

Stereochemical configuration of poly (2-hydroxy ethyl methacrylate) by NMR spectroscopy

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Poly (2-hydroxy ethyl methacrylate) has been prepared by free radical bulk polymerization at 80°C and characterization of its microstructure has been carried out using one-dimensional (¹H, ¹³C{¹H}) and two-dimensional (HSQC, TOCSY and HMBC) NMR spectra. The methyl, methylene and carbonyl carbon resonance signals have been found to be sensitive to various configurational sequences. 2D TOCSY spectrum has been used to examine the coupling between bonded protons. 2D HMBC spectrum shows long range coupling between quaternary, methylene and carbonyl carbon with methyl protons.

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Polymeric hydrogels such as poly (2-hydroxy ethyl methacrylate) (PHEMA) are of considerable importance as biomaterials and have been studied extensively¹⁻⁴. Two-dimensional NMR techniques along with one-dimensional NMR have more potential to investigate absolute configurational assignments^{5,6}. PHEMA has the potential to be an effective tool in imparting desired properties for soft contact lenses; it is a suitable biomaterial for implantation because of its lack of toxicity and high resistance to degradation⁷. Yoon *et al.*⁸ have investigated the conformational analysis of PHEMA. They have calculated the characteristic ratios of isotactic and syndiotactic PHEMA from conformational energy based on statistically averaged geometry and statistical weights. They reported that syndiotactic chain is more folded than isotactic chain. Brar *et al.*⁹⁻¹³ have reported the NMR studies of various homopolymers and copolymers of vinyl monomers. Various coworkers¹⁴⁻¹⁶ have reported the controlled polymerization of PHEMA by atom transfer radical polymerization. We report here the configurational assignments of PHEMA by one- and two-dimensional NMR spectroscopy. 2D HSQC, TOCSY and HMBC spectra have been used to confirm the configurational assignments in one-dimensional ¹³C{¹H} NMR spectrum.

Materials and Methods

2-Hydroxy ethyl methacrylate monomer was

distilled under reduced pressure and stored below 5°C. PHEMA was synthesized using AIBN as an initiator at 80°C under nitrogen atmosphere by precipitation in hexane. PHEMA was further purified using hexane/methanol system. The 1D and 2D NMR spectra were recorded on Bruker DPX-300 spectrometer in CD₃OD. ¹H and ¹³C measurements made at the frequencies 300.13 and 75.5 MHz, respectively and calibrated with respect to the solvent signal. Gradient HSQC and HMBC experiments were recorded using the pulse sequence invigtpt and inv4gplplrnd of the Bruker software, respectively. The spectra were acquired with 512 increments in F₁ dimension and 2048 data points in F₂ dimension. TOCSY experiments were performed using standard pulse sequence. 32 Scans were accumulated for 512 experiments with 2 s delay time¹⁷.

Results and Discussion

¹³C{¹H} NMR studies

The ¹³C{¹H} NMR spectrum of PHEMA is divided into four resonance envelopes. The resonance signal around δ 20.0 ppm is assigned to α-CH₃ carbon. The splitting within this resonance signal indicates its sensitivity towards configurational sequences. The resonance signals around δ 22.3, δ 20.0 and δ 17.8 ppm are assigned to mm, mr and rr triads, respectively (Fig. 1a). These resonance signals are further confirmed by 2D HSQC spectrum as shown in

