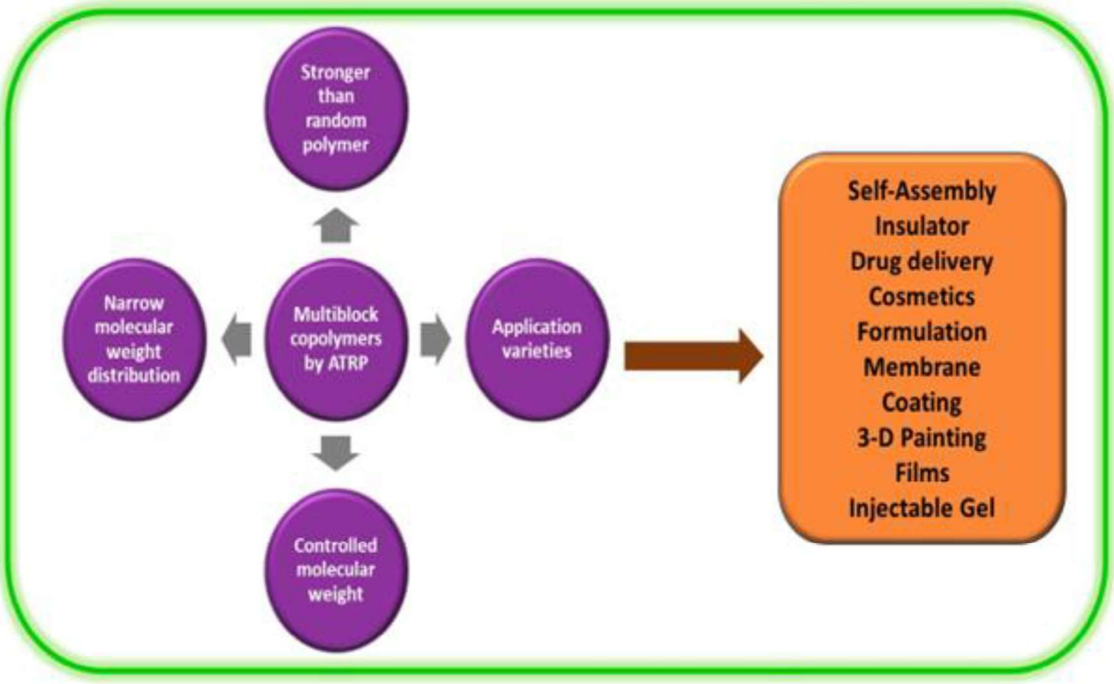
Chapter 2

Scope of study of multiblock copolymers via Atom Transfer Radical Polymerization Technique



2.1 Experimental section

2.2. Materials and methods

The monomer styrene (Sigma Aldrich, 99%) was washed with a 5% NaOH solution, washed with distilled water, passed through activated neutral and basic alumina to remove inhibitors, and then dried overnight with a molecular sieve. Same as MMA (Aldrich, 99% (USA)) and tBA (Aldrich, 99%) was passed through activated alumina and dried it overnight. DMDBHD (Sigma Aldrich, 97%) was obtained from Aldrich and used without further purification, PMDETA (Sigma Aldrich, 99%), and CuBr (Sigma Aldrich, 99%) was washed with glacial acetic acid, ethanol, diethyl ether respectively. The purity of the final product was 99%, and process of vacuum drying will begin. Toluene as a solvent (99.5%, Sigma Aldrich) was purified under reduced pressure and passed through a molecular sieve overnight. THF (LOBA CHEMIE, 99.8%) and methanol were used as received, as were all other reagents.

2.2.1. FT-IR

The method is based on the observation that chemical compounds exhibit significant selective infrared absorption. The molecules of chemical substances vibrate at various rates after absorbing IR radiation, generating a closely packed absorption band known as the IR absorption spectrum. This spectrum corresponds to the distinctive functional group and bond present in chemical substances. As a result, a chemical substance's IR spectrum serves as a fingerprint for identification. The KBr pellet approach was used to perform FT-IR on an 8400 s SHIMADZU spectro-photometer during scanning at wavelength range of 4000-400 cm^{-1} at 28°C.

