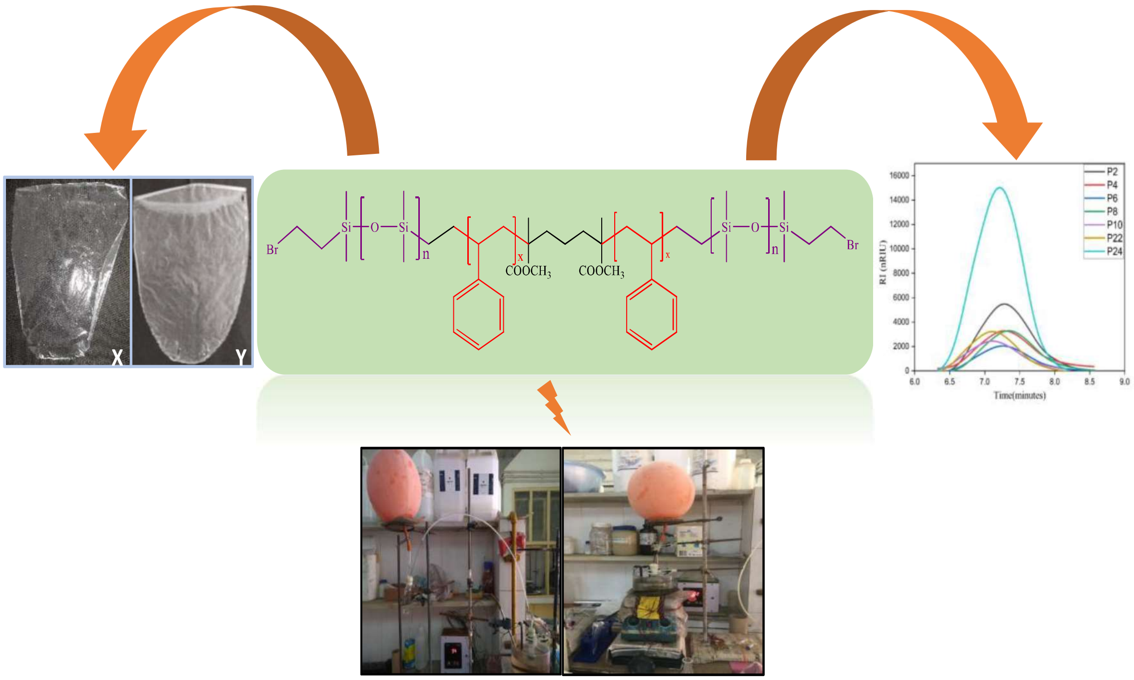
Chapter 4

Synthesis and Characterization of well-defined triblock copolymers via ATRP: PDMS-*b*-PS-*b*-PDMS



4.1. Introduction

The modifications in the structural arrangement, functionality, surface topology that are done by ATRP very systematically[1]. Block and graft copolymers[2] of PDMS are expected to have unique physical properties, making them potential options for materials such as thermoplastic elastomers, silicone rubber compatibilizers, and supercritical carbon dioxide surfactants. PDMS is the choice of material for a wide range of applications, because it owns many advantages, such as stability to UV, nontoxicity, thermostability, hydrophobicity[3], good gas permeability[4], low-coefficient friction, low-surface tension[5], biocompatibility[6], and commercial availability. However, its application is limited because of its critical film-forming property, poor cohesion, and low-glass transition temperature, which induce the cumbersome curing process of PDMS and poor mechanical performance. So many modification methods had been applied to improve mechanical performance of PDMS. Specifically, hybrid polymers containing PDMS have been reported for many different applications such as nanotechnology, electronics, filtration, two-dimensional liquid chromatography, and adsorption, among many others.

PDMS-*b*-PS-*b*-PDMS soft–hard–soft triblock copolymers have been prepared by the anionic polymerization by the acid-catalyzed insertion. The triblock copolymers have been prepared by the anionic polymerization of octamethylcyclotetrasiloxane or hexamethylcyclotrisiloxane initiated by the living anionic ends of PS[7]. Also, the triblock PDMS-*b*-PS-*b*-PDMS have been prepared by two-stage anionic polymerization process. The first stage involved anionic polymerization of styrene initiated by lithium naphthalene. In the second stage hexamethylcyclotrisiloxane was polymerized on the thus formed styrene macroanions. Silanol end-groups were neutralized with acetic acid[8]. Here, in this work the triblock copolymer PDMS-*b*-PS-*b*-PDMS were prepared by ATRP. By changing the initiator/monomers (styrene) mole ratios, triblock copolymers of various molecular weights and different polystyrene and polysiloxane block lengths were obtained, which is not reported yet.

Synthesis of Br-PS-Br homopolymer[9] via ATRP technique is already represent in the chapter 2 of this thesis, which will be use as a macroinitiator for the preparation of triblock copolymer. Preparation of triblock copolymer using ATRP technique by taking poly(dimethylsiloxane) vinyl terminated as monomer is the new target and challenge. The idea comes from the one of the research paper of PS-*b*-PDMS-*b*-PS[10].

4.2. Experimental Section

4.2.1. Preparation of high molecular weight homopolymer

Synthesis of bi-functional bromo-terminated polystyrene (macroinitiator) using PMDETA as a ligand and copper as a catalyst. First, making styrene inhibitor free (monomer purification). Styrene contains MEHQ as an inhibitor which inhibits polymerization reaction of styrene, so it was important to remove inhibitor first. Inhibitor was removed by washing styrene with 5% aqueous solution of NaOH in separating funnel. Collect the organic layer and was passed it through basic alumina column (pH>8).

