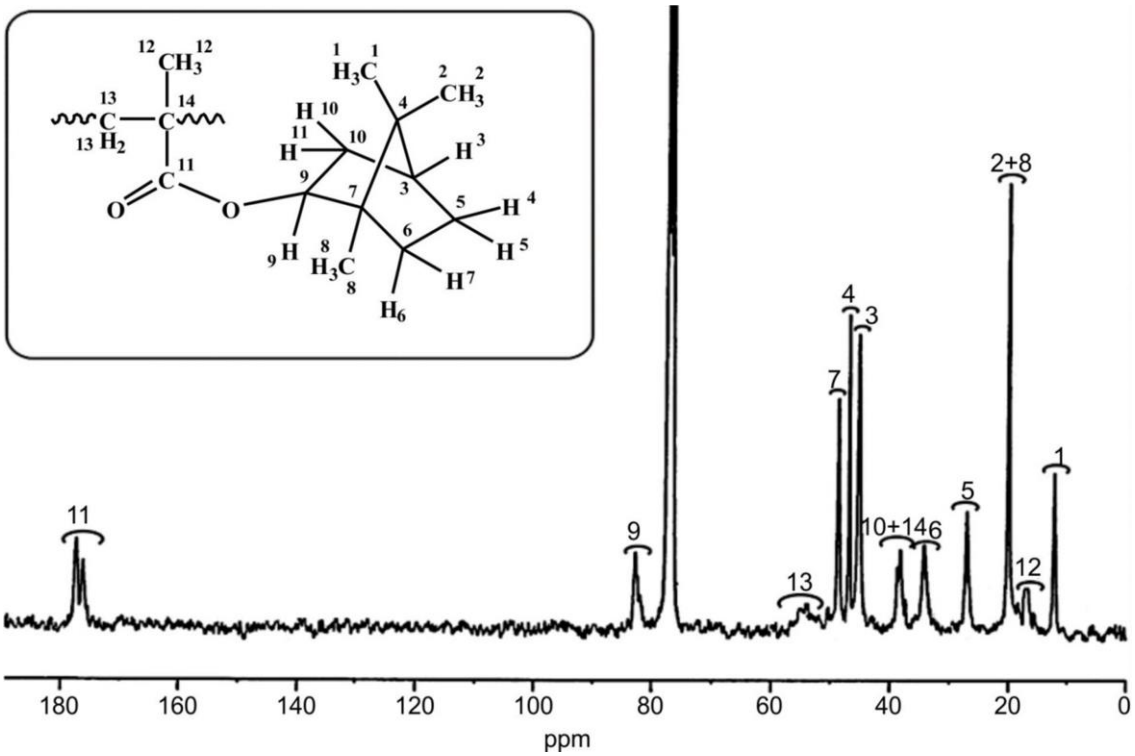


Fig. 1a. $^{13}C\{^1H\}$ NMR spectrum of PiBMA in $CDCl_3$ at 25°C.

