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Two-dimensional NMR studies of acrylate copolymers*

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Abstract: High-resolution NMR spectroscopy is the most versatile, reliable, and generally acceptable technique for the determination of the microstructure of polymers. 2D NMR techniques, along with 1D NMR, have more potential to study absolute configurational assignments and sequence distribution of copolymers. Physical and chemical properties of polymers are influenced fundamentally by their microstructure. We discuss the detailed microstructure analysis of a large number of homopolymers, copolymers, and terpolymers. 2D NMR study of poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), and poly(methacrylonitrile) (PMAN) is discussed in this article. In addition to homopolymers, 2D heteronuclear single-quantum coherence (HSQC), total correlation spectroscopy (TOCSY), and heteronuclear multiple-bond correlation (HMBC) study of different copolymers such as poly(methyl methacrylate-*co*-methyl acrylate), poly(styrene-*co*-methyl methacrylate), and poly(methyl methacrylate-*co*-methacrylonitrile) have also been reported here. This in turn helps in microstructural analysis of terpolymers such as poly(methacrylonitrile-*co*-styrene-*co*-methyl methacrylate), poly(acrylonitrile-*co*-methyl methacrylate-*co*-methyl acrylate), and poly(ethylene-*co*-vinyl acetate-*co*-carbon monoxide).

Keywords: NMR; homopolymers; copolymers; terpolymers; HSQC; TOCSY; HMBC.

INTRODUCTION

NMR spectroscopy has been an indispensable tool for structural investigation in the polymers field. NMR is being used for checking the purity of polymers, elucidation of polymerization mechanism, tacticity determination, analysis of monomer sequence in copolymers, and polymer dynamics [1–6]. NMR also plays an important part in determination of end-group functionality as well as copolymer compositions. NMR parameters such as chemical shifts, relaxation rates, etc. depend on the local environment and dynamics of the nuclei. The study of these NMR parameters thus acts as a powerful tool for characterization and structural studies of polymers, as evident by a large amount of work carried out in this field [7–9]. The stereochemical studies using isotactic parameters obtained from NMR data are also very useful in the determination of polymerization mechanisms. Hence, NMR spectroscopy is invaluable in the current research and development in polymer science for providing new polymers with unique advantages [10–13]. Multidimensional high-resolution NMR has made a more detailed understanding of polymer microstructure possible.

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POLYMER MICROSTRUCTURE

Microstructure is used to describe the specific repeat unit structures, sequencing of repeat units, average composition, compositional distribution, and number-average sequence lengths of monomer addition [14,15]. The determination of intramolecular (triad distribution, tacticity) and intermolecular (chemical composition and molar mass distribution) copolymer microstructure is generally recognized as a prerequisite, since revealing the molecular microstructure may supply information about monomer addition, e.g., about the preference of monomer to add in a co-iso or co-syndiotactic configuration. Moreover, knowledge about inter- and intramolecular structures is of paramount importance for understanding relations between structure and polymer properties. The development of new polymers and investigation of new uses for existing polymers constantly generate a need for techniques that can give both qualitative and quantitative information about polymer microstructure. This information obtained from microstructure can further be used to synthesize the copolymers with desired physicochemical properties and to give information about the mechanism of copolymerization [16,17]. This information in turn can be used for quality control purposes during the synthesis of polymers, for establishing structure–property relationship [18,19]. Physical properties (i.e., crystallinity, glass transition temperature (T_g), tensile strength, etc.) and chemical properties (i.e., reactivity, type of interactions, degradation mechanism, etc.) of polymers are influenced fundamentally by the microstructure, which involves sequence distribution (compositional) and stereochemical (configurational) arrangements of various monomer units in polymer chain. Structurally monomer repeat units are called compositional sequences, i.e., we can have 3 diads, 6 triads, etc. In configurational arrangement, we have 6 diads and 20 triads [13]. NMR has been extensively used for the microstructure determination of polymers in solutions [20,21]. It is often observed that polymers with similar monomer compositions have different mechanical, thermal, optical, or electrical properties as a consequence of difference in microstructure. Various 1D and 2D NMR techniques have been widely used to understand the microstructure of various polymers.

1D NMR TECHNIQUES

^{1}H NMR spectroscopy was used for the determination of microstructure of polymers, as a result of its relatively high sensitivity [13]. Differences in chemical shifts of various ^{1}H nuclei, which are in different stereochemical and compositional environment, are usually small, causing the broad and overlapping signals. ^{1}H NMR spectra of vinyl polymers are usually overlapped and complex. ^{13}C{^{1}H} NMR has proved to be a more effective technique than ^{1}H NMR for characterizing the stereochemical structure of polymers. Quantitative gated decoupled ^{13}C{^{1}H} NMR technique contains information concerning the relative number and types of carbon nuclei in polymers. Copolymer composition can be calculated from ^{1}H and quantitative ^{13}C{^{1}H} NMR techniques. Composition data can be used to determine reactivity ratios of monomers in copolymers using the Kelen–Tudos (KT) method [22] and nonlinear error-in-variable method (EVM) [23]. Reactivity ratios along with copolymer compositions can be used to calculate diad, triad, tetrad, pentad, etc. sequences using various theoretical programs [24], which helps in studying the microstructure of copolymers. Propagation statistics of polymers can be explained by various statistical models. The most frequently used statistical models are Bernoullian [25] and first-order Markov [26,27]. The Bernoullian model describes a random distribution of monomer units where the probability of a monomer addition is independent of the outcome of any previous addition, while in first-order Markov sequence, the mode of addition of the approaching monomer is influenced by the stereochemistry of the chain end. Bernoullian and first-order Markov statistical models can be examined for the most practical aspects of polymer applications, that is, NMR chemical shift assignments, sequence distribution, and number-average sequence lengths. The effect of tacticity and comonomer sequence on chemical shift provides important structural information of the polymers [28,29]. However, along with natural line-broadening resulting from the rapid spin–spin relaxation, these factors can also

result in overlapped $^{13}C\{^1H\}$ NMR spectra as well. For polymers with broad and poorly resolved resonances, various modern 1D NMR techniques like spin-echo [30], insensitive nuclei-enhanced polarization transfer (INEPT) [31], and distortionless enhancement by polarization transfer (DEPT) can be used to simplify the spectrum [32]. DEPT is a spectral editing technique, which is typically based on the differences in polarization transfer due to the number of directly bonded protons [33]. It helps to distinguish between methine, methylene, methyl, and quaternary carbon signals, in the overlapped $^{13}C\{^1H\}$ NMR spectrum.

2D NMR TECHNIQUES

2D NMR has proved to be a most powerful and useful technique as increased resolution can be achieved by spreading the spectrum along a second dimension. It also provides additional microstructural information and confirms the assignments already done by 1D experiment. 2D NMR techniques, such as inverse heteronuclear correlation (HETCOR), heteronuclear single-quantum coherence (HSQC), gradient heteronuclear single-quantum coherence (gHSQC), heteronuclear multiple-quantum coherence (HMQC), ^1H-^1H correlation spectroscopy (COSY), total correlation spectroscopy (TOCSY), heteronuclear multiple-bond correlation (HMBC) and gradient heteronuclear multiple-bond correlation (gHMBC), etc. [34–38] have been used to assign the complex ^1H and $^{13}C\{^1H\}$ NMR spectra. A major benefit of 2D NMR is resurgence of interest in using ^1H NMR for polymer characterization. McCord et al. [39] have reported $^{13}C\{^1H\}$ and 2D NMR analysis of polypropylene. These polymers have unusually complex structure and can only be assigned with the help of 2D NMR experiments. Brar et al. have reported the configurational assignments of poly(vinyl acetate) [40], poly(vinyl alcohol) [41], and poly(*n*-butyl acrylate) [42] using 2D HSQC, TOCSY, and HMBC experiments. 2D NMR has emerged as the most effective technique to study the polymer structure. Useful results have been obtained for biological macromolecules, in which overlapping of resonances entirely precludes the analysis of certain spectral regions. A brief introduction of various 2D techniques that are used in microstructure determination of polymers is given below.

2D homonuclear correlation spectroscopy

2D homonuclear correlation techniques that are widely used for microstructure determination of polymers are COSY, TOCSY, and nuclear Overhauser enhancement spectroscopy (NOESY).

COSY

Correlation spectroscopy is a homonuclear 2D technique that is used to correlate the chemical shifts of proton nuclei that are J-coupled to one another. COSY relies on J-coupling to provide spin–spin correlation, and its cross-peaks indicate which protons are close to which other protons through the bonds of molecule. In COSY, cross-peaks have zero integrated intensity and coherence transfer is restricted to directly spin-coupled nuclei.

TOCSY

Total correlation spectroscopy provides a different mechanism of coherence transfer than COSY. In TOCSY, cross-peaks are generated between all members of a coupled spin network. An advantage is that net coherence transfer produced can be arranged to create pure absorption mode spectra with positive intensity peaks (rather than differential coherence transfer which causes spectra with equal positive and negative intensities). In TOCSY, oscillatory exchange is established which proceeds through the entire coupling network so that there can be net magnetization transfer from one spin to another even without direct coupling. TOCSY spectrum has superior signal-to-noise (S/N) ratio for molecules with short relaxation times like macromolecules.

NOESY

Nuclear overhauser effect spectroscopy is a 2D spectroscopy method that identifies the spins undergoing cross-relaxation and measures the cross-relaxation rates. Most commonly, NOESY is used as a homonuclear ^{1}H technique. In NOESY, direct dipolar coupling provides the primary means of cross-relaxation, so spins undergoing cross-relaxation are those that are close to one another in space. Thus, cross-peaks of a NOESY spectrum indicate which protons are close to which other protons in space.

2D heteronuclear correlation spectroscopy

2D heteronuclear correlation techniques that are widely used for microstructure determination of polymers are HETCOR, HMQC, HSQC, and HMBC.

HETCOR

Heteronuclear (X, H) shift correlation spectroscopy is a technique that can be used to determine which protons of a molecule are bonded to which ^{13}C nuclei (or other X nuclei). HETCOR makes use of large one-bond heteronuclear J-coupling (J_{XH}) for polarization transfer, so only ^{13}C's bonded directly to protons are detected. 2D HETCOR spectrum has a projection onto an F_2 axis that is a $^{13}C\{^{1}H\}$ spectrum with all quaternary carbons missing, and a projection onto an F_1 axis that is a proton spectrum.

HMQC

Heteronuclear multiple-quantum correlation experiment correlates the chemical shift of proton with chemical shift of directly bonded carbon (or nitrogen). This experiment utilizes one-bond couplings. HMQC spectroscopy is an inverse chemical shift correlation experiment in comparison to HETCOR and determines which proton of a molecule is bonded to which ^{13}C nuclei (or other X nuclei). The advantage of HMQC over HETCOR is that in HMQC, the nucleus with the highest $\gamma(^{1}H)$ is detected, so it is possible to obtain the highest sensitivity. HMQC uses a multiple-quantum filter to suppress the signals of those protons that are not attached to ^{13}C. HMQC is a poor choice for molecules having short T_2 values (e.g., macromolecules).

HSQC

Heteronuclear single-quantum correlation experiment correlates the chemical shift of proton with chemical shift of directly bonded carbon (or nitrogen). This experiment utilizes one-bond couplings. HSQC and HMQC both provide exactly the same information. Differences are technical and involve S/R ratio. HSQC will give sharper lines (with higher S/N ratio), especially for $-CH_2$ since ^{1}H-^{1}H homonuclear coupling in an F_1 axis is not suppressed in HMQC. HSQC is more sensitive to pulse width calibrations, but HMQC can suffer T_2 sensitivity losses in viscous and high molecular weight compounds.