Table 4.1. Synthesis of bi-functional bromo-terminated polystyrene

Materials	role	Volume (ml)	Quantity (g)	M.W (g/mol)	moles	Mole ratio
Styrene	monomer	10	9.06	104	0.0871	2000
DMDBHD	initiator	-	0.0150	346	4.35×10^{-5}	1
CuBr	catalyst	-	0.0062	143	4.35×10^{-5}	1
PMDETA	ligand	0.02	0.0150	173	8.7×10^{-5}	2

Took 3 vials, cleaned and thoroughly dried them. Then add as following: Vial 1: CuBr, Vial 2: styrene(monomer)+ PMDETA(ligand), Vial 3: DMDBHD +toluene(solvent). Kept all the three vials under N_2 environment using N_2 balloon for 10-20 minutes. Expeled out all the oxygen present in the vials.

Catalyst purification

CuBr used as a catalyst should first be purified as following

Took 0.0062g of CuBr on a filter paper on funnel. Washed the catalyst with glacial acetic acid followed by alcohol and then with acetone for 3-4times till the colourless liquid emerges out from the funnel end. The resultant CuBr obtained was in pure form. Heated the CuBr vial with magnetic stirrer in oil bath for 10-20 minutes under N_2 atmosphere, added the solution of vial 2 to vial 1 through cannula followed by subsequent addition of vial 3 to vial 1. The prepared mixture was heated at 100°C for 4-5 h. The hot green solution of vial obtained after the reaction was dissolved in 50 mL of tetrahydrofuran. Pass this solution through alumina column. The Product obtained from the reaction mixture was heated to evaporate maximum THF. The resultant solution was taken in additional funnel, the solution was poured dropwise in the beaker containing methanol. The solid white precipitates are observed which were collected and then purified. The product was dissolved in THF and then reprecipitated in methanol then dried and process was repeated 3-4 times and dried under the oven.

Calculation of theoretical molecular weight homopolymers:

The final product from the overall reaction mixture was 8.66g.

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

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

= 8.66/9.06 x 100

= 95.58

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

=346 + 2000/1 x 104 x 0.95589

M_n theoritical = 199152

4.2.2. Preparation of tri block copolymer via ATRP

Table 4.2. Synthesis of triblock copolymer by using Bromo terminated polystyrene as a macroinitiator

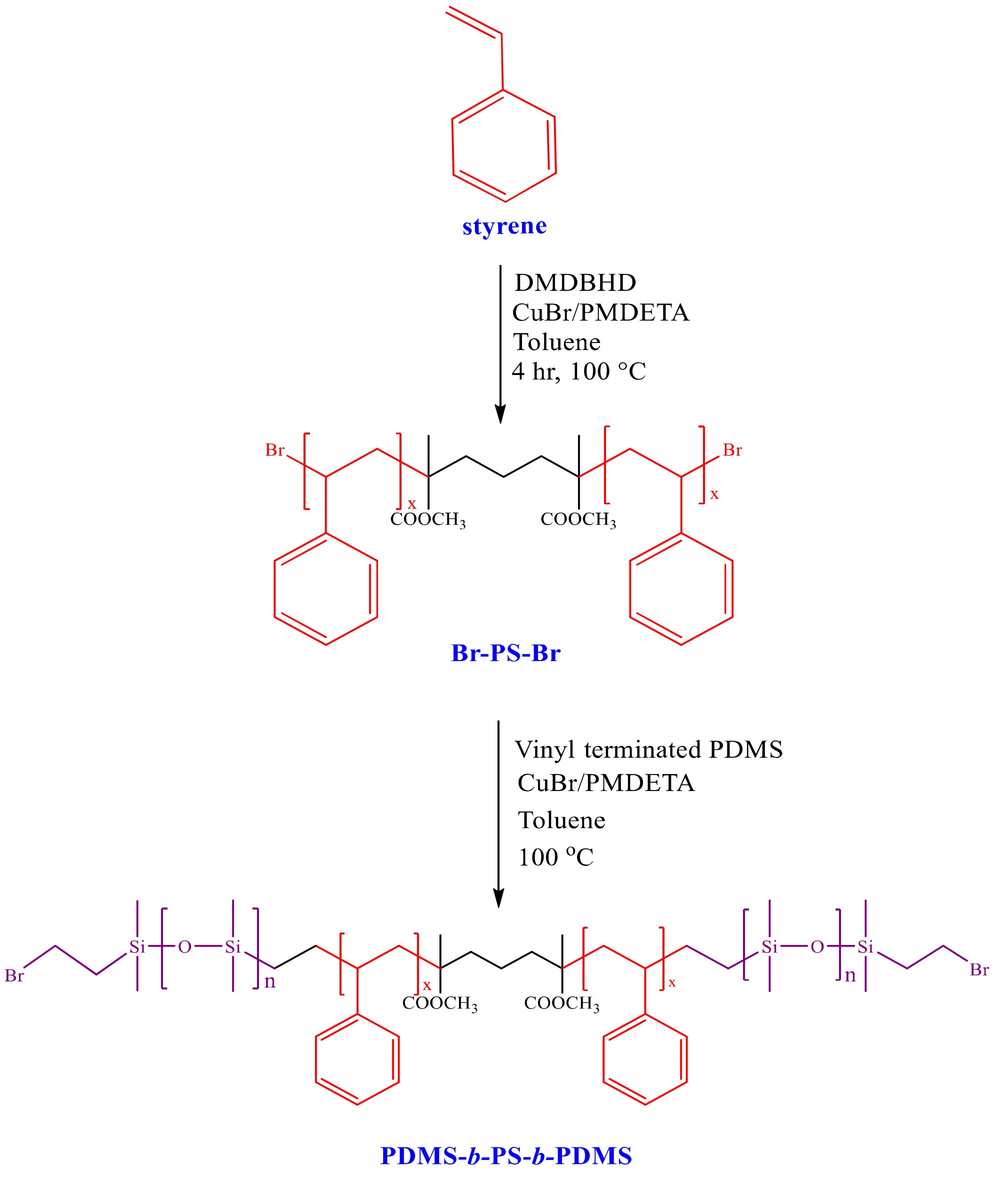
Materials required	role	Volume (ml)	Quantity (g)	M.W (g/mol)	moles	Mole ratio
Vinyl terminated PDMS	monomer	3	2.89	20121	0.000143	10
polystyrene	macroinitiator		2.84	199152	0.0000143	1

