# Synthesis and characterization of multiblock copolymers and nanocomposites by atom transfer radical polymerization

**<u>EXECUTIVE SUMMARY</u> of**

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**By**

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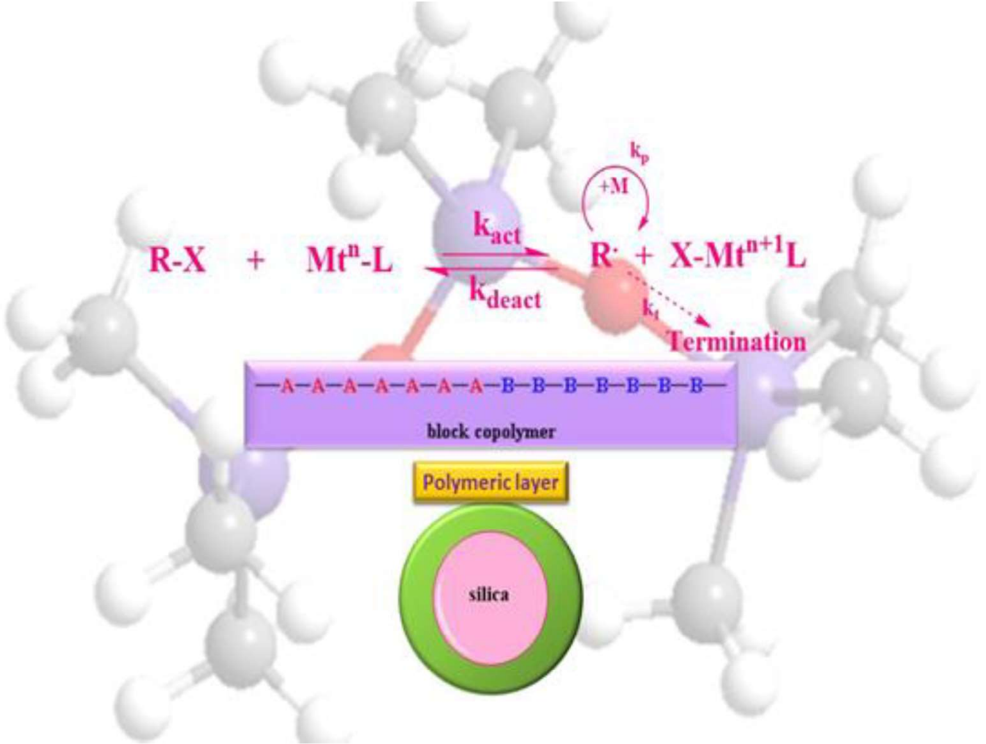
# Chapter 1: General Introduction