HMBC

Heteronuclear multiple-bond correlation spectroscopy is a modified version of HMQC suitable for determining long-range ^{1}H-^{13}C connectivity. This is useful in determining the structure as well as proton and ^{13}C assignments of molecules. HMBC is an inverse experiment that has higher sensitivity. HMBC experiment differs from HMQC and HSQC in that multiple-bond couplings over two or three bonds (J = 2–15 Hz) are utilized. Cross-peaks are between protons and carbons that are two or three bonds away (and sometimes up to four or five bonds away). Direct one-bond cross-peaks are suppressed.

NMR OF HOMOPOLYMERS

It is well recognized that physical and mechanical properties of vinyl polymers are critically dependent upon their tacticity, i.e., stereochemical configuration. Tacticity measurements require a technique that allows a meso configuration to be distinguished from a racemic configuration. The power of NMR to determine the configuration of vinyl polymer chains arises from its sensitivity to equivalence and non-

equivalence of similarly bonded nuclei. Various stereochemical arrangements such as diads, triads, etc., in homopolymers can be distinguished by 1D techniques such as ^{1}H, $^{13}C\{^{1}H\}$, and DEPT NMR spectroscopy. Nakayama et al. [43] have used 2D incredible natural abundance double-quantum transfer experiment (INADEQUATE) spectrum to assign the resonance signals in PVC up to tetrad and pentad sequences on the basis of carbon–carbon connectivity and rectified the previous assignments. The tacticity of poly(methacrylonitrile) (PMAN) [33] has been analyzed up to hexad level for proton and up to tetrad level for carbon nuclei by applying double quantum filtered (DQF)-COSY and HETCOR experiments. Both 1D and 2D experiments such as DQF-COSY and ^{1}H detected $^{1}H/^{13}C$ shift correlated NMR spectroscopy have been used in combination to assign various stereochemical sequences in poly(pentyl acrylate), poly(*tert*-butyl acrylate) [44], poly(*trans*-4-acryloyloxyazobenzene), and poly(*n*-butyl methacrylate) [45]. Along with HMBC experiments, HSQC and TOCSY have been used to assign the complex and overlapped ^{1}H NMR spectrum of poly(*n*-butyl acrylate), poly(methyl acrylate) (PMA) [46], and poly(2-hydroxy ethyl methacrylate) [47]. Rinaldi et al. [48] have illustrated the combined use of isotopic labeling and modern NMR techniques like 2D INADEQUATE NMR experiments to provide direct evidence of head-to-head or tail-to-tail enchainment present in the backbone of poly(styrene), thus supporting the assumption that free-radical polymerization of polystyrene terminates primarily via combination. Detailed comprehensive microstructural analysis of poly(methyl methacrylate) (PMMA) was done by Brar et al. with the help of HSQC, TOCSY, and HMBC experiments [36]. Dais et al. [49] have reported the complete assignments of proton and carbon spectra of poly(*N*-vinylcarbazole) (PVK) by employing a number of modern gradient 2D NMR experiments like COSY, TOCSY, HMQC, and HMBC. Brar and Dutta [50] have assigned the stereochemical structure of poly(*N*-vinyl-2-pyrrolidone) using 1D and 2D NMR. Methine and methylene carbon resonances were assigned up to pentad and tetrad level configurational sequences by 2D HSQC/TOCSY experiments. Microstructure analysis of a large number of homopolymers has been discussed, and detailed microstructure analysis of PMMA, PMA, and PMAN is given in this article.

2D NMR study of poly(methyl acrylate)

2D HSQC and TOCSY NMR experiments were employed to resolve the highly overlapping and complex ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of polymers. Methylene proton resonance signals that were overlapped and could not be assigned by ^{1}H NMR spectra alone were assigned with the help of one–one correlation between carbon and proton signals in HSQC spectra. TOCSY spectra were used to confirm 1-, 2-bond geminal couplings between nonequivalent protons of β-methylene group. Protons in racemic configuration are in same environment, resulting in a single cross-peak in 2D HSQC spectrum. Two nonequivalent methylene protons in meso configuration result in two cross-peaks in HSQC spectrum and a cross-correlation peak in TOCSY spectrum (H_A proton was attributed to proton having high chemical shift and H_B having lower chemical shift). Thus, TOCSY spectra enable differentiation between meso and racemic protons and confirm the HSQC assignments. Complete spectral assignment of carbonyl carbons was done with the help of HMBC spectra. Carbonyl carbon was found to be sensitive up to pentad configurational sequences and shows 3- and 4-bond coupling with methine and methylene protons.

Detailed microstructural analysis of PMA [46] has been done by Brar et al. Completely assigned HSQC NMR spectrum of PMA is shown in Fig. 1. Meso configuration of methylene region gives two cross-peaks due to two methylene protons (H_A and H_B) having different environment, and racemic configuration gives one cross-peak in between these two cross-peaks as shown in Scheme 1. Relative intensity of these peaks in ^{1}H spectrum as well as in 2D HSQC spectrum is in the ratio of 1:2:1, which shows that 50 % of PMA is in isotactic and 50 % is in syndiotactic configuration. A cross-peak around δ 41.25/2.35 ppm is assigned to the methine region. These assignments were further confirmed by TOCSY NMR experiment, which shows coupling between methylene and methine protons in various configurations. In TOCSY spectrum (Fig. 2), cross-peaks centered at δ 1.92/2.32 (1) and δ 1.49/2.32

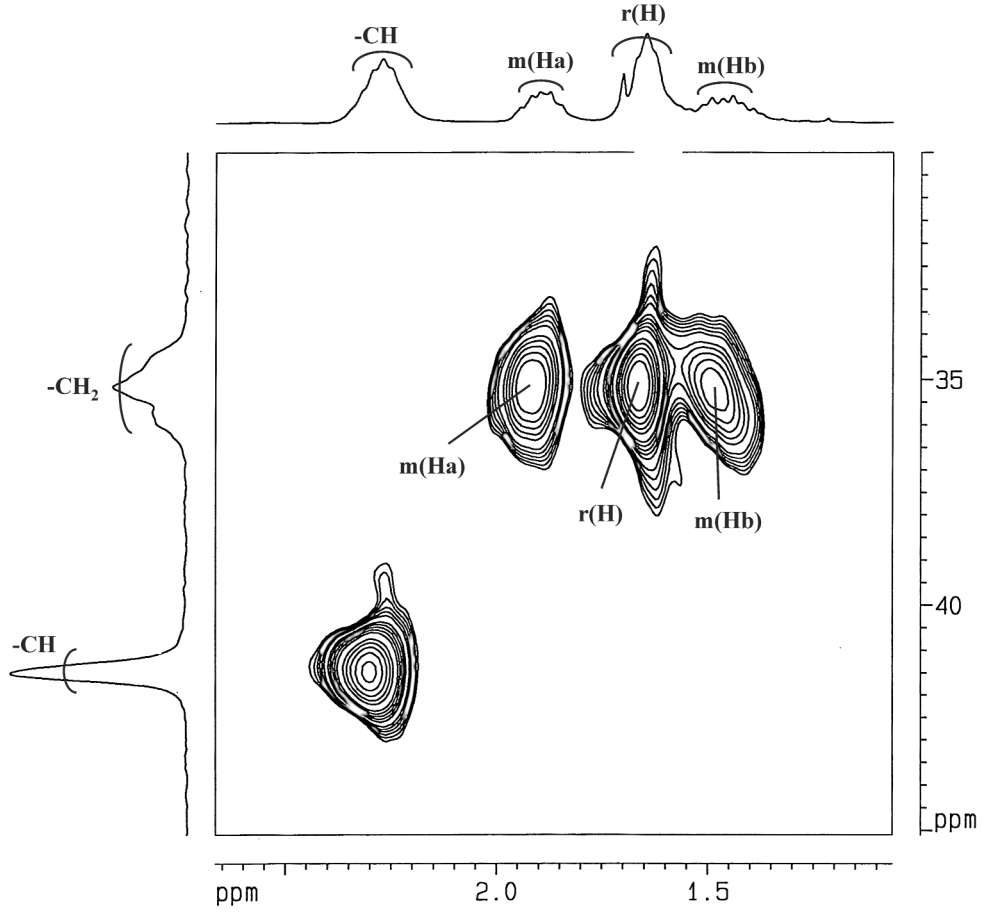
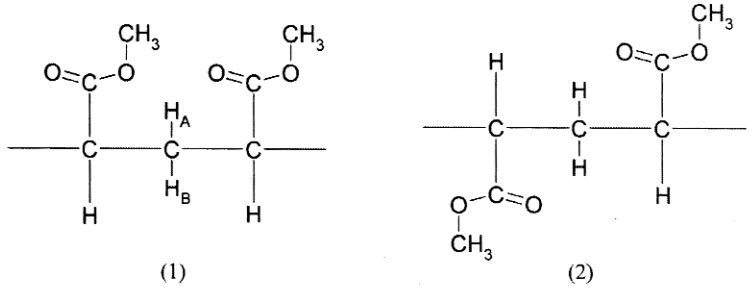


Fig. 1 2D NMR HSQC NMR spectrum of PMA in $CDCl_3$ at 45 °C.



(1) (2)

Scheme 1 Meso and racemic diads of PMA.

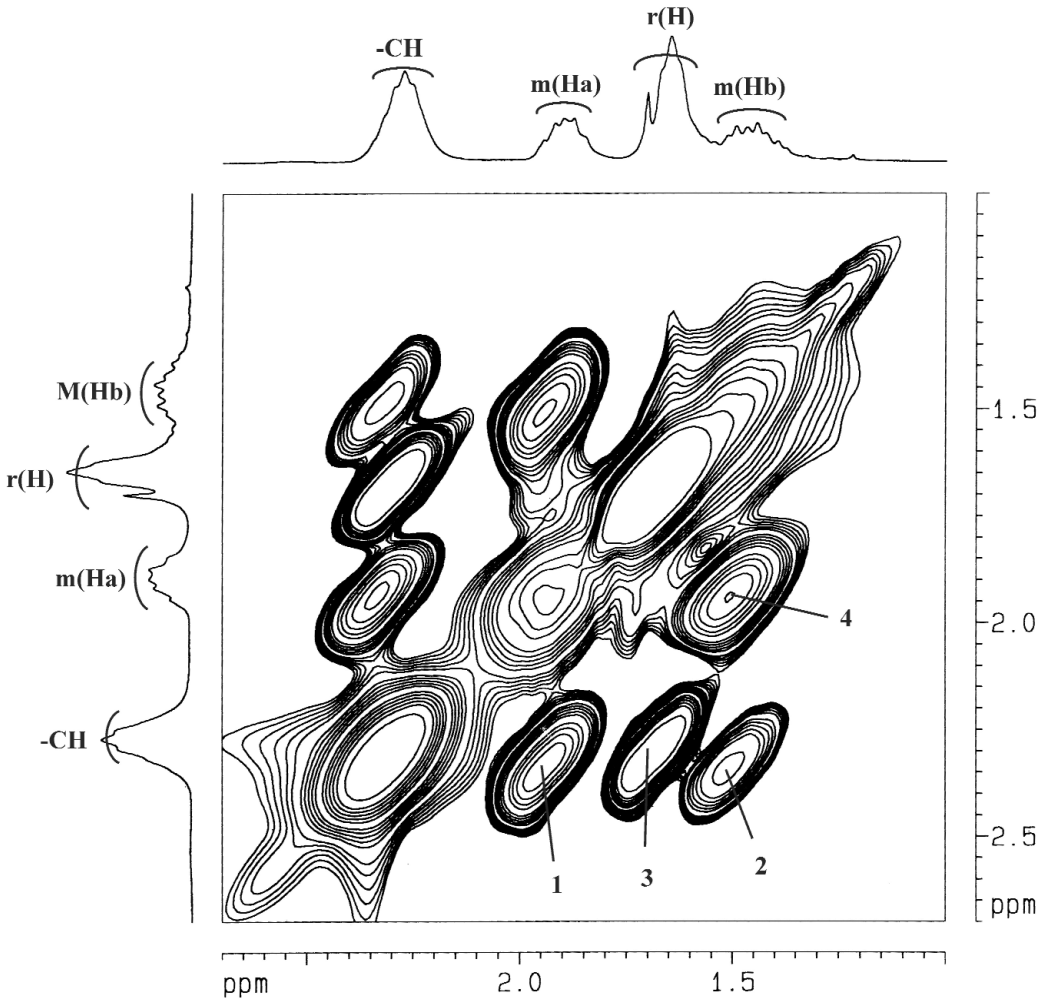


Fig. 2 2D TOCSY NMR spectrum of PMA in $CDCl_3$ at 45 °C.

