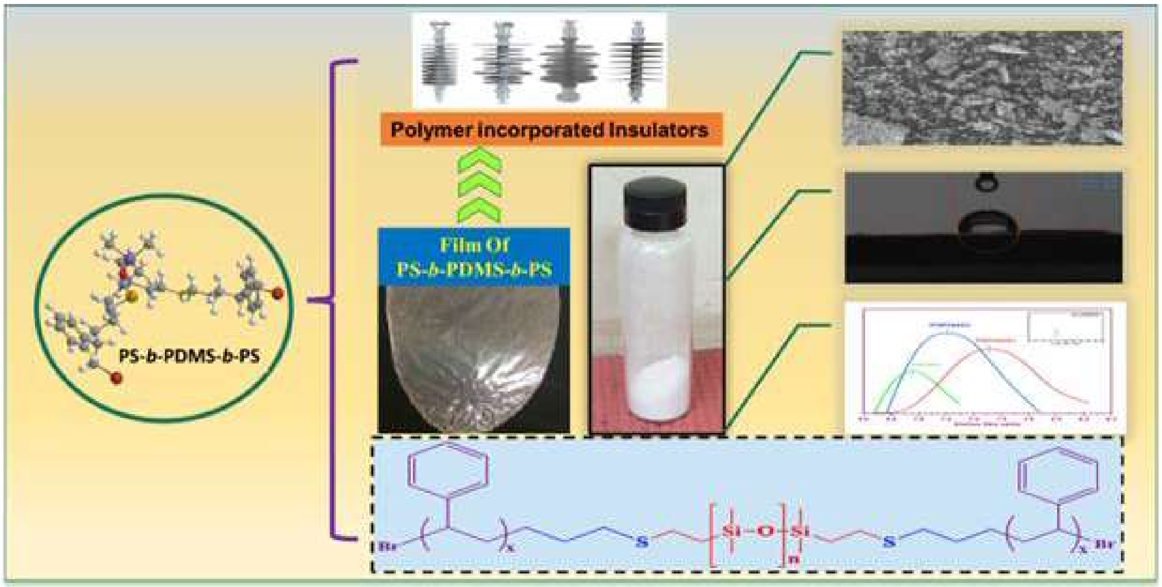
Chapter 3

Synthesis and characterization of ABA type triblock copolymer of polydimethylsiloxane: PS-*b*-PDMS-*b*-PS



"The scheme and Figures given in this Chapter are published in my publication[1]"

3.1. Introduction

In the list of inorganic polymers, PDMS is the most common and important inorganic polymer. It is known for its various applications like formulation, cosmetics[2], drug delivery[3], insulators[4–6], membranes[7, 8], injecting gel, coating[9], film etc. PDMS is currently utilised often with a variety of functional groups, including -OH, $-NH_2$, $-CH_2=CH_2$, and others. PDMS has a high bond energy because of the presence of a methyl group and the siloxane backbone. PDMS has a few interesting properties, such as a low glass transition temperature, low surface tension, biocompatibility. It has also the capacity to resist higher temperatures, moisture, oxidation, and UV radiation. Here, PS is non-polar and PDMS is polar. These two copolymers have been different fractions of PS and these PS block lengths is expected to exhibit unique properties that can be modified as required. In L/CRP method has become advanced, and the polymerization procedure has been quick and simple. Recent studies of synthesis of block copolymers via ATRP gives the formation of different structure, its topology with verities in composition[10, 11].

This chapter illustrate the interesting approach of the reaction between vinyl terminated PDMS and 3-chloropropane-1-thiol. This is used as a macroinitiator (MI) and styrene as a monomer. The final product obtained the PDMS and PS blocks. This MI prepare by the successive reaction of Thiol-Michael addition[12, 13]. Because it is hydrophobic nature, this newly synthesised polymer will be investigated in this study with the goal of discovering more applications for it in insulating coating materials and evaluating the features it possesses. In recent decades, there has been a shift away from the usage of ceramic insulators and toward polymeric insulators as a replacement. Polymeric insulators have been shown to be superior to ceramic insulators in terms of both cost and performance. It is possible to modify and change the flow property of silicon by changing the type of fillers that are present in the silicon rubber. Because of its benefits, such as control over molecular weight and polydispersity index, as well as its linear structure through a unique Thiol-Michael addition reaction and this macroinitiator, the ATRP technique utilised here has not been used for ATRP research till now. The purpose of the study was to functionalize vinyl terminated poly(dimethylsiloxane), and the 3-Chloro-1-propanethiol was found to be the most simple and effective method of double bond conversion because the direct attachment of the -Si in vinyl terminated PDMS makes it extremely difficult to form double bonds. Previous research indicates that a variety of halogenating reagents are used in the process of chlorination and bromination (halogenation). The modification of PDMS was quite difficult, and our goal was to use some novel reagents for halogenation, specifically in vinyl terminated PDMS and the final yield of also functionalize vinyl terminated PDMS is 67%. It is confirmed by the FT-IR, NMR, analysis its molecular weight and PDI obtained through GPC, DLS, SEM, EDX, and contact angle is also the important part of this chapter.

