Chapter 4: Microstructures present in ARGET-ATRP prepared PMMA

Abstract

This chapter reports the analysis of different microstructures present in poly(methyl methacrylate) (PMMA) using1D and 2D NMR spectroscopy. The PMMA used in this study has been prepared via activators regenerated by electron transfer atom transfer radical polymerization (ARGET-ATRP) in DMF at ambient temperature using methyl 2-chloro propionate (MCP) as initiator, $CuBr_2$ as catalyst in combination with N, N, N´, N´´, N´´- pentamethyldiethylenetriamine (PMDETA) as ligand and ascorbic acid as reducing agent. ^{13}C NMR, which provides good information about tacticity of a polymer, has been used extensively along with ^{1}H NMR spectroscopy to extract the information about the different microstructures present in PMMA. Heteronuclear multiple-bond correlation (HMBC), heteronuclear single-quantum coherence (HSQC), and total correlation spectroscopy (TOCSY) were also used to study the position of protons, couplings with carbon etc. in the PMMA.

4.1. Introduction:

Polymers are widely prepared using conventional free radical polymerization which has limitations like uncontrolled molecular weight, molecular architecture and dispersity. But, with the advent of controlled radical polymerization (CRP) these limitations are mitigated. It helps in synthesizing polymers with controlled and desired properties. There are different types of CRPs methods has been established and among these, atom transfer radical polymerization (ATRP) is the most commonly used technique.[185, 221, 22] In ATRP a repetitive transfer process of a halogen or pseudo-halogen atom between an alkyl halide R-X and a redox active transition-metal complex Cu(I)X/ligand is takes place. But, it has a limitation of control of molecular weight at high conversion.[223, 179a]

To overcome this limitation and to prepare polymer with control over molecular weight a new technique viz. Activators Generated by Electron Transfer (ARGET) ATRP is used. Matyjaszewski et al. reported the synthesis of high molecular weight polymer using ARGET-ATRP technique.[184] In ARGET-ATRP there is use of higher oxidation state catalyst in *ppm* level and a proper reducing agent and free radical thermal initiator like AIBN.[224, 225] In this chapter the microstructure of PMMA prepared via ARGET-ATRP has been studied. The term microstructure is used for the specific structure of the repeat unit and sequencing of the repeat unit. By definition, polymer is a large molecule consisting of small repeating units.[226] These units can arrange themselves in different ways along the backbone of the chain. This alignment of the repeating unit in the chain is described by polymer microstructure.[227] From the polymer microstructure various information like, tacticity, stereochemistry of different group, number-average sequence lengths and degree of polymerization can be obtained.[227, 228] It has strong influence on both physical and chemical properties of the polymer.[229] For example, the isotactic PMMA melts at 160 °C and syndiotactic PMMA at 200 °C; similarly, isotactic polystyrene melts at 240 °C and syndiotactic polystyrene at 200 °C. In addition, the crystallinity of the polymers also varies with the degree of the tacticity.[230] Hence, the study of microstructure is very important and it helps to understand the relationship between the polymer properties and its structure and to prepare a new copolymer of required physicochemical properties.[228] The study of microstructure of polymers for both homopolymer[226, 231] and copolymer[227, 207, 232, 233] is possible with NMR spectroscopy as the chemical shift obtained in NMR spectroscopy is affected by the configuration of the chain.[231] To elucidate the complete structure of the polymer using only ^{1}H NMR spectroscopy is not sufficient as major portion of the information remains unseen due to the presence of multiple peaks of broad range. Therefore ^{13}C NMR spectra are used along with ^{1}H NMR spectra to study the complete structure of polymer.[230] The ^{13}C NMR spectrum of polymer with carbonyl carbons e.g. acrylic polymer gives detailed information about uneven distribution of configurational sequences.[231, 234, 235] The microstructure of polymer obtained also varies with the type of polymerization techniques: syndiotactic polymer is mainly obtained from free radical polymerization technique, a range of tacticities can be obtained from anionic polymerization but PMMA formed via group transfer polymerization is mainly syndiotactic.[236]

4.2. Preparation of poly (methyl methacrylate):

PMMA ($\overline{M_n} = 7700\, a.u., PDI = 1.55$) used for this investigation was prepared via ambient temperature *ARGET-ATRP* as reported in our earlier report.[20] The structural characterization of the PMMA was carried out by ^{1}H and ^{13}C NMR spectroscopy.

4.3. Characterization:

4.3.1. NMR spectroscopy:

The 1D and 2D NMR spectra of PMMA were recorded on Bruker NMR Spectrometer in solvent $CDCl_3$. ^{1}H and ^{13}C experiments were carried out at frequencies of 400 and 800 MHz, respectively and calibrated with respect to the solvent signal. Gradient HMBC and HSQC experiments were recorded using the pulse sequence *hmbcgpndqf* and *hsqcetgp* of Bruker software, respectively. The spectra acquired in HMBC with 1200 increments in the F1 dimension and 1216 data points in F2 dimension. Total correlation spectroscopy (TOCSY) experiment was performed using standard pulse sequence of 8 scans, accumulated for 440 experiments with 1.5 delay time. HSQC experiment was acquired with 100 increment in F1 dimension and 1208 data points in F2 dimension.