(2) ppm were assigned to the coupling between methylene and methine protons in meso (*m*) configuration (a and b, respectively), and a cross-peak centered at δ 1.68/2.30 (3) ppm was assigned to the coupling between methylene and methine proton in racemic (*r*) configuration. A cross-peak centered at δ 1.49/1.92 (4) ppm was assigned to the geminal coupling between two methylene protons (a and b) in meso configuration. HMBC spectrum enabled us to study [46] 3-bond couplings between carbonyl carbon, and neighboring methylene and methine protons is shown in Fig. 3. In HMBC spectrum, four sets of cross-peaks appeared due to the interaction of methine and methylene protons in different configurations with carbonyl carbon (Scheme 2). Set A of cross-peaks was assigned to the interaction of carbonyl carbon with methine proton. Cross-peaks set B and D were assigned to the interaction of carbonyl carbon with methylene protons in meso configuration (i.e., Ha and Hb, respectively) while set C was due to the interaction with protons in racemic configuration. On the basis of the above assignments, a broad carbonyl carbon signal was assigned to the overlap of four *mr* centered pentad configurations. Signals at δ 175.00, δ 174.85, and δ 174.70 ppm were assigned to *rmrr*, *mrmr*+ *mmrr*, and *mmrm* pentad configurations, respectively. All of the assignments of 2D HMBC spectrum of PMA are given in Table 1.

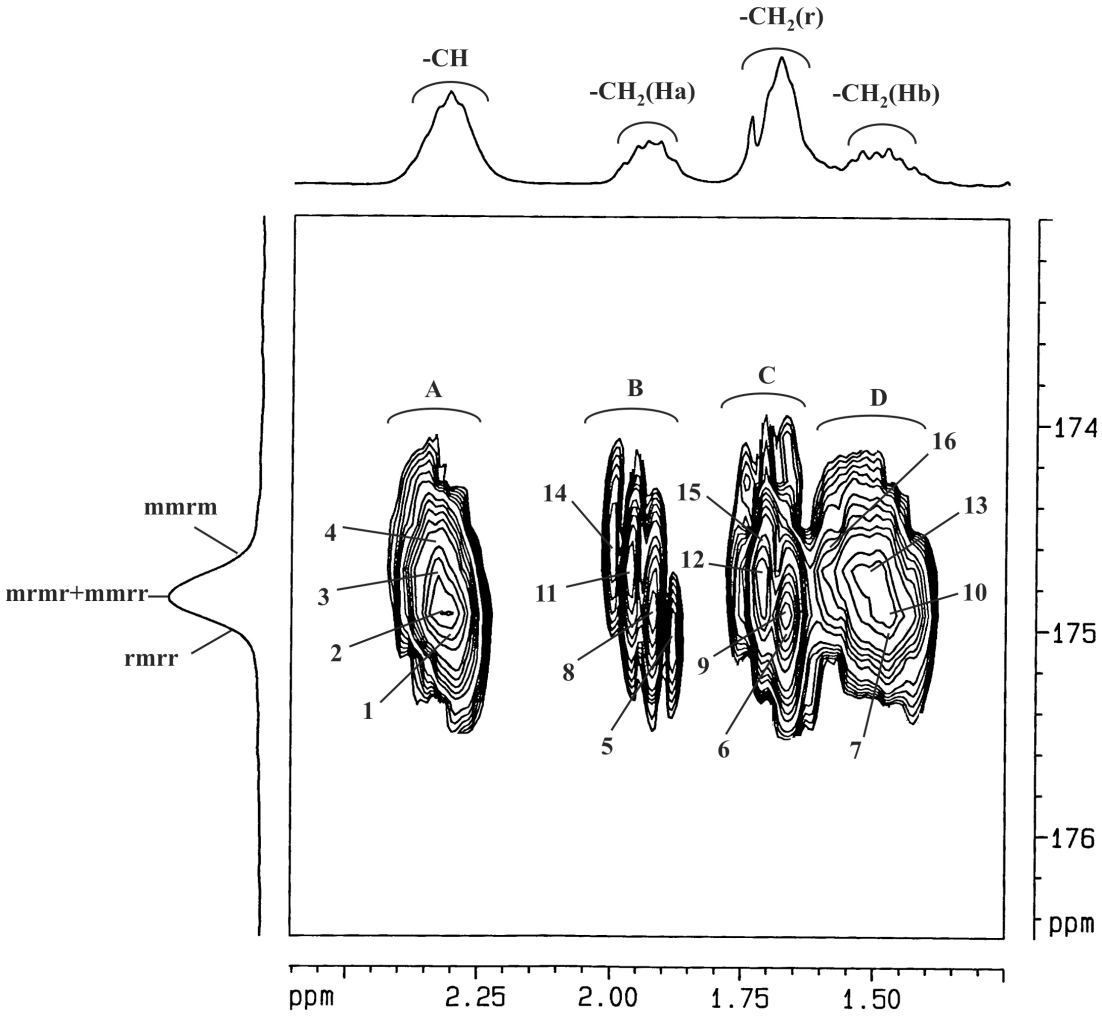
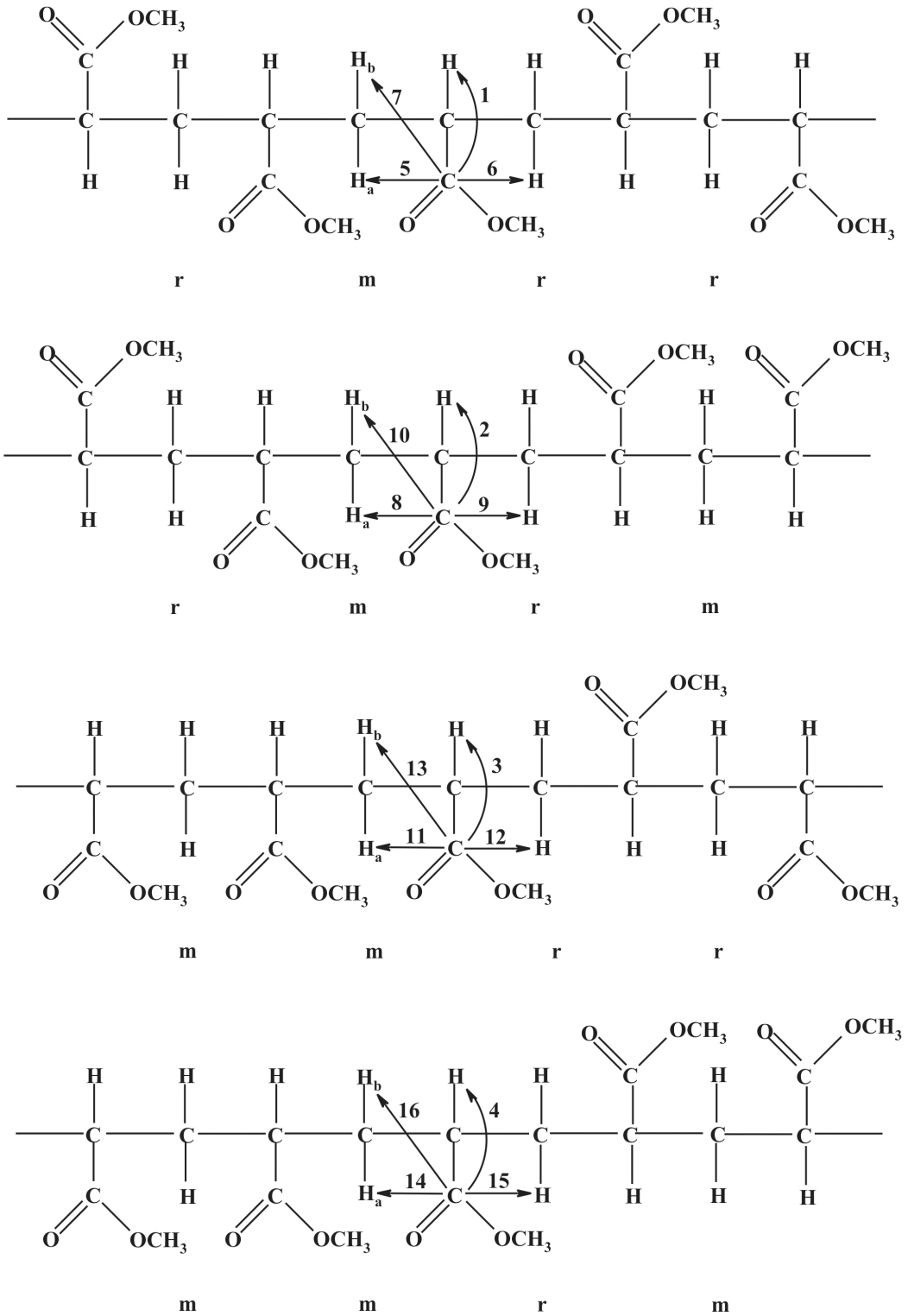


Fig. 3 2D HMBC NMR spectrum of PMA in $CDCl_3$ at 45 °C.



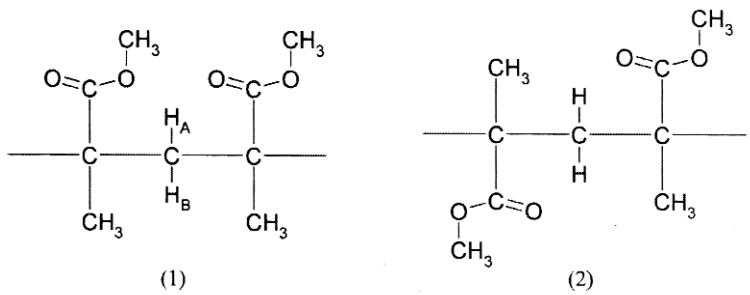
Scheme 2 Depiction of carbonyl carbon couplings with different protons in *mr*-centered pentads of PMA.

Table 1 Coupling of carbonyl carbon with methine and methylene protons of PMA based on the 2D HMBC spectrum.