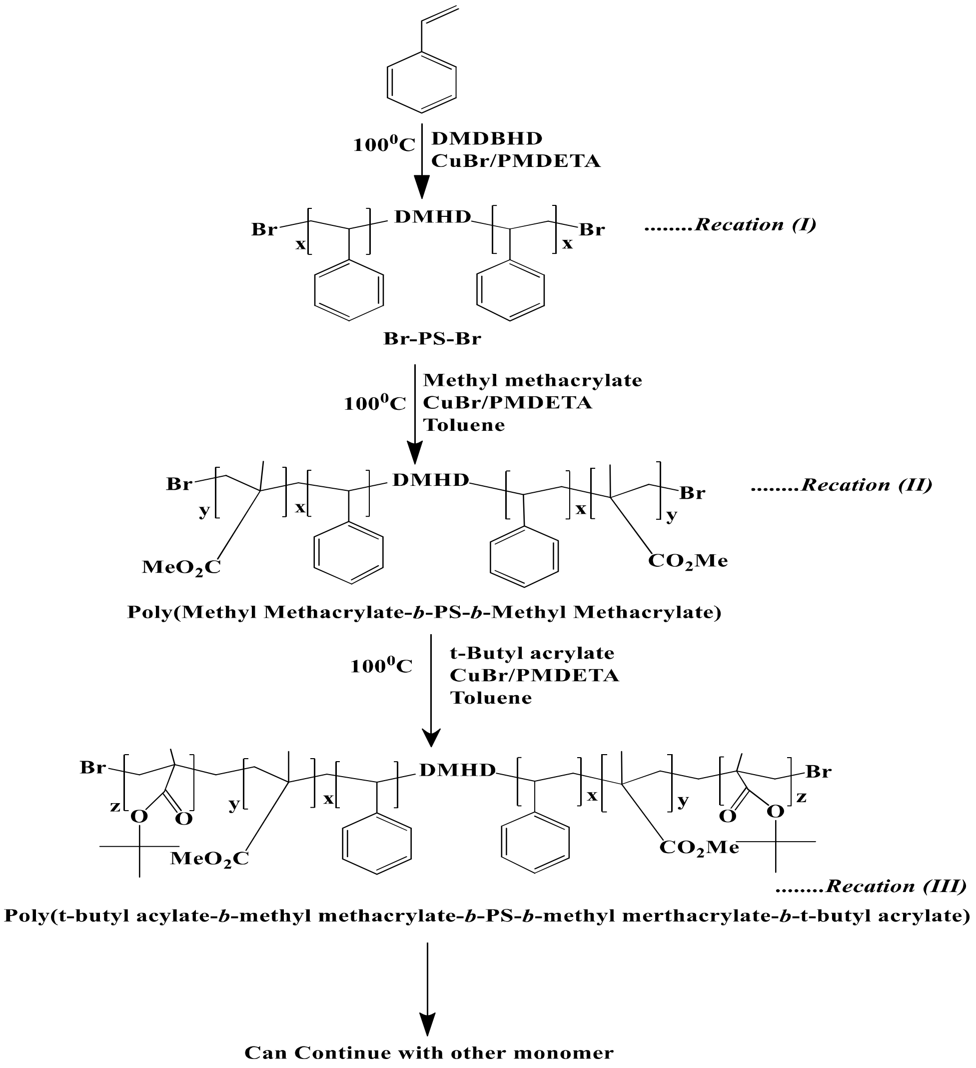
2.1.1. Synthesis of bi-functional bromo-terminated polystyrene (Macroinitiator)

In the synthesis of di-functional bromo-terminated polystyrene (macroinitiator) PMDETA was used as a ligand and copper as a catalyst. Styrene contains 4-Methoxyphenol (MEHQ) as an inhibitor which inhibits polymerization reaction of styrene, so it was important to remove inhibitor first. The inhibitor was removed by washing styrene with 5% aqueous solution of sodium hydroxide (NaOH) in separating funnel. The organic layer was collected and passed through basic alumina column (pH>8). 3 vials were cleaned with distilled water and dried. Vial 1 contained purified Copper(I)Bromide (CuBr) catalyst, vial 2 contained styrene(monomer)+PMDETA(ligand) and vial 3 contained ligand (PMDETA) with solvent as a toluene. Here the synthesis was based on solution ATRP because it provides good media and regulates overall conditions. All the 3 vials were kept under inert atmosphere using argon balloon for 15 minutes to expel out all the oxygen present in the vials. CuBr was used as a catalyst and was first purified before use.

Purification of catalyst

CuBr was taken on a filter paper on a funnel. The catalyst was washed with glacial acetic acid followed by alcohol and then with acetone for 3-4 times till the colorless liquid emerges out from the funnel end. The CuBr obtained was then taken for the reaction. Heated the CuBr vial with magnetic stirrer in oil bath for 15 mins under argon atmosphere. Now add the solution of vial 2 to vial 1 through cannula tube followed by subsequent adding of vial 3 to vial 1. Heated the mixture to 100°C for 4-5 hours. The hot green solution of vial obtained after the reaction was dissolved in 50 mL of tetrahydrofuran (THF) and passed through alumina column. Product was then heated to evaporate maximum THF. The resultant solution was taken in an additional funnel, then the solution was poured dropwise in the beaker containing methanol. Solid white precipitates are observed which were collected and then purified. The product was redissolved in THF and then reprecipitated in methanol then dried and this process was repeated 3-4 times. The purified product was then made completely dry. Figure 2.1 illustrates the general laboratory setup for the synthesis of multiblock copolymers by ATRP, and all the required calculations and materials are given in Table 2.1.