3.2 Experimental section

3.2.1. Synthesis of PDMS-MI (macroinitiator) via Thiol-Michael addition

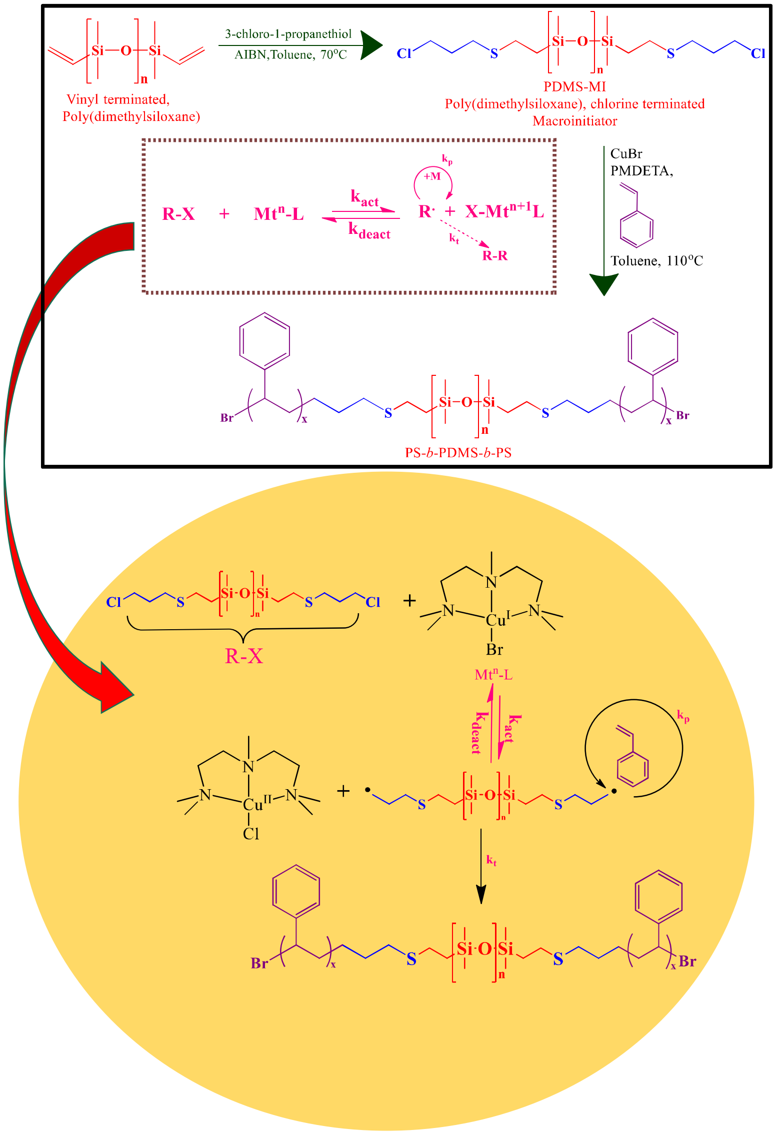
The MI has been synthesized through the thiol-Michael addition procedure. 9.65 g of vinyl-terminated PDMS was added to a dry, 100 ml, 3-necked round-bottom flask with a magnetic stir bar, and 25 ml of toluene was diluted into it. This was done in an argon atmosphere with a rubber septum sealed around the flask. The flask was then completely closed, the mixture was added, and it was stirred in an oil bath for 20 hours at 65 0.5°C. The additional Azobisisobutyronitrile (AIBN) (0.2 g, 1.15 mmol) and 3-chloropropane-1thiol (0.12 g, 1.15 mmol) were then added. The reaction mixture was vigorously stirred, gently poured into a methanol solution, and allowed to cool at room temperature before filtering to remove unreacted particles (500 mL). To remove unreacted thiols, this process was repeated two more times. These thiols can be physically verified by smell and chemically verified by NMR analysis. The PDMS-MI product was vacuum-pressed dried at 50°C. As a result, we were able to produce a pale yellow, hazy liquid that we later used as a macroinitiator in an ATRP procedure. The yield of PDMS-MI that was synthesized is 6.5g (67%).

3.2.2. Synthesis of PS-*b*-PDMS-*b*-PS (triblock copolymer) by ATRP

First, a dry 100 mL two-necked round-bottom flask was filled with purified CuBr (0.006 g, 0.047 mmol), sealed with a rubber septum under a flowing stream of argon, and heated at 60°C to remove oxygen. Deoxygenated PMDETA (0.01 g, 0.094 mmol) in styrene (27 mL) was added to this via a cannula tube in a high argon atmosphere. Deoxygenated PDMS-MI (0.965 g, 0.047 mmol) was added to the aforesaid flask, creating a homogeneous solution, and gradually raising the temperature. The solvent used was 20 mL of toluene. The flask was submerged for varying lengths of time in a silicon oil bath that was kept at 100°C. By exposing the reaction to air, the reaction was stopped, and the mixture was then diluted with 200 mL of THF. It was run through an activated neutral alumina column to get rid of the catalyst-ligand combination from this reaction mixture. Rota evaporation was used to concentrate the solution, and a sizable amount of methanol was used to precipitate the polymer out. In a similar fashion, the polymer was dried, diluted in a small amount of THF, and precipitated out in methanol; the pure polymer was thus purified three times. Then, at 50°C, it was vacuum-dried. 18 h, 30 h, and 48 h, respectively, while a similar reaction is carried out.

The given below is the scheme of synthesis of MI and ABA type of triblock copolymer via ATRP.

Scheme 2. Synthesis of PDMS-MI by Thiol-Michael addition reaction and addition of a block of styrene as a monomer.



3.3. Materials and methods

The required materials are Poly(dimethylsiloxane), vinyl terminated from Sigma Aldrich having the M_w~25000. Chlorinating agent: 3-Chloro-1-propanethiol from Sigma Aldrich with 98% purity. The initiator AIBN used. Styrene as monomer used after the purification (washing by 5% NaOH, distilled water, passed through neutral/basic alumina, preserved it for 24 h under molecular sieve). The catalyst CuBr purchased from Sigma Aldrich and have been 98% purity, which was washed by glacial acetic acid, ethanol, diethyl ether respectively. PMDETA is the ligand, methanol and THF are the solvent and was purchased from LOBA CHEMIE (99.8%), and additional reagents were applied as received.

3.3.1. FT-IR

Using FT-IR analysis with ALPHA (Bruker Optics Inc., Germany), the functional group of the synthesized polymer was identified at 28°C. Liquid chemicals were sandwiched between a NaCl pellet while solid KBr pellets were used to study each compound. The spectra was then acquired by scanning the pallets using an FT-IR spectrometer between 400 and 4000 cm^{-1} in wavelength.