CuBr	catalyst		0.0020	143	0.0000143	1
PMDETA	ligand	0.0059	0.0049	173	0.0000286	2

Took 3 vials, cleaned and made them dry. Then add as following, Vial 1: CuBr, Vial 2: Vinyl terminated PDMS + PMDETA, Vial 3: polystyrene as a macroinitiator in toluene. Kept all the three vials under N_2 environment using N_2 balloon for 10-20 minutes. Expel out all the oxygen present in the vials. CuBr used as a catalyst was first be purified in the following manner.

Take 0.0020g of CuBr in filter paper on funnel. Wash the catalyst 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. Resultant CuBr obtained was said to be pure, heat the CuBr vial with magnetic stirrer in oil bath for 10-20 minutes under N_2 atmosphere. Add the solution of vial 2 to vial 1 through cannula followed by subsequent adding of vial 3 to vial 1 was heated the mixture to 100°C for 24 h.

Figure 4.1 Experimental setup of Triblock copolymers.



Scheme 3 Synthesis of triblock copolymer (PDMS-*b*-PS-*b*-PDMS).

The hot green solution of vial obtained after the reaction was dissolved in 50 mL of tetrahydrofuran. Passed the solution through alumina column. Product was then heated to evaporate maximum THF. The resultant solution was then taken in additional funnel, then the solution was poured dropwise in the beaker containing methanol. The solid white precipitates are observed which were collected and then purified. The product is dissolved in THF and then reprecipitated in methanol then dried and process were repeated 3-4 times. The purified product was completely dry.

Calculation of theoretical M.W of triblock copolymer

The final product from the overall reaction mixture was 2.180g.

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

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

= 2.180/2.89 x 100

= 72.53

M_n = 199152 + 10/1 x 20121 x 0.7543

M_n theoritical = 350924

4.2.3. Preparation of film (Homopolymer and triblock copolymer)

Polystyrene (Br-PS-Br) and triblock copolymer (PDMS-*b*-PS-*b*-PDMS) dissolved separately in chloroform to prepare 18% dope solution. Then polymeric dope solution cast on a glass plate using applicator and thin film formed via dry phase inversion process shows in Figure 4.2.

Figure 4.2 Thin film of (X) Br-PS-Br (Y) PDMS-*b*-PS-*b*-PDMS.

4.3. Materials and methods

Monomer styrene (Aldrich, 99%) purified by 5% NaOH solution then distilled water then passing through the neutral alumina column. Vinyl terminated poly(dimethyl siloxane) (Aldrich, M_w~25000). DMDBHD, 97% (purity) was obtained from Aldrich. CuBr (Aldrich, 99.99%) was purified by glacial acetic acid followed by absolute ethanol and ether. PMDETA from Aldrich 99% (Purity). Toluene, THF, methanol, and chloroform (LOBA CHEMIE, 99%).

FT-TR analysis from ALPHA (Bruker optics Inc, Germany) at 28°C. All the compounds were performed by KBr pellet and scanned over a wavelength range of 4000-400 cm^{-1}. ^{13}C and ^{1}H spectra from BRUKER 400 MHz, all samples performed under $CDCl_3$ solvent by complete dissolution of the polymer. The elemental studied by EDS analysis, JEOL JSM-

5610LV Scanning Electron Microscope from Akishima, Tokyo, Japan was used. GPC from Agilent Technologies was used to estimate the number average and weight average molecular weight as well as the polydispersity index (M_n, M_w, PDI), all the samples were taken 1 mg and dissolved as in HPLC grade of THF. The thermal stability analyzed by the instrument Exstar (Stage II TG/DTA-6300) use for the TGA analysis. To investigate the variation in wetting properties, contact angle measurement ACAMNSC 03, Apex Instruments Pvt. Ltd. The probe liquid for each measurement was de-ionized water.

4.4. Results and discussion

FT-IR was one of the very useful analytical tools to detect the presence of certain functional group and identify the organic materials.