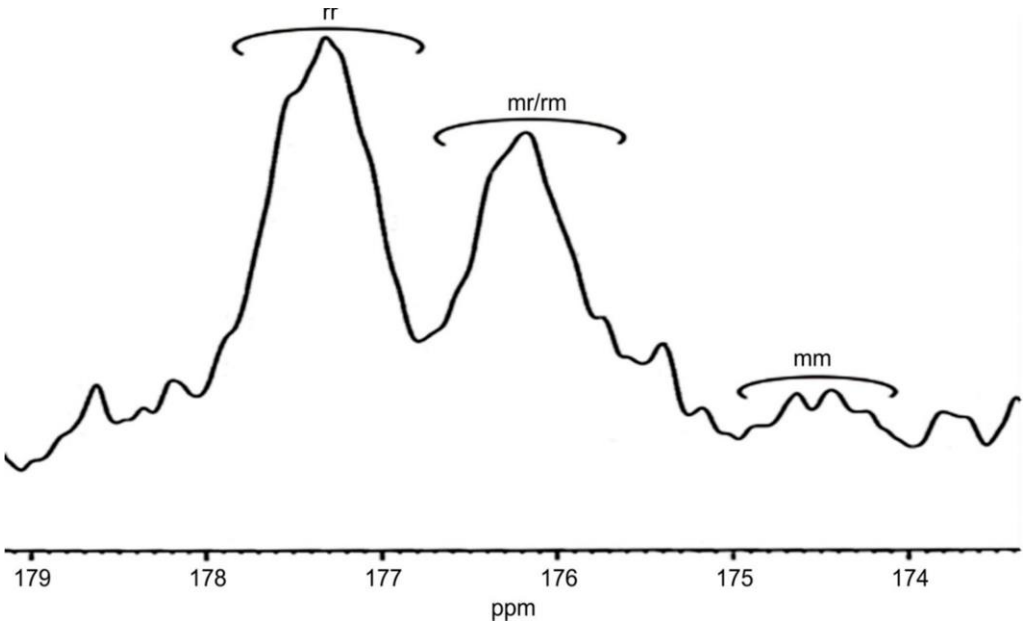


Fig. 1b. Expanded backbone carbonyl carbon region of $^{13}C\{^{1}H\}$ NMR spectrum of PiBMA in $CDCl_3$ at 25 °C