4.4. Results and discussion:

The tacticity of the polymer PMMA synthesized via ARGET-ATRP[96, 97] has been studied by ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectra of PMMA are divided into four resonance regions. The first region from 16-20 *ppm* is assigned to α-methyl carbon resonances, shown in Figure 4.1(a). The splitting in this region from low to high chemical shift is assigned to different tactic configurations: *rr*, *rm/mr* and *mm* triads. A single peak was observed for triad *rr* at 16.5 *ppm* and *mr* triad was observed to be splitted into two peaks at 18.8 and 19.0 *ppm*. Further, for *mm* triads, two obtained peaks at 21.2 and 21.7 *ppm* were assigned to *rmmr* and *rmmm/mmmr* pentads respectively as earlier assigned by A. S Brar [92(a)] The second region from 44-45.6 ppm is assigned to quaternary carbon shown in Figure 4.1(b). The peaks at 44.6, 44.9 and 45.6 *ppm* within this region are assigned to the *mm*, *rm/mr* and *rr* triads respectively.

The third region for methylene and methoxy region is in the range of 52-55 *ppm* as shown in Figure 4.1(c). The single peak at 52.0 *ppm* was assigned to Methoxy ($–OCH_3$) group, while the peak in the large chemical shift region from 51.7-54.6 *ppm* is assigned to methylene carbon resonances. It has also been reported that tetrads will have the order *rmr, rrr, mmr, mrr, mmm* and *mrm* from high to low chemical shift.[92(a)]