Figure 4.3 represent the band of Br-PS-Br that appear the C-H stretching at 2800-3000 cm^{-1}, C-H bending (methyl group) are attributed at 1494 cm^{-1}. The ester group confirmed at 1732 cm^{-1} and end group bromine (C-Br) band at 696 cm^{-1}. The characteristic bands of PDMS, -Si-CH_3 in 1261 cm^{-1}, Si-O-Si in 1020–1074 cm^{-1} and -CH_2-Br in 690 $cm^{-1}$are appear. These results shows brominated polystyrene as a homopolymer, and the vinyl terminated poly(dimethylsiloxane) successfully bound and extend the chain of PDMS-*b*-PS-*b*-PDMS triblock copolymer.

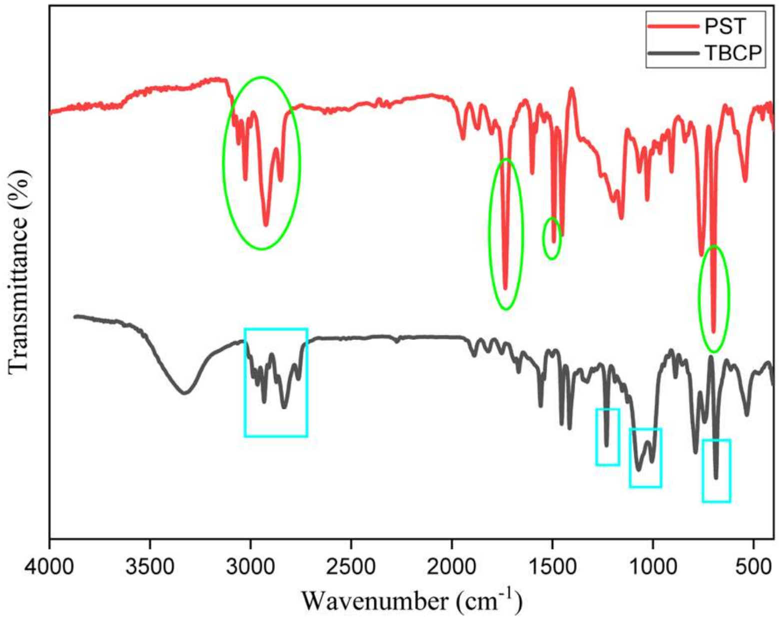


Figure 4.3. FT-IR spectra of polystyrene and triblock copolymer.

NMR was a nuclei specific spectroscopy that has far reaching applications throughout the physical sciences and industry. NMR uses a large magnet to probe the intrinsic spin properties of atomic nuclei. Like all spectroscopies, NMR uses a component of electromagnetic radiation to promote transitions between nuclear energy levels (Resonance). NMR was used for structure determination of molecules.

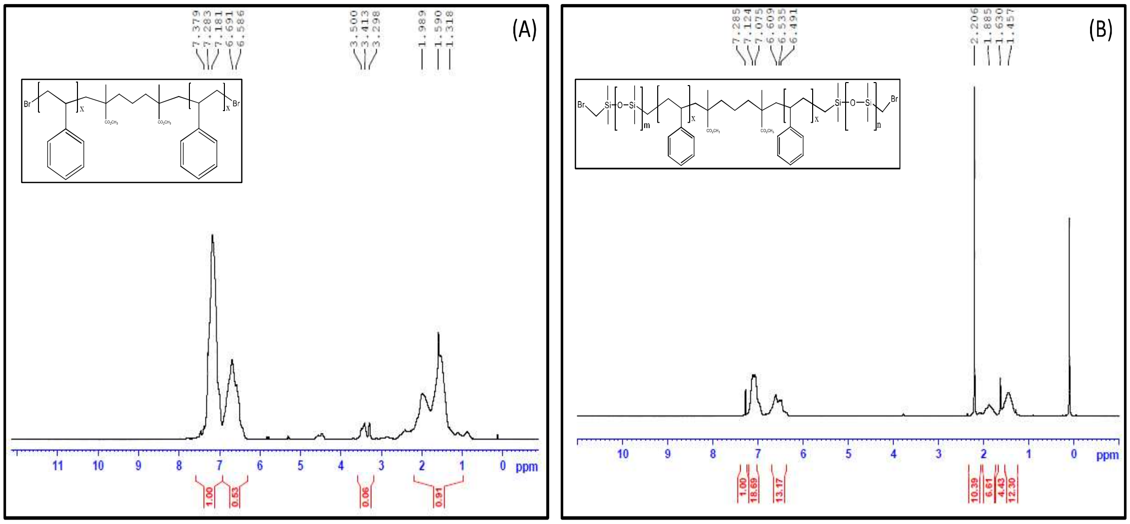


Figure 4.4. ^{1}H NMR Spectra of (A) Br-PS-Br (B) PDMS-*b*-PS-*b*-PDMS.

Figure 4.4 (A) shows the Br-PS-Br with halogen exchange mechanism that the signal at 3.5 δ ppm attributes to the end functional group C-Br bond, the aromatic ring of polystyrene shows spectra at 7.2 δ ppm, spectra of (-CH_3) methyl group at 1.9 δ ppm and the methylene (-CH_2) at 1.5 δ ppm. These data show the successful polymerization of polystyrene homopolymer by ATRP. ^{1}H-NMR spectra of PDMS at 0.1 ppm (-$Si(CH_3)_2O$-) and the characteristic ^{1}H-NMR peaks of PDMS-*b*-PS-*b*-PDMS triblock copolymer at 0.1 ppm (-$Si(CH_3)_2O$-), 1.4–2.2 ppm (-CH_2-CH-), and 6.0–7.2 ppm (benzene), which were assigned to PS as described above. The results showed that the final product included PDMS and PS phase structure PDMS-*b*-PS-*b*-PDMS in Figure 4.4 (B).