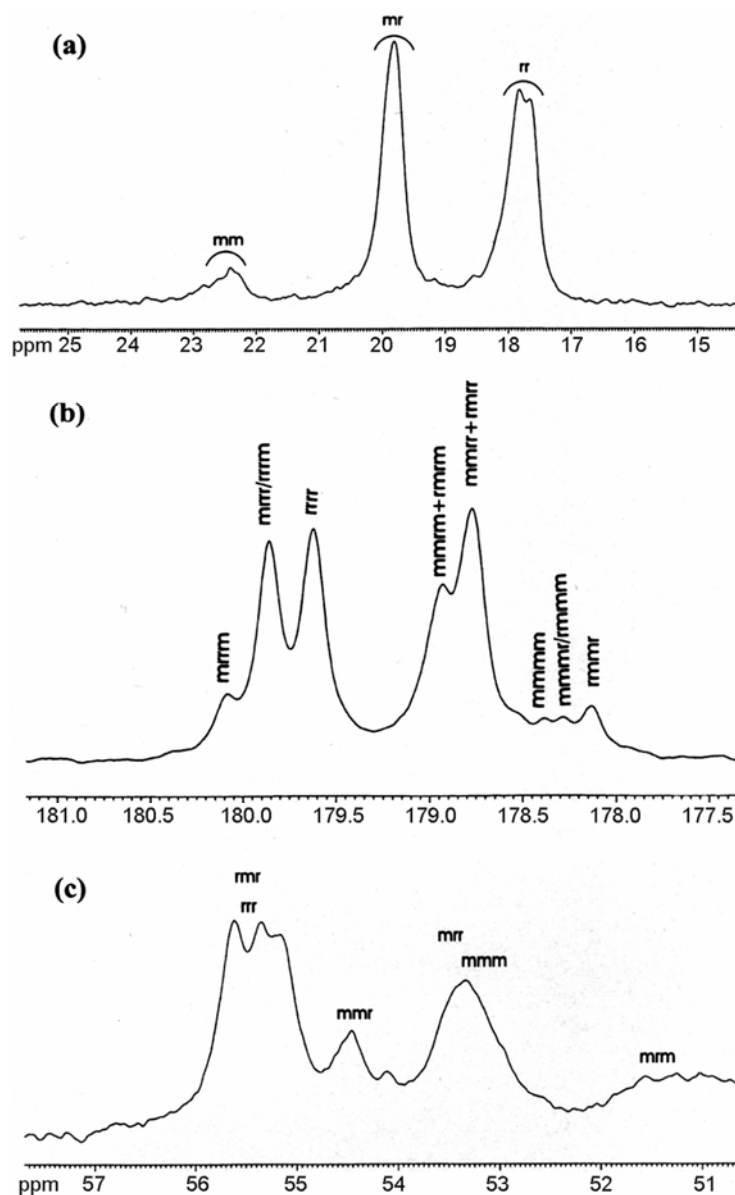


Fig. 1 — The expanded $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of: (a) α -methyl region, (b) carbonyl carbon region, and (c) β -methylene region of PHEMA.

Fig. 2a. The resonance signal around δ 46.5 ppm is assigned to quaternary carbon of PHEMA. The signals around δ 47.0, δ 46.5 and δ 46.1 ppm are assigned to mm, mr and rr triads, respectively.

The multiplet around δ 179.50 ppm is assigned to carbonyl carbon. The expanded carbonyl carbon is shown in Fig. 1b. The three envelopes of resonance around δ 178.00–178.45, δ 178.50–179.20 and δ 179.40–180.20 ppm are assigned to mm, mr/rm and rr triads, respectively. The central carbonyl carbon in rr triad is deshielded in comparison to mm triad because of the ring current created due to H-bonding.

In central methyl group, reverse trend is observed. Further splitting of mm triad is assigned up to pentad level of configurational sensitivity. In this way, the resonance signals at δ 178.10, δ 178.30 and δ 178.45 ppm are assigned to rmmr, mmmr/rmmm and mmmm, respectively according to their intensity variation. The mr centered triad is divided into two pentads, which are assigned as mmrr+rmrr and mmmr+mmrm pentads at δ 178.72 and δ 178.93 ppm, respectively. Similarly, rr centered triad is further divided into rrrr, mrrr/rmrr and mrrm pentads which are assigned to the signals at δ 179.60, δ 179.87 and