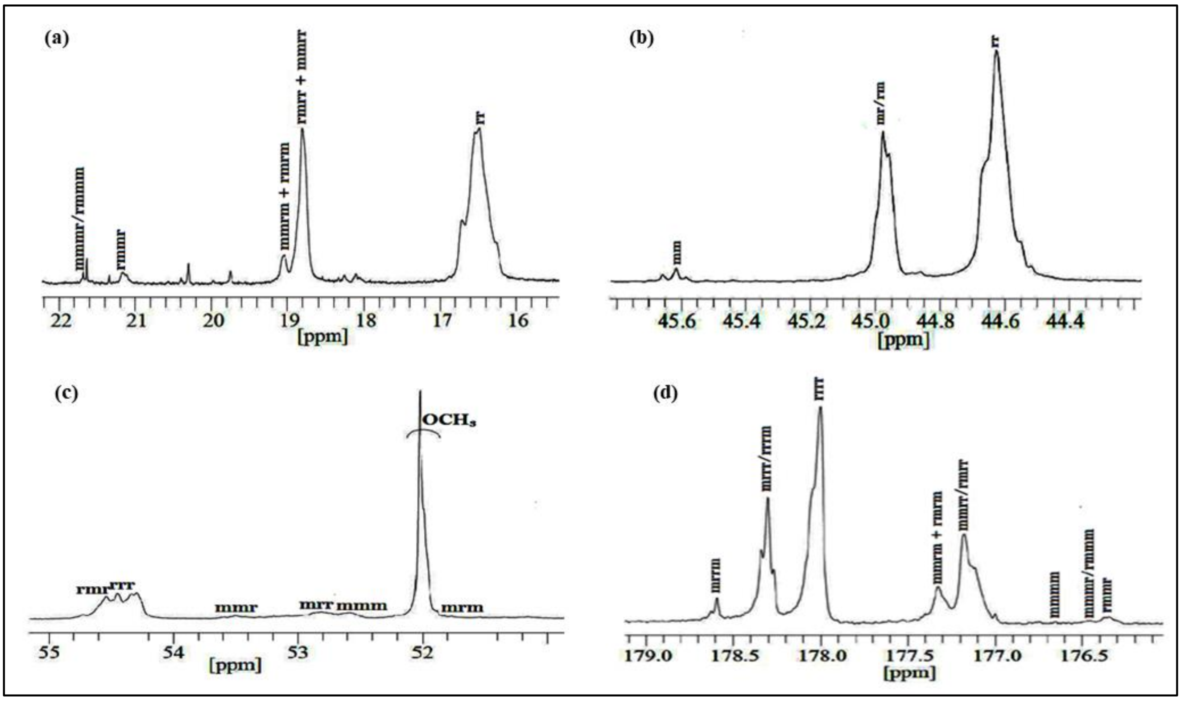
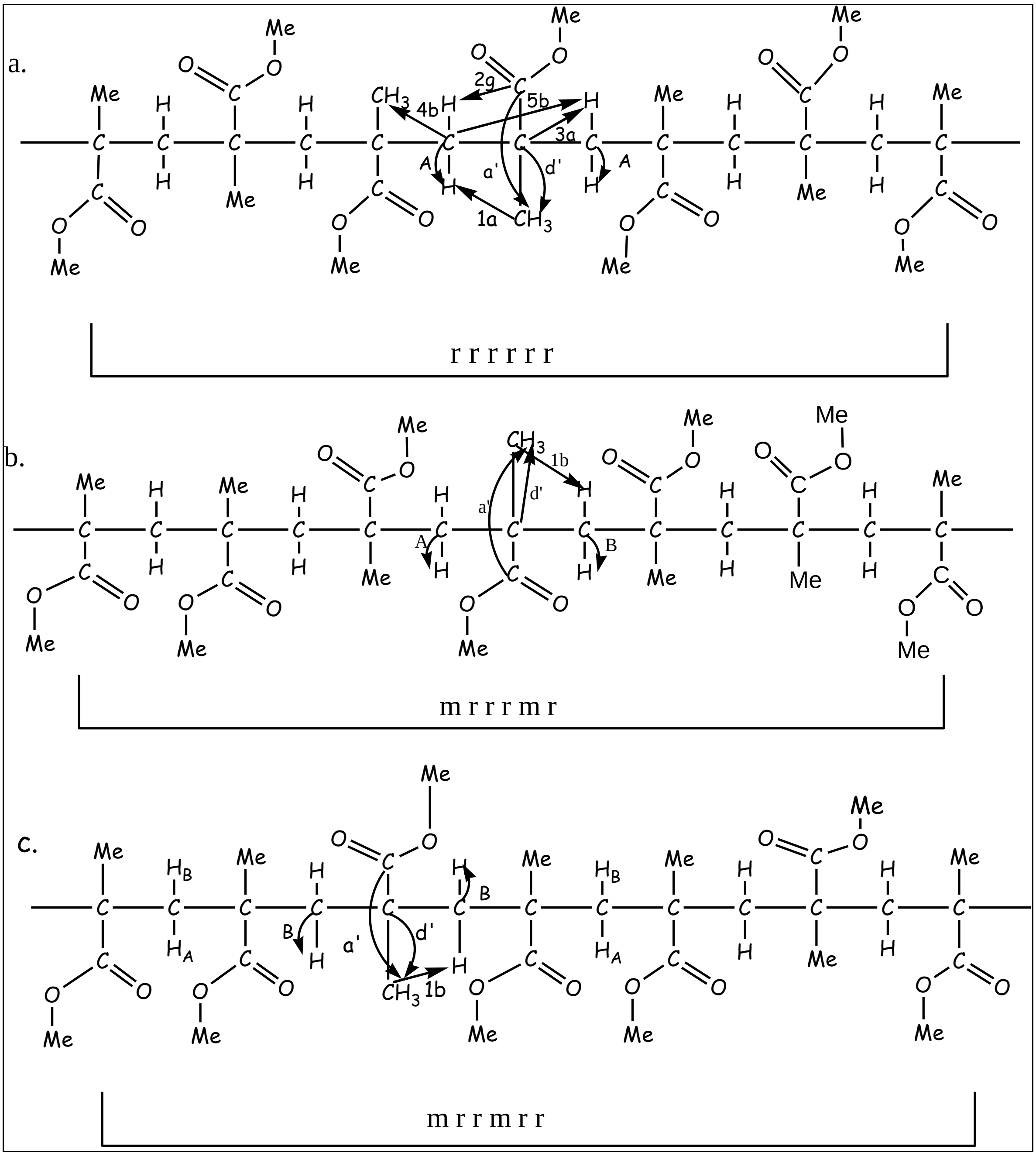
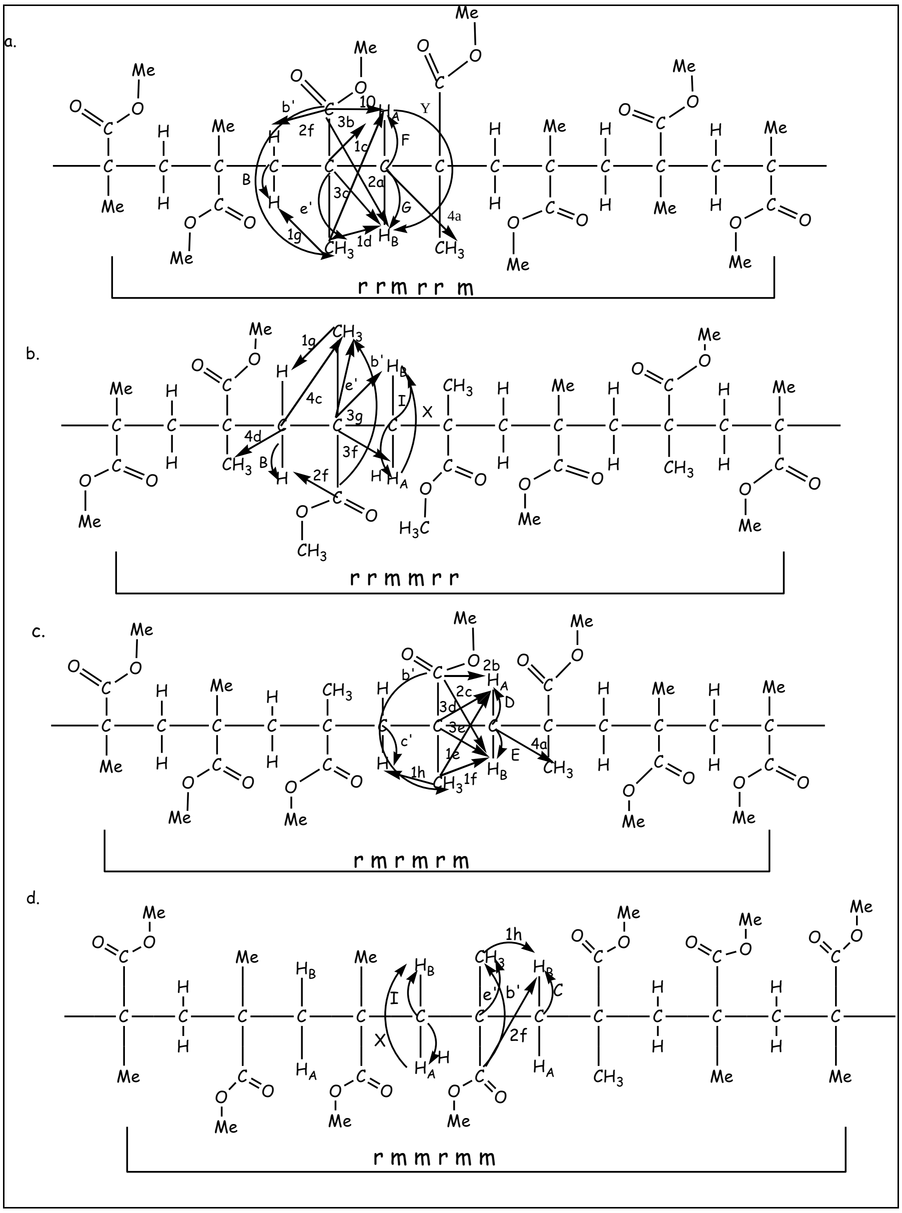