3.3.2. GPC

The polydispersity index, number of average molecular weights, and weight average molecular weights are all determined with the help of the GPC equipment (M_n, M_w, and PDI). The equipment from the Agilent 1200 Infinity series is used to perform GPC with a PLgel Mixed-B column that has a pore size of 10 m and a refractive index (RI) detector at a flow rate of 1 mL min^{-1}. Alternatively, GPC can be performed with a PLgel Mixed-B column that has a pore size of 10 m and a RI detector at the same flow rate. THF was used as the elution solvent at a temperature of 40 degrees Celsius, and polystyrene standards were utilized to standardize the apparatus. At a concentration of 5 mg each polymer, all the polymers were dissolved in HPLC-grade THF. THF is a solvent used in high-performance liquid chromatography.

3.3.3. ^{13}C NMR

Because the primary carbon isotope cannot be distinguished using NMR, only the ^{13}C isotope of carbon, which has a naturally occurring abundance of only 1.1%, may be detected using the ^{13}C NMR technique. The typical shifts in chemical states have a substantially wider dynamic range compared to proton NMR. The BRUKER 500 MHz Spectrometer AVANCE

NEO was the manufacturer of the device. Under the conditions of the $CDCl_3$ solvent, each of the samples is conducted by completely dissolving the polymer.

3.3.4. TGA

The mass of a sample is determined using this thermal analysis technique as the temperature changes over time. The SDT Q600 V20.9 Build 20 equipment was used to analyze polymeric samples in an enclosed setting at a heating rate of 10°C/min.

3.3.5. EDS

The EDS analysis, which is the elemental analysis, was performed using a JEOL JSM-5610LV Scanning Electron Microscope from Akishima, which is in Tokyo, Japan. The samples were distributed evenly across a piece of double-sided adhesive carbon tape measuring 10mm X 10mm.

3.3.6. DSC

In this thermoanalytical approach, the difference between the amount of heat needed to raise the temperature of a sample and a reference is evaluated as a function of temperature. The glass transition temperature of the PS-b-PDMS-b-PS triblock copolymer provided was determined using the internal standard and the NETZSCH DSC 200 F3 instrument. An aluminum pan containing 6 mg of sample was heated at 10°C/min in a nitrogen atmosphere with temperatures ranging from -125°C to 300°C.

3.3.7. SEM

The morphological analyses of the triblock copolymer PS-*b*-PDMS-*b*-PS were conducted with a reduced magnification of 500X utilizing a FEG-SEM 450 field emission gun scanning electron microscope. Following the application of gold plating, the samples were examined.

3.3.8 DLS

The Zetasizer ZS90 was used to measure the PS-*b*-PDMS-*b*-PS triblock copolymer's synthesized particle size (Malvern Instruments, Worcester, UK). A 5 Mw He-Ne laser (632.8 nm) operating at 25°C and a scattering angle of 90° was used for the analysis.

3.3.8 Contact Angle Analyzer

The hydrophobicity of the film of the synthesized polymer PS-*b*-PDMS-*b*-PS triblock copolymer surface was evaluated by contact angle measurement ACAMNSC 03, Apex Instruments Pvt. Ltd., to examine the fluctuation in wetting characteristics. For each measurement, de-ionized water was used as the probe liquid.

3.4. Results and Discussion

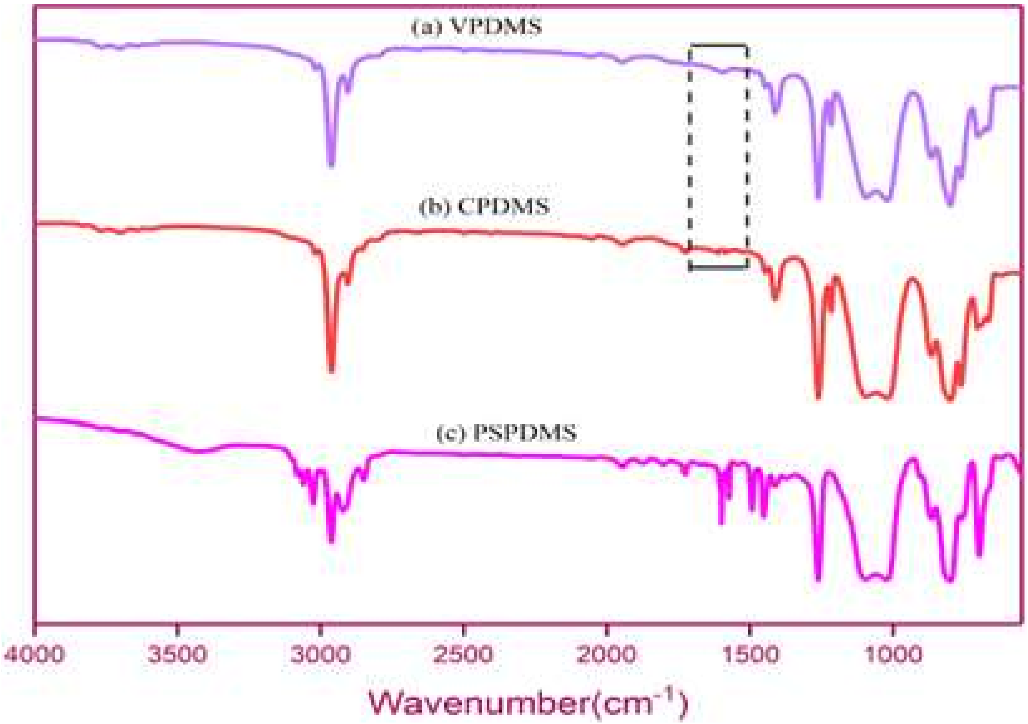


Figure 3.1. FT-IR spectrum (a) (VPDMS) Vinyl terminated poly(dimethylsiloxane), (b) (CPDMS) PDMS-MI, (c) (PSPDMS) triblock copolymer.

The FT-IR spectrum in Figure 3.1 above was used to verify the functionality of the synthesized macroinitiator made from vinyl terminated PDMS, as stated in Scheme 2.