Cross-peak no.	Type of carbon	Coupled to proton of	Cross-peak position $^{13}C/^{1}H$; ppm
1.	>CO of *rmrr*	–CH of *rmrr*	175.04/2.27
2.	>CO of *rmrm*	–CH of *rmrm*	174.85/2.30
3.	>CO of *mmrr*	–CH of *mmrr*	174.70/2.32
4.	>CO of *mmrm*	–CH of *mmrm*	174.60/2.34
5.	>CO of *rmrr*	$-CH_2$ of *mrr* (H_A)	175.04/1.88
6.	>CO of *rmrr*	$-CH_2$ of *mrr*	175.04/1.65
7.	>CO of *rmrr*	$-CH_2$ of *mrr* (H_B)	175.04/1.46
8.	>CO of *rmrm*	$-CH_2$ of *mrm* (H_A)	174.85/1.92
9.	>CO of *rmrm*	$-CH_2$ of *mrm*	174.85/1.67
10.	>CO of *rmrm*	$-CH_2$ of *mrm* (H_B)	174.85/1.48
11.	>CO of *mmrr*	$-CH_2$ of *mrr* (H_A)	174.70/1.95
12.	>CO of *mmrr*	$-CH_2$ of *mrr*	174.70/1.70
13.	>CO of *mmrr*	$-CH_2$ of *mrr* (H_B)	174.70/1.50
14.	>CO of *mmrm*	$-CH_2$ of *mmr* (H_A)	174.60/1.98
15.	>CO of *mmrm*	$-CH_2$ of *mrm*	174.60/1.72
16.	>CO of *mmrm*	$-CH_2$ of *mmr* (H_B)	174.60/1.52

2D NMR study of poly(methyl methacrylate)

Analysis of couplings by 2D HSQC, TOCSY, and HMBC spectroscopy enable the unambiguous and comprehensive assignments of carbon and proton resonances of vinyl polymers [39,51,52]. In PMMA, α-methyl, methylene, carbonyl, and quaternary carbon resonances are configurational-sensitive [36]. Unlike α-methyl, quaternary, and carbonyl carbon resonances, methylene carbon and proton resonances do not follow chemical shift order so are consequently difficult to assign. Assignments of methylene resonances thus provide a good base for 2D NMR analysis. The main structural difference between meso and racemic (Scheme 3) diad of PMMA is that, in the case of meso diad, methylene proton H_A is flanked by two carbonyl groups and H_B by two methyl groups, while in racemic configuration both of the protons have symmetrically placed substituents. Nonequivalent methylene protons (H_A and H_B) of meso diad show two different couplings with methylene carbon, giving rise to two cross-peaks in 2D HSQC spectrum. Nonequivalent H_A and H_B protons gave a cross-correlation peak in 2D TOCSY spectrum. Two equivalent methylene protons of racemic diad couple with methylene carbon giving a single cross-peak in 2D HSQC spectrum. 2D HSQC spectrum of methylene region showing carbon resonances ranging from δ 51.0 to 55.5 ppm coupled with proton resonances ranging from δ 1.4 to 2.1 ppm is shown in Fig. 4. Cross-peaks I, II, and III correspond to *r* centered tetrads having single cross-peaks in 2D HSQC spectrum, assigned to *rrr*, *mrr*, and *mrm* tetrads, respectively. Cross-peaks IV/V and VI/VII correspond to rmr tetrad and are higher-order-sensitive. Owing to *m*-centered methylene group, couplings IV/VI and V/VII were assigned to H_A and H_B protons, respectively. Nonequivalent H_A and H_B protons of *rmr* tetrad show a cross-correlation peak in 2D TOCSY spectrum labeled "b" in Fig. 5. Cross-peaks VIII and IX were attributed to H_A and H_B of *mmr* tetrad and nonequivalent protons gave cross-correlation peak "a" in 2D TOCSY spectrum. Proton resonances assigned using 2D HSQC spectrum and confirmed by 2D TOCSY spectrum were applied to analyze 2D HMBC spectrum (Fig. 6). Cross-peaks 1 and 3 were assigned to the couplings between α-methyl protons of *rr* triad with methylene carbon of *rrr* and *mrr* tetrads, respectively. Cross-peaks 2, 4, and 7 were attributed to couplings between α-methyl protons of *mr* triad with methylene carbons of *rmr*, *mrr*, and *mrm* tetrads, respectively. Couplings between α-methyl protons of *mm* triad with methylene carbon of *mmr* and *mmm* triad resulted in cross-peaks 5 and 6, respectively. Cross-peak 8 was assigned to the coupling of methylene pro-



Scheme 3 MmM and MrM diads of PMMA.

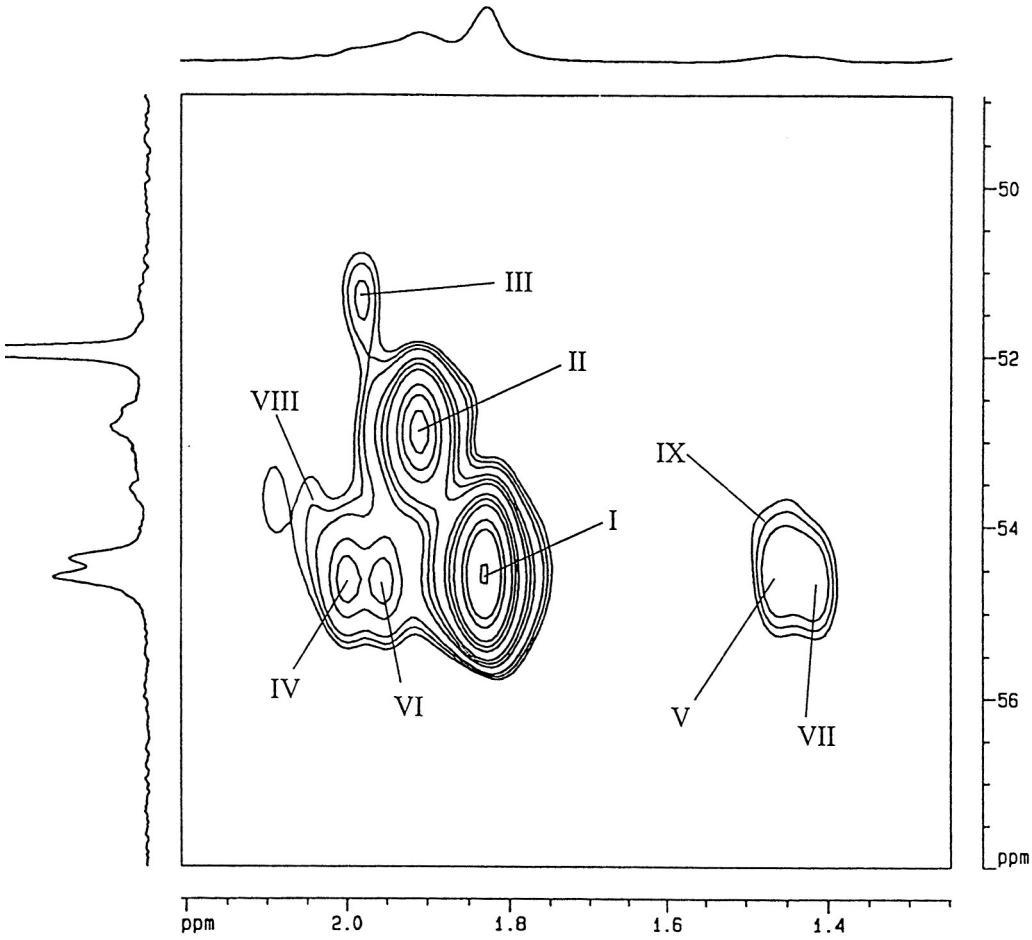


Fig. 4 2D HSQC NMR spectrum of methylene region of PMMA at 45 °C.

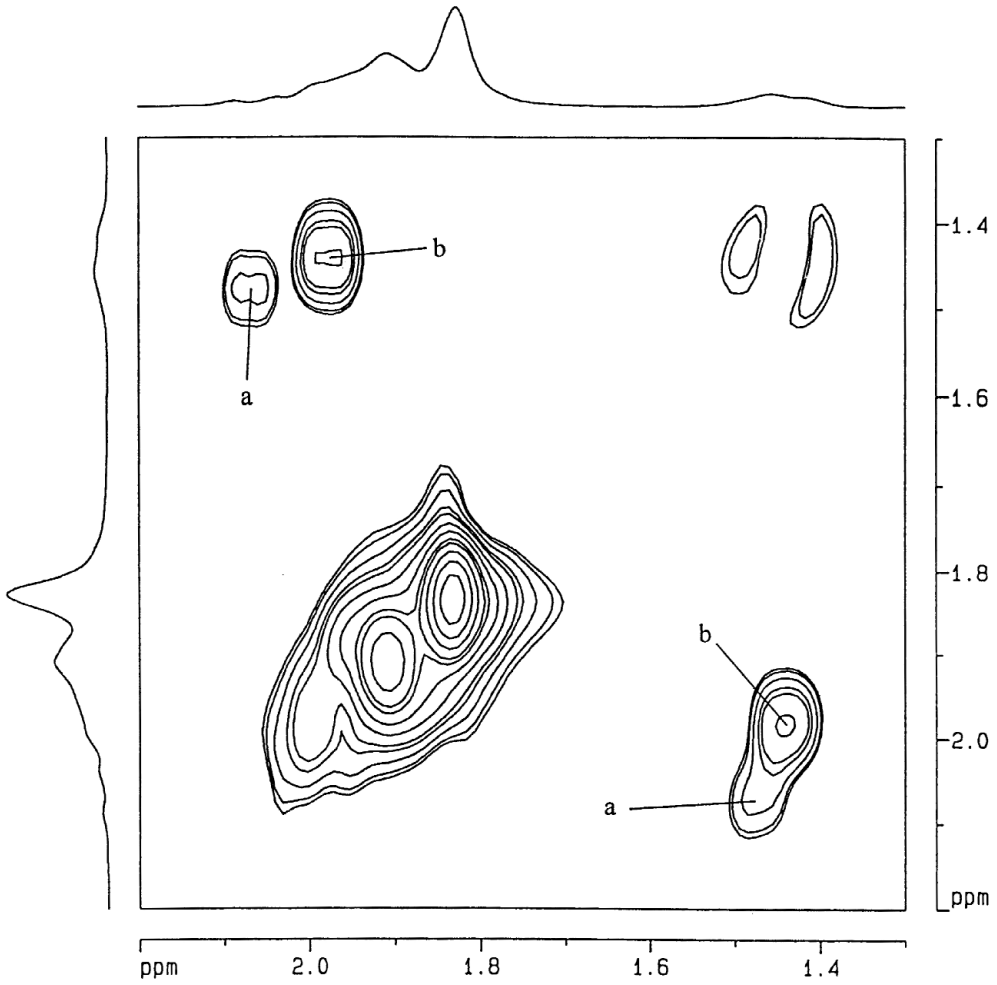


Fig. 5 2D TOCSY NMR spectrum of PMMA at 45 °C.

ton of *rmr* tetrad with methylene protons of the adjacent *mrm* unit. Similarly, cross-peak 9 was assigned to the coupling between methylene carbon and protons of adjacent *m* tetrads in *rrrr* pentad. Cross-peaks 10/12 and 11/13 were assigned to the couplings between methylene protons of *rmr* tetrad with methylene carbon of *mrr* unit in *rmrr* pentad. Cross-peak 14 was assigned to the coupling of mrr methylene carbon with m protons in *mm* pentad. Assignments of methylene carbon and proton resonances are shown in respective 1D NMR projection in Fig. 6. 2D NMR spectral analysis further substantiated the assignments of carbon and proton resonances.