Figure 4.1: Expanded ^{13}C NMR spectra of: (a) α-methyl carbon, (b) quaternary carbon, (c) methylene and methoxy region, (d) carbonyl carbon region

As shown in Figure 4.1(d), the fourth region from 176.5-179.0 *ppm* is assigned to carbonyl carbon. Three sets of resonances for carbonyl carbon were observed from 176.3-176.6, 177.0-177.4 and 177.9-178.7 *ppm* and were assigned as *mm, rm/mr* and *rr* triads respectively. The peaks at 176.3, 176.4 and 176.6 *ppm* assigned to *rmmr, mmmr/rmmm* and *mmmm* pentads on splitting by the *mm* triads were observed. As the same peaks for *rrrr, rrrm/mrr* and *mrrm* pentads of centered *rr* were observed at 178.0, 178.3 and 178.6 *ppm* respectively. The *mmrr/rmrr and mmrm*+*rmrm* pentads of centered *mr* triads with the different intensities were observed at 177.2 and 177.3 *ppm*.



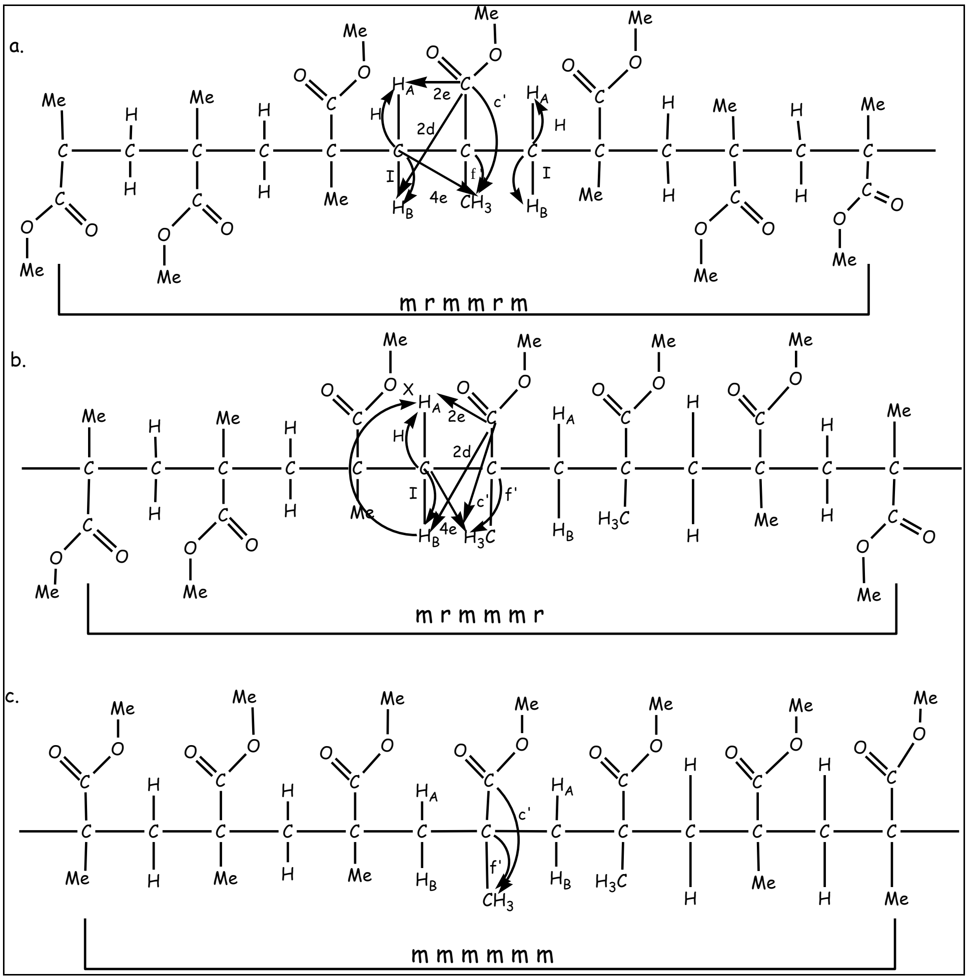
Scheme 4.1: Schematic representation of couplings in pentads with *rr* centered [227(a)]



Scheme 4.2: Schematic representation of couplings in pentads with *mr* centered [227(a)]

Researchers have already discussed about the assignments of carbon of methylene group and reported about the order of the tetrads, that tetrads will have *rrr*, *rmr, mrr,mmr, mrm* and *mmm* order from high to low chemical shift.[227] HSQC provides correlation between carbon and its attached protons.

In PMMA, methylene proton depends on diad of repeating unit. There are two similar protons of methylene of *r* diad due to same environment of functional group. Therefore, there will be only one crosspeaks in 2D HSQC between methylene carbon and protons. But in case of *m* diad methylene protons will be different to each other due to different environment of functional groups. Therefore, in 2D HSQC two crosspeaks will be observed between methylene carbon and its corresponding attached protons.