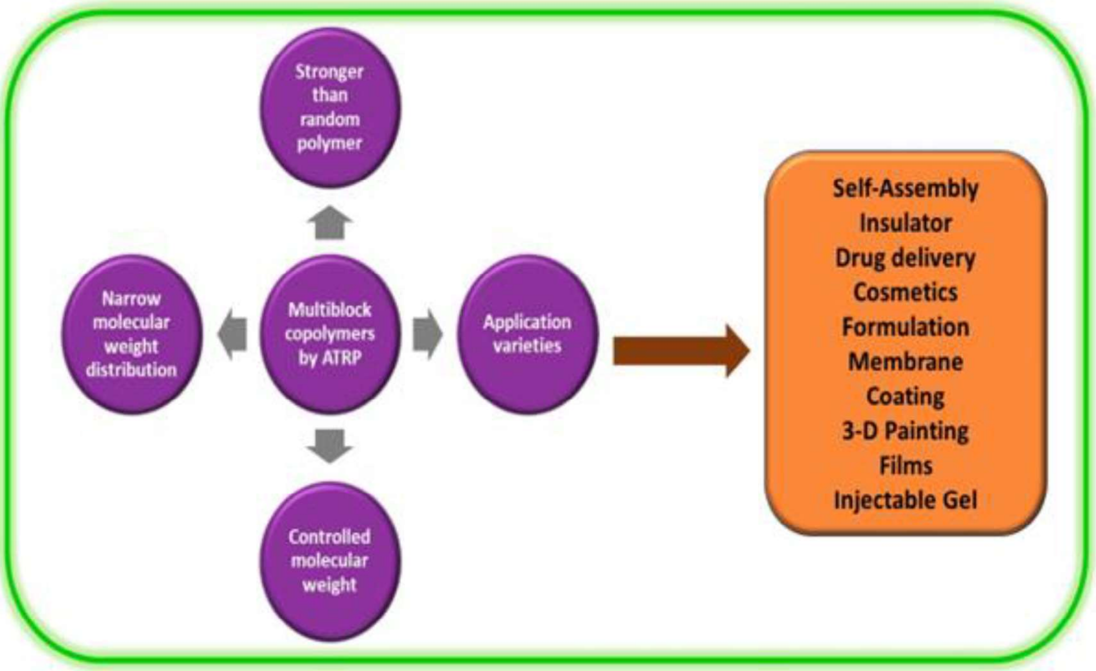
Polymers form through the repetitive combination of basic chemical building blocks with unique structural characteristics. There are two main traditional categories for the polymerization process: (i) addition polymerization and (ii) condensation polymerization. Alongside polymerization, the synthesis of polymers using controlled/living radical polymerization (CRP) methods represents a rapidly advancing domain within the fields of chemistry and polymer science. Controlled/"Living" Radical Polymerization (CRP) methods have successfully been employed to synthesize copolymers that incorporate a diverse range of readily (co)polymerizable monomers while maintaining a narrow molecular weight distribution. The effectiveness of all these "controlled" methods hinges on establishing a rapid dynamic equilibrium between a limited number of actively forming free radicals and a significant proportion of inactive or dormant species. Since the advent of CRP techniques, the scientific literature has been primarily influenced by successful macromolecular engineering strategies such as nitroxide-mediated polymerization (NMP), organo-tellurium-mediated live radical polymerization (TERP), reversible addition-fragmentation transfer polymerization (RAFT), and atom transfer radical polymerization (ATRP). In Atom Transfer Radical Polymerization (ATRP), minimal amounts of transition metals, acting as catalysts alongside ligands, have been utilized. ATRP involves a reversible redox process in which an organic halide undergoes catalysis by a transition metal compound, typically a cuprous halide. The key to successful ATRP lies in rapid initiation and deactivation, resulting in a narrow molecular weight distribution, ensuring that all propagating species commence growth simultaneously. Consequently, ATRP provides a versatile platform for exploring various copolymerization options.



Different transition metal catalysts, including Cr, Fe, Mo, Mn, Co, Os, Re, Ru, Cu, Pd, and Ni, exhibit varying capabilities in facilitating ATRP. Among these metals, copper stands out with robust evidence supporting its widespread use as a catalyst, particularly in studies examining the redox potential of other metals. A recently developed catalyst, known as Photo-ATRP, utilizes photoinitiators and photosensitizers to generate photosensitive active sites. This investigation holds promise for enhancing our understanding of the recyclability and reusability of photocatalysts, potentially addressing issues related to material discoloration caused by certain highly pigmented photocatalysts.