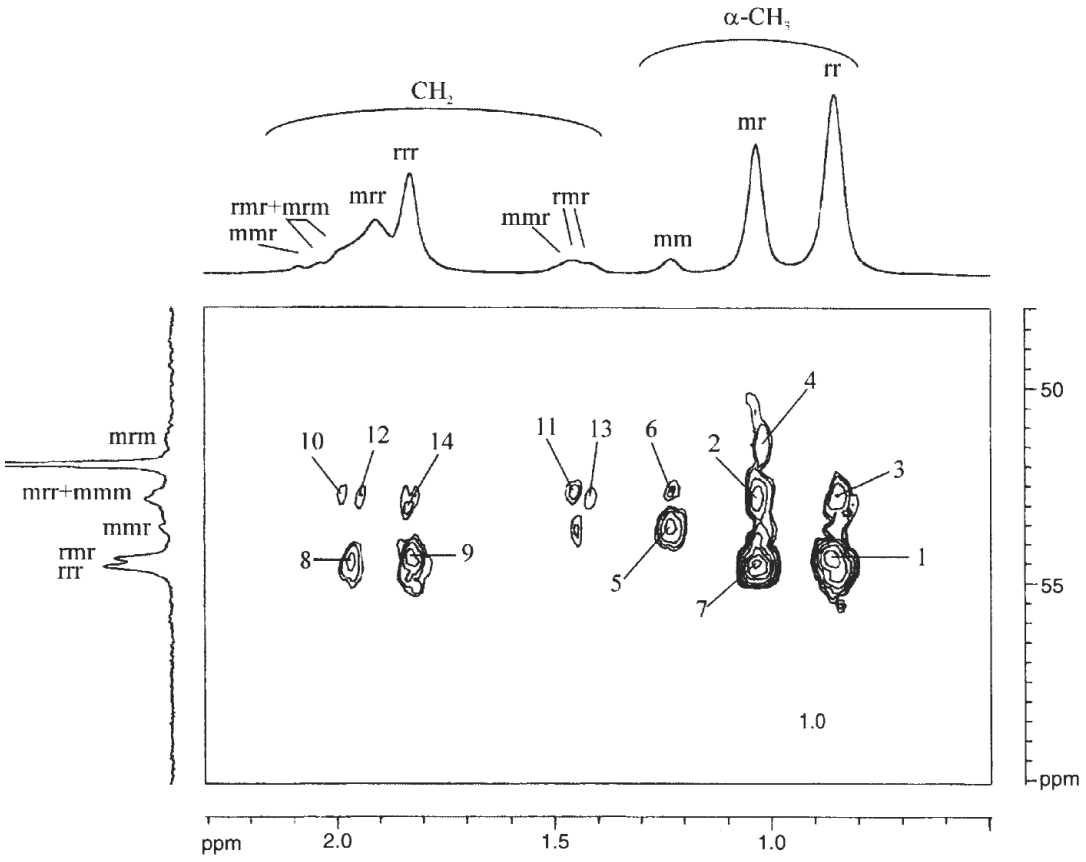


Fig. 6 2D HMBC NMR spectrum showing 3-bond couplings between methylene carbons with α-methyl protons and adjacent methylene protons of PMMA at 45 °C.

2D NMR study of poly(methacrylonitrile)

^{13}C NMR spectra of atactic and syndiotactic-rich PMAN [53] along with 2D (^{1}H-^{13}C COSY) NMR spectra of α-methyl and methylene regions of atactic PMAN were assigned completely. Values of tetrads and pentads were calculated from triads obtained from α-methyl carbon of PMAN. By comparing the calculated values with observed ones, and by taking 2D NMR spectra into consideration, both α-methyl carbon and proton absorptions were assigned up to pentads, and methylene carbon absorptions up to tetrads (partly up to hexads) levels.

NMR OF COPOLYMERS

Microstructure determination becomes slightly more complicated when two or more monomers have been copolymerized together. In copolymers, the arrangement of repeat units along the polymer backbone must be established in addition to determination of modes of addition, chirality, and molecular weight. Comonomer sequence distribution in copolymer is statistically controlled by mechanism of copolymerization, and it has been suggested that it would be a more sensitive method for distinguishing the alternative mechanism. One of the earliest copolymers studied by NMR was styrene/methyl methacrylate copolymer. Kapur and Brar [54] have analyzed the copolymer sequences of methyl methacrylate/acrylonitrile copolymers using carbonyl and nitrile carbon resonances. Gallardo et al.

[55] have used ^{1}H and $^{13}C\{^{1}H\}$ NMR for microstructural analysis of *p*-acryloyloxy-acetanilide and *N*,*N*-dimethyl acrylamide copolymers, which are of biomedical importance. Kim and Harwood [56] have analyzed the sequence distribution in methyl acrylate/methyl methacrylate copolymers by $^{13}C\{^{1}H\}$ NMR spectroscopy. Llauro et al. [57] have investigated the microstructure of ethylene/butadiene copolymer using ^{1}H and $^{13}C\{^{1}H\}$ NMR. Guerra et al. [58] have reported the sequence analysis of poly(ethylene terphthalate) terpolyester containing isophthalic and *tert*-butyl isophthalate units by $^{13}C\{^{1}H\}$ NMR.

It is often observed that sequence determination by ^{1}H and $^{13}C\{^{1}H\}$ NMR experiments is difficult to assign due to large-scale overlapping of the resonating signals. Carbon-13 DEPT and 2D NMR experiments have been extensively used for the analysis of compositional and configurational sequences in copolymers. Brar et al. [59] have completely assigned the complex ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of acrylonitrile/methyl methacrylate copolymers to compositional (tetrad, pentad, and hexad levels) and configurational (triad level) sequences with the help of inverse-HETCOR and DEPT experiments. DEPT is extensively used for the analysis of overlapped carbon resonances in $^{13}C\{^{1}H\}$ NMR spectrum, thus it helps in compositional and configurational assignments. Huthchinson et al. [60] studied the short-chain branching structures for a wide range of ethylene copolymers of various composition, prepared by high-pressure free radical polymerization, with the help of ^{1}H, $^{13}C\{^{1}H\}$, and 2D NMR techniques (HSQC-TOCSY). Proton-detected HMQC and HMBC experiments have been routinely used for the characterization of biological molecules.

The microstructure of a large number of copolymers such as methyl methacrylate/methyl acrylate (A/B) [61,62], 2-hydroxy ethyl methacrylate/2-vinyl pyridine [63], acrylonitrile/methyl methacrylate [59], and ethyl methacrylate/acrylonitrile [64] have been investigated by Brar et al. Recently, they have assigned the complex carbon and proton NMR spectra of glycidyl methacrylate/vinyl acetate, methacrylonitrile/methyl methacrylate [65], *N*-vinyl-2-pyrrolidone/acrylonitrile, *N*-vinyl-2-pyrrolidone/methyl acrylate, glycidyl methacrylate/methyl styrene [66], and glycidyl methacrylate/butyl acrylate [67] in terms of compositional and configurational sequences with the help of DEPT, HSQC, TOCSY, and NOESY NMR experiments. They have also assigned the complex ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra of a large number of copolymers such as styrene/*n*-butyl acrylate [68], styrene/methyl methacrylate [69], *N*-acryloylcarbazole/methyl methacrylate [70], *N*-acryloyl carbazole/methacrylonitrile [71], and acrylonitrile/methyl acrylate [72] with the help of DEPT, HSQC, TOCSY, and HMBC experiments. This article explains the detailed 2D NMR study of poly(methyl methacrylate-*co*-methyl acrylate), poly(styrene-*co*-methyl methacrylate) and poly(methyl methacrylate-*co*-methacrylonitrile) that helps in microstructural analysis of poly(methacrylonitrile-*co*-styrene-*co*-methyl methacrylate) and poly(acrylonitrile-*co*-methyl methacrylate-*co*-methyl acrylate).

2D NMR study of poly(methyl methacrylate-*co*-methyl acrylate)

Analysis of methylene, α-methyl, and methine carbon and proton resonances of methyl acrylate/methyl methacrylate (A/B) copolymer [61,62] can be done with the help of HSQC and TOCSY spectra. Carbonyl carbon assignments based on experimental analysis of their coupling with methylene and α-methyl protons (assigned with the help of 2D HSQC and TOCSY spectra) using HMBC spectra can be done to overcome any speculation in the resonance analysis. 2D HSQC spectrum of A/B copolymer with composition (F_A = 0.58) is given in Fig. 7, and all of the assignments are listed in Table 2. Methylene protons H_A and H_B of both AmB- and ArB-centered tetrads are nonequivalent as shown in Scheme 4, thus resulting in two cross-peaks by coupling with methylene carbon in 2D HSQC spectra (Fig. 7). H_A and H_B protons of AmB and ArB being nonequivalent gave cross-correlation peaks I to VI in 2D TOCSY spectrum (Fig. 8), enabling the differentiation between cross-peaks of AmB and ArB in different tetrads in 2D HSQC spectra. AA and BB diad-centered tetrads show compositional and conformational sensitivity. The methine group of methyl acrylate can be assigned up to a triad level of com-

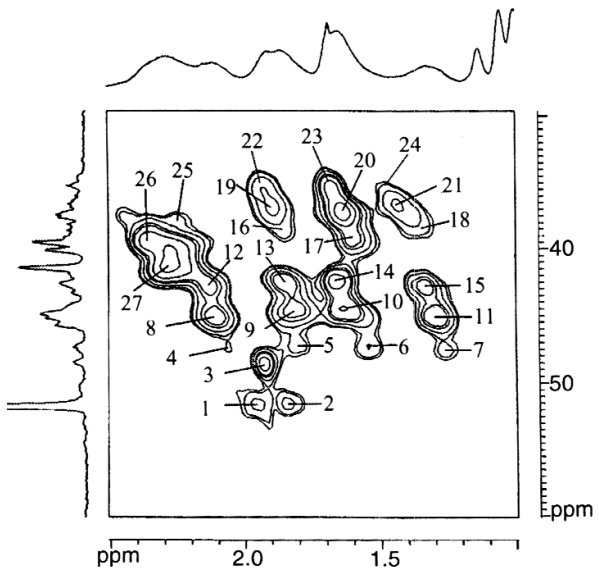
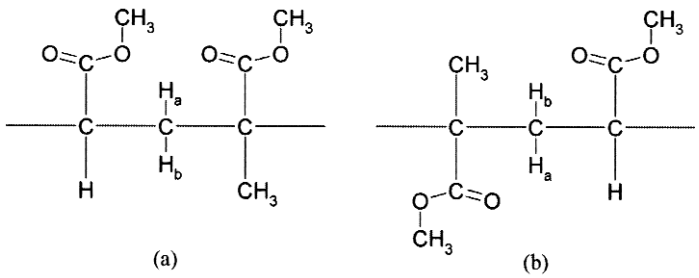


Fig. 7 2D HSQC NMR spectrum of methyl acrylate/methyl methacrylate (A/B) copolymer (F_A = 0.58), showing methylene and methine region at 45 °C.

Table 2 Assignments of the methylene carbon resonances of methyl acrylate (A)/methyl methacrylate (B) copolymer from the 2D HSQC spectrum.