Scheme 4.3: Schematic representation of couplings in pentads with *mm* centered [227(a)]

4.4.1. 2D HSQC study:

The coupling of methylene region covering carbon resonances and proton resonances ranging from 51.0-54.5 *ppm* and 1.4-2.2 ppm is showed in the 2D HSQC spectrum Figure 4.2. Direct attached carbon with protons (^{13}C-^{1}H) couplings between methylene carbon and proton are labelled from *A* to *I* in Schemes (1, 2 and 3) which resulted to corresponding crosspeaks shown in Figure 4.2.

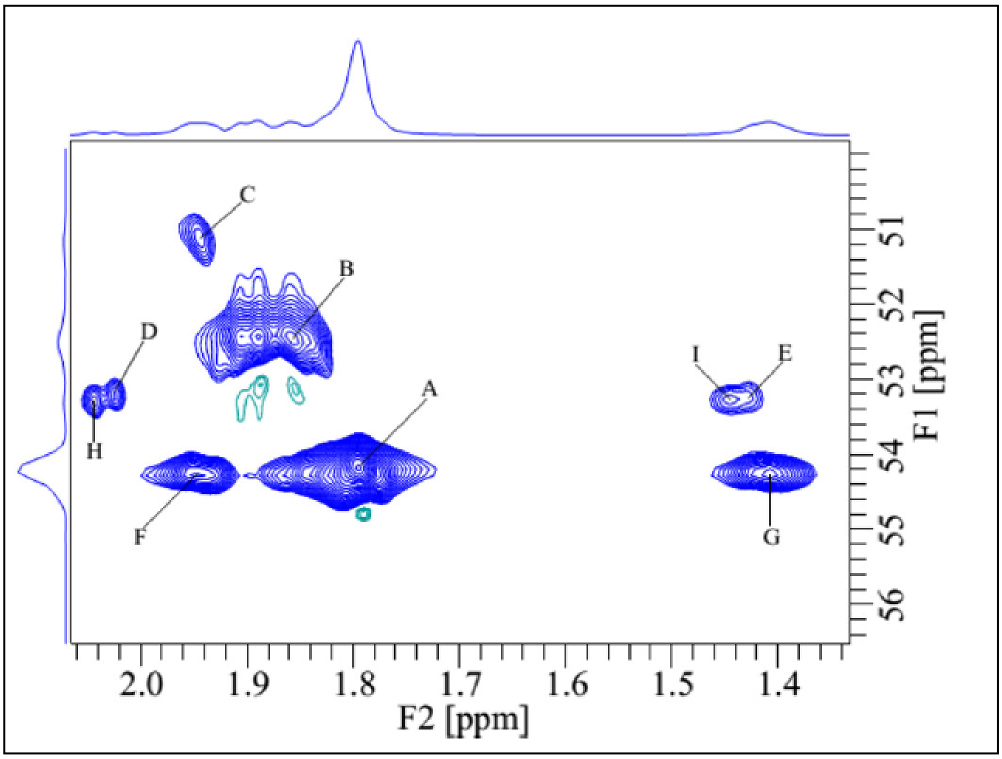


Figure 4.2: The HSQC NMR spectrum of methylene region of PMMA.

In Figure 4.2, crosspeaks between methylene carbon and its protons *A* [as shown in Scheme 4.1(a) and 4.1(b)], proton *B* [as shown in Scheme 4.1(b), 4.1(c), 4.2(a) and 4.2(b)] and proton C [as shown in Scheme 4.2(c) and 4.2(d)] are seen. Crosspeaks of couplings *D* and *E* [Scheme 4.2(c)] and *F* and *G* [Scheme 4.2(a)] observed for *rmr* tetrad and coupling *D/E* and *E/F* were assigned to H_A and H_B protons, respectively. The couplings *H* and *I* were assigned to H_A and H_B of *mmr* tetrad [Scheme 4.2(b) and 4.2(d)] and [Scheme 4.3(a) and 4.3(b)].Crosspeaks *H* and *I* due to these couplings in 2D HSQC are shown in Figure 4.2.