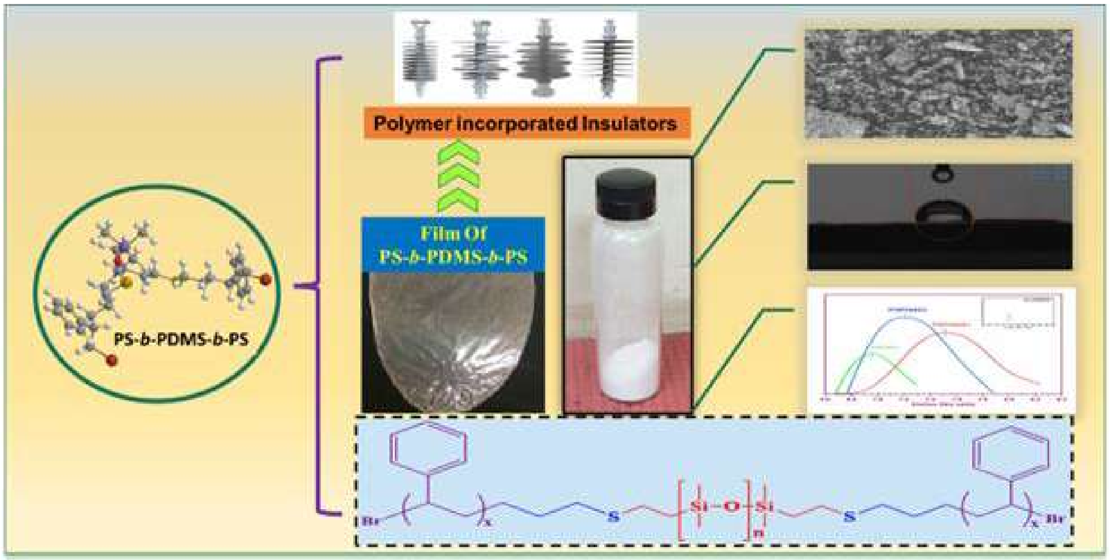
## Chapter 2: Scope of study of multiblock copolymers via Atom Transfer Radical Polymerization Technique

Utilizing Atom Transfer Radical Polymerization (ATRP), block copolymers such as BAB and CBABC with controlled molecular weights and narrow molecular weight distributions, comprising styrene, methyl methacrylate, and t-butyl acrylate, have been successfully synthesized. The research delves into the block copolymer's structural characteristics, living nature, and thermal properties of the artificially produced polymers. The ATRP process ensures precise control over molecular weight and molecular weight distribution for these block copolymers. The synthesized pentablock copolymer has undergone analysis using FT-IR, $^{1}$H, $^{13}$C, GPC, and TGA techniques.



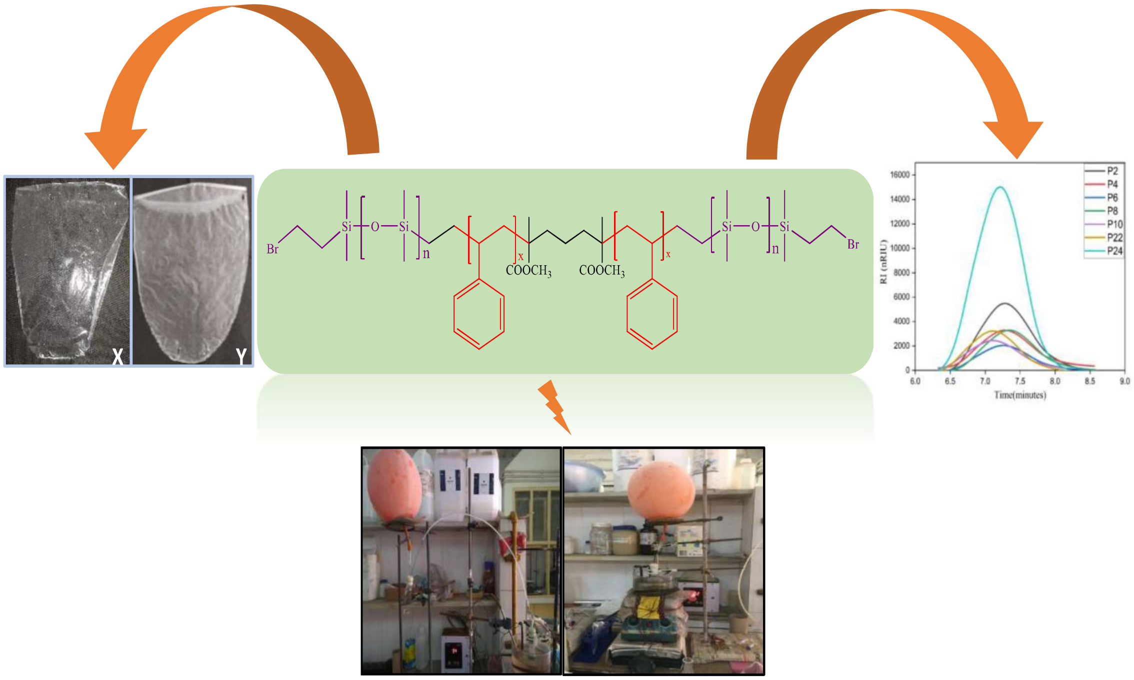
## Chapter 3: Synthesis and characterization of ABA type triblock copolymer of polydimethylsiloxane: PS-*b*-PDMS-*b*-PS