Figure 3.1 shows the FT-IR spectra of the following materials: (a) vinyl terminated pure PDMS (VPDMS), (b) chlorinated PDMS (CPDMS), and (c) PSPDMS (PS-b-PDMS-b-PS polymer). In this graph, there is a strong Si-O-Si band at 1044 cm^{-1}, a CH_3 characteristic band at 1259 cm^{-1}, a C-Si-C band at 804 cm^{-1}, and a very minor band for the C=C characteristic band at 1604 cm^{-1}. Figure 3.1(b) shows the chlorine-terminated PDMS spectrum; the sharp bands of Si-O-Si, CH_3, and C-Si-C are still present. However, after the functionalization of the -C=C-, this stretching band at 1604 cm^{-1} was disappear[14], along with 692, 758, 2928, 2990, and 3029 cm^{-1} as shown in Figure 3.1(c) for the addition of styrene to both ends. This information demonstrates how the double bond at the ends of PDMS vanished and how adding PS was successful[15, 16].

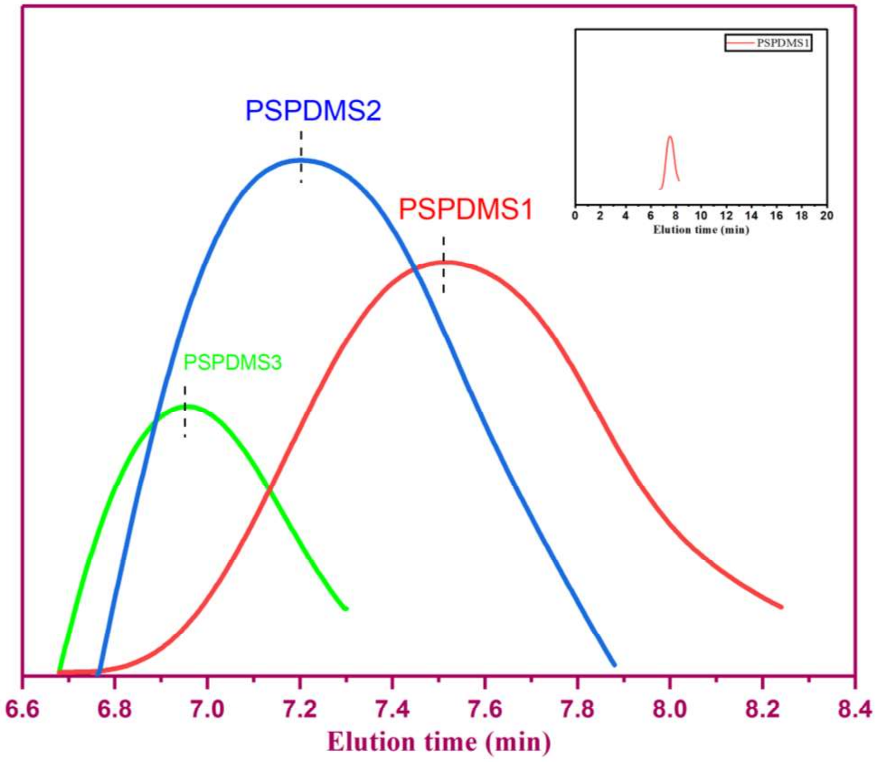


Figure 3.2. GPC chromatographs of (a) PSPDMS1, (b) PSPDMS2, (c) PSPDMS3. The complete thermogram for PSPDMS1 is shown in the inset.

Table 3.1. Synthesis of PS-*b*-PDMS-*b*-PS triblock copolymers

Polymer Series	**[M]:[I] Ratio**	**Conversion (%)**	**M_n, theoretical (g/mol)**	**M_n, GPC (g/mol)**	**Reaction (h)**	**PDI**
PSPDMS1	5000:1	3.6	39078	31159	18	1.2
PSPDMS2	5000:1	7.5	59153	58225	30	2.0
PSPDMS3	5000:1	20	122490	114849	48	1.9

Table 3.1 presents the polymer series, reaction parameters, MW and PDI data. Styrene:PDMS-MI:CuBr:PMDETA:= 5000:1:1:2 was the ratio that was used in all three of the

experiments. This ratio has a very high monomer ratio since the pristine vinyl terminated PDMS itself has Mn and Mw that are quite high, and therefore the high monomer ratio was used. It was a very slow reaction that begins after 8 to 9 hours and produces a hazy solution by precipitating the reaction mixture into methanol. High molecular weights are produced by the pure PDMS itself (M_w ~25000), the chain length, and the PDI values of the final triblock. The PDMS-macroinitiator has a 1.31 polydispersity. The three series of polymers shown in the given GPC chromatographs in Figure 3.2 have increasing retention times, indicating that the polymeric chains in these series have increased molecular weights.

The M_n derived from the theoretical value is close to the experiment value, with the highest conversion at 48 hours with 20% conversion, having greater M_n, theory = 122490 and M_n, GPC = 114849 with 1.95 PDI[16]. While the block copolymer PSPDMS1 had a PDI of 1.2, pure poly(dimethylsiloxane) with a vinyl termination has a PDI of 1.3. The reaction time for the other two block copolymers in the series, PSPDMS2 and PSPDMS3, was extended from 30 to 48 h. Triblock copolymer was made using PDMS-macroinitiator (MI) with an average M_w of 25000 and a 5000:1 (M:I) monomer ratio as the starting material. The molecular weight of the synthesized triblock copolymer increased, according to the GPC analysis, and the molecular weight that was discovered is in good agreement with the theoretically predicted molecular weight. The molecular weight order (M_n Theoretical, GPC) is seen to increase linearly with time in Figure 3.3.