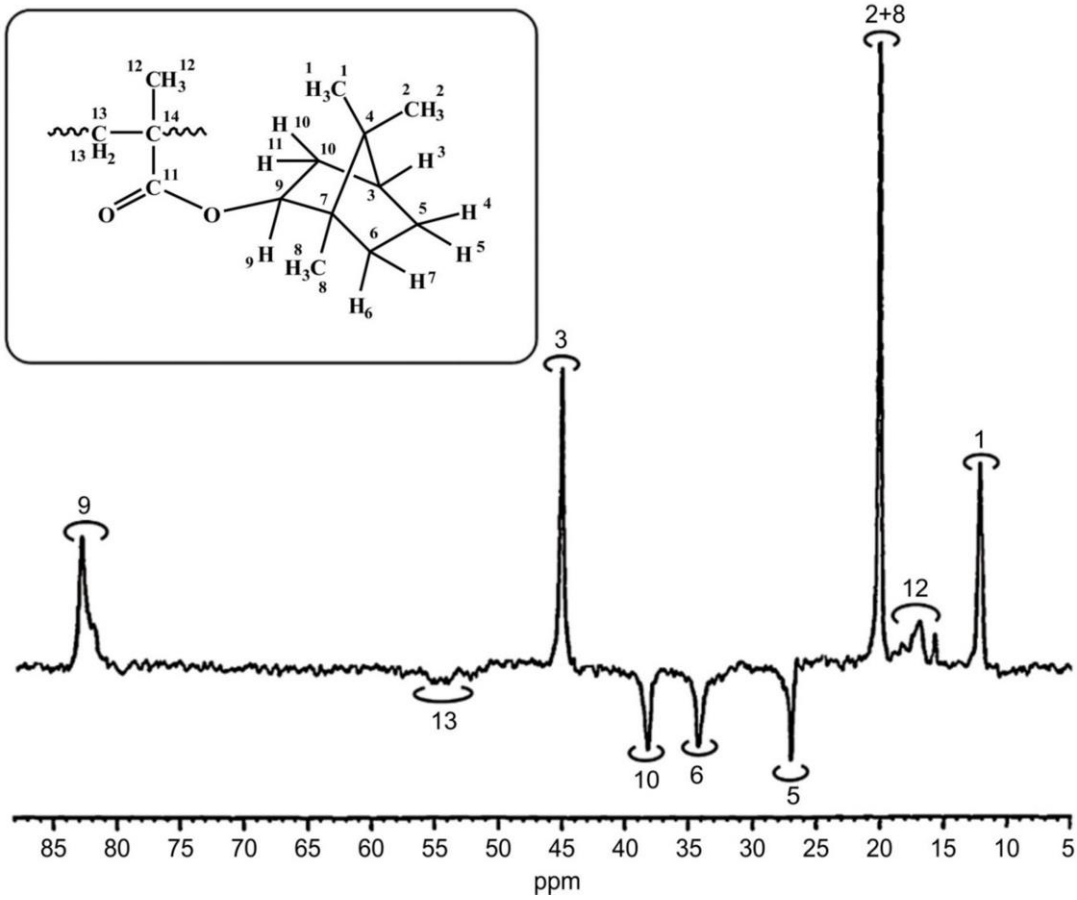


Fig. 2. DEPT-135 NMR spectrum of PiBMA in $CDCl_3$ at 25 °C

Carbonyl carbon (C_{11}) is responsible for the multiplet between δ 173.8 and 178.2. Fig. 1b depicts the extended carbonyl carbon area wherein three resonance envelopes at δ 177.3, 176.2, and 174.4 attributed to the rr, rm/mr, and mm triads, can be clearly seen. The stereoregularity and polydispersity index (Mw/Mn) (PDI) using the two initiators in the synthesis process was also calculated. It was discovered that PiBMA produced using ATRP had a random structure, with mm = 4%, mr = 42%, and rr = 53% and PiBMA synthesized with AIBN showed similar values rr = 52%, mr = 43%, and mm = 4%. PiBMA synthesized by ATRP had a polydispersity index (Mw/Mn) (PDI) of 1.19, whereas PiBMA synthesized by AIBN had a PDI of 1.84 as measured by Gel Permeable Chromatography.

3.2. HSQC (2D) and TOCSY (2D) NMR analysis:

In spectra where overlapped proton signals could not be allocated by ^{1}H NMR analysis, 2D HSQC spectrum is particularly useful to assign the proton signals and can be additionally confirmed by 2D TOCSY results.

Fig. 3a shows three cross peaks, designated as 1, 2, and 3, which have been respectively attributed to CH_3 carbons namely C_1, C_2, and C_8. The downfield position of the peak due to carbon C_2 compared to that of carbon C_1 is attributed to its equatorial position. Although carbon C_2 and C_8 have similar environments, the proton attached to C_8 appears more downfield due to the presence of an adjacent oxygen atom, leading to distinctive cross peaks. The α-CH_3 carbon (C_{12}) backbone was designated to the triad level of stereochemical arrangements in PiBMA using HSQC assignments. Cross peaks 4, 5, and 6 were designated to rr, mr/rm, and mm triads of α-CH_3 carbon (C_{12}), respectively. In Fig. 3b, a solitary cross peak 18 is generated by the two backbone methylene (CH_2) protons (H_{13}) of the racemic diad (r), whereas the meso diad (m) produces cross peaks 17 and 19 due to the non-equivalence of Ha and Hb protons. The presence of cross peaks 7 and 8 due to the H_4 axial proton and cross peaks 9 and 10 due to the H_5 equatorial proton of methylene (CH_2) carbon (C_5) confirms the geminal coupling. The presence of cross peaks 11 and 12 due to the H_6 axial proton and cross peaks 13 and 14 due to the H_7 equatorial proton of carbon atom C_6 confirms the different peaks for these protons (Table-1) [20]. Table-2 shows heteronuclear coupling amidst nonequivalent hydrogen nuclei of PiBMA obtained through a two dimensional total correlation spectroscopic analysis *viz*.- TOCSY (Fig. 4), wherein it can be seen that that correlation peaks 26, 27, and 28 are due to the coupling of CH_3 protons (H_1+H_2) with CH_2 protons (H_5)e, (H_6)a, and (H_4)a, respectively.