Following the appropriate end functionalization of vinyl-terminated PDMS, ATRP (Atom Transfer Radical Polymerization) was employed to produce a series of triblock copolymers of ABA type, specifically polystyrene-*b*-poly(dimethylsiloxane)-*b*-polystyrene (PS-*b*-PDMS-*b*-PS). The creation of a halo-terminated macroinitiator involved combining vinyl-terminated PDMS with 3-chloropropane thiol. Subsequently, ABA-type block copolymers were synthesized using this macroinitiator, and characterization of the resulting copolymers was conducted to confirm the presence of PDMS and PS blocks. The high molecular weight of the final block copolymer was verified through theoretical molecular weight calculations and Gel Permeation Chromatography (GPC). Results indicate successful bonding of PS chains to the PDMS backbone, with the molecular weight increasing linearly during controlled polymerization. The functionality of the given polymer was confirmed through FT-IR analysis, $^{1}$H NMR spectra, and $^{13}$C NMR spectra. The introduction of PS and PDMS led to improved thermal stability, validated by thermogravimetric analysis. EDS analysis confirmed the halogen content, while SEM was utilized to examine nanoaggregate morphology and DLS to confirm particle size. The triblock copolymer exhibited good thermal stability according to thermogravimetric analysis. Contact angle analysis demonstrated increased hydrophobicity of PS due to the formation of PDMS blocks.



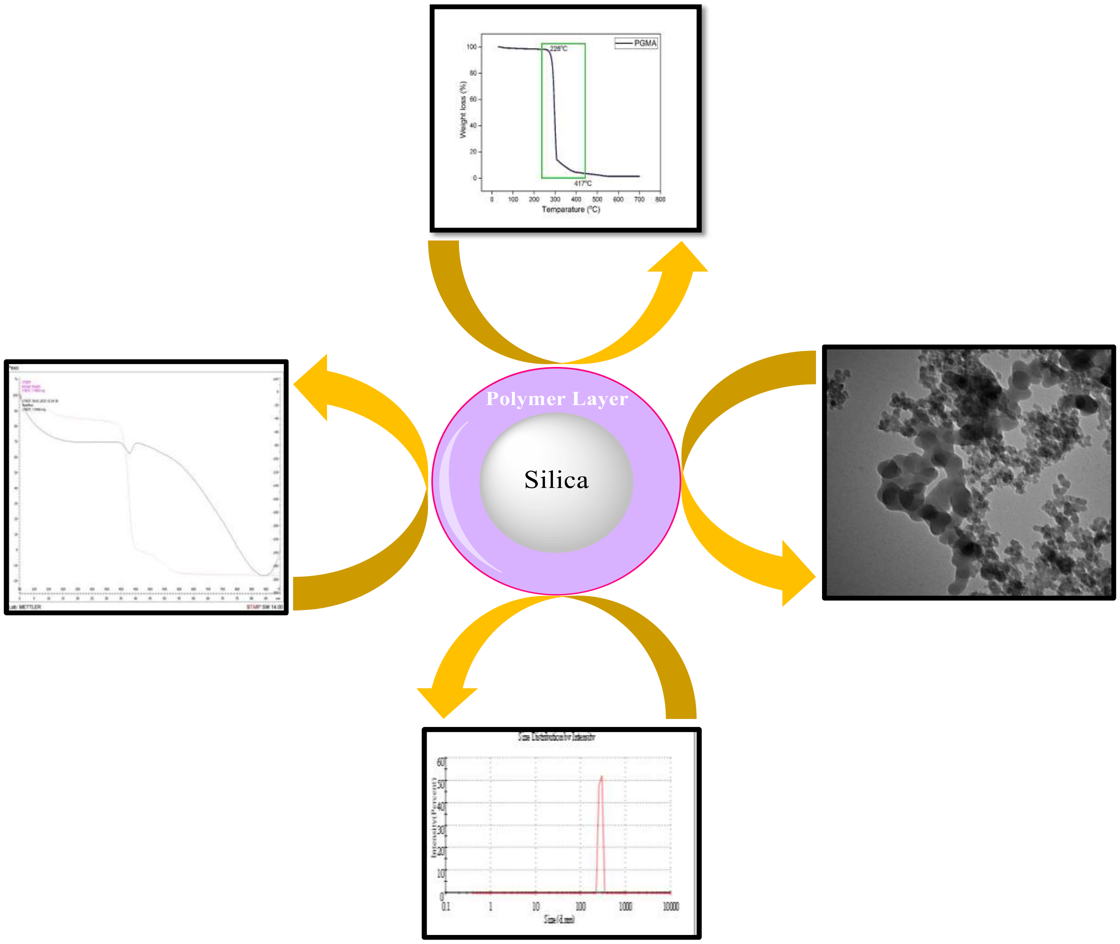
## Chapter 4: Synthesis and Characterization of well-defined triblock copolymers via ATRP: PDMS-*b*-PS-*b*-PDMS