Figure 2.1 Laboratory setup for the ATRP system.



Scheme 1 Synthesis of reaction (I) is for Br-PS-Br, reaction (II) is for PMMA-*b*-PS-*b*-PMMA, reaction (III) for PtBA-*b*-PMMA-*b*-PS-*b*-PMMA-*b*-PtBA.

Table 2.1 Preparation of bi-functional polystyrene and require materials.

Materials required	role	Volume (ml)	Quantity (g)	MW (g/mol)	moles	Mole ratio
Styrene	monomer	10	9.09	104.5	0.087	20
DMDBHD	initiator	0.94	1.50	346	0.00435	1
CuBr	catalyst	-	0.62	143	0.00435	1
PMDETA	ligand	1.35	1.505	173	0.0087	2

The final product from the overall reaction mixture was 7.59g.

% conversion = weight of product obtained / weight of a starting product x 100

= 7.59/9.09

= 0.834

83%

M_n theoritical = I + [M]/I x M.W of monomer x conversion

Mn = 346 + 20/1 x 104.5 x 0.834

M_n theoritical = 2080

2.1.2. Synthesis triblock copolymer: PMMA-*b*-PS-*b*-PMMA

The synthesized Br-PS-Br was used for the next synthesis of triblock copolymer (PMMA-*b*-PS-*b*-PMMA) as a macroinitiator. In which CuBr as a catalyst, PMDETA as a ligand and toluene use for proving media of the reaction mixture at 100°C. The calculations and required materials are given in Table 2.2.

Table 2.2 Preparation of triblock copolymer and require materials

Materials required	role	Volume (ml)	Quantity (g)	M_w(g/mol)	moles	Mole ratio
Polystyrene	Macroinitiator	-	2	2080	0.00096	1
MMA	Monomer	10	9.6	100.12	0.096	100
CuBr	Catalyst	-	0.14	143	0.00096	1
PMDETA	Ligand	0.39	0.33	173	0.0019	2

The final product from the overall reaction mixture was 3.4g

% conversion = weight of product obtained / weight of a starting product x 100

= 3.4/9.6

= 0.34

34%

M_n theoritical = I + [M]/I x M.W of monomer x conversion

M_n = 2080 + 100/1 x 100.12 x 0.34

M_n theoritical = 5484

2.1.3. Synthesis of pentablock copolymer: PtBA-*b*-PMMA-*b*-PS-*b*-PMMA-*b*-PtBA

At last, these synthesized triblock copolymer (reaction (II)) worked as a macroinitiator and t- butyl acrylate is the monomer for the next synthesis. All the reaction conditions was same as the reaction (I, AND II). The preparation of pentablock copolymer and require materials given in Table 2.3.

Table 2.3 Preparation of pentablock copolymer and require materials

Materials required	role	Volume (ml)	Quantity (g)	M_w(g/mol)	moles	Mole ratio
t-butyl acrylate	monomer	10	7.0	128.17	0.054	100
Triblock copolymer	macroinitiator	-	3	5484	0.00054	1
CuBr	catalyst	-	0.07	143	0.00054	1
PMDETA	ligand	0.22	0.18	173	0.0010	2

The final product from the overall reaction mixture was 4.0g

% conversion = weight of product obtained / weight of a starting product x 100

= 4.0/7.0

= 0.57

57%

M_n theoritical = I + [M]/I x M.W of monomer x conversion

M_n = 5484 + 100/1 x 128.17 x 0.57

M_n theoritical = 12789

2.2.2. ^{1}H NMR

NMR technique has become the prominent technique for determining the structure of organic compounds. Of all the spectroscopic methods, it is the only one for which a complete analysis and interpretation of the entire spectrum is normally expected. ^{13}C and ^{1}H spectra from BRUKER 400 MHz, all samples were performed under $CDCl_3$ solvent by complete dissolution of the polymer.

2.2.3. GPC

GPC is a form of SEC that uses size to separate analytes. The method is frequently used for polymer analysis. When describing polymers, the PDI as well as the molecular weight must be taken into consideration. PLgel Mixed-B column with pore size of 10 m and refractive index

RI detector at a flow rate of 1 ml min^{-1} are used to perform GPC using equipment from the Agilent 1200 Infinity series. when the temperature is 40°C. All the samples were taken 1 mg and dissolved as in High-Performance Liquid Chromatography (HPLC) grade of THF.

2.2.4. TGA

TGA is a type of thermal analysis in which the mass of a sample is measured as the temperature changes over time. The SDT Q600 V20.9 Build 20 equipment was used to analyze polymeric samples in an enclosed environment at a heating rate of 10°C/min.