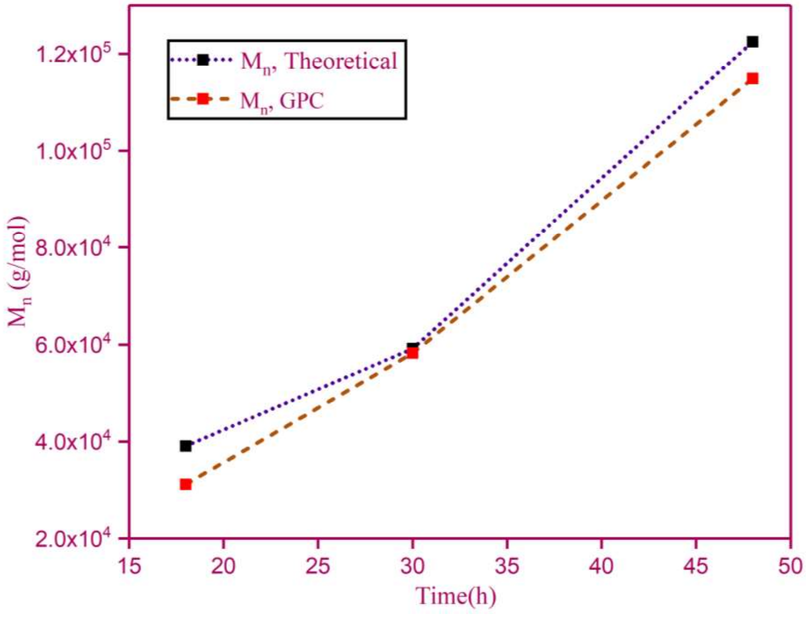


Figure 3.3 Kinetics of PS-*b*-PDMS-*b*-PS triblock copolymer.

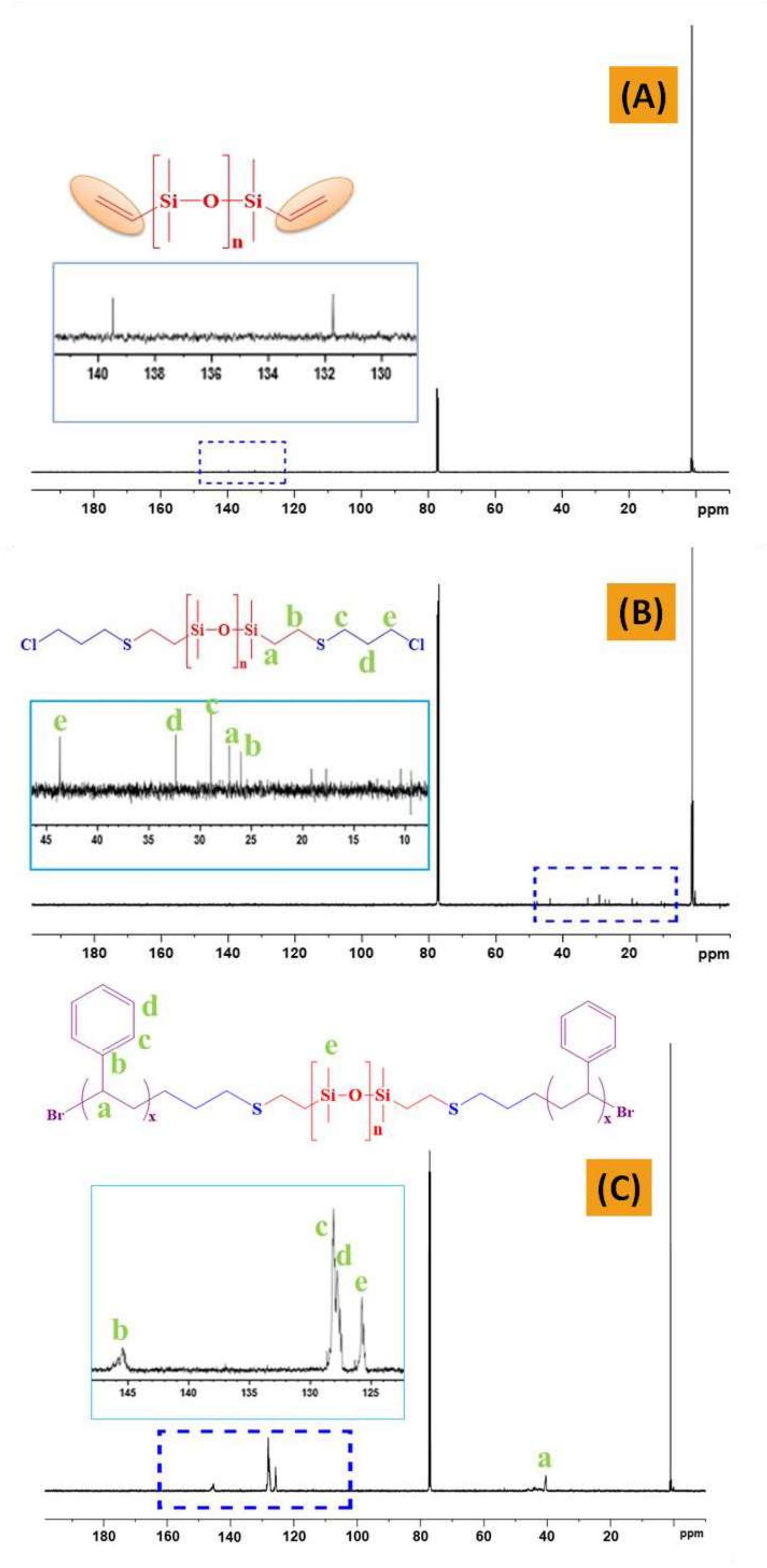


Figure 3.4. ^{13}C NMR spectra of (A) VPDMS (B) CPDMS (C) PSPDMS.