To produce the triblock copolymer PDMS-*b*-PS-*b*-PDMS, initial steps involved the preparation of dibromo-terminated polystyrene, which was subsequently utilized as a macroinitiator for the ATRP-driven synthesis of the triblock copolymer. The confirmation of the macroinitiator and the final product involved various analyses, including FT-IR, $^{13}C$ NMR, $^{1}H$ NMR, EDS, and GPC. FT-IR analysis was employed to validate the functionality of the synthesized material, while $^{1}H$ NMR spectra confirmed the presence of protons. The structural characterization of the resulting triblock copolymer, featuring PDMS at the end chain, is detailed. The percentage of bromine content indicated the end functionality for attaching monomeric units. The synthesized triblock copolymer exhibited a higher molecular weight, as corroborated by theoretical and GPC analyses, along with the desired PDI (Polydispersity Index), suggesting that the polymerization proceeded in according to first-order kinetics.



## Chapter 5: Blending of polymer with fumed silica as a filler

The introduction of fumed silica is previously explained in chapter 1 of this thesis, whereas the present chapter summarizes the synthesis of PMMA via ATRP technique, and its comparative study with the grafted polymer, $SiO_2$-g-PMMA. In this work, the brominated fumed silica as a macro initiator is used to prepare $SiO_2$-g-PMMA, and $SiO_2$-g-PGMA grafted polymers. The synthesis of this brominated fumed silica was carried out by the purification of the fumed silica and its functionalization with Bromine (-Br) group, and then its grafting process was carried out by MMA as well as GMA monomer via ATRP. The synthesis of PMMA via ATRP was confirmed via FT-IR analysis, whereas the formation of $SiO_2$-g-PMMA, and $SiO_2$-g-PGMA were confirmed by FT-IR and EDS analysis. The information of surface morphology and its particle size was given by the TEM analysis. Moreover, the DLS analysis confirmed that after monomer attachment, and on increasing the functionalization of bromine, the particle size of the silica grafted material was increased, and the percentage weight loss of the grafted polymers obtained from TGA analysis was used to calculate percentage grafting (%G) was calculated using the results of TGA analysis of $SiO_2$-g-PMMA, and $SiO_2$-g-PGMA.