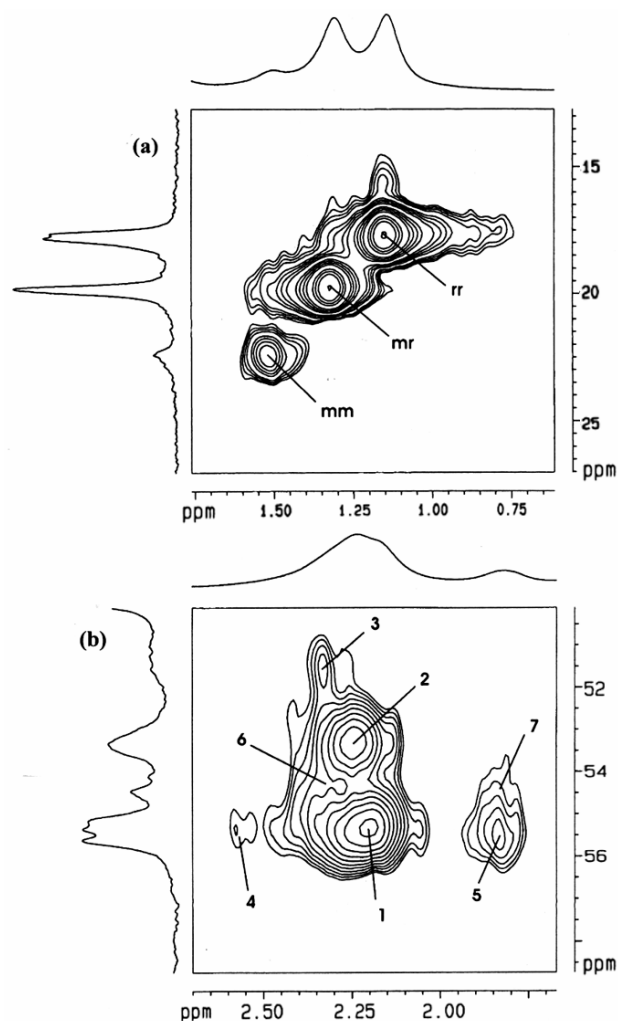


Fig. 2 — The expanded HSQC NMR spectra of: (a) α -methyl region, and (b) β -methylene region of PHEMA.

δ 180.10 ppm, respectively. In case of PHEMA, the percentage (relative abundance) of mr triad (48%) is more in methyl and carbonyl carbons than in rr triad (44%) because of H-bonding. This observation is different from PMMA where rr configuration is more predominant. In rr triad, two bulky methyl groups are placed opposite to each other. So, the steric hindrance is minimum and hence contribution of rr triad will be more than sterically unfavorable mm configuration. So, the resonance signal of low intensity is assigned to mm triad (8%), while the resonance signal of higher intensity is assigned to rr triad.

The broad multiplet around δ 53.0 ppm is assigned to β -methylene carbon. The β -methylene carbon resonances exhibit large chemical shift dispersion from δ 56.0 - 51.0 ppm as shown in Fig. 1c. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of PHEMA is almost

identical to PMMA except pendant group. Various coworkers¹⁷⁻¹⁹ have reported that tetrads will have the order rmr, rrr, mmm, mrr, mmm and mrm from high to low chemical shift in PMMA and similar trend is also observed during the present investigations. Assignments of these tetrads are confirmed by 2D HSQC and 2D TOCSY spectra.

2D HSQC and TOCSY studies

The two methylene protons of r diad having similar environment give a single cross-peak in 2D HSQC spectrum, while the two methylene protons of m diad (Ha and Hb) will be in different environments. Thus Ha and Hb protons of m diad will give two cross-peaks in 2D HSQC spectrum and these protons in m diad will give a cross correlation peak in 2D TOCSY spectrum. The one bond coupling between methylene carbon and proton is shown in 2D HSQC spectrum (Fig. 2b). The cross-peaks 1, 2 and 3 are assigned to rrr, mrr+mmm and mrm tetrads, respectively. The cross-peaks 4 and 5 are assigned to Ha and Hb protons of rmr tetrad, respectively, while the cross-peaks 6 and 7 are assigned to Ha and Hb protons of mmm tetrad, respectively.