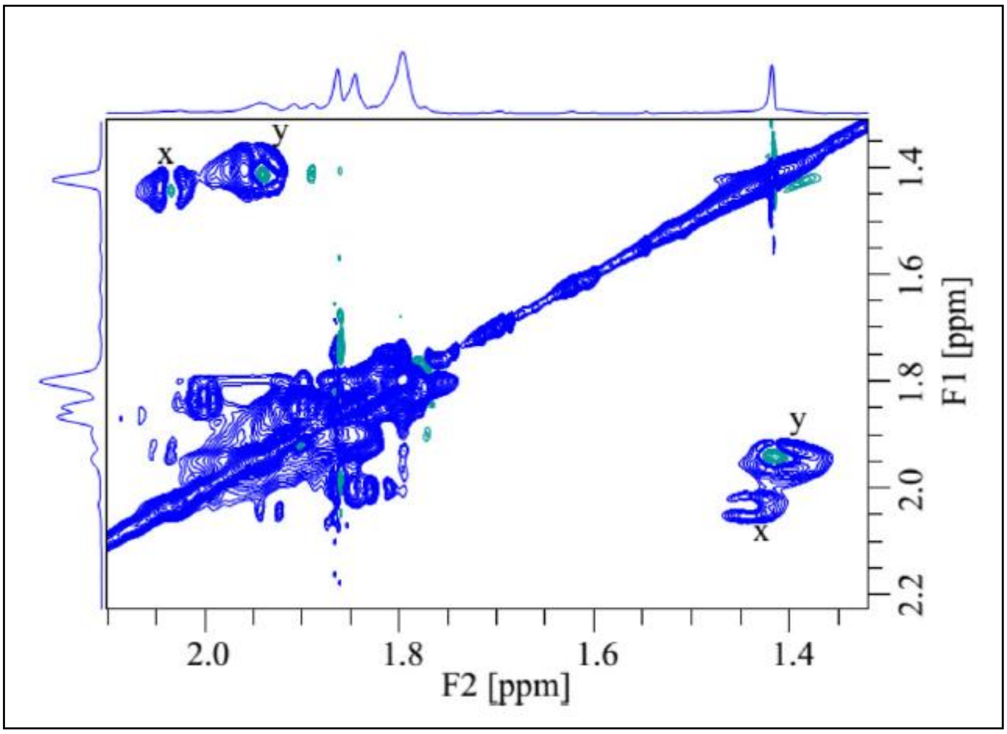


Figure 4.3: 2D TOCSY spectrum presenting couplings of protons with *m* centered methylene tetrads in PMMA

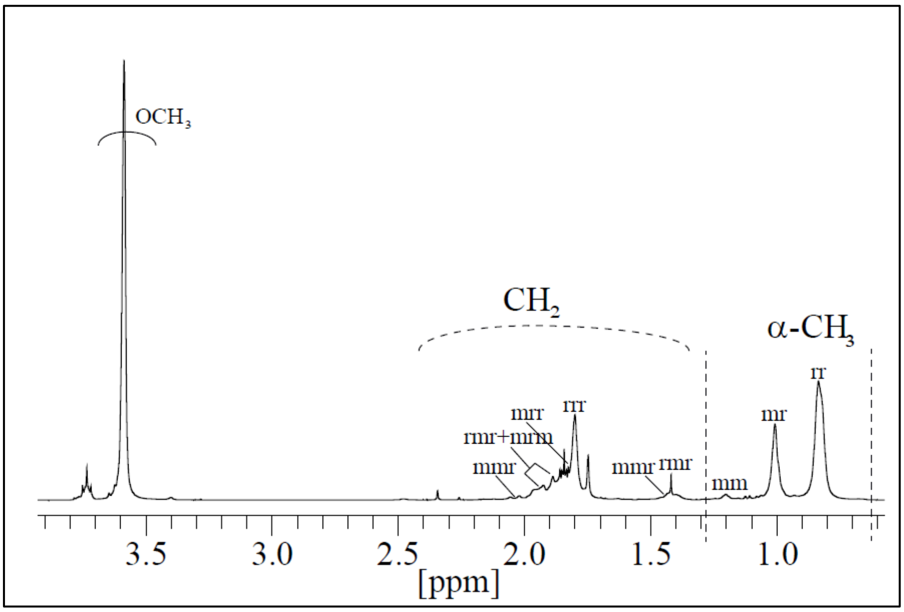


Figure 4.4:^{1}H NMR spectrum showing methylene and *α*-methyl protons of PMMA.

4.4.2. 2D TOCSY and HMBC study:

In 2D TOCSY spectrum two cross-correlation peaks are observed labelled as ‘Y’ between non-equivalent protons and the other labelled as ‘X’ is the result of another nonequivalent proton shown in Figure 4.3. The assignments of different interactions in the 2D TOCSY and HMBC NMR for ^{13}C-labeled PMMA have been found consistent with some earlier reports.

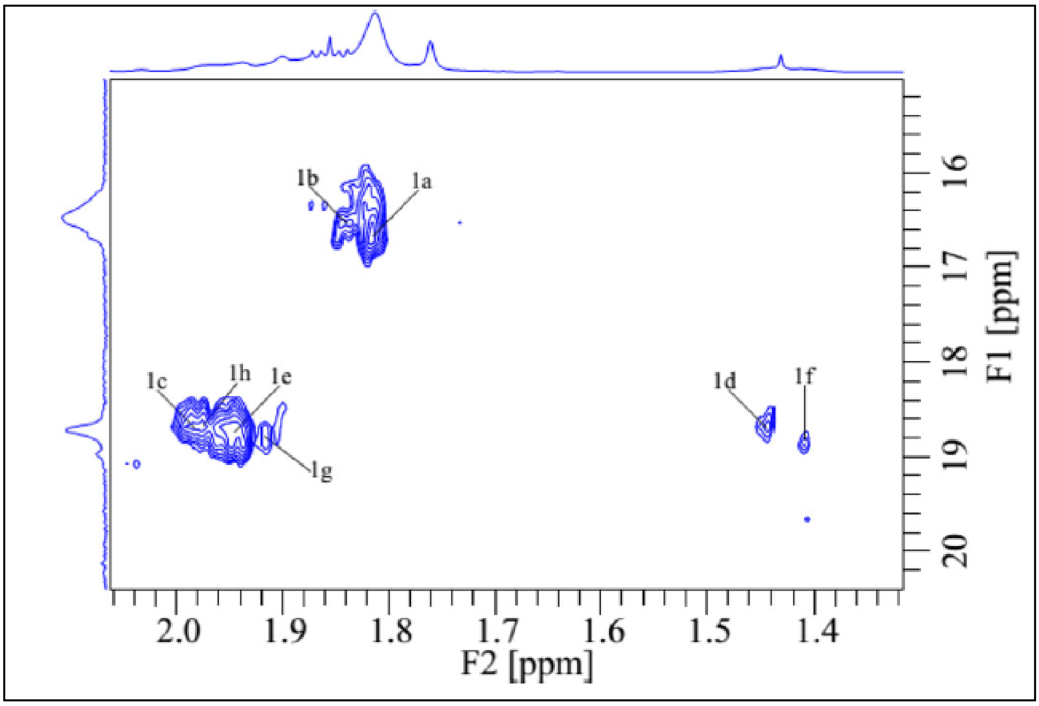


Figure 4.5: 2D HMBC spectrum presenting three bond couplings between α-methyl carbon and methylene protons.