## Chapter 6: Summary, Conclusions & Future Directions

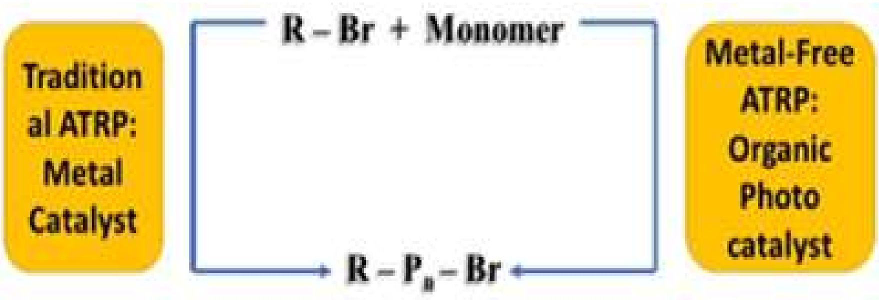
To comprehend ATRP, the initial focus was on synthesizing a styrene homopolymer, utilizing CuBr as the catalyst. Copper complexes had to be stable in both monomers and organic solvents throughout polymerization. Ligands played a crucial role by influencing the redox potential of the CuIIL/CuIL couple, and a more stable ligand led to a more reactive CuI complex. The increase in the number of monomer chains corresponded to an increase in the molecular weight of the final product. This sequential approach was extended to the addition of different monomers, ultimately resulting in a pentablock copolymer. Chapter 1 provides a foundational understanding of multiblock copolymer synthesis through ATRP, laying the groundwork for further modifications in conditions, monomers, and M:I ratios in subsequent chapters.

The synthesis of a macroinitiator using vinyl-terminated PDMS provided a robust signal for its preparation, albeit with challenges such as handling difficulties due to high viscosity and the inherent high molecular weight. Adjusting M:I ratios played a pivotal role in ATRP, necessitating a higher styrene monomer ratio. Thiol-Michael addition reaction with 3-Chloro-1-propanethiol proved to be an effective method for synthesizing the macroinitiator, while past researchers also explored the use of brominating agents like BIBB for functionalized vinyl-terminated reactions. The successful synthesis of the triblock copolymer PS-b-PDMS-b-PS through ATRP, incorporating ideas about changing monomer and initiator positions, provided strong results and insights into the technique. Chapter 4 further confirmed the possibility of using vinyl-terminated PDMS as a monomer. PDMS-*b*-PS-*b*-PDMS synthesis was attempted for the first time using ATRP. The high molecular weight of vinyl-terminated PDMS necessitated a higher molecular weight macroinitiator for the solid end product. A higher monomer ratio in the macroinitiator synthesis facilitated compatibility for further polymerization with vinyl-terminated PDMS. Results, supported by FT-IR and NMR data, revealed a triblock copolymer with increased molecular weight, validated by theoretical and GPC analyses, desired PDI, and first-order kinetics. Contact angle analysis indicated hydrophobicity, and the inclusion of PDMS enhanced thermal stability. Although initial molecular weights deviated from theoretical values due to uncontrolled radical dissociation, this work suggests potential extensions by adjusting M:I ratios and extending chains with additional monomeric units in the future

Fumed silica, known for its large particle size, serves as an effective filler and nanocomposite material. Coated with oil, it undergoes a removal process before functionalization for the synthesis of macroinitiator (MI) through ATRP and subsequent monomer additions. TEM analysis confirms the grafting of fumed silica, paving the way for nanocomposite formation using a triblock copolymer from Chapter 3. Pristine silica, functionalized silica, and grafted silica are incorporated into nanocomposites, demonstrating enhanced thermal stability in TGA data. Future prospects involve exploring varying percentages of nanomaterials to further improve stability with polymers.

## Recommendations/ Suggestions

1. ATRP's evolution begins with the metal catalyst and progresses through numerous difficulties with catalyst purity and coloring. Further research reveals metal-free ATRP. The use of a photoredox catalyst replaces the need for a metal catalyst. These findings may offer up alternative opportunities to better understand the recycled content and reusability of photocatalysts, in addition to potentially addressing material discoloration due to the highly coloured existence of many of these photocatalysts.



2. The block copolymers of PDMS have high hydrophobicity so that it will use as non-conductive materials as an application. Styrene can be replaced by the other monomer which will have non-conductive properties.
3. The nano filler fumed silica has the excellent capacity to make nano composite with different polymers or even block copolymers. It will be used as a coating material, and it is also important to consider.
4. The synthesis of block copolymers of PDMS will be use in membrane technology by using Fumed silica, CNTs as a filler for the gas separation.

My perspective is very optimistic because I believe that with the knowledge that is currently available, there are only a few limits that can be explored by using ATRP. Additionally, with the advancement of better polymerization methods, processes, and techniques, I believe that things that have been thought to be impossible will be accomplished in the future.

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