Synopsis of the thesis

Titled

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

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Chapter 1: General Introduction

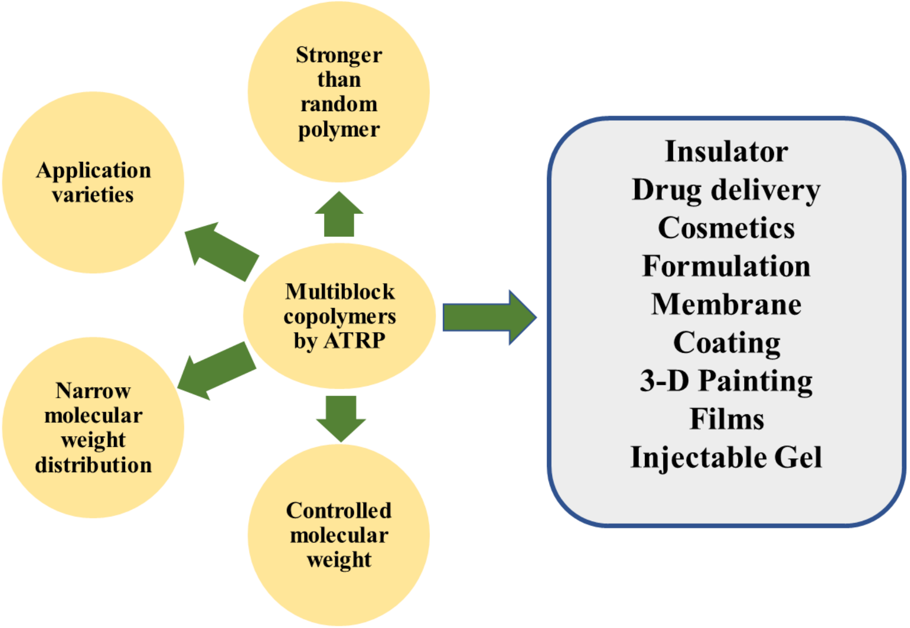
Polymers are created by repeatedly combining small, simple chemical building blocks with distinctive structural properties. The two traditional classifications for the polymerization process are (i) addition polymerization and (ii) condensation polymerization. One of the most quickly evolving fields of chemistry and polymer science, in addition to polymerization, is the synthesis of polymers by controlled/living radical polymerization (CRP) methods. The synthesis of copolymers integrating a variety of radically (co)polymerizable monomers and having a narrow molecular weight dispersion has been accomplished using the Controlled/"Living" Radical Polymerization (CRP) techniques. All of these "controlled" techniques rely on creating a quick dynamic equilibrium between a small number of free radicals that are developing and a large portion of dormant species. Since the development of the CRP techniques, the literature has been dominated by effective macromolecular engineering approaches as nitroxide mediated polymerization (NMP), organo-tellurium mediated live radical polymerization (TERP), reversible addition-fragmentation transfer polymerization (RAFT), and atom transfer radical polymerization (ATRP). Low concentrations of transition metals have been employed in Atom Transfer Radical Polymerization (ATRP), which used as a catalyst along with a ligand. Atom transfer radical polymerization is a reversible redox process that an organic halide goes through, catalyzed by a transition metal compound such a cuprous halide. A quick initiation is necessary for a successful ATRP, as is a quick deactivation that leads to a narrow molecular weight distribution so that all propagating species start growing at the same moment. Thus, ATRP opens a wide range of copolymer possibilities.

Various transition metal catalysts, such as Cr, Fe, Mo, Mn, Co, Os, Re, Ru, Cu, Pd, and Ni, have varied capabilities to conduct ATRP. As compared to other transition metals, copper has the strongest evidence in favor of its extensive usage as a catalyst and the study of other metals' redox potential. A novel kind of catalyst called Photo-ATRP uses substances called photoinitiators and photosensitizers to create photosensitive active sites. This research may open up new possibilities for a better understanding of the recycled content and reusability of photocatalysts, in addition to perhaps resolving material decolorization brought on by the presence of some of these highly coloured photocatalysts. This thesis will explain it using the given content.