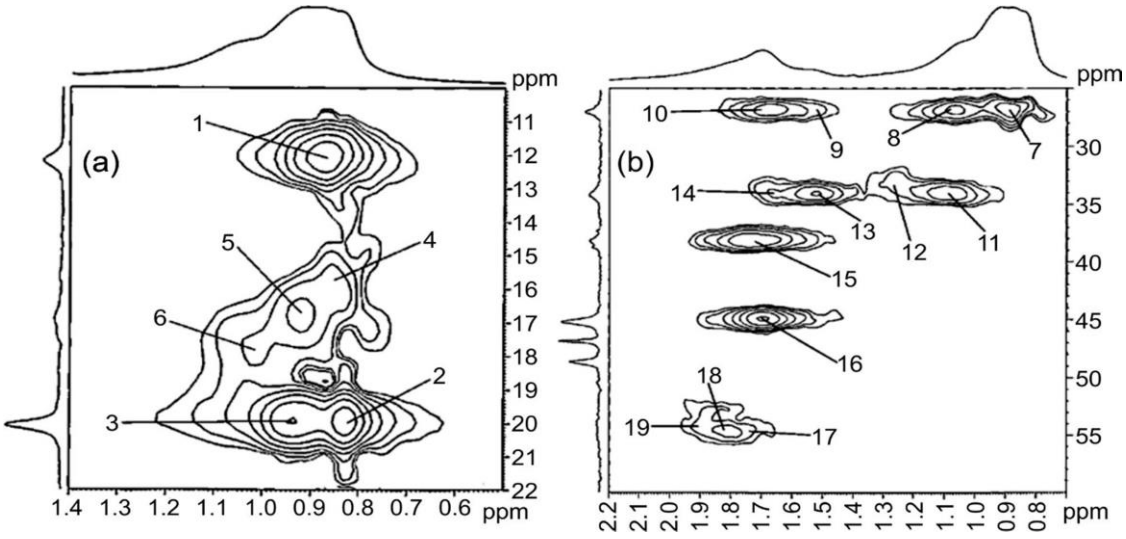


Fig. 3. (a) Expanded 2D HSQC spectrum of methyl region and (b) expanded 2D HSQC spectrum of PiBMA in $CDCl_3$ at 25 °C

Table-1. Assignments of different carbon in 2D HSQC spectrum of PiBMA

Cross peak no.	Cross peak assignment	Peak position, 2D HSQC ($^{13}C/^{1}H$), δ;ppm
1.	CH_3 (C_1/H_1),a	12.08/0.87
2.	CH_3 (C_2/H_2),e	19.90/0.85
3.	CH_3(C_8/H_8)	19.90/0.95
4.	α- CH_3(C_{12})(rr)	15.82/0.84
5.	α- CH_3(C_{12})(mr/rm)	16.91/0.92
6.	α- CH_3(C_{12})(mm)	18.271.02
7.	CH_2(C_5/H_4),a	27.14/0.88
8.	CH_2(C_5/H_4),a	27.14/1.06
9.	CH_2(C_5/H_5),e	27.14/1.51
10.	CH_2(C_5/H_5),e	27.16/1.68
11.	CH_2(C_6/H_6),a	34.24/1.08
12.	CH_2(C_6/H_6),a	33.96/1.26
13.	CH_2(C_6/H_7),e	34.24/1.52
14.	CH_2(C_6/H_7),e	34.18/1.68
15.	CH_2 (C_{10}/H_{10}+H_{11})	38.30/1.72
16.	CH (C_3)	45.02/1.69
17.	CH_2(C_{13}), m(H_a)	54.81/1.74
18.	CH_2(C_{13}), r	54.82/1.82
19.	CH_2(C_{13}), m (H_b)	54.82/1.91

Table-2. ^{1}H-^{1}H cross correlation between nonequivalent protons of PiBMA in 2D TOCSY spectrum