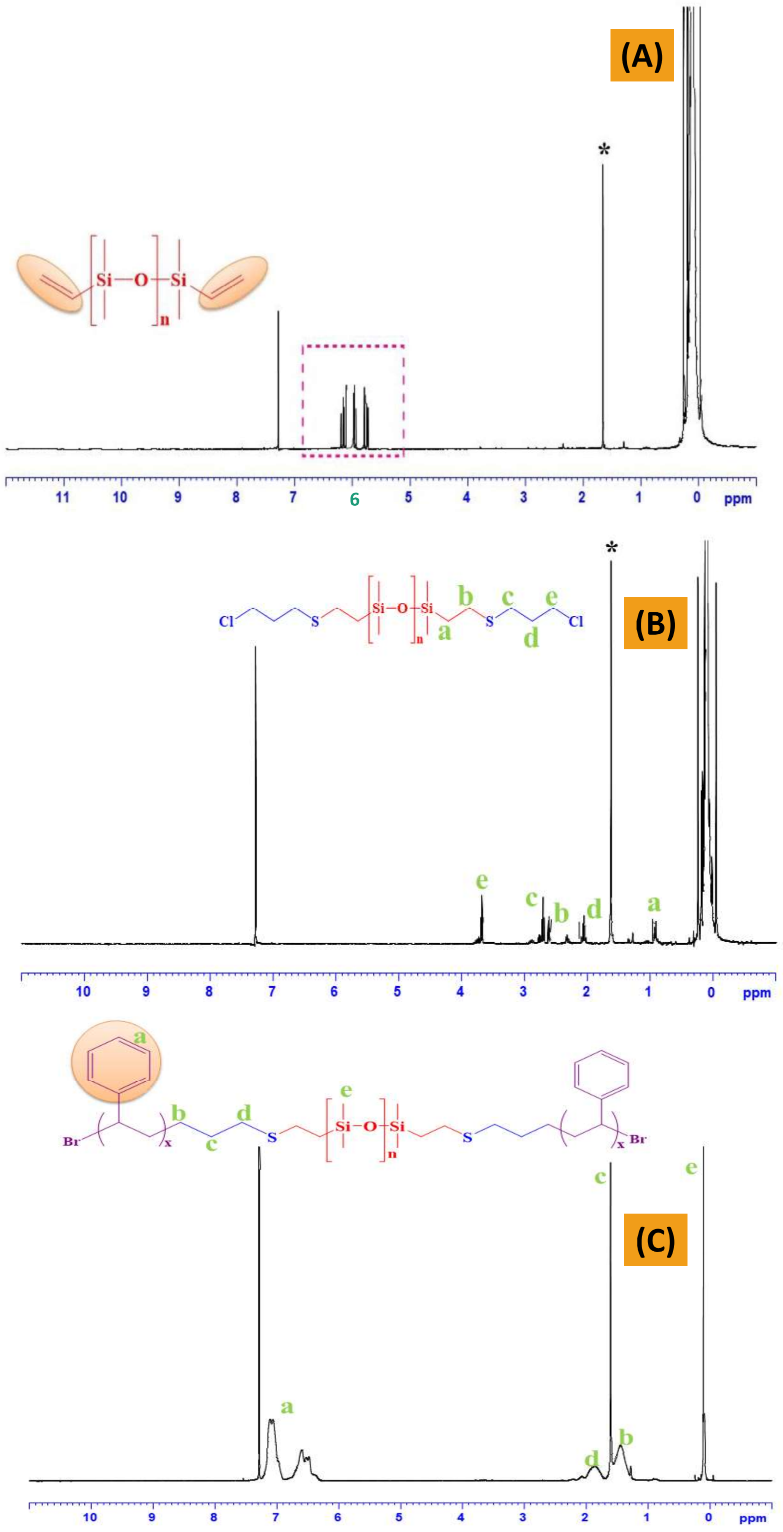


Figure 3.5. ^{1}H NMR spectra of (A) VPDMS (B) CPDMS (C) PSPDMS (* is for wet CDCl3 trace)

As seen in Figure 3.4. The structural analysis of a triblock copolymer produced has shown the polystyrene end chain during polymerization. The spectra of the specified polymer synthesized in $CDCl_3$ solvent are given in ^{13}C NMR. The VPDMS spectra shown in graph **(A)**, two different signals at 131δ ppm and 139δ ppm respectively are for the vinyl group. The peaks at 0.8-1.4δ ppm are assigned to the carbons of $-CH_3$ groups of $-Si(CH_3)_2O$ of synthesized PDMS-MI In **(B)** CPDMS. The signals **a** and **b** are between 25 and 27 ppm for the $-CH_2-CH_2-$ signal, **c** is at 28 ppm for the methylene group ($-CH_2-S$), and **d** and **e** are at 43 ppm for the terminal carbon with connected chlorine. The triblock copolymer with signals **b**, **c**, **d**, and **e** at 125-128 and 145 ppm are for carbon and 145 ppm for benzene, respectively, whereas **'a'** at 43 ppm, which was clearly indicative of PS, contained carbon and benzene, respectively (polystyrene). According to the findings, the final copolymer had PDMS and PS phase structures. Figure 3.5(A) shows the ($-Si(CH_3)_2O-$) resonance at 0.1 ppm, the $-CH_2=CH_2$ resonance at 5.7 to 6.2 ppm, which entirely vanished in Figure 3.5(B), and the -CH2-Cl resonance at 3.6 ppm, which validated the end functional group. Figure 3.5(C) signals for the benzene ring from 6.4 to 7.4 ppm. These ^1H NMR results clearly demonstrate the attachment of the PS backbone to the PDMS chain.