2.3. Results and Discussion

FTIR is one of the very useful analytical tools to detect the presence of certain functional groups and identify organic materials. In the Figure 2.2 shows the Br-PS-Br band exhibits C-H stretching between 2800 and 3000 cm^{-1} and C-H bending (methyl group) at 1448 cm^{-1}. The end group bromine (C-Br) band is at 698 cm^{-1}, and the ester group is confirmed at 1732 cm^{-1}.

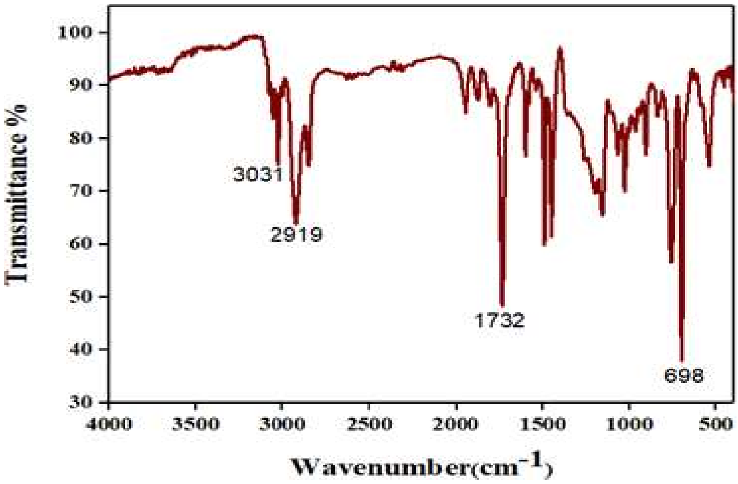


Figure 2.2 FT-IR spectra of Br-PS-Br (polystyrene as homopolymer).

For the synthesis of PMMA-*b*-PS-*b*-PMMA, the stretching of ester and C-H group at 1730-1750 cm^{-1}, 2800-3000 cm^{-1} respectively. Bending of methyl group at 1448 cm^{-1} given in Figure 2.3. The C=O stretching in Figure 2.4. Shows at around 1732 cm^{-1}, -CH_3 stretching vibration at 2940 cm^{-1} and 971 cm^{-1} gives the end group (halogen) functional group. These graphs are the clear indications of the functional group which are present in the synthesized pentablock copolymer.

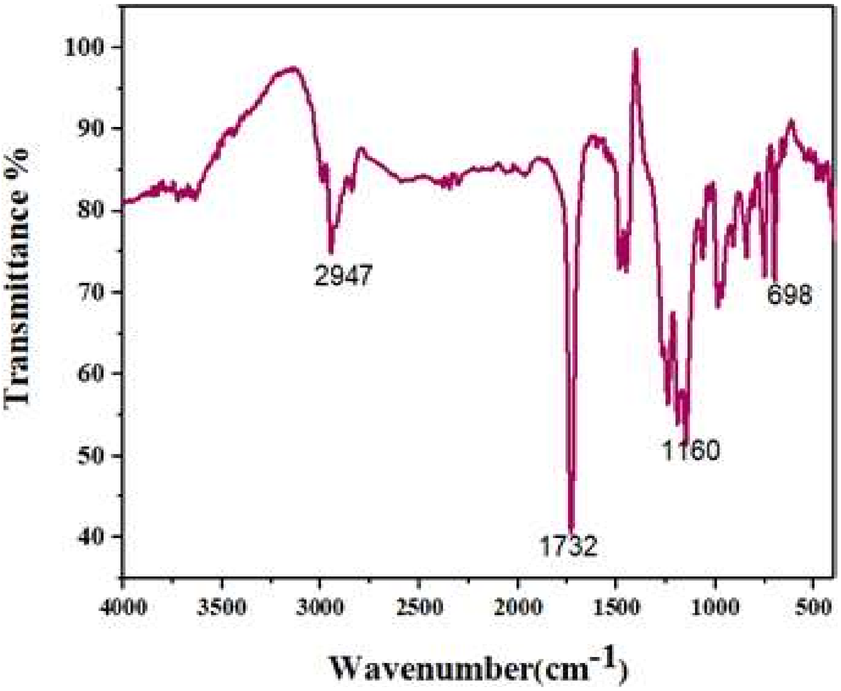


Figure 2.3 FT-IR Spectra of PMMA-b-PS-b-PMMA.