Correlation peak no.	Coupled proton I	Coupled proton II	Peak position, δ (2D TOCSY $^{1}H/^{1}H$); ppm
20.	CH_2(H_{13}),m(H_a)	CH_2(H_{13}),m(H_b)	1.71/1.92
21.	CH_2(H_5)a CH_2(H_{13}),r	CH(H_3)	1.50/1.69
22.	CH_2(H_6)a	CH_2(H_5)e	1.29/1.50
23.	CH_2(H_6)a	CH(H_3)	1.24/1.69
24.	CH_2(H_4 + H_6)a	CH_2(H_5)e	1.05/1.70
25.	CH_2(H_4 + H_6)a CH_2(H_4)a	CH_2(H_7)e	1.05/1.53
26.	CH_3(H_1 + H_2)	CH_2(H_5)e	0.88/1.48
27.	CH_3(H_1 + H_2)	CH_2(H_6)a	0.85/1.26
28.	CH_3(H_1 + H_2)	CH_2(H_4)a	0.85/1.04
29.	OCH(H_9)	CH_2(H_{10} + H_{11})	4. 34/1.72
30.	OCH(H_9)	CH_2(H_6)a	4.48/1.28

Fig. 3b shows the cross peak 15, designated to the CH_2 carbon C_{10}, and the peak 16, which was attributed to carbon C_3. The peaks 21 and 23 corresponded to the interaction respectively between CH_2 protons H_5 and H_6 and CH proton H_3 while peak 22 corresponded to the interaction between CH_2 protons H_5 and H_6. These assignments are listed in Table-2. In addition, the couplings between the OCH proton H_9 with CH_2 protons (H_{10}+H_{11}) and with CH_2 proton H_6 were responsible for coupling peaks 29 and 30, respectively. Therefore, the results obtained from the HSQC spectrum were subsequently validated through the TOCSY experiment.