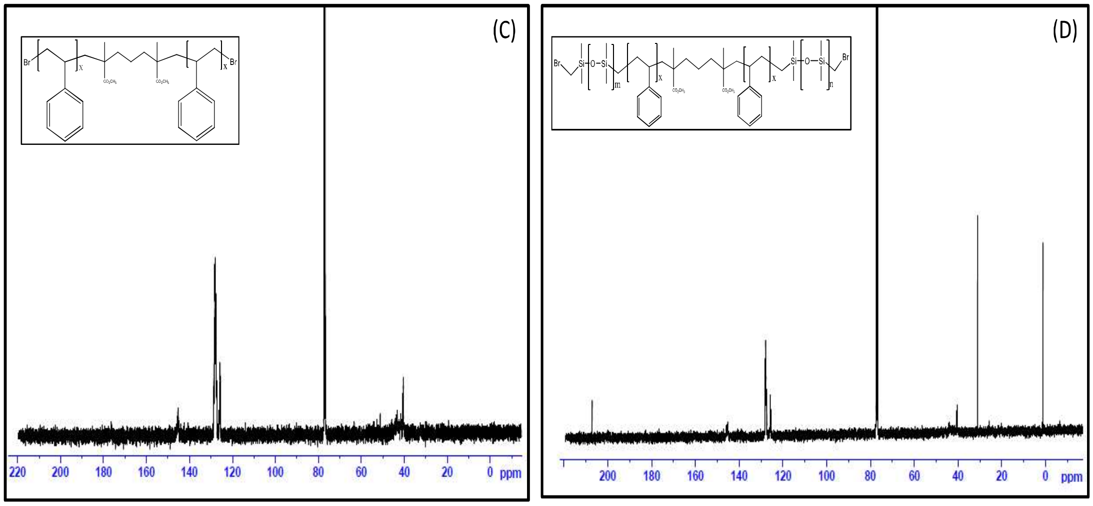


Figure 4.5. ^{13}C NMR Spectra of (C) Br-PS-Br (D) PDMS-*b*-PS-*b*-PDMS.

The Figure 4.5, the synthesized homopolymer Br-PS-Br gives spectra at 125-128 δ ppm for the carbon and 145 δ ppm for benzene with end functional group at 43 δ ppm respectively. After the preparation of triblock copolymer with the vinyl terminated poly(dimethylsiloxane) confirmed spectra at 0.8 δ ppm that were assigned to the carbon of -CH$_3$ of -Si(CH$_3$)$_2$O. The signals for methylene group (-CH$_2$CH$_2$-) at 31 δ ppm and 40 δ ppm for the terminal carbon with bromine. These ^{1}H NMR and ^{13}C NMR spectra gave the clear indication of successfully synthesized the triblock copolymer.

GPC was a type of SEC, that separates analytes based on size. The technique was often used for the analysis of polymer. When characterizing polymers, it was important to consider the polydispersity index (PDI) as well the molecular weight. Polymer can be characterized by a variety of definitions for molecular weight including the M_n, M_w, M_z, or the M_v, GPC allows for the determination of PDI as well as M_v and based on other data, the M_n, M_w, and M_z can be determined. Most samples can be thoroughly analyzed in an hour or less.

Table 4.3 Summarizes the triblock copolymer series, the parameters of the reaction, and the results of the M_n, and PDI

Time (h)	conversion (%)	$M_{n,\ Theotitical}$	$M_{n,\ GPC}$	PDI
2	**0.79**	**200741**	**168866**	**2.17**
4	**1.4**	**201968**	**116347**	**3.32**
6	**1.7**	**202572**	**161929**	**2.21**
8	**1.8**	**202834**	**160134**	**2.26**
10	**3.5**	**206194**	**154390**	**2.31**
22	**64**	**327926**	**185188**	**1.89**
24	**75.4**	**350924**	**196255**	**1.88**

Table 4.3 summarizes the triblock copolymer series, the parameters of the reaction, and the results of the molecular weight and molecular weight distribution. The kinetics of the reaction taken for the determination of monomer conversion. Here, the solution was taken from the reaction mixture via injection and directly poured into the methanol solvent during the reaction. Where the precipitation formed was filtered and dried under the oven and weighed. Polymers with the different time duration shows the increasing order of the % conversion.