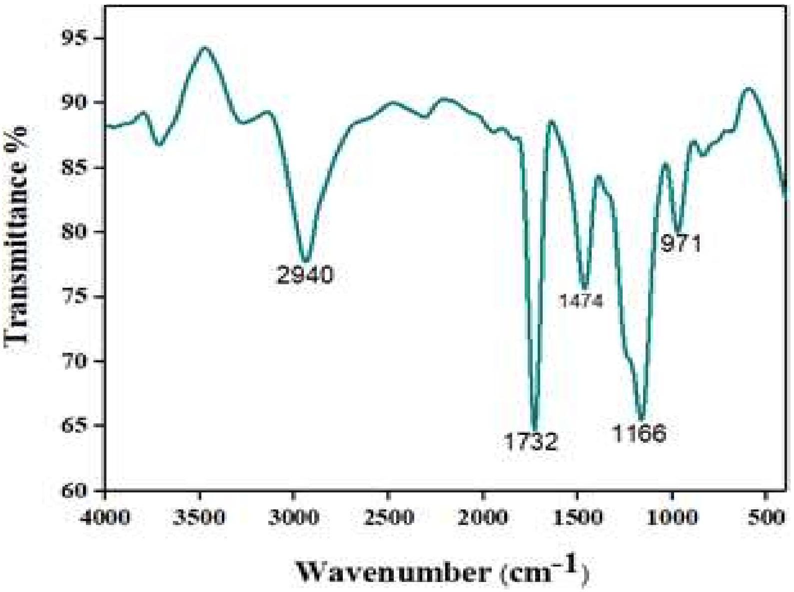


Figure 2.4 FT-IR Spectra of PtBA-*b*-PMMA-*b*-PS-*b*-PMMA-*b*-PtBA.

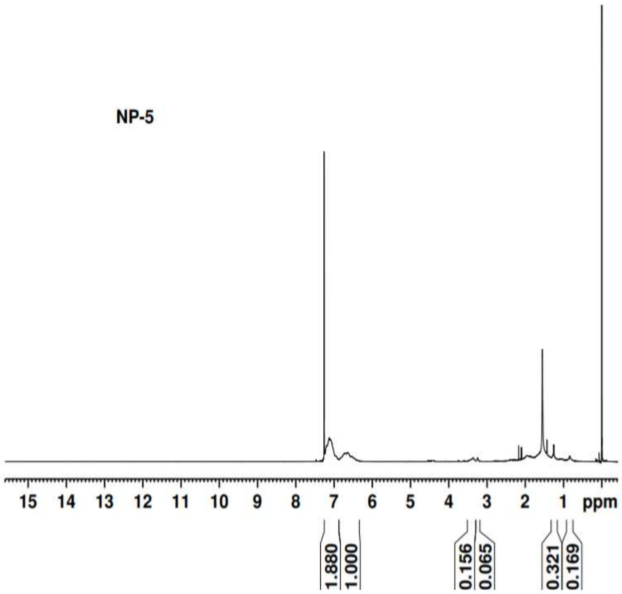


Figure 2.5 ^{1}H NMR Spectra of Br-PS-Br.

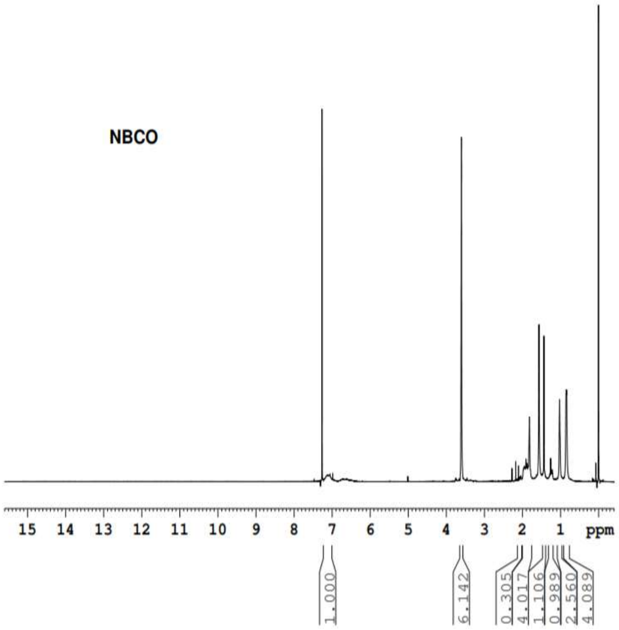


Figure 2.6. ^{1}H NMR Spectra of PMMA-*b*-PS-*b*-PMMA.