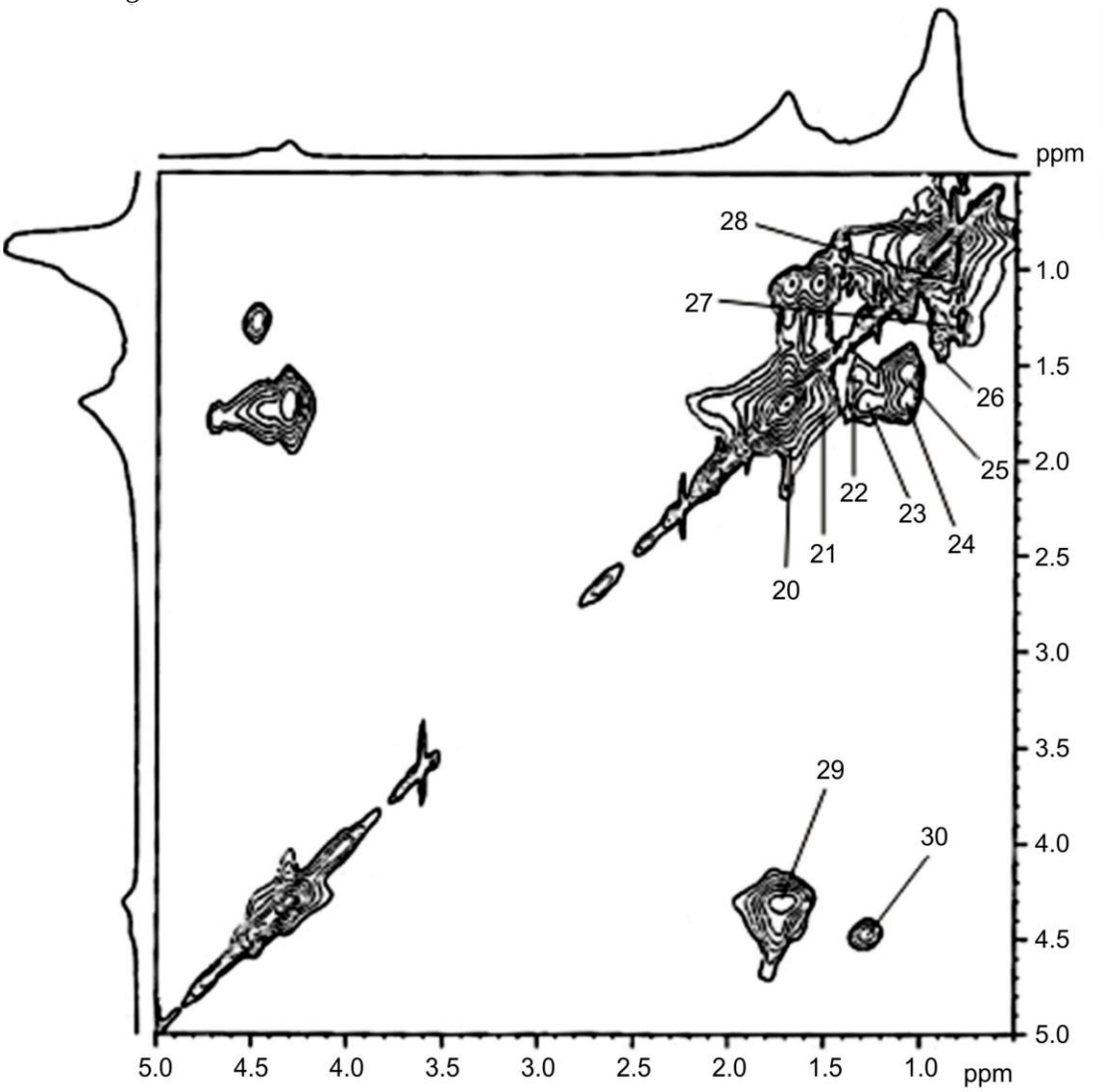


Fig. 4. 2D TOCSY spectrum of PiBMA in $CDCl_3$ at 25 °C

3.3. 2D HMBC Studies

Distant interaction between quaternary carbon and CH_2 carbons with CH_3 protons is visible in the 2D HMBC spectrum (Fig. 5). The assigned Cross peaks are listed in Table-3 where the various interactions between protons and carbon atoms and the resulting peaks positions are tabulated.