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

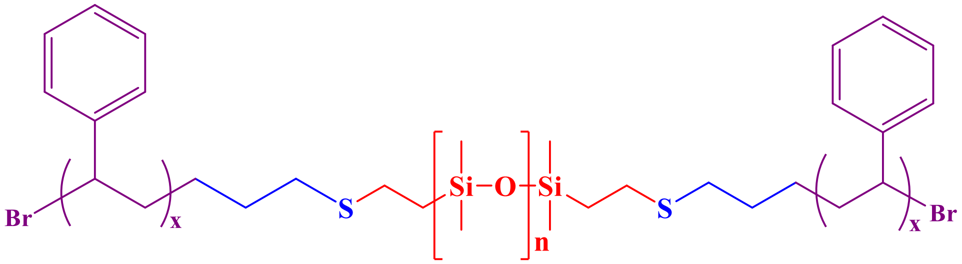
Polymerization Technique

BAB and CBABC tri and pentablock copolymers of styrene, methyl methacrylate, and t-butyl acrylate with controlled molecular weights and narrow molecular weight distributions can be successfully synthesized using ATRP. The study has been done on the block copolymer structure, living nature, and thermal characteristics of the synthetic polymers. Molecular weight and molecular weight distribution are well-controlled during the atom transfer radical polymerization process used to create the block copolymers. The FT-IR, ^{1}H, ^{13}C, GPC, and TGA analyses of the synthesized pentablock copolymer.



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

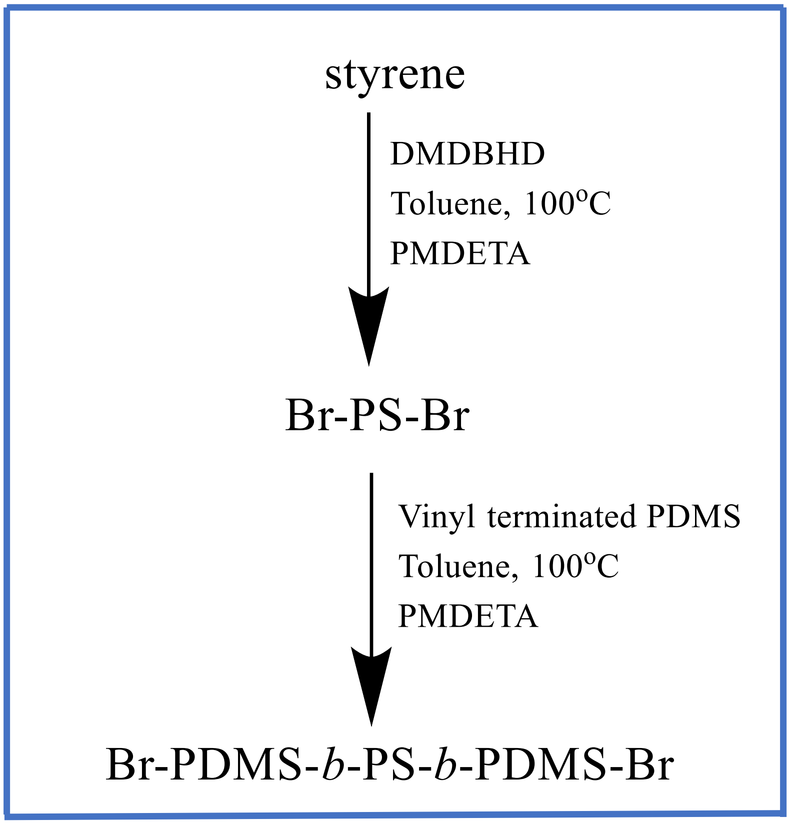
After proper end functionalization of vinyl-terminated PDMS, ATRP (Atom Transfer Radical Polymerization) was used to create a series of ABA-type polystyrene-b-poly(dimethylsiloxane)-b-polystyrene (PS-*b*-PDMS-*b*-PS) triblock-copolymers. To create a halo terminated macroinitiator, vinyl terminated PDMS was combined with a 3-chloropropane thiol. The synthesis of block copolymers of the ABA type was then carried out using this macroinitiator. To confirm the presence of PDMS & PS blocks, the resulting block copolymers were characterized. The high molecular weight of the ultimate block copolymer was confirmed using the theoretical molecular weight and GPC. The findings demonstrate that the PS chains were successfully bonded to the PDMS backbone and that, throughout the controlled polymerization, the molecular weight increased linearly with time duration. FT-IR analysis, ^{1}H NMR spectra, and ^{13}C NMR spectra were used to confirm the given polymer's functionality. After PS and PDMS were added, the thermal stability improved. The halogen content is also confirmed by the EDS analysis. While SEM was used to examine the morphology of the nanoaggregates, DLS was used to confirm the particle size. Thermogravimetric analysis showed that this triblock has good thermal stability. Contact angle analysis proved that the formation of PDMS blocks increased hydrophobicity of PS. Here is the reaction of the final polymeric chain which is given below.