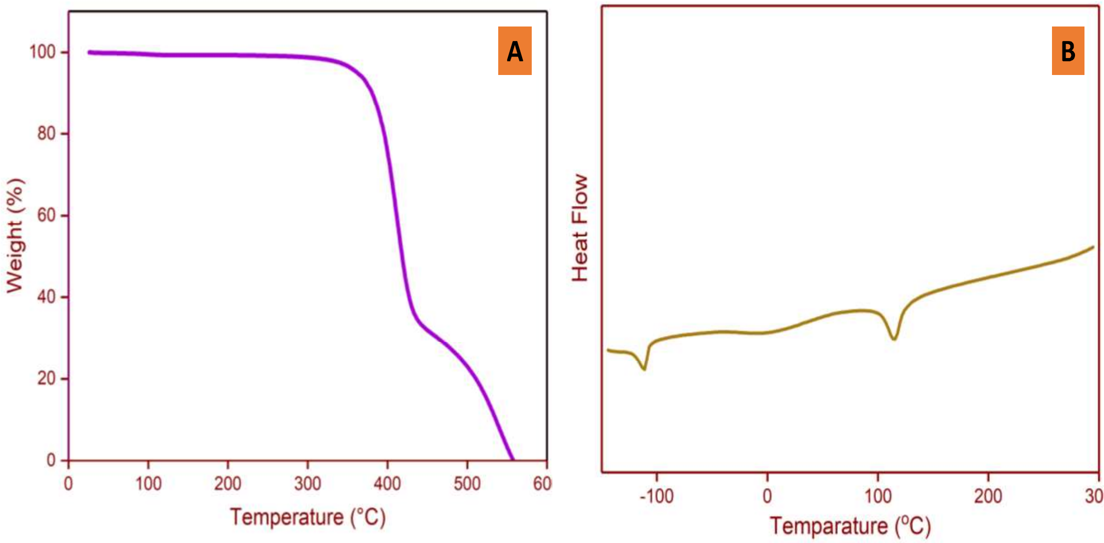


Figure 3.6. TGA curve of (A) PS-*b*-PDMS-*b*-PS, (B) DSC thermograms of PS-*b*-PDMS-*b*-PS.

Figure 3.6 (A) displays the TGA thermograms of materials heated at a rate of 10 °C/min under inert atmospheric conditions, scanning from 25°C to 600°C. The decomposition is two-staged, begins at greater than 300°C, and has outstanding thermal stability. According to the thermogram, the first breakdown is related with heat degradation of the PS chain, whereas the second phase is associated with thermal degradation of the PDMS main chain. Two stages of triblock copolymer degradation demonstrate the independent breakdown of two copolymer components. The addition of PDMS increased the thermal stability because the PDMS decomposition temperature (Td) at 550°C is greater than the PS segment's Td at 435°C[16]. Furthermore, Figure 3.6 (B), which shows the DSC scanning, verifies the Tg values for the polystyrene block at 108°C and the PDMS soft block at -114°C [14, 17]. The DSC thermogram for the PS-*b*-PDMS-*b*-PS triblock copolymer with a PDMS Centre block and polystyrene terminal blocks confirms the phase separated morphology of an ABA type block copolymer[18].

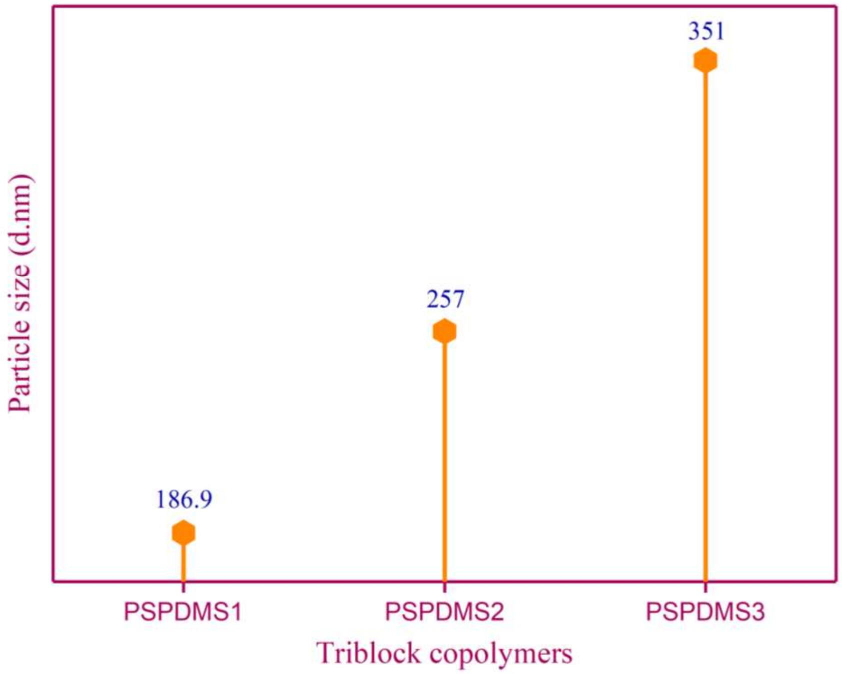


Figure 3.7 DLS image of PS-*b*-PDMS-*b*-PS triblock copolymer particles.

A freshly synthesized sample was mixed with deionized water and diluted to the desired concentration. The particle size of the three distinct triblock copolymers was investigated further using DLS tests. The particle sizes of three distinct polymers were increased as the monomer attachment during polymerization was increased. DLS measurements show in Figure 3.7 that the aggregate diameters were 186.9 nm, 257 nm, and 351 nm, respectively. This single peak in the size distribution demonstrated the linear chain of the ABA triblock copolymer and confirmed the triblock copolymer's narrow dispersity.

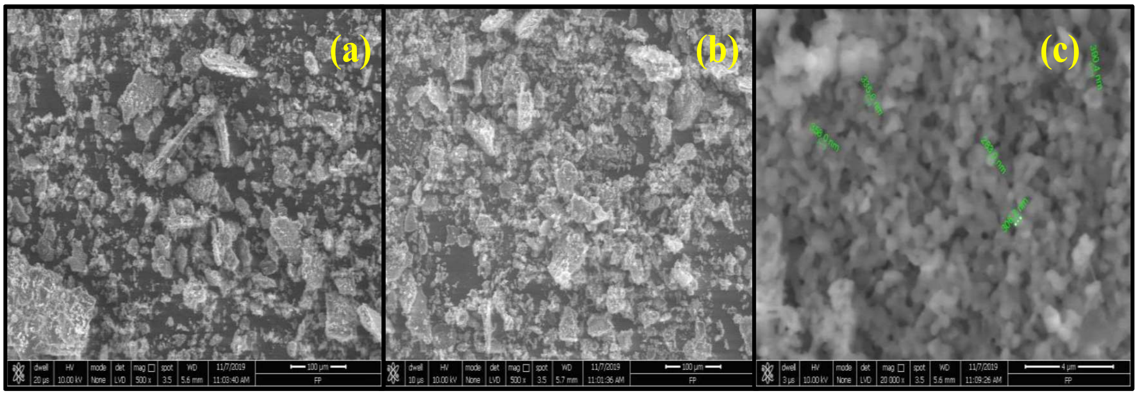


Figure 3.8. SEM images of PS-*b*-PDMS-*b*-PS triblock copolymer particles.