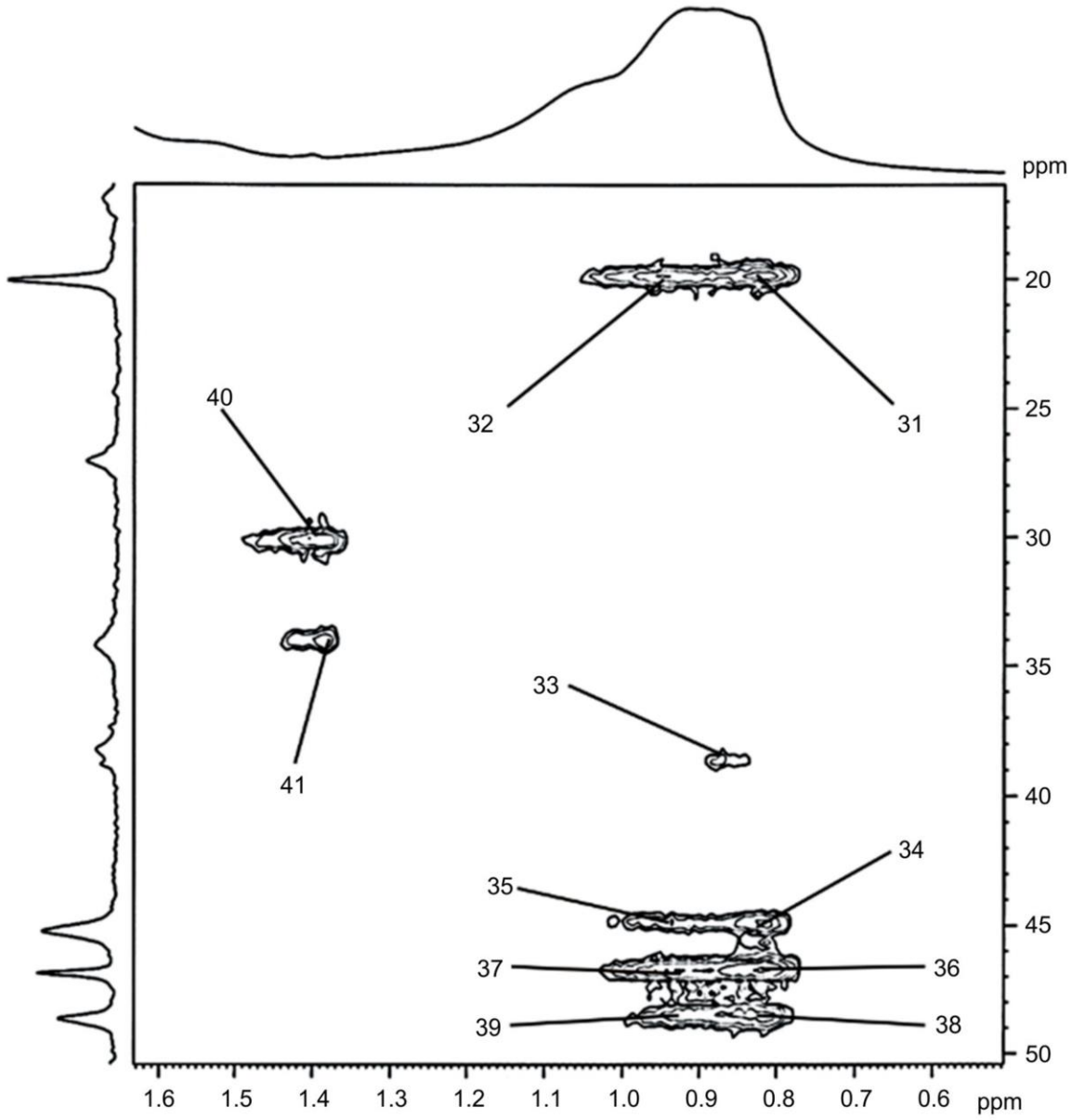


Fig. 5. 2D HMBC spectrum of PiBMA in $CDCl_3$ at 25 °C

Table-3. Assignments of different carbon atoms in 2D HMBC spectrum of PiBMA

Cross peak no.	Type of Carbon	Coupled to proton of	Peak position, δ; ppm
31.	Methyl (C_2)	Methyl (H_1)	19.86/0.88
32.	Methyl (C_2)	Methyl (H_8)	19.86/0.95
33.	Quaternary carbon (C_{14})	α-Methyl (H_{12})	38.32/0.88
34.	Methine (C_3)	Methyl (H_1 + H_2)	45.05/0.88
35.	Methine (C_3)	Methyl (H_8)	45.05/0.95
36.	Quaternary carbon (C_4)	Methyl (H_1 + H_2)	47.05/0.88
37.	Quaternary carbon (C_4)	Methyl (H_8)	47.00/0.95
38.	Quaternary carbon (C_7)	Methyl (H_1 + H_2)	49.01/0.88
39.	Quaternary carbon (C_7)	Methyl (H_8)	49.03/0.95
40.	Methylene (C_5)	Methylene (H_6)a	27.19/1.22
41.	Methylene (C_6)	Methylene (H_5)e	34.30/1.45