PS-*b*-PDMS-*b*-PS

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

To prepare the triblock copolymer PDMS-b-PS-b-PDMS, dibromo terminated polystyrene was first prepared and then used for the subsequent reaction in triblock copolymer via ATRP. FT-IR, ^{13}C NMR, ^{1}H, EDS, and GPC analysis were used to confirm the macroinitiator and final product. Furthermore, FT-IR analysis confirmed the functionality of the synthesized material, and ^{1}H NMR spectra confirmed the presence of proton. The structural characterization of a synthesized triblock copolymer with PDMS at the end chain is presented here. The bromine content percentage also demonstrated the end functionality that will be used for the attachment numbers of monomeric units. This synthesized triblock copolymer has a higher molecular weight, which is confirmed by theoretical and GPC analysis, as well as the desired PDI and the polymerization proceeded according to first-order kinetics.



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

The synthesis of PMMA via ATRP was confirmed by FT-IR analysis. The purification of fumed silica and its functionalization was confirmed by EDS and FT-IR analysis. Furthermore, polymer grafted from fumed silica was successfully prepared by the ATRP technique. After the grafting, the particle size is increasing which was confirmed by DLS. The percentage grafting (%G) of the final material and % weight loss of the ATRP reaction is confirmed by the TGA analysis. The polymer grafted silica material will be further used as a filler next to the polymer and checked for its hydrophobicity by contact angle analysis and its surface topology by TEM.

Chapter 6: Summary, Conclusions & Future Directions

This chapter includes a summary of each chapter, as well as the merits and downsides of the study provided in the thesis. Furthermore, due to the limits of the study, new possibilities for future research might be studied.

❖References

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❖Conferences

1. Attended: IWA, The 6th International Water Accusation Regional Membrane Technology Conference 11th December 2018
2. Poster Presentation: 56th Annual Convention of Chemist 2019 organized by 'INDIAN CHEMICAL SOCIETY' NOVEMBER 14-16, 2019, Raipur-492010, Chhattisgarh, India
3. Attended: UGC-CPEPA Sponsored, National Seminar on Applied Polymer Science and Technology (NSAPST-2019) Organized by Department of Chemistry, Sardar Patel University, Vallabh Vidhyanagar-388120, Gujarat, India
4. Oral presentation: 9th biennial symposium on "Emerging trends in separation science and technology (SESTEC-2020) Organized by BARC, Mumbai, India
5. Oral presentation: International Conference on "Advances in Sustainable Research for Energy and Environmental Management (ASREEM-2021)", August 6th, 2021, Department of Chemical Engineering, Sardar Vallabhbhai National Institute of Technology Surat-395007, Gujarat, India
6. Oral presentation: 12th International Conference (Virtual) on "Advancements in polymeric (APM-2021)", March 9th, 2021, Bhubaneswar, India

❖ List of Publications Related to Thesis

1. **B. Mistry**, C. N. Murthy, In the Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, August 2022, "Synthesis of ABA type triblock copolymer from poly(dimethylsiloxane) macroinitiator: A novel attachable initiator for atom transfer radical polymerization". (Accepted-19th September 2022, IF: 2.216)

❖ Publication Not- related to Thesis

1. **B. Mistry**, H. K. Machhi, R. Vithalani, D. Patel, C. K. Modi, M. M. Lad, K. R. Surati, S. S. Soni, P. K. Jha and S. R. Kane, In the Journal of Sustainable Energy Fuels, 2019, DOI: 10.1039/C9SE00338J. "Harnessing the N-Dopant Ratio to Carbon Quantum Dots for Enhancing the Power Conversion Efficiency of Solar Cell". (IF: 5.503)
2. Sneha Soly, **Bhavita Mistry**, C. N. Murthy, In Polymer International, November 2021, entitled "Photo-mediated metal-free atom transfer radical polymerization: recent advances

in organocatalysts and perfection towards polymer synthesis”. DOI: 10.1002/pi.6336, (IF: 2.990)

❖ Book Chapter

1. N. S. Joshi, D. K. Pandey, **B. Mistry**, D. K. Singh, In the Springer Nature, Metal Oxide Nanoparticles: Synthesis, Properties, Characterization, and Applications. (Under Communication)

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