2D TOCSY NMR spectra of PHEMA recorded at 4 ms and 80 ms are shown in Fig. 3. At low mixing time (Figs 3a, 3c), one can see the direct coupling (AM spin type) between the bonded protons, whereas at higher mixing time (Fig. 3b, 3d), one can see the relay coupling (AMX spin type) through magnetization transfer. The Ha and Hb protons of rmr tetrad give the cross correlation peak 1, while the cross correlation peak 2 is assigned to coupling of non-equivalent protons (Ha and Hb) of mmm tetrad. The cross-peaks 3 and 4 are assigned to the interaction of $-\text{CH}_2\text{O}$ protons with $-\text{OCH}_2$ protons and with $-\text{OH}$ protons, respectively. The additional cross-peak 5, which appears in TOCSY spectrum recorded at 80 ms only (Fig. 3d), is assigned to the coupling of $-\text{OCH}_2$ protons with $-\text{OH}$ proton.

The ^1H NMR spectrum is assigned completely using 2D HSQC and TOCSY spectra. The resonance signal around δ 1.31 ppm is assigned to α - CH_3 hydrogen of PHEMA. The multiplicity in this signal indicates its sensitivity to configurational sequence. The resonance signals at δ 1.50, δ 1.31 and δ 1.15 ppm are assigned to mm, mr and rr triad sequences. The resonance signal around δ 2.24 ppm is assigned to β -methylene protons. The resonance signals around δ 3.99, δ 4.27 and δ 5.50 ppm are assigned to $-\text{CH}_2\text{O}$, $-\text{OCH}_2$ and $-\text{OH}$ protons, respectively.