3.4. ^{1}H NMR Studies

With the use of 2D HSQC and TOCSY spectra, the overlapping and intricate ^{1}H NMR spectrum as can be seen in Fig. 6 has been completely resolved. The peaks at δ 0.82 and 0.95 appear as a consequence of the CH_3 protons (H_1) and (H_2) and (H_8) respectively found on the isobornyl ring whereas the signal between δ 0.84 - 1.02 is identified as H_{12} α-CH_3 proton. The CH (H_9) proton on the isobornyl ring is evident at about δ 4.48. The backbone CH_2 protons (H_{13}) are responsible for the broad signal between δ 1.72 - 1.94. The equatorial CH_2 protons H_5 and H_7 resonate in a down field region between δ 1.51- 1.70 whereas the H_4 and H_6 axially oriented protons absorb in an up field region between δ 0.88-1.26. CH_2 protons (H_{10}), (H_{11}) and H_3 hydrogen (CH) attached to C_3 carbon are responsible for the overlapping signal between δ 1.65-1.75.

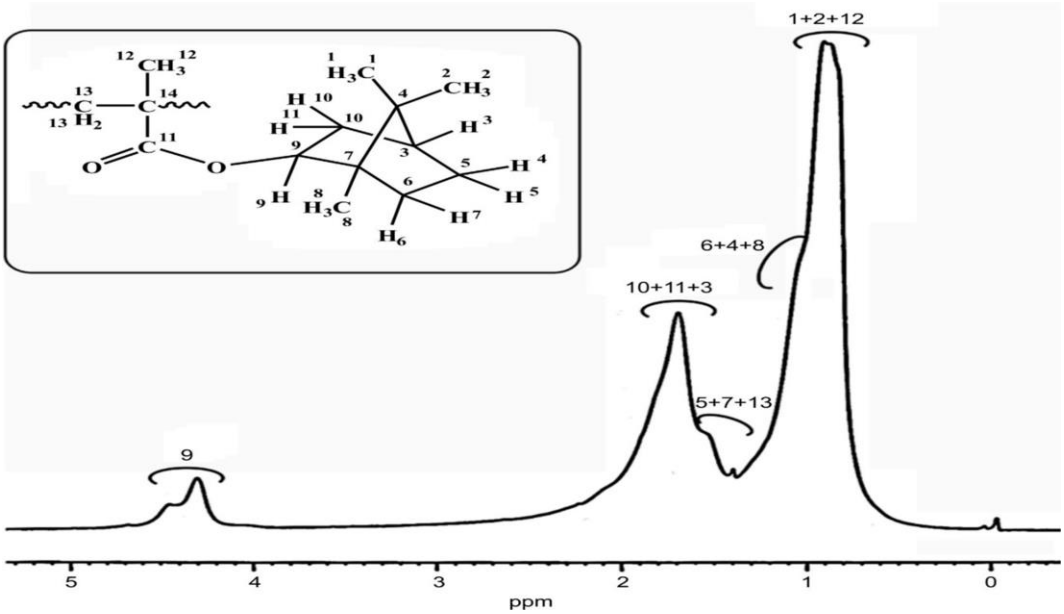


Fig. 6. ^{1}H NMR spectrum of PiBMA in $CDCl_3$ at 25 °C

4. CONCLUSIONS

We have successfully synthesized PIBMA by ATRP method as well as free radical polymerization method using AIBN as the initiator. The former method yielded a structure that was almost random, with mm = 4%, mr = 42%, and rr = 53%, whereas the latter also yielded similar values rr = 52%, mr = 43%, and mm = 4%. The use of 2D NMR spectroscopy enabled the determination of the sequence of PIBMA configurations. The assignment of both carbon and proton resonances was completed using HSQC and TOCSY spectra at different levels of configuration. The $^{13}C\{^{1}H\}$ spectrum revealed that both α-CH_3(C_{12}) and carbonyl (C_{11}) carbons were designated within triad while the CH_2 carbon adjacent to a carbonyl group could be designated within diad level of stereochemical arrangements. The quaternary carbon in the proton-decoupled carbon-13 NMR spectrum too was assigned using HMBC NMR spectrum.

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Statement of Conflict of Interest: The authors have no competing interests to declare that are relevant to the content of this paper.

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