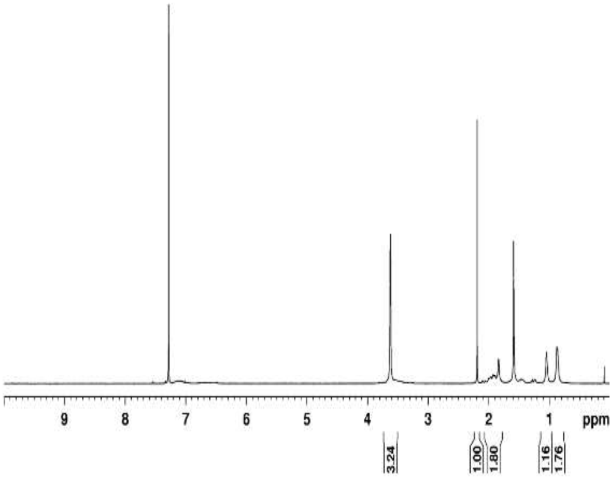
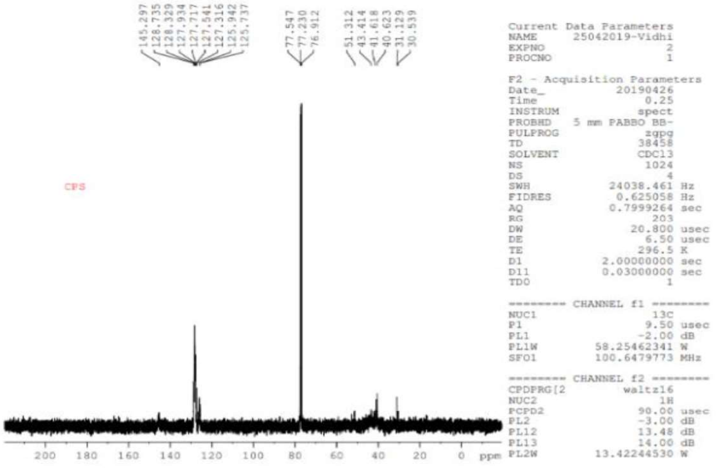


Figure 2.7. ^{1}H NMR Spectra of PtBA-*b*-PMMA-*b*-PS-*b*-PMMA-*b*-PtBA.

Here, in Figure 2.5 the aromatic protons of polystyrene are attributed at 6.5 to 7.2 ppm. The signals of Methylene (-CH_2) group gives chemical shift at 1.4 ppm and 1.2 to 2 ppm for methyl proton. The triblock copolymer in $CDCl_3$ showed a signal at 3.7 ppm for -OCH_3 group of PMMA, methyl protons (-$C(CH_3)OCH_3$) appears the signals at 0.8 to 1.9 ppm and methylene group at 1.6 ppm. According to the ^{1}H NMR spectra, the polymer chain and MMA have completely bonded during synthesis given in Figure 2.6. The methyl proton of -$C(CH_3)(COOC_4H_9)$ and -$O(CH_2)_3CH_3$ attributing the signals at 0.8-1.1 ppm and methylene group revealing the signal at 1.6 ppm in Figure 2.7. ^{1}H NMR spectra gives the confirmation of Polystyrene (PS), PMMA and Poly(t-butyl acrylate) (PtBA) successfully bounded linearly in polymeric chain.



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PL13                 14.00 dB
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Figure 2.8. ^{13}C NMR Spectra of Br-PS-Br.

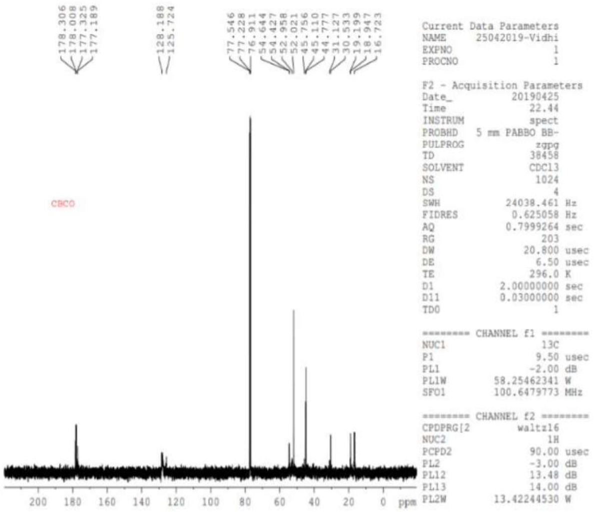

Figure 2.9. ^{13}C NMR Spectra of PMMA-*b*-PS-*b*-PMMA.

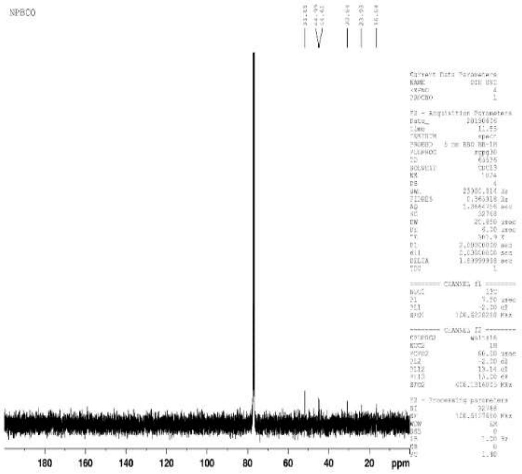

Figure 2.10. ^{13}C NMR Spectra of PtBA-*b*-PMMA-*b*-PS-*b*-PMMA-*b*-PtBA.

The aromatic ring of polystyrene given the spectra at 130 ppm in Figure 2.8, while in Figure 2.9 shows the $R_2C=O$ at 178 ppm for PMMA and C-O group at 50 ppm in Figure 2.10 appears the carbon schalaton which are the strong avidence of the successfully atachment of the pentablock copolymer.