Cross-peak no.	Cross-peak assignment	Cross-peak position, ppm
1.	ABBB	51.5/1.95
2.	ABBB	51.5/1.84
3.	ABBA	48.4/1.92
4.	BAmBB (H_A)	47.3/2.04
5.	BArBB (H_A)	47.0/1.77
6.	BArBB (HB)	47.0/1.52
7.	BAmBB (H_B)	47.3/1.23
8.	AAmBB/BAmBA (H_A)	44.8/2.1
9.	AArBB/BArBA (H_A)	44.3/1.82
10.	AArBB/BArBA (H_B)	44.3/1.62
11.	AAmBB/BAmBA (H_B)	44.8/1.29
12.	AAmBA (H_A)	42.6/2.13
13.	AArBA (H_A)	42.2/1.84
14.	AArBA (H_B)	42.2/1.65
15.	AAmBA (H_B)	42.6/1.33
16.	BAmAB (H_A)	38.4/1.86
17.	BArAB	38.8/1.62
18.	BAmAB (H_B)	38.4/1.37
19.	AAmAB (H_A)	36.5/1.89
20.	AArAB	36.9/1.63
21.	AAmAB (H_B)	36.4/1.43
22.	AAmAA (H_A)	35.3/1.93
23.	AArAA	35.1/1.67
24.	AAmAA (H_B)	35.3/1.46



Scheme 4 AmB and ArB diads showing nonequivalent H_A and H_B methylene protons in methyl methacrylate/methyl acrylate (A/B) copolymer.

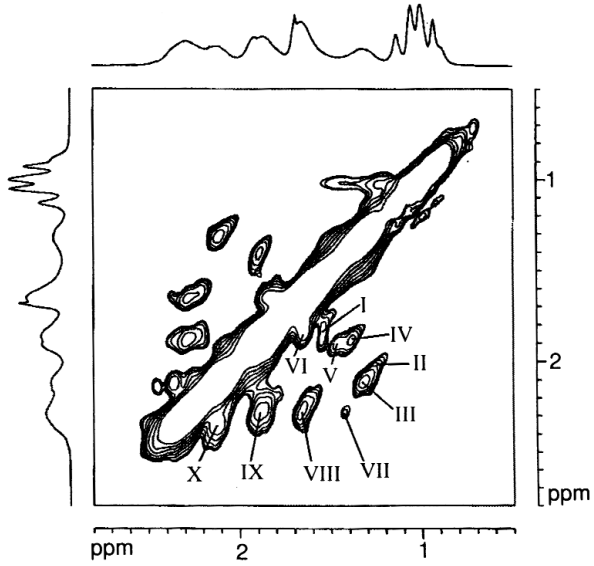


Fig. 8 2D TOCSY NMR spectrum of methyl acrylate/methyl methacrylate (A/B) copolymer (F_A = 0.58), at 45 °C.

positional sensitivity in the copolymer, based on 2D HSQC assignments. The methine group of methyl acrylate can be assigned up to a triad level of compositional sensitivity. 2D TOCSY studies were used to ascertain these assignments by analyzing 1,3-bond order couplings between methylene and methine protons of A monomer in AA- and AB-centered methylene cross-correlation peaks VII to X as shown in Fig. 8. HMBC spectral analysis enabled us to assign carbonyl carbon resonances by analyzing 3-bond coupling with α-methyl protons of the same methyl methacrylate (B) monomer unit, enabling us to assign B-centered triads (Fig. 9). The rest of the carbonyl carbon resonances were analyzed from the couplings of methylene protons with carbonyl carbon. All of the assignments of 2D HMBC spectral analysis are given in Table 3.

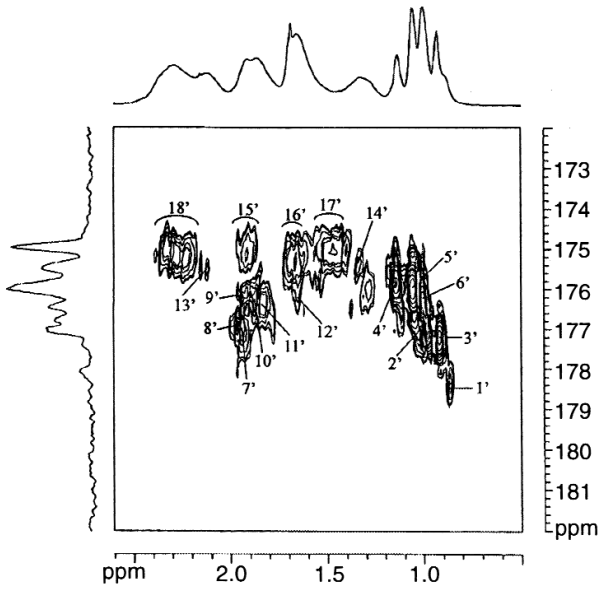


Fig. 9 2D HMBC NMR spectrum of methyl acrylate/methyl methacrylate (A/B) copolymer ($F_A = 0.58$), showing the couplings of methylene carbon with α-methyl protons.

Table 3 Coupling of carbonyl carbon with α-methyl protons and methylene protons in methyl methacrylate/methyl acrylate (A/B) copolymer observed from the 2D HMBC spectrum.

Cross-peak no.	Carbonyl carbon nuclei	Proton nuclei	Cross-peak position, ppm
1'	BrBrB	α-CH_3 BrBB	177.9/0.86
2'	BrBA	α-CH_3 BrBA	176.6/0.99
3'	BrBA	α-CH_3 BrBA	176.9/0.91
4'	ABA	α-CH_3 ABA	175.8/1.14
5'	ABA	α-CH_3 ABA	175.9/1.05
6'	ABA	α-CH_3 ABA	176.1/1.00
7'	ABrB	CH_2 ABBA	177.1/1.92
8'	ABrB	CH_2 ABBB	177.0/1.96
9'	ABmB	CH_2 ABBA	176.1/1.92
10'	ABmB	CH_2 ABBB	176.1/1.86
11'	BArB	CH_2 BArBA (H_A)	176.4/1.82
12'	BArB	CH_2 BArBA (H_B)	176.3/1.64
13'	AAmB	CH_2 AAmBA (H_A)	175.4/2.12
14'	AAmB	CH_2 AAmBA (H_B)	175.4/1.33
15'	AAA	CH_2 AmA (H_A)	174.7/1.90
16'	AAA	CH_2 ArA	174.7/1.65
17'	AAA	CH_2 AmA (H_B)	174.7/1.4

2D NMR study of poly(styrene-*co*-methyl methacrylate)

Analysis of carbonyl region long-range couplings between carbon and proton nuclei in poly(styrene-*co*-methyl methacrylate) [69] is very helpful in understanding the microstructure of polymers. Expanded carbonyl region in $^{13}C\{^1H\}$ NMR spectrum of S/M copolymer is very complex. The carbonyl carbon region in PMMA has been assigned to MmMmM, MmMrM, and MrMrM at δ 178.0, 177.0, and 177.2 ppm, respectively. By comparing the variation in intensity of signals with copolymer composition along with homopolymer, various triad sequences in carbonyl carbon region are assigned. A comparison of carbonyl carbon region for different compositions of S/M copolymer with PMMA is shown in Fig. 10. Region VIII corresponds to MrMrM triad sequence, whereas regions IX, X, and XI were assigned to

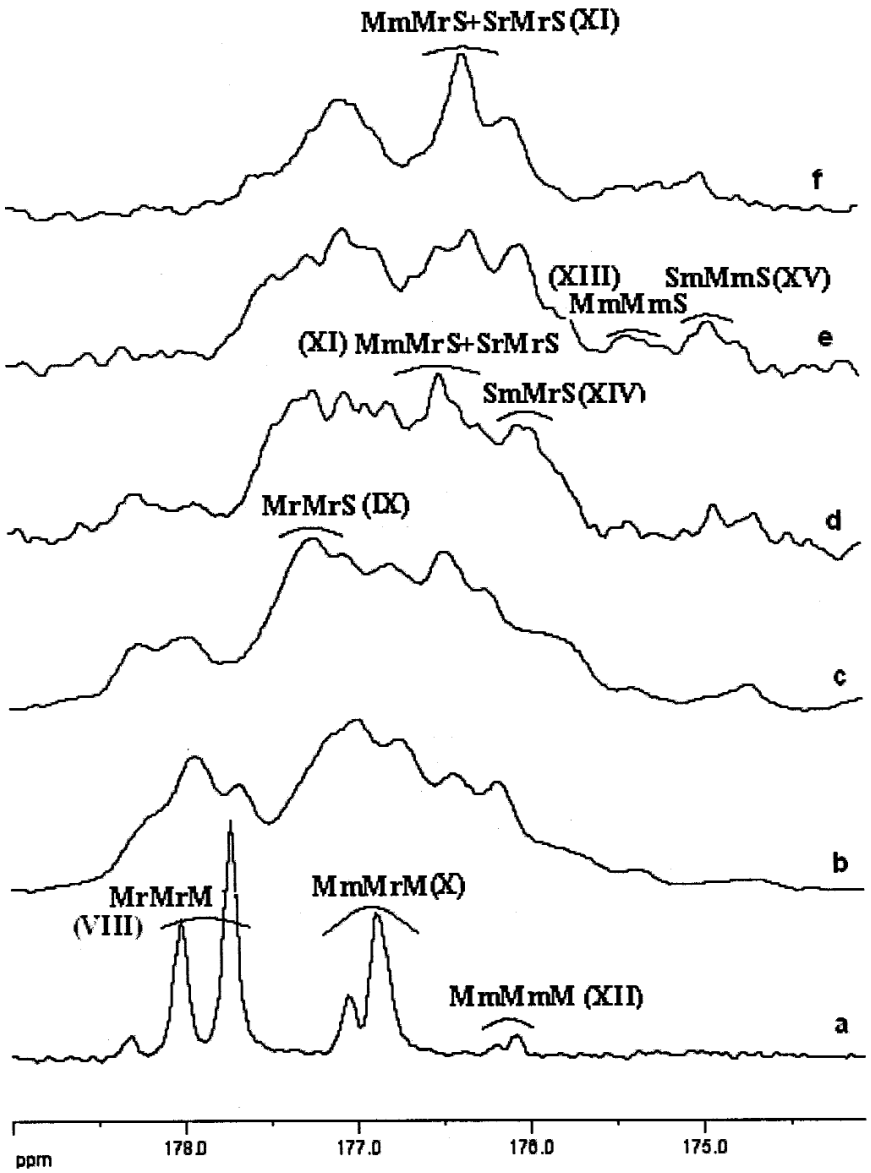


Fig. 10 Expanded carbonyl carbon signals of M unit in $^{13}C\{^1H\}$ NMR spectra of S/M copolymers in $CDCl_3$ at 25 °C: (a) PMMA, (b) $F_M = 0.75$, (c) $F_M = 0.61$, (d) $F_M = 0.51$, (e) $F_M = 0.38$, and (f) $F_M = 0.25$.

MrMrS, MmMrM, and MmMrS + SrMrS triads, respectively. Region XII was assigned to MmMmM triad sequence. By observing the change in intensities of signals with increase in styrene content in copolymers, region XIII was assigned to MmMmS triad, whereas regions XIV and XV were assigned to SmMrS and SmMmS triads, respectively, which were later confirmed by HMBC. 2D HMBC study of S/M copolymer is helpful in the assignment of the carbonyl region. Long-range coupling of carbonyl carbon with α-methyl protons are shown in expanded HMBC spectrum (Fig. 11). Completely assigned ^{1}H NMR spectrum obtained from 2D HSQC was used to confirm the assignments done with the help of 2D HMBC spectrum. Considering the coupling of α-methyl protons with carbonyl carbon, only M-centered triads will be observed. Cross-peaks 1 and 2 centered at δ 177.5/0.70 and 176.8/0.87 ppm are assigned to couplings of carbonyl carbons in MrMrM and MmMrM triads with α-CH_3 protons in MrMrM and MmMrM triads, respectively. Cross-peaks 3 and 4 centered at δ 177.2/0.56 and 176.5/0.65 ppm are assigned to coupling of carbonyl carbons with α-methyl protons in MrMrS and MmMrS triads, respectively. Cross-peak 5 centered at δ 176.7/0.48 ppm is assigned to coupling of carbonyl carbon with α-methyl protons in the SrMrS triad.

