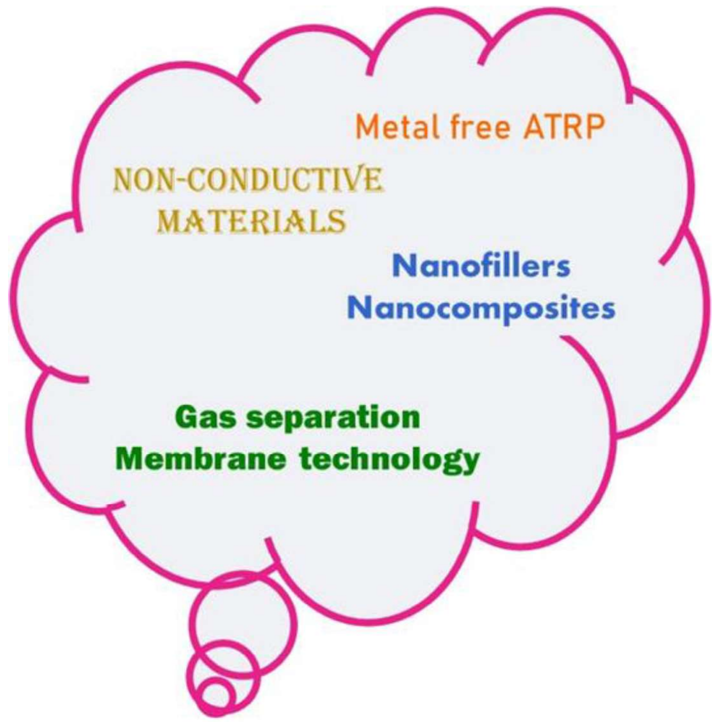

Chapter 6

Summary, Conclusions & Future Directions

6.1. Summary and Conclusion

The ATRP approach, its workings, benefits, drawbacks, contributing elements, etc. are all represented in this thesis. This method is used for any PDMS-based synthesis involving various monomers, including styrene, MMA, GMA, and tBAc. This technique was used in the past by researchers using different conditions. The aim was to determine if the monomer that we chose would be polymerized by this approach or not, which means that this method does not always give a high yield of the final material and can change some other possibilities. Some of the things we tried worked out successfully, and others provided knowledge on what will work best for ATRP. The work is considered novel by itself, based on the outcomes of various synthesis. The following are the key conclusions of this study:

❖ Scope of study of multiblock copolymers via Atom Transfer Radical

For the understanding of ATRP, first the basic synthesis of a homopolymer of styrene monomer gave the idea about how it will work. All the reactions were put with CuBr Catalyst because free copper ions, Cu^{+} and Cu^{2+}, have essentially no catalytic potential. During the polymerization process, copper complexes must be stable in monomer and organic solvents. By stabilizing or destabilizing the Cu^{II} state of the complex, ligands impact the redox potential of the couple $Cu^{II}L/Cu^{I}L$. The relationship between a low Cu^{I}/Cu^{II} redox potential and in comparison, to the Cu^{I} state, relative stabilization of the Cu^{II} state occurs in interaction with the ligand. As an ATRP catalyst, a more stable ligand will produce a more reducing and hence more reactive Cu^{I} complex. As the number of monomer chain increase the MW of final product was also increased, and this tradition is followed up to the addition of two different monomers and finally it became pentablock copolymer. The chapter 1 is giving the basic handle of synthesized multiblock copolymer by successful method of ATRP. This was help us to modify the other conditions, monomers, and M:I ratios for synthesized various MI for the next.

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

From the synthesis of multiblock copolymer, the synthesis of macroinitiator by using vinyl terminated PDMS gave the strong signal for its preparation. Off course loss of difficulties were arises like, due to its high viscosity the handling of overall material was too much difficult, it has its own higher MW, which was difficult in overall conclusion of the preparation, the adjustment of M:I ratios was the key factor of the ATRP so, the amount of monomer (styrene) ratio was taken very much high.

The synthesis of the MI by Thiol-Michael addition reaction by 3-Chloro-1-propanethiol was the most effective one. Some other brominating agents like BIBB also use for the functionalized vinyl terminated reaction by the past researchers. The synthesis of MI by the Thiol-Michael addition reaction and then ATRP by styrene monomer was not polymerized till now. So, the overall efforts of this synthesis of triblock copolymer PS-*b*-PDMS-*b*-PS was given the strong results and indication about this ATRP technique. By this synthesis some ideas came whether the monomer and initiator position can be changed. Whether the vinyl terminated PDMS as monomer possible? Which was confirmed by the chapter 4.

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

Synthesis of PDMS-*b*-PS-*b*-PDMS first time attempt by the ATRP technique. From the past by the living anionic polymerization process. As above mentioned, the MW of vinyl terminated PDMS become very high so the Mw of macroinitiator should be higher for the solid product of the final material. So, the higher ratio of monomer for the synthesis of MI gives high molecular weight and which will be compatible for the further polymerized with vinyl terminated PDMS. According to the results and discussion this study is proven by the FT-IR and NMR data.

This synthetic triblock copolymer has a larger molecular weight, as shown by theoretical and GPC analyses, the desired PDI, and first-order kinetics were used during polymerization. There is no physical mix indicated by the single GPC curve, which indicates a linear polymer chain. This chapter shows interesting data of contact angle analysis shows its hydrophobic nature. The use of PDMS also improves thermal stability. Uncontrolled radical dissociation is observed concurrently, and this causes the production of strongly crosslinked molecules with extremely high molecular weights. At first, molecular weights do not match to theoretical values. This work may be extended in future by changing the M:I ratios and chain can be extended by numbers of monomeric units.

- ### Blending of polymer with fumed silica as a filler

The fumed silica is great particle size, so it is used as a filler and nanocomposite. Fumed silica was coated with oil so it should be completely removed from oil and then it was used for functionalization so basically the target was to make MI then ATRP followed by different monomers. After synthesis of this grafted fumed silica the TEM analysis shows the black circle for pristine silica only and when it will coated by polymer it have which layer around it. This TEM analysis confirmed grafting fumed silica and the next step is to make nanocomposite with another polymer. For that, in chapter 3 the prepared triblock copolymer is used as a polymer and these pristine silica, functionalized silica and grafted silica, all were making a nanocomposite and its TGA data shows its thermal stability. This work, by the changing of different percentage of nano materials will increase its stability with polymer, these will make it future prospect.

❖ Future Directions

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.

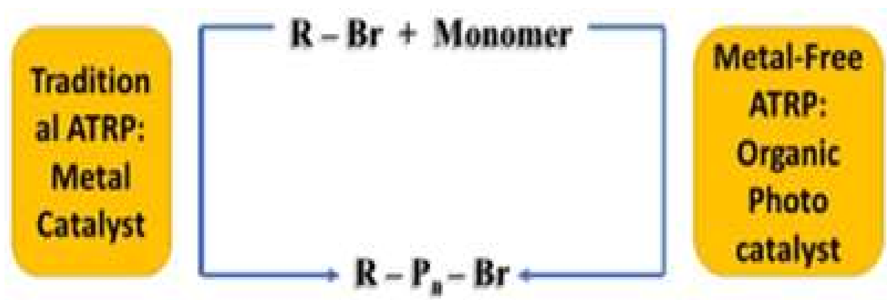

Figure 6.1 Difference between tradition metal catalyst and metal-free ATRP.

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.