2D HMBC NMR experiment is a very useful method to study tacticity in high molecular weight polymer by extracting stereo chemical information.[237] This technique gives crosspeaks between carbon and proton that are separated by two, three and sometimes four bonds (in conjugated systems). The HMBC NMR spectrum of PMMA is shown in Figure 4.5 and shows the couplings between carbon of α-methyl group and protons of methylene groupof the molecule. Crosspeak *1a* is assigned to the coupling *1a* [Scheme 4.1(a)] between carbon of α-methyl group of *rr*-triad with protons of methylene group of *rrr* tetrad and crosspeak *1b* [Scheme 4.1(b)] and [Scheme 4.1(c)] for the coupling *1b* between *rr* of

α-methyl carbon and *mrr* of methylene. The two resonance signals of triad *mr* is shown in Figure 4.1(b) and further *mmrm* and *rrmr* pentads were assigned to signals at high and low chemical shift by comparing intensities of the signals.[221] The correlations between α-methyl carbon and methylene protons are very similar to those reported in the previous HMBC NMR result.[227, 237]

In the 2D HMBC spectrum, the couplings *1e* and *1d* shown in Scheme 4.2(a) and couplings *1d* and *1f* shown in Scheme 4.2(c) corresponds to crosspeaks *1e* and *1d*, and crosspeaks *1e* and *1f* observed at low and high chemical shift signal. Further Brar et. al. assigned the crosspeak 3, crosspeak 4, crosspeak 5 and crosspeak 6 to methylene of *rmr* tetrads by correlating HSQC and TOCSY spectrum. The crosspeaks *1g* shown in Scheme 4.2(a) and Scheme 4.2(b) is for the coupling between *mr* carbon of α-methyl group with *mrr* proton of methylene groupand the crosspeaks *1h* Scheme 4.2(c) and Scheme 4.2(d) is assigned to *mrm* methylene.

Figure 4.6 shows the 2D HMBC spectrum of 3 bonds coupling of carbon of carbonyl group with protons of α-methyl group and with adjacent protons of methylene group. The coupling *a′* corresponding to crosspeak *a′* between protons of α-methyl group of *rr* triad with *rr* triad of carbonyl carbon is shown in Scheme 4.1 and the couplings *b′* and *c′* for *mr* and *mm* triads shown in Scheme 4.2and Scheme 4.3corresponds to crosspeaks *b′* and *c′*.

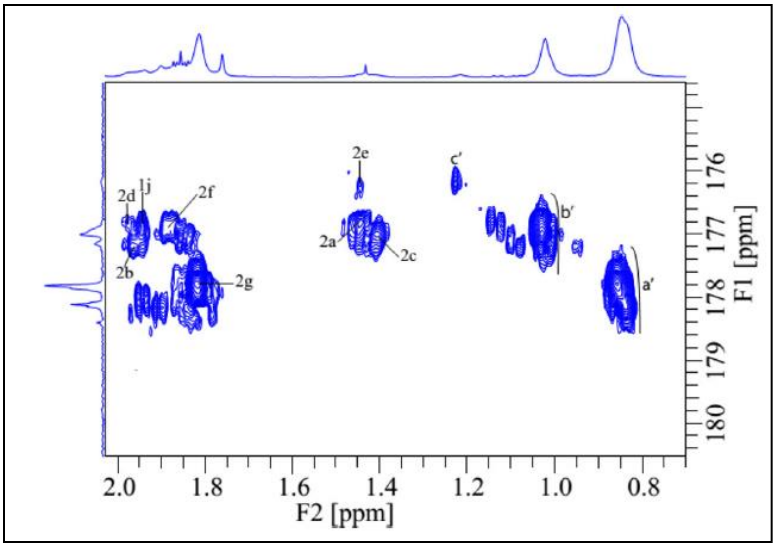


Figure 4.6:2D HMBC spectrum presenting couplings of: (i) methylene protons with carbonyl carbon and (ii) α-methyl protons with carbonyl carbon.

The couplings *1j* and *2a* (Scheme 4.2(a)) and couplings *2b* and *2c* (Scheme 4.2(c)) were assigned for *rmr* tetrad of *rmrr* and *rmrm* pentad based on the argument done by Brar et. al.[227] The couplings *1j*, *2a*, *2b* and *2c* correspond to crosspeaks *1j*, *2a*, *2b* and *2c* shown in Figure 4.6. Coupling *2f* (Scheme 4.2(a) and Scheme 4.2(b)) between carbon of carbonyl group of *rrmr* or *mmrr* pentad and protons of methylene group of *mrr* tetrad corresponds to crosspeak *2f*. Couplings *2d* and *2e* shown in Scheme 4.3(a) and Scheme 4.3(b) and coupling *2g* (Scheme 4.1(a)) corresponds to crosspeaks *2d*, *2e* and *2g*.