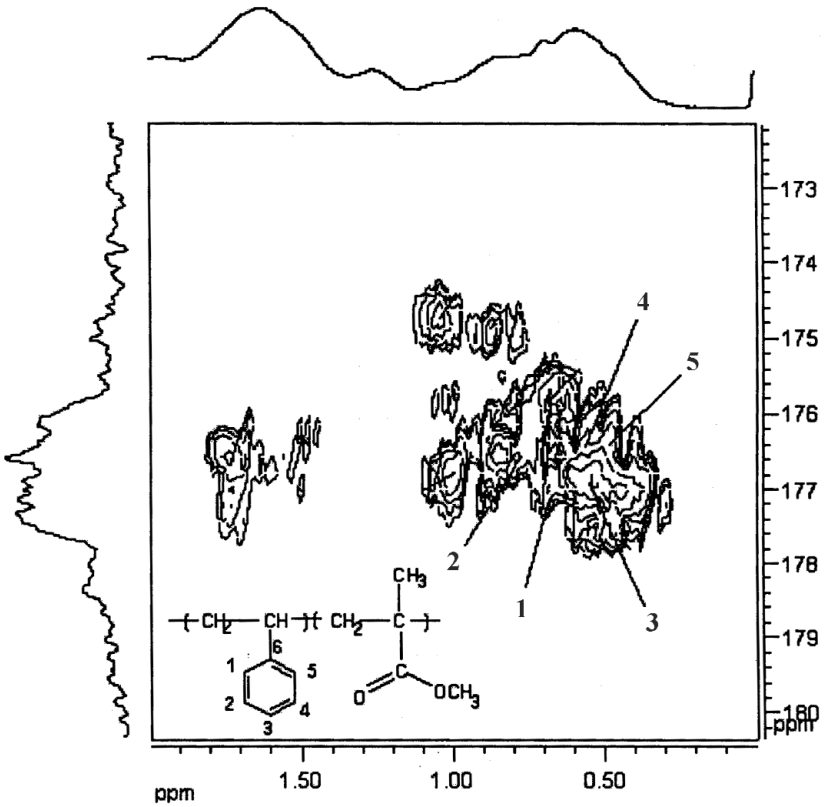


Fig. 11 Expanded 2D HMBC NMR spectrum of S/M copolymer (F_M = 0.51), indicating the couplings of carbonyl carbon with the α-methyl region in $CDCl_3$ at 25 °C.

2D NMR study of poly(methyl methacrylate-*co*-methacrylonitrile)

α-CH_3 carbon region of both MMA (A) and MAN (B) units in $^{13}C\{^1H\}$ NMR spectrum of poly(methyl methacrylate-*co*-methacrylonitrile) [65] is very complex because of overlapping and spreading over a wide range of chemical shifts due to tacticity effects in both PMMA and PMAN. As both the units show configurational and compositional effects, the spectrum is quite complex so it was resolved with the help of 2D HSQC spectrum (Fig. 12). Overlapped multiplet in the methyl carbon region is assigned to both compositional and configurational sequences. Assignments of various signals have been carried out with the help of spectra of PMMA, PMAN, and by observing change in intensity of signals with change in composition of copolymers. All of the assignments of α-CH_3 carbon region in 2D HSQC NMR are given in Table 4.

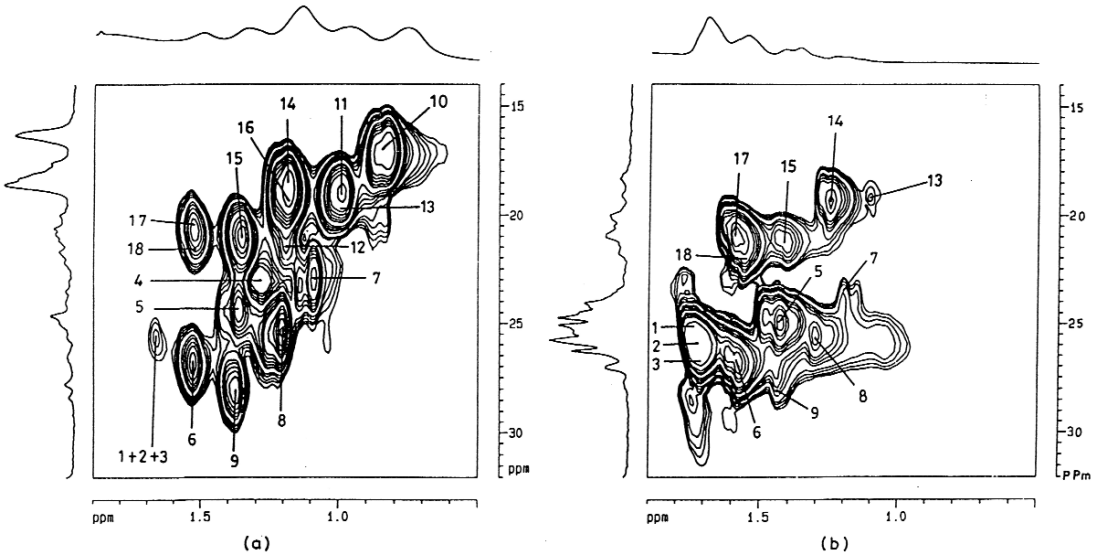


Fig. 12 Expanded α-methyl carbon region in 2D HSQC spectra of methacrylonitrile/methyl methacrylate (A/M) copolymers with compositions (a) $F_A = 0.23$ and (b) $F_B = 0.79$ in $CDCl_3$ at 25 °C.

Table 4 Compositional and configurational assignments of α-CH_3 carbon signals of methacrylonitrile/methyl methacrylate (A/M) copolymer from 2D HSQC NMR spectra.

Cross-peak no.	Cross-peak assignment	Cross-peak position, ppm
1.	ArArA	25.3/1.75
2.	ArAmA	26.0/1.71
3.	AmAma	26.9/1.70
4.	ArArM	23.0/1.29
5.	ArAmM	24.5/1.38
6.	AmAmM	26.7/1.52
7.	MrArM	23.0/1.11
8.	MrAmM	25.5/1.20
9.	MmAmM	28.0/1.39
10.	MrMrM	16.8/0.88
11.	MrMmM	18.9/1.12
12.	MmMmM	21.2/1.19
13.	MrMrA	19.9/1.01
14.	MrMmA	18.4/1.20
15.	MmMmA	21.2/1.38
16.	ArMrA	19.5/1.19
17.	ArMmA	20.5/1.52
18.	AmMmA	21.5/1.51

NMR OF TERPOLYMERS

Microstructure determination becomes very complicated when more than two monomeric units have been incorporated in polymerization. It is difficult to resolve these complicated arrangements of repeating units along the polymer backbone. Rinaldi and coworkers studied the stereosequence of different triads in different copolymers and terpolymers by various 2D NMR techniques [73]. Composition analysis of butyl acrylate/methylmethacrylate/α-methyl styrene terpolymers was carried out by McManus et al. [74] Thermogravimetric analysis (TGA) of acrylamide/acrylic acid/acrylonitrile terpolymers was performed by Rakshit and coworkers [75]. Various coworkers have reported the reactivity ratios of different terpolymers [76,77]. Brar et al. have reported the microstructure of various terpolymers and copolymers by 2D NMR [78–80]. In this review, 2D NMR study of different terpolymers like poly(methacrylonitrile-*co*-styrene-*co*-methyl methacrylate), poly(acrylonitrile-co-methyl methacrylate-*co*-methyl acrylate), and poly(ethylene-*co*-vinyl acetate-*co*-carbon monoxide) are discussed in detail.

2D NMR study of poly(methacrylonitrile-*co*-styrene-*co*-methyl methacrylate)

The methyl region of methacrylonitrile (N) and methyl methacrylate (M) units in 1D (^{1}H and ^{13}C{^{1}H}) NMR spectra of methacrylonitrile/styrene/methyl methacrylate (N/S/M) [80] terpolymers is quite complex and overlapped. This region can be assigned with the help of HSQC spectra. 2D HSQC spectra of two compositions of N/S/M terpolymer are shown in Fig. 13. In N/S copolymers, S-unit adjacent to N-centered triad leads to shielding of methyl carbon of N-unit (SNS < NNS < NNN, in increasing order of chemical shifts). Similarly, in N/M copolymer, the addition of methyl methacrylate unit (M) adjacent to N-centered triad leads to shielding of methyl carbon (MNM < NNM < NNN, in increasing order of chemical shifts). The CH_3 group in N-monomeric unit of terpolymer shows compositional sensitivity.

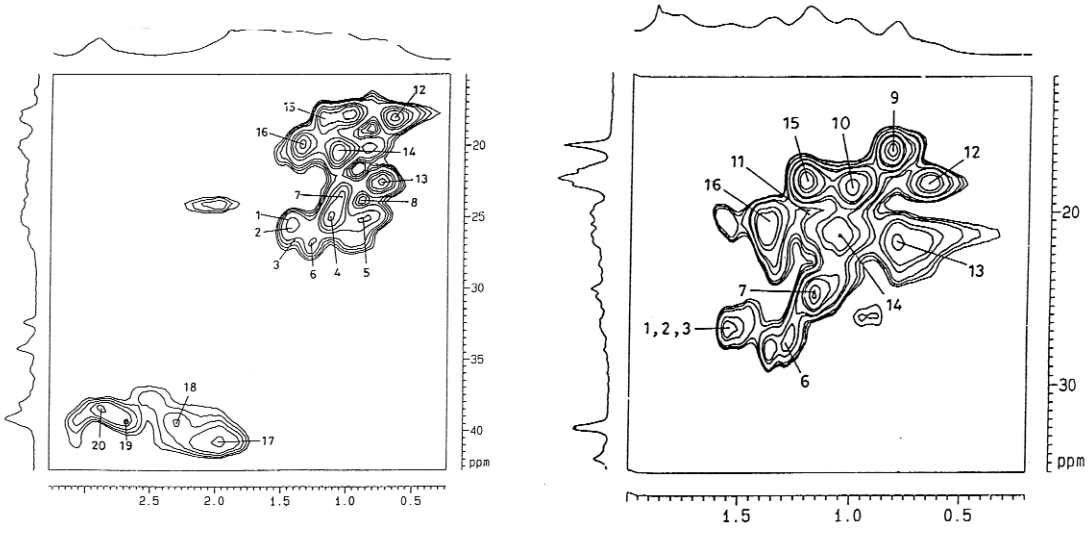


Fig. 13 Expanded 2D HSQC spectra of methacrylonitrile/styrene/methyl methacrylate (N/S/M) terpolymers with compositions (N, S, M = mol % in the terpolymer) (a) 0.33, 0.33, 0.34 and (b) 0.27, 0.13, 0.60.