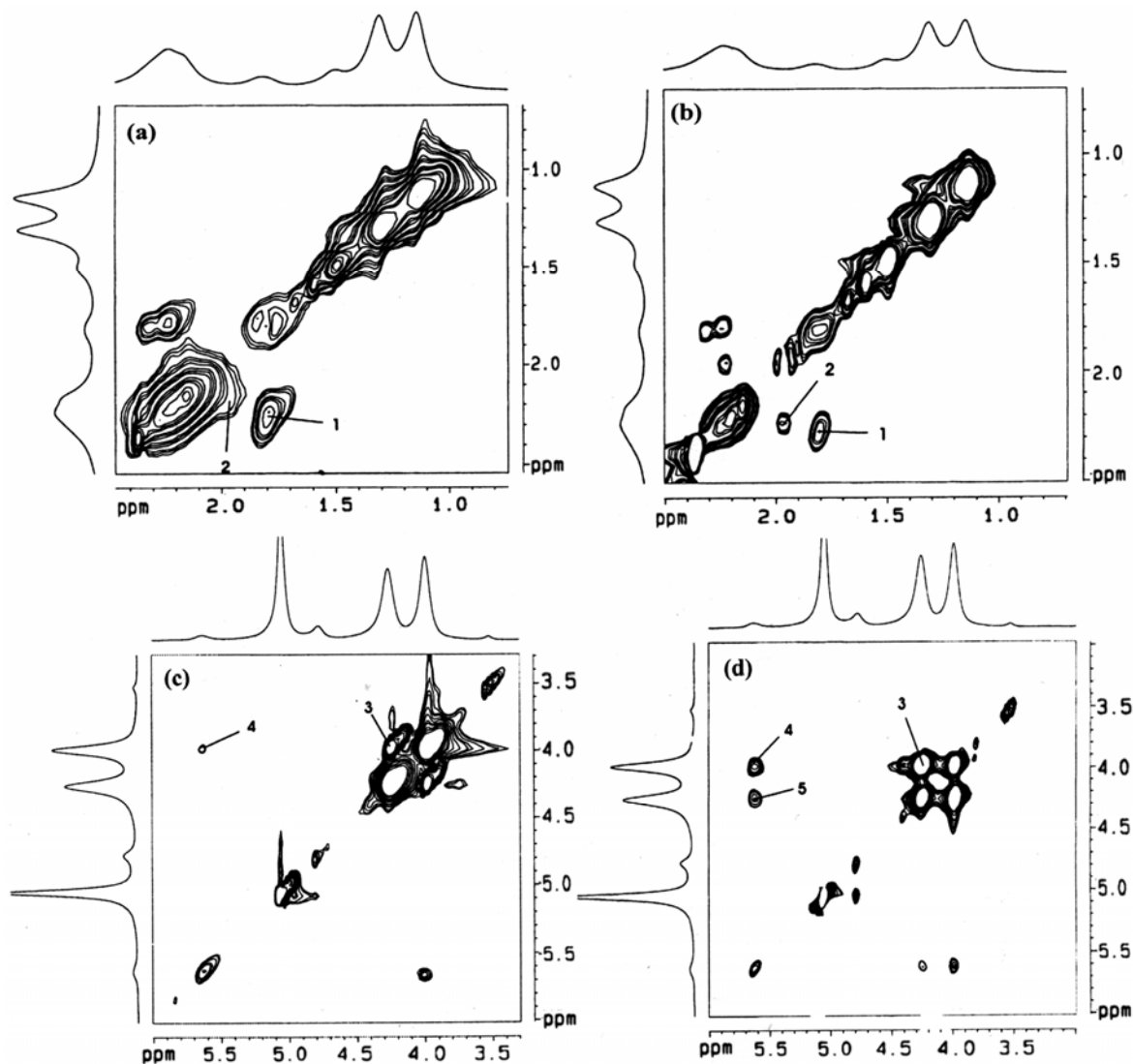


Fig. 3 — 2D TOCSY spectra of PHEMA showing various couplings in: (a) α -methyl and methylene region at 4 ms, (b) α -methyl and methylene region at 80 ms, (c) $-\text{OCH}_2$ and $-\text{CH}_2\text{O}$ region at 4 ms, and (d) $-\text{OCH}_2$ and $-\text{CH}_2\text{O}$ region at 80 ms.

2D HMBC studies

The 2D heteronuclear multiple bond correlation (HMBC) has become a powerful technique for the detection of heteronuclear long range couplings. 2D HMBC spectrum showing long range coupling between quaternary and methylene carbons and α -methyl protons is shown in Fig. 4a. The interaction of quaternary carbon of PHEMA with methyl hydrogen appears around δ 46.85/1.31 ppm. The cross-peaks 1, 2 and 3 are assigned to the interaction of quaternary carbon with methyl hydrogen in rr, mr and mm configuration, respectively, while the cross-peaks 4, 5 and 6 are assigned to the interaction of β -methylene carbon with methyl hydrogen in rr, rm and mm configuration, respectively. The cross-peaks 7, 8

and 9 are assigned to the coupling of carbonyl carbon with α - CH_3 protons in mm, mr and rr configuration (Fig. 4b), respectively.

Conclusions

The characterization of microstructure of PHEMA has been done with the help of 2D NMR spectroscopy. Methyl and methylene carbon region and proton resonances were assigned completely by HSQC, TOCSY spectra up to different configurational levels. The relative abundance of mm, mr and rr diads in methyl and carbonyl carbons was found to be 8%, 48% and 44%, respectively. Proton-proton correlation in neighbouring group was assigned completely by low and high mixing time