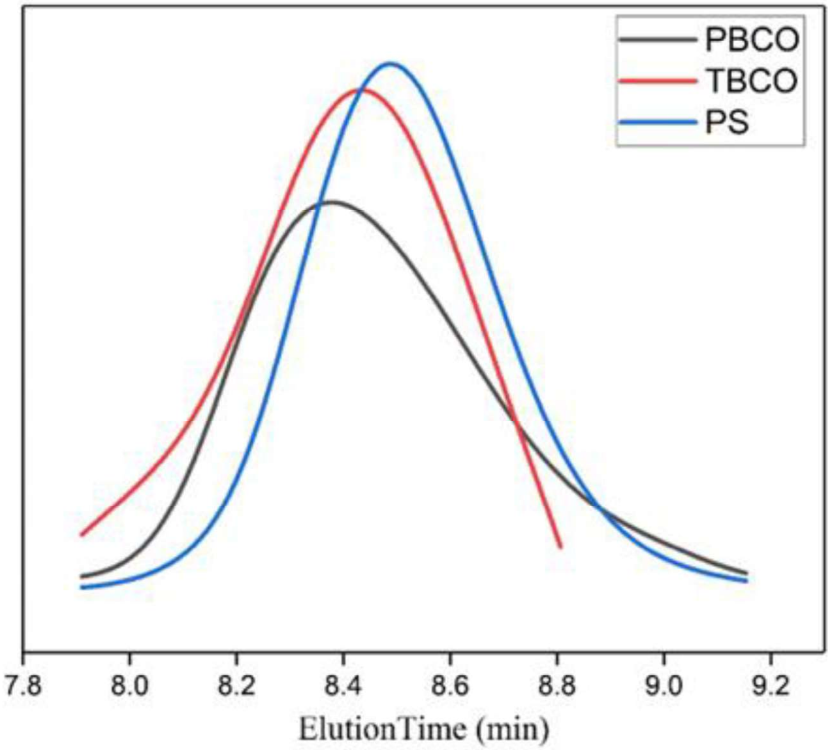

Figure 2.11. GPC thermograph of Br-PS-Br, PMMA-*b*-PS-*b*-PMMA, PtBA-*b*-PMMA-*b*-PS-*b*-PMMA-*b*-PtBA.

GPC traces for the progress of ATRP reaction of Br-PS-Br is in Figure, The molecular weight of the macroinitiator was , Number Average Molecular Weight (M_n)=2134 g/mol, and PDI is 1.19 which is denoted by blue line in Figure 2.11. As the number of monnomers are added to the homopolymer the Mn will increased linearly. Triblock copolymer peak shifted to higher moleculer weights with monomer conversion are single peak that confirmed that the product is the PMMA-*b*-PS-*b*-PMMA block copolymer M_n=3138 g/mol, M_w/M_n=1.2. At last the progress of ATRP reaction of PtBA-*b*-PMMA-*b*-PS-*b*-PMMA-*b*-PtBA is in Figure 2.11, The molecular weight of the final product is, M_n=12572 g/mol, and M_w/M_n =1.3. The given below is Figure 2.12 is the plot of three different plot of polymers such as Br-PS-Br, PMMA-*b*-PS-*b*-PMMA and PtBA-*b*-PMMA-*b*-PS-*b*-PMMA-*b*-PtBAwhich gives the value of M_n from the theoritical and from GPC are very near to each other with linear increse the monomeric chain.

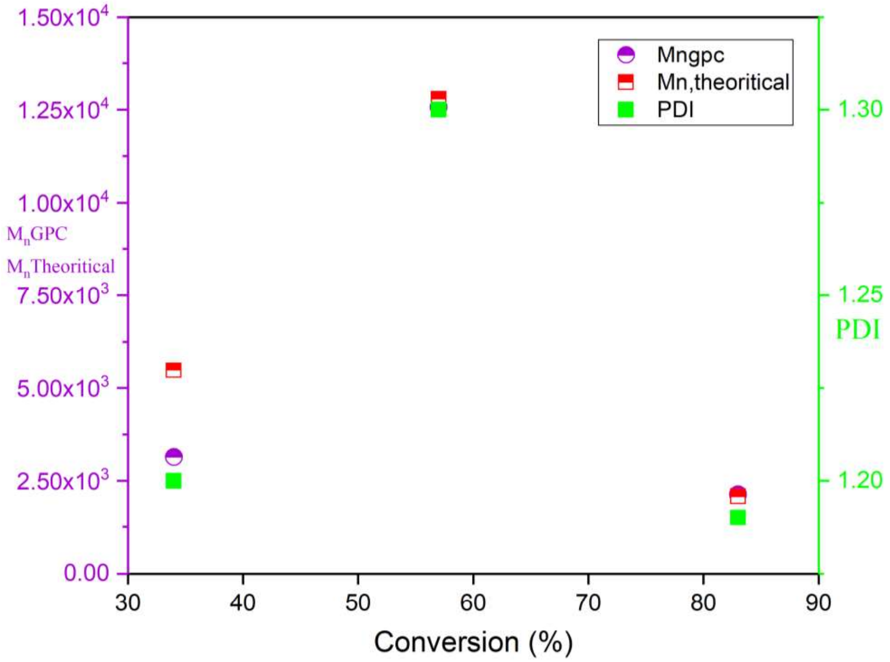

Figure 2.12. Plot of variation of molecular weight and PDI with conversion for all three polymers.