Assignments of methyl carbon resonances of N-monomeric unit in terpolymer are done on the basis of change in intensity of signals with change in composition of terpolymers and by comparing methyl carbon resonances in HSQC spectra of N/S and N/M copolymers. Methyl carbon resonances of M-monomeric unit in terpolymer also show compositional and configurational triad sensitivity. All of the assignments have been done by comparing methyl carbon resonances in HSQC spectra of S/M and N/M copolymers. In S/M copolymers, S-unit adjacent to M-centered triad in S/M copolymers leads to shielding of both methoxy and carbonyl carbons (SMS < MMS < MMM, in increasing order of chemical shifts), at the same time, methyl carbon (M-unit) follows the similar arrangement in triads distribution (SMS < MMS < MMM). Besides this in N/M copolymers, addition of methacrylonitrile unit adjacent to M-centered triad leads to shielding of carbonyl carbon (NMN < NMM < MMM, in increasing order of chemical shifts), at the same time deshielding of methyl carbon of M-centered triads (MMM < NMM < NMN). In N/M copolymers, the addition of methacrylonitrile unit adjacent to M-centered triad leads to shielding of carbonyl carbon (NMN < NMM < MMM, in increasing order of chemical shift), at same time deshielding of methyl carbon of M-centered triads. So it follows the reverse trend for methyl carbon of M-centered triads (MMM < NMM < NMN). Along the proton axis, methine proton of S-unit can be assigned by comparing the spectra of N/S and S/M copolymers and on the basis of variation in intensity of signals with change in composition of terpolymers. All 2D HSQC assignments are given in Table 5.

Table 5 Compositional and configurational assignments of α-CH_3 and methine carbon signals of methacrylonitrile/styrene/methyl methacrylate (N/S/M) terpolymers from the 2D HSQC NMR spectra.

Cross-peak no.	Cross-peak assignment	Cross-peak position, ppm
1.	NrNrN	24.8–25.3/1.50–1.55
2.	NrNmN	25.3–26.4/1.46–1.50
3.	NmNmN	26.4–27.0/1.40–1.46
4.	NNS	24.5–26.0/1.15
5.	SNS	24.3–25.8/0.80–0.98
6.	NNM	26.5–28.5/1.22–1.38
7.	MNM	23.5–24.5/1.02–1.20
8.	MNS	22.5–24.0/0.82–0.95
9.	MrMrM	16.5/0.82
10.	MrMmM	18.5/0.99
11.	MmMmM	20.5/1.17
12.	MMS	18.0/0.65
13.	SMS	21.5–23.0/0.60–0.82
14.	NMS	21.0/1.10
15.	MMN	18.0/1.20
16.	NMN	20.5/1.40
17.	MSS	40.7/1.88–2.20
18.	NSS	39.4/2.20–2.40
19.	MSM	39.2/2.51–2.85
20.	NSN	38.5/2.86–3.17

2D NMR study of poly(acrylonitrile-*co*-methyl methacrylate-*co*-methyl acrylate)

Microstructure analysis of acrylonitrile/methyl methacrylate/methyl acrylate terpolymers (A/B/M), synthesized by ATRP is being reported using NMR techniques [82]. Methine carbon region of A-unit in $^{13}C\{^1H\}$ NMR spectrum is very complex because of the overlapping of various conformational and configurational placements and also due to residual signals of α-methyl carbon of B-unit. Complexity and overlapping of α-methyl region in $^{13}C\{^1H\}$ NMR spectrum was resolved by employing 2D HSQC spectra of A/B/M terpolymers with different compositions. 2D HSQC spectra of A-unit of terpolymers (Fig. 14) revealed that cross-peaks 1–9 and 10–21 were ascribed to A-centered triads of A/M copolymer (AAA, AAM, MAM) and A-centered triads of A/B copolymer (AAB and BAB), respectively. Cross-peaks 1, 2, and 3 were assigned to ArArA, ArAmA, and AmAmA triads, respectively, by comparing with 2D HSQC spectra of poly(acrylonitrile). Cross-peaks 4, 5, and 6 were assigned to ArArM, ArAmM, and AmAmM, while cross-peaks 7, 8, and 9 were assigned to MrArM, MrAmM, and MmAmM triads, respectively, on comparison with 2D HSQC spectra of A/M copolymers and change in intensity of signals with change in composition of terpolymers. Cross-peaks 10, 11, and 12 were assigned to AArArBA, AArAmBA, and AAmAmBA pentads, respectively. Variation of terpolymer composition does not impart any effect on the intensity of these cross-peaks; hence were attributed to configurational sensitivity within these pentads. Only one cross-peak, 13, was assigned to the overlap of MAB triad and AAABB pentad sequences and only one cross-peak 14 was assigned to BAABB pentad, which suggests that the methine proton of these AAB-centered triad is insensitive to configurational arrangement (Fig. 14c). Similarly, in the BAB-centered triad region, cross-peaks 15–21 were assigned. Cross-peaks 15, 16, and 17 were assigned to ABrArBA, ABrAmBA, and ABmAmBA pentads, respec-

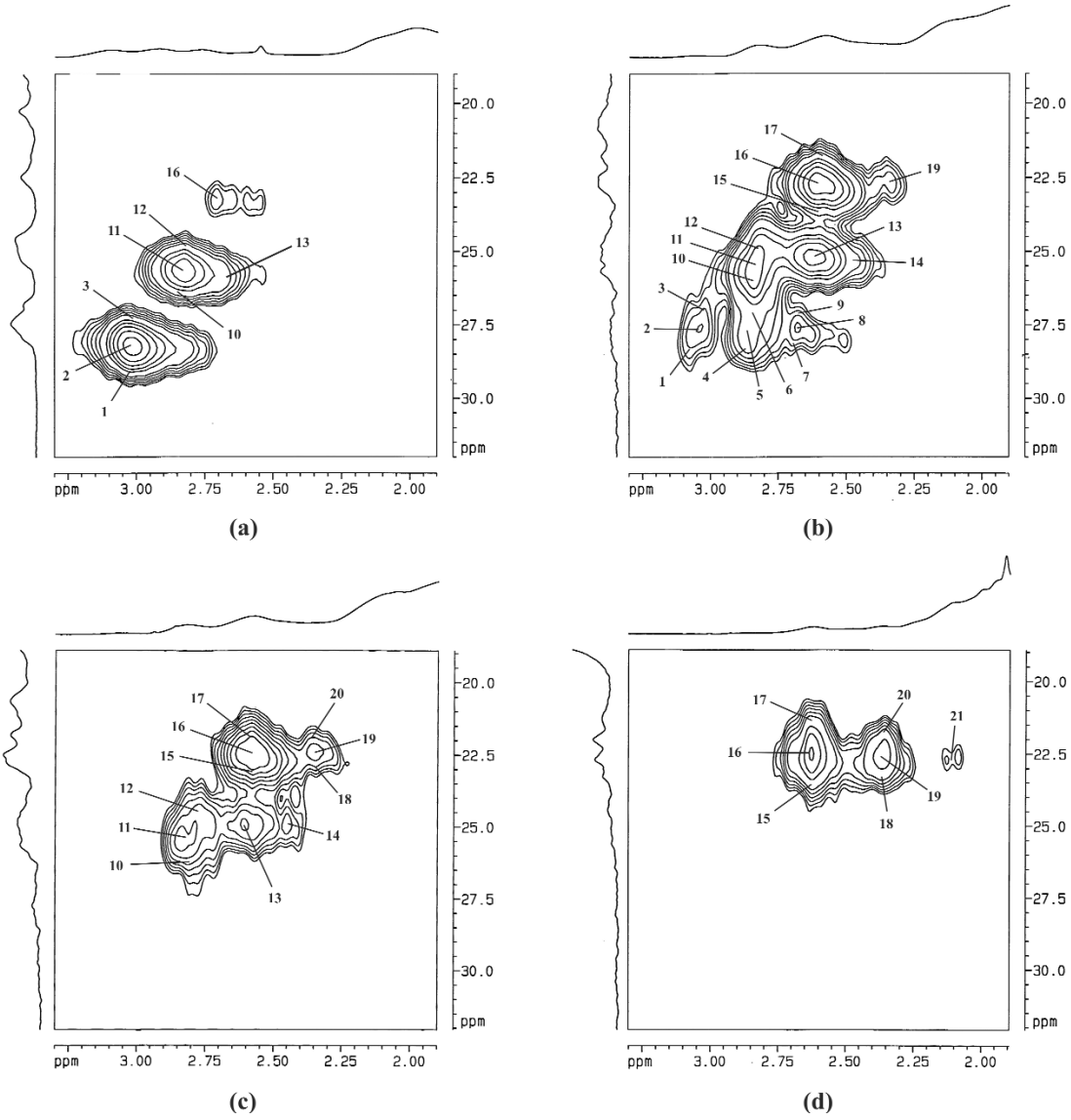


Fig. 14 Expanded methine region of acrylonitrile (A) in 2D HSQC spectra of acrylonitrile/methyl methacrylate/methyl acrylate (A/B/M) terpolymers with compositions (A, B, M = mol % in the terpolymer) (a) 0.59, 0.18, 0.23 (b) 0.35, 0.28, 0.37 (c) 0.33, 0.45, 0.22 and (d) 0.16, 0.67, 0.17.

tively. Cross-peaks 18, 19, and 20 were assigned to BBrArBA, BBrAmBA, and BBmAmBA pentads while cross-peak 21 was assigned to BBABB pentad, respectively.

2D NMR study of poly(ethylene-*co*-vinyl acetate-*co*-carbon monoxide)

A systematic study of poly(ethylene-*co*-vinyl acetate-*co*-carbon monoxide) [73] with varying amount of monomers demonstrates the utility of 2D NMR techniques in characterizing complex polymers. Techniques were useful for unequivocal assignments of resonances from a range of triad monomer sequence structures and for identifying tacticity effects, which was not possible by 1D NMR. gHSQC ex-

periments allowed separation and identification of methyl, methylene, and methine resonances from each other; HSQC-TOCSY proved to be a valuable adjunct to gHMBC, often giving information on 2-bond correlations which are not evident in gHMBC spectra. A few chain ends and short-chain branching structures can also be identified from 2D NMR experiments. In accordance with the study of EV polymers of McCord et al. [81], no evidence was found for quaternary carbons, indicating that chain transfer to the acetate methine does not occur at a detectable level. Although it was possible to assign all the major triads, many resonances could not be assigned due to spectral overlap; hence, work is continuing using 3D NMR with isotopic labeling to selectively study the resonances in congested regions of these spectra.

CONCLUSIONS

2D NMR has emerged as the most effective technique for microstructural analysis of different homopolymers, copolymers, and terpolymers. It is very difficult to resolve these complicated arrangements of repeating units along the polymer backbone. Assignments of various signals have been carried out with the help of spectra of homopolymers and by observing the change in intensity of signals with change in composition of copolymers. Overlapped and complex multiplet in methyl carbon region of various copolymers and terpolymers can be assigned to both compositional and configurational sequences with the help of 2D HSQC spectra. Analysis of methylene, α-methyl, and methine carbon and proton resonances of different copolymers can be done with the help of 2D HSQC and TOCSY spectra. Carbonyl carbon assignments based on experimental analysis of their couplings with methylene protons and α-methyl protons (assigned from 2D HSQC and TOCSY spectra) using HMBC spectra was done to overcome any speculation in resonance analysis. Thus, 2D NMR is a very useful technique for the study of polymer structure. The use of 2D NMR to interpret 3D structures of molecules in solution underpins much of modern chemistry research. Multidimensional magnetic resonance may be use to characterize a new material, elucidate a protein structure, synthesize a new drug, or evaluate the possibility of disease; scientists are involved in a wide variety of endeavors.

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