Figure 3.8 illustrates the block copolymer's strong phase segregation and nano aggregation properties, which are due to the PDMS and PS segments (Figure 3.8a and b). The triblock copolymer has spherical particles with an average size of 335 nm, according to SEM images (Figure 3.8c).

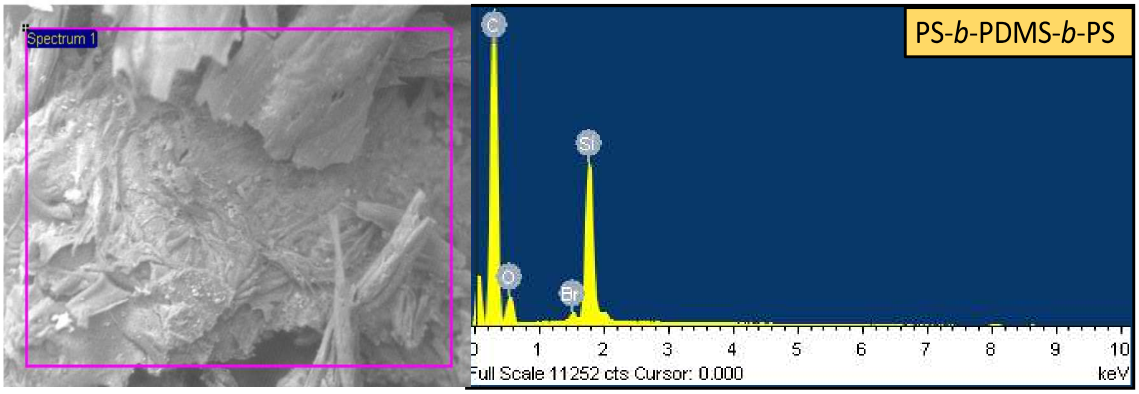


Figure 3.9. EDS image of PS-*b*-PDMS-*b*-PS triblock copolymer.

Figure 3.9 represent the elemental composition of the final functionalized PDMS can be determined by EDS. Images from an EDS examination show that there is 0.56% bromine present in this sample, with the other components being C, O, and Si. The PS-b-PDMS-b-PS triblock copolymer's end functional group was also confirmed by this data. The final polymer of the bromine end group works as a macroinitiator for subsequent reactions, and the chain can be extended up to multiple monomeric units.

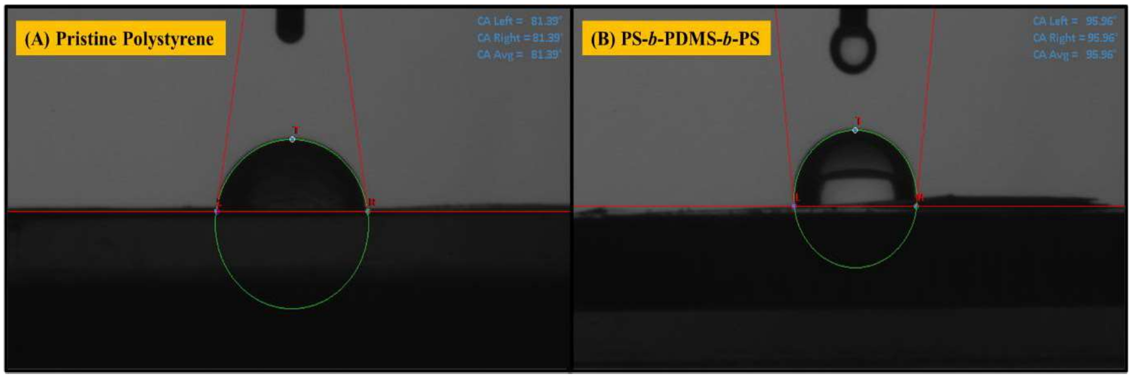


Figure 3.10 Water contact angle for (A) Pristine polystyrene film and (B) PS-*b*-PDMS-*b*-PS Triblock copolymer film.

The water contact angle test was used to examine the surface wettability of the resultant films. The film of pure polystyrene and synthesized PS-*b*-PDMS-*b*-PS triblock copolymer was created by solubilizing it in $CHCl_3$ solvent. The film of pristine polystyrene, as seen in Figure 3.10(A), had a contact angle of 81.39° and was improved by the triblock copolymer PS-*b*-PDMS-*b*-PS, which exhibits higher hydrophobicity at 95.96° shown in Figure 3.10(B). These synthetic triblock copolymers exhibit hydrophobic surfaces and have the potential to be employed as nonconductive materials.

3.5. Conclusions

PDMS-MI was successfully synthesised using the Thiol-Michael addition procedure for the synthesis of PS-b-PDMS-b-PS triblock copolymer (ABA type), as shown by the ^{13}C NMR, 1H NMR, and FT-IR spectrum. Theoretical, GPC, and desired PDI studies all support the synthetic polymer's larger molecular weight. In a controlled manner, the molecular weight increases linearly. The produced triblock copolymers decomposed at temperatures above 300°C, demonstrating the great thermal stability of triblock copolymer, while DSC spectra provide information on the morphology of phase separation. By using DLS analysis, it was discovered that particle sizes were growing as monomer conversion increased. Strong nanoaggregates are shown by SEM examination in terms of their size and form, and their hydrophobicity is increased by the addition of PDMS to PS.

3.6. References

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