Figure 4.7 shows the 2D HMBC spectrum of PMMA. It shows couplings between carbon of quaternary and methylene group and protons of *α*- methyl group. Couplings *d′*, *e′* and *f′* (Scheme 4.1-4.3) of the carbon of quaternary group with *rr*, *mr* and *mm* triads with protons of *α*- methyl group, respectively corresponds to crosspeaks *d′*, *e′* and *f′*.
Crosspeaks *3a,3b,3c,3d,3e,3f* and *3g* corresponds to couplings *3a,3b,3c,3d,3e,3f* and *3g* between quaternary carbon and methylene proton for different assignments of proton H_A and H_B of methylene. Coupling *3a* is shown in Scheme 4.1(a), 4.3(a) and 4.3(b) in Scheme 4.2(a), couplings *3d* and *3e* in Scheme 4.2(c) and couplings *3f* and *3g* in Scheme 4.2(b).

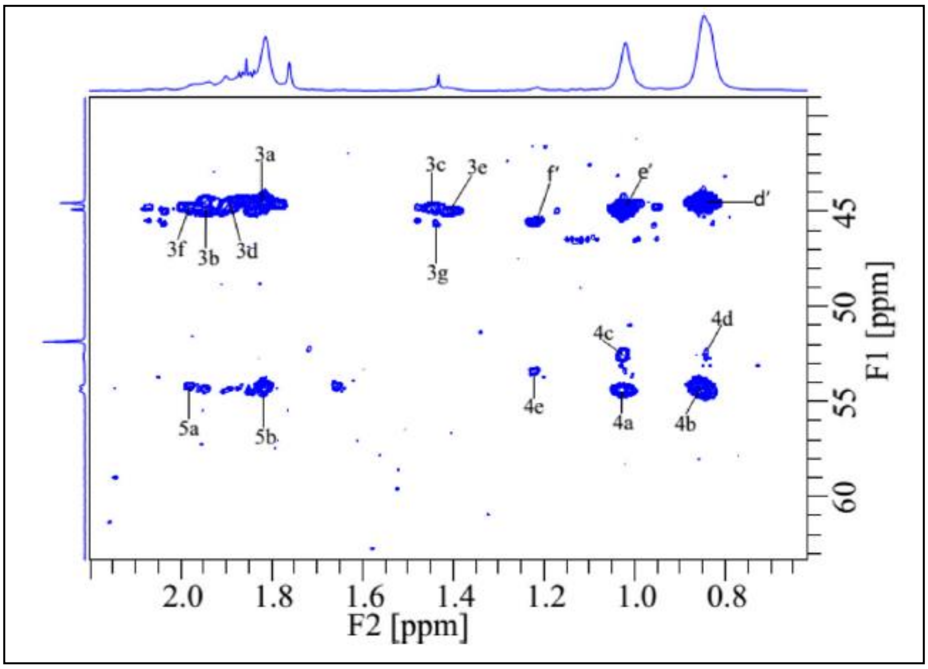


Figure 4.7: 2D HMBC spectrum presenting couplings of: (i) quaternary carbon with methylene protons and (ii) *α*-methyl protons and methylene carbon with *α* -methyl protons and adjacent methylene carbon.

In Figure 4.7 shows the couplings of α- methyl protons with methylene carbon. The crosspeaks *4a* (as shown in Scheme 4.2(a) and 4.2(c)), *4b* (as shown in Scheme 4.1(a)), *4c* and *4d* (shown in Scheme 4.2 (b)) and *4e* (shown in Scheme 4.3(a) and 4.3(b)) corresponds to coupling *4a*, *4b, 4c*, *4d* and *4e*. The crosspeaks *4a* and *4b* are assigned to interaction of *rmr* and *mrr* of methylene carbon with α- methyl protons in *mr* configuration. While crosspeaks *4d* and *4e* are assigned to interaction of carbon of methylene group with *mrr* and *mmr* tetrad with protons of α- methyl group with *rr* and *mm* diad configuration, respectively. The crosspeak *5a* is due to the interaction of either *rrr* or *rmr* tetrad carbon with *mrm* tetrad proton, thus it is not assigned particularly or the crosspeak *5b* is assigned to interaction of *rrr* carbon with *rrr* methylene tetrad, respectively. The crosspeaks obtained and discussed were similar to that obtained by Brar and Kawamura.[238]

4.5. Conclusion:

The different techniques of 2D NMR spectroscopy helped to assign the different arrangements of the repeating unit along the polymer chain. ^{1}H NMR spectra alone cannot give complete information due to presence of multiple peaks of broad range and therefore, along with ^{1}H NMR, ^{13}C NMR spectra were also carried out to study the complete structure of the polymer, PMMA. 2D NMR spectra (TOCSY and HSQC) were recorded to assign the different proton attached to methylene carbon. HMBC spectra helped to assign the couplings between ^{13}C of α-methyl and ^{1}H protons of methylene group. The spectra recorded was seen to be similar to the one recorded for PMMA prepared via conventional FRP, except the crosspeaks for coupling between *mr* triad of α-methyl protons with *mrm* tetrad methylene, coupling between ^{13}C of methylene group of *mrr* tetrad with protons (H_A and H_B) of *rmr* tetrad and coupling between ^{13}C of methylene group of *mrr* tetrad with *rrr* proton in the *mrrr* pentad were not found in our prepared homopolymer PMMA via ARGET-ATRP. Hence, 2D NMR spectrum was found to be helpful to study the homopolymer of PMMA prepared via ARGET-ATRP.