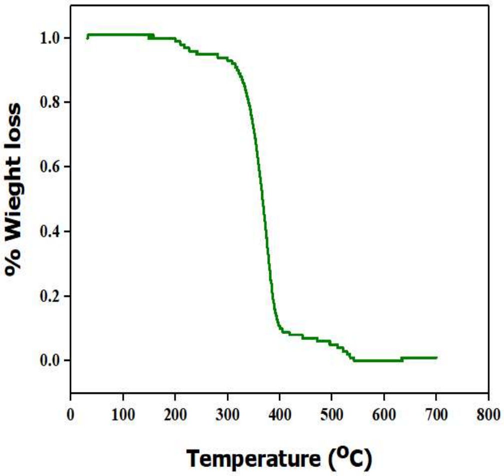

Figure 2.13. TGA plot of Br-PS-Br.

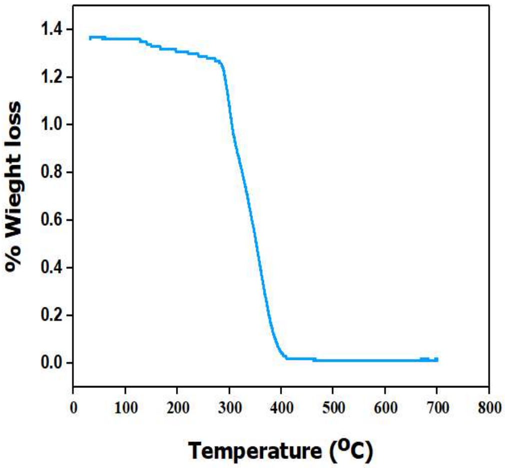

Figure 2.14. TGA plot of PMMA-*b*-PS-*b*-PMMA.

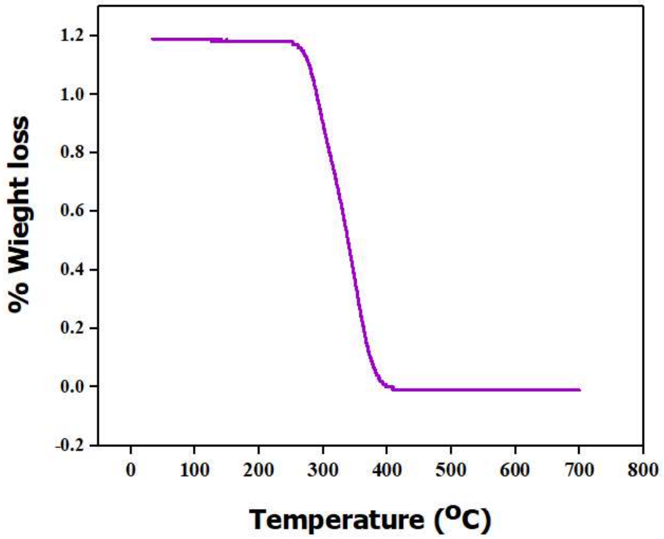

Figure 2.15. TGA plot of t-PBA-*b*-PMMA-*b*-PS-*b*-PMMA-*b*-t-PBA.

TGA curve of-Br PS-Br shows degradation of PS chain start at 200°C to 550°C, given in Figure 2.13. For PMMA-*b*-PS-*b*-PMMA triblock copolymer is decomposes 310°C to 400°C in Figure 2.14. In Figure 2.15, PtBA-PMMA-PS-PMMA-PtBA pentablock copolymer decomposition starts at 280°C up to 400°C. This data indicates the excellent thermal stability of synthesized polymers.

2.4. Conclusion

This work illustrates that ATRP can be successfully used for synthesis of homopolymers as well as pentablock copolymer (multiblock) of styrene , MMA , tBA with controlled molecular weights and narrow molecular weight distributions as found from GPC. The FT-IR data, NMR studies gives its confirmation of attachment of functional group. The end group of halogens is useful for the addition of the next to the required monomer and chain will be extended up to the number. The block copolymers are synthesized via solution ATRP and structure of block copolymers, living nature and thermal properties of the synthesized polymers have been studied. The synthesis of multiblock copolymers are the first step to perform ATRP and with the help of this confirmation, other monomers and their structural change are also possible by changing M:I ratios and reaction conditions.