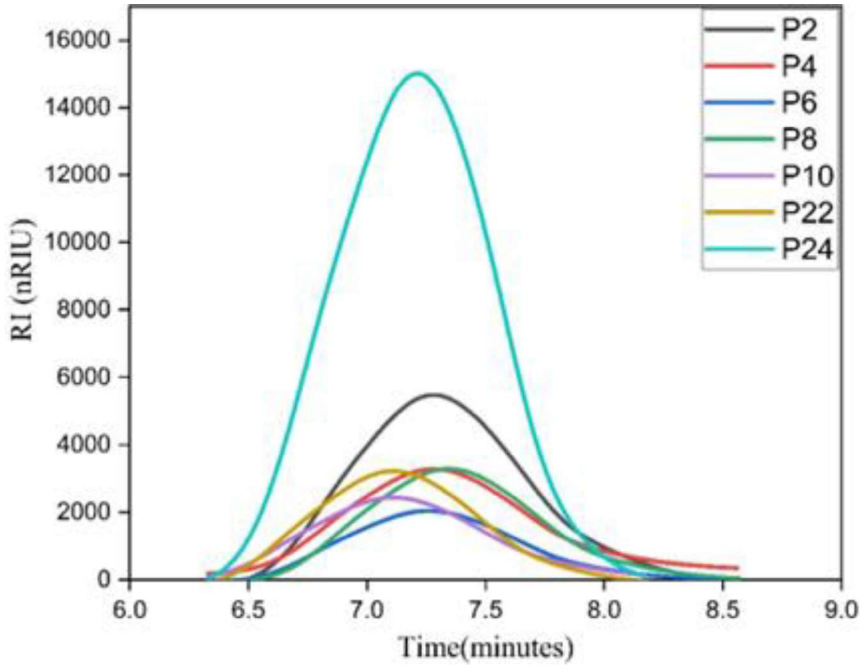


Figure 4.6. GPC traces of (1) P2, (2) P4, (3) P6, (4) P8, (5) P10, (6) P22, and (7) P24.

The GPC thermographs (traces) in Figure 4.6, show the different retention time of the all the given 7 series of polymers but at the same time overall retention time of P2 compared with P24 is increased that implied polymeric chains where of higher molecular weight.

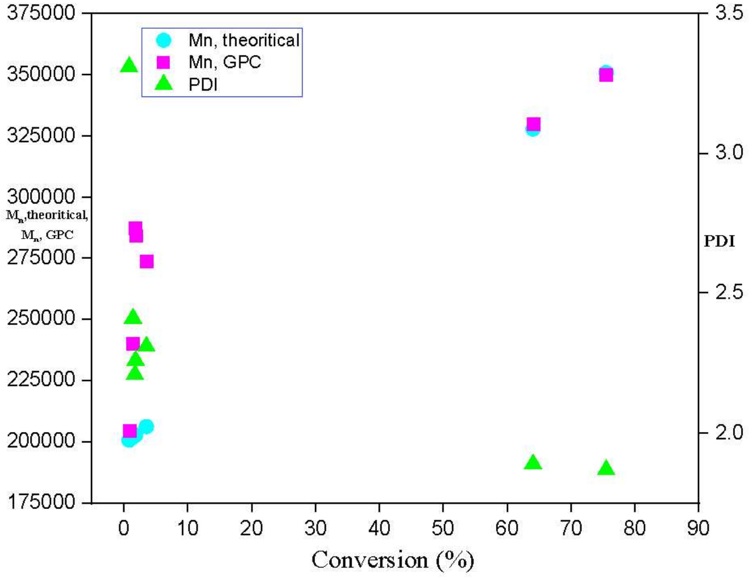


Figure 4.7. Plot of variation of molecular weight and PDI with conversion for triblock copolymers (PDMS-*b*-PS-*b*-PDMS).

The given graph in Figure 4.7 shows polydispersity index, theoretical molecular weight, and molecular weight through GPC as a function of monomer conversion for the ATRP of triblock copolymers. This data from the kinetics studies tells that the higher molecular conversion PDI becomes lower. A linear increase of number average molecular weight as well as from GPC.

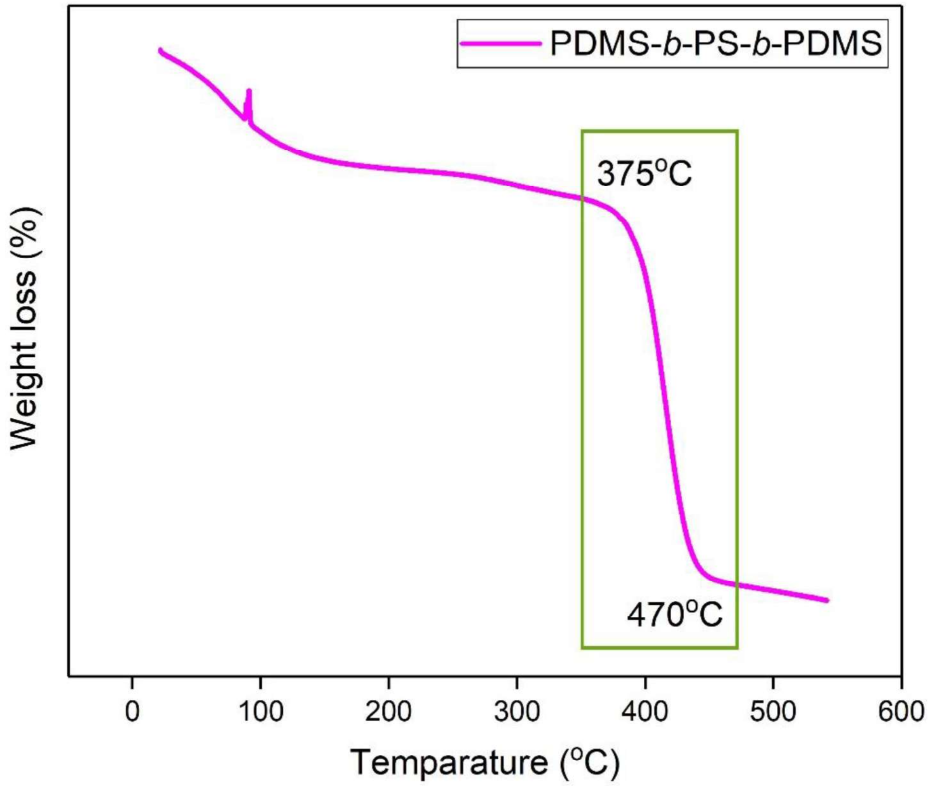


Figure 4.8. TGA curve of PDMS-b-PS-b-PDMS.