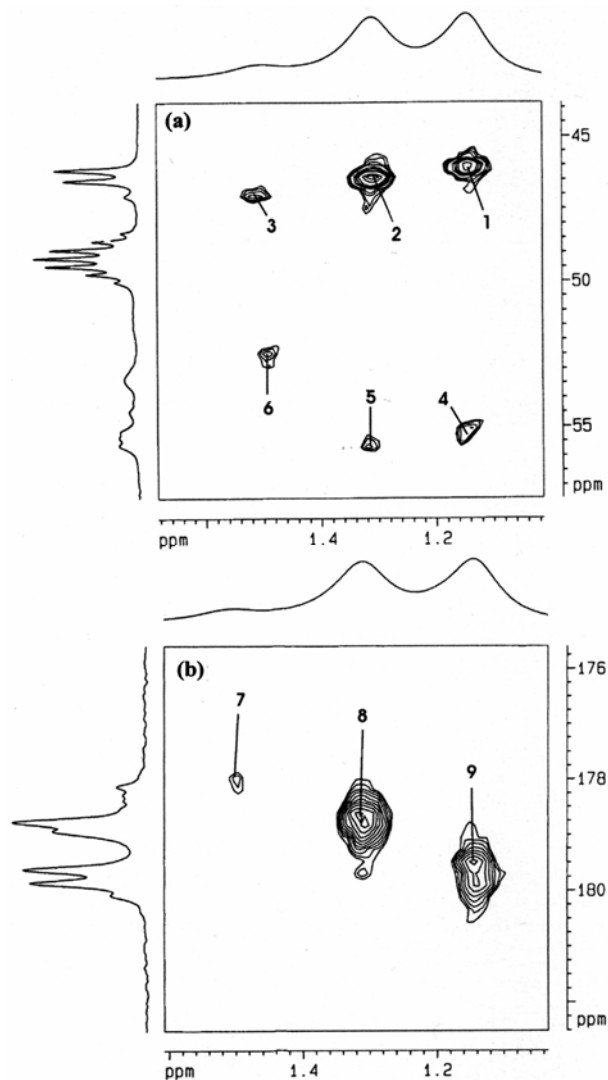


Fig. 4 — 2D HMBC spectra of PHEMA showing long range coupling of: (a) methylene and quaternary carbon with methyl protons, and (b) carbonyl carbon with methyl protons.

TOCSY spectra. The assignment of methylene carbon resonance signal up to tetrad level was confirmed by

2D HSQC and TOCSY spectra. Coupling of carbonyl carbon resonances with methyl protons has been assigned completely by HMBC spectrum.

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References

- 1 Mark H F, Bikalas N M, Overberger C G & Menges G, *Encyclopedia Polym Sci Eng*, 1 (1985) 234.
- 2 Jeyauthi R & Rao P K, *Biomaterials*, 11 (1990) 238.
- 3 Ratner B D, *J Biomed Mater Res*, 279 (1993) 283.
- 4 Fernandez – Garcia M, Torrado M F, Martinez G, Sanchez – Chaves M & Madruga E L, *Polymer*, 41 (2000) 8001.
- 5 Matsuzaki K, Uryu T & Asakura T, *NMR Spectroscopy and Stereoregularity of Polymers* (Japan Scientific Societies Press, Tokyo) (1996).
- 6 Bovey F A & Mirau P A, *NMR of Polymers* (Academic Press, New York) 1996.
- 7 Montheard J P, Chatzopoulos P M & Chappard D, *J M S Rev Macromol Chem Phys*, C 32 (1992) 1.
- 8 Yoon J H, Shin J M, Kang Y K & Jhon M S, *J Poly Sci Part A: Poly Chem*, 29 (1991) 393.
- 9 Brar A S & Singh P K, *Indian J Chem*, 45 A (2006) 581.
- 10 Puneeta & Brar A S, *Int J Plastic Tech*, 8 (2004) 371.
- 11 Brar A S, Markanday M & Gandhi S, *Indian J Chem*, 44 A (2005) 58.
- 12 Brar A S & Singh P K, *Indian J Chem*, 45 A (2006) 1605.
- 13 Brar A S, Hooda S & Goyal A K, *Indian J Chem*, 45 A (2006) 1981.
- 14 Beers K L, Boo S, Gaynor S G & Matyjaszewski K, *Macromolecules*, 32 (1999) 5772.
- 15 Coca C B, Jasieczek K L, Beers & Matyjaszewski K, *J Poly Sci Part A: Poly Chem*, 36 (1998) 1417.
- 16 Robinson L, Khan M A, Paz Benez M V, Wang X S & Armes S P, *Macromolecules*, 34 (2002) 3155.
- 17 Brar A S, Singh G & Shanker R, *J Mol Str*, 703 (2004) 69.
- 18 Kawamura M, Toshima N & Matsuzaki K, *Macromol Chem Rapid Commun*, 14 (1993) 719.
- 19 Kawamura M, Toshima N & Matsuzaki K, *Macromol Chem Phys*, 194 (1994) 2677.