# CHAPTER VII

## Summary and Conclusions

## 7.1. Summary and Conclusions

The objective of this research was to investigate and prepare well-defined polymeric materials using "Living"/Controlled Radical Polymerization techniques (L/CRP). Initiallly the research was focused on the synthesis of various acrylic homopolymer and block copolymers particularly by ATRP, but the scope evolved as the knowledge gained in ATRP and was used to exploit opportunities in the similar fields of L/CRP like TERP and Living anionic Polymerization.

The main findings of this work are:

Atom transfer radical polymerization (ATRP) technique was successfully applied for the synthesis of poly(*n*-butyl methacrylate-*b*-styrene-*b*-*n*-butyl methacrylate) (PBMA-*b*-PS-*b*-PBMA), (BAB) and poly(methyl methacrylate-*b*-*n*-butyl methacrylate-*b*-styrene-*b*-*n*-butyl methacrylate-*b*-methyl methacrylate) (PMMA-*b*-PBMA-*b*-PS-*b*-PBMA-*b*-PMMA), (CBABC) linear tri- and pentablock copolymers, respectively in solution for the first time. Difunctional polystyrene macroinitiator that contains bromide end-group was prepared by ATRP of styrene using dimethyl-2,6-dibromoheptanedioate (DMDBHD) as an initiator. The formation of block copolymers was confirmed by gel permeation chromatography (GPC), Nuclear magnetic resonance ($^1$H NMR) and differential scanning calorimeter (DSC) techniques. A good agreement between the theoretical and experimental molecular weights was found. The molecular weight distribution (MWD) was narrow and did not change much with the progress of the reaction. Linear increase in the number average molecular weight ($M_n$) with conversion was observed indicating the polymerizations followed a 'living'/controlled process. Both, BAB and CBABC block copolymers showed core-shell type flower-like micellar structures when toluene was used as a selective solvent for A block. This system can thus be tuned to fit particular monomers or catalyst systems resulting in unique supramolecular structures and offers the control needed to synthesize well-defined polymers for specific applications.

The feasibility of producing nano-sized polymer particles for the first time using true emulsion ATRP using mixed ligand system with low surfactant concentration at room temperature was studied. The factors affecting polymerization, particle size, and molecular weight were investigated to provide initial information for eventual application to large scale industrial applications of PMMA. The preliminary results shows that ATRP in a true emulsion using mixed ligand system and by differential addition of the monomer is possible, at room temperature but additional investigations are necessary to understand the role of all components involved.

Well-defined polystyrene-*b*-poly (2-vinylpyridine) (PS-*b*-P2VP) and (P2VP-*b*-PS) an amphiphilic diblock cooligomer (which acts like a surfactants) of low molecular weight were successfully designed and synthesized for the first time via TERP. Thus, TERP provides a facile route for the synthesis of AB and BA diblock copolymers from Styrene and 2-vinylpyridine respectively. The versatility and mild reaction conditions of this new method would be suitable for the mass production of structurally defined macromolecules. Block copolymer have been increasingly used to organize mesostructured composite solids, because the architectures of the amphiphilic block copolymers can be rationally adjusted to control the interactions between the inorganic and organic species, self-assembly, and especially processibility is more than possible with low molecular weight surfactants. For mesoporous composites by electrostatic interaction, P2VP block of P2VP-*b*-PS was quarternized by reaction with excess methyl iodide. The quarternized Q-P2VP-*b*-PS has a hydrophilic pyridium block and hydrophobic polystyrene block so it dissolved and formed micelles in toluene. The $TiO_2$ was selectively embedded in P2VP domains. To remove polymer, sintering and oxygen plasma etching were used. Thin films were prepared by spin-coating for application such as optical catalysts, chemical sensors, and dye-sensitized solar cell.

A novel, cheap and readily available coupling agent has been successfully employed in the anionic polymerization at room temperature leading to the concurrent synthesis of the three different block copolymers; di-, tri-, and star-block polymers of polystyrene-*b*-polyisoprene (SI). SI block copolymers have been found to be valuable in diverse applications. High degree of control over the molecular weight and weight fractions of various SI block copolymers has been demonstrated by changing the molar ratios of initiator to the coupling agent. In spite of using bi-functional coupling agent star-block copolymer along with the di- and tri- block copolymers were obtained at the same time. The most probable mechanism which explains the results and is most logical based on the scientific facts already known has also been proposed. This is the first report of the formation of a star-block copolymer with the help of a bi-functional coupling agent employing anionic polymerization at room temperature.

In conclusion, the work carried out here in "Living"/Controlled Polymerizations