Figure 4.8 shows that in inner an atmosphere, TGA thermograms of substances heated from 25°C to 600°C at a rate of 10 °C/min. the degradation temperature of the final product PDMS-*b*-PS-*b*-PDMS start at 375°C to 470°C. This result give the excellent thermal stability and it withstand the high temperature. As the attachment of PDMS with PS the thermal stability is increased.

EDX was an analytical technique used for the elemental analysis or chemical characterization of a sample. In Figure 4.9, EDX analysis images confirm bromine content of 0.44% in the homopolymer polystyrene and this function group represented as a macroinitiator for another monomer.

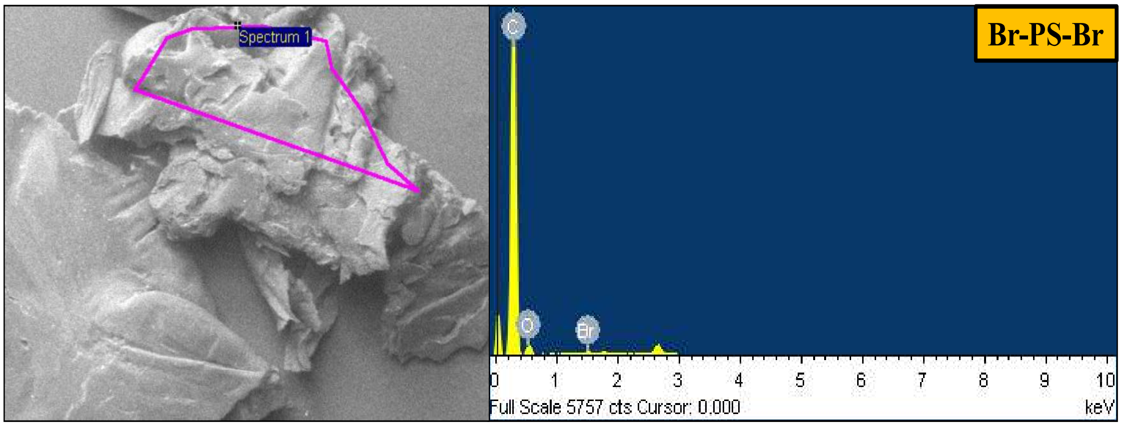


Figure 4.9 EDX analysis of Br-PS-Br.

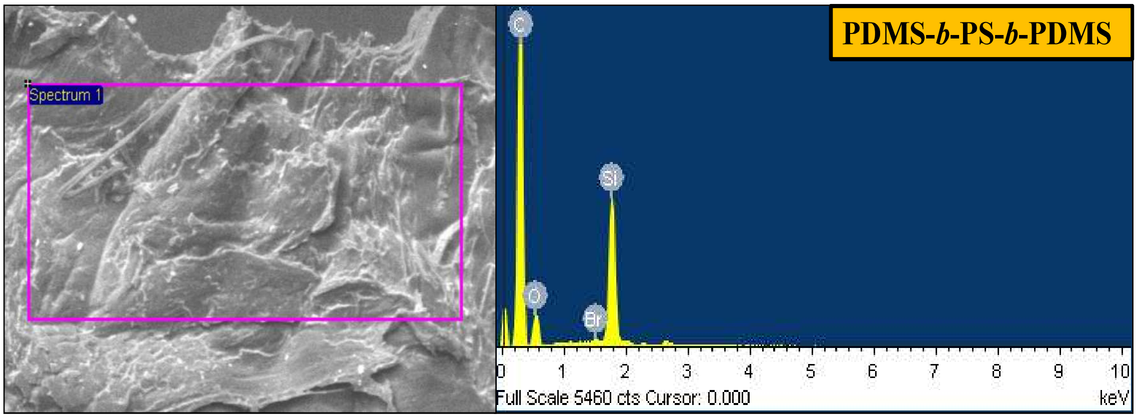


Figure 4.10. EDX analysis of PDMS-*b*-PS-*b*-PDMS.

In Figure 4.10, The successful PDMS-*b*-PS-*b*-PDMS triblock copolymer also shows the end functional group with 0.17% and rest was other elements including C, O and Si. The % of Si was not shown in the polystyrene homopolymer. This data confirmed the functionality, and the chain can be extended up to several monomeric unit.

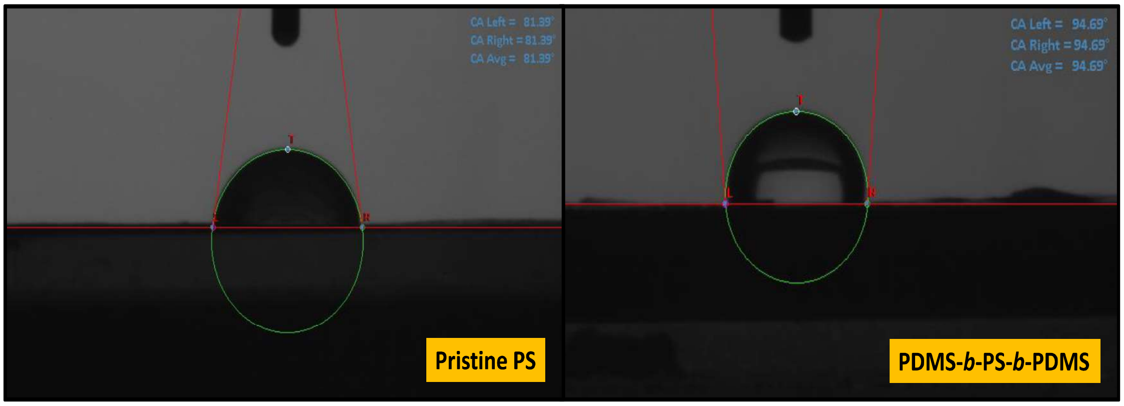


Figure 4.11. Contact angle analysis of Pristine PS comparison with PDMS-*b*-PS-*b*-PDMS.

The triblock copolymer PDMS-*b*-PS-*b*-PDMS, which has a higher hydrophobicity at 94.69°, enhanced the film of pure polystyrene, as shown in Figure 4.11, which had a contact angle of 81.39°. These synthesized triblock copolymers have surface that are hydrophobic and could be used to make nonconductive materials.

4.5. Conclusions

This work illustrates that, for the preparation of triblock copolymer PDMS-*b*-PS-*b*-PDMS first to prepared dibromo terminated polystyrene which was used for the further reaction in triblock copolymer via ATRP. This macroinitiator as well as final product was confirmed by FT-IR, ^{13}C NMR, ^{1}H, EDX and GPC analysis. Furthermore, the functionality of the synthesized material confirmed by the FT-IR analysis and the presence of proton was confirmed by ^{1}H NMR spectra. Here, structural characterization of synthesized triblock copolymer with the PDMS at the end chain. The % of bromine content also proved the end functionality which will used for the attachment numbers of monomeric units. This synthesized triblock copolymer has a higher molecular weight confirmed by theoretical as well as GPC analysis and desired PDI and the polymerization followed first-order kinetics. The single GPC curve indicate the linear polymer chain and there is not any physical blend. The contact angle analysis proved its hydrophobicity. The thermal stability is also increase by addition of PDMS. At the same time uncontrolled radical dissociation observed and its leads to formation of highly crosslinked structures with very high molecular weights. Molecular weights do not follow the theoretical values at initial stage.

4.6. References

[1] Matyjaszewski, K.; Xia, J. Atom Transfer Radical Polymerization. *Chem Rev*, **2001**. https://doi.org/10.1021/cr940534g.

[2] Davis, K. A.; Matyjaszewski, K.; Höcker, H. Statistical, Gradient, Block, and Graft Copolymers by Controlled/Living Radical Polymerizations. *Advances in Polymer Science*. 2002. https://doi.org/10.1007/3-540-45806-9_1.

[3] Karunakaran, M.; Shevate, R.; Peinemann, K. V. Nanostructured Double Hydrophobic Poly(Styrene-b-Methyl Methacrylate) Block Copolymer Membrane Manufactured via a Phase Inversion Technique†. *RSC Adv*, **2016**, *6* (35), 29064–29071. https://doi.org/10.1039/c6ra02313d.

[4] Merkel, T. C.; Bondar, V. I.; Nagai, K.; Freeman, B. D.; Pinnau, I. Gas Sorption, Diffusion, and Permeation in Poly(Dimethylsiloxane). *J Polym Sci B Polym Phys*, **2000**, *38* (3). https://doi.org/10.1002/(SICI)1099-0488(20000201)38:3<415::AID-POLB8>3.0.CO;2-Z.

[5] Owen, M. J.; Dvornic, P. R. Silicone Surface Science; 2012. https://doi.org/10.1007/978-94-007-3876-8_14.

[6] Kuddannaya, S.; Bao, J.; Zhang, Y. Enhanced in Vitro Biocompatibility of Chemically Modified Poly(Dimethylsiloxane) Surfaces for Stable Adhesion and Long-Term Investigation of Brain Cerebral Cortex Cells. *ACS Appl Mater Interfaces*, **2015**, *7* (45). https://doi.org/10.1021/acsami.5b09032.

[7] Sargent, J. R.; Weber, W. P. Novel Synthesis of Triblock PDMS-PS-PDMS Copolymers. *J Polym Sci A Polym Chem*, **2000**, *38* (3). https://doi.org/10.1002/(SICI)1099-0518(20000201)38:3<482::AID-POLA13>3.0.CO;2-D.

[8] Dems, A.; Strobin, G. Synthesis and Properties of Well-Defined Multiblock Copolymers: Polystyrene-Block-Polydimethylsiloxane. *Die Makromolekulare Chemie*, **1991**, *192* (11).

[9] Kumar, S.; Lee, J. S.; Murthy, C. N. Synthesis and Characterization of BAB and CBABC Tri- and PentaBlock Copolymers via Atom Transfer Radical Polymerization. *Macromol Res*, **2011**. https://doi.org/10.1007/s13233-011-1012-8.

[10] Mistry, B.; Murthy, C. N. Synthesis and Properties of ABA Type Triblock Copolymer

from Poly(Dimethylsiloxane) Macroinitiator: Development of Novel Attachable Initiators for Atom Transfer Radical Polymerization. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, **2022**. https://doi.org/10.1080/10601325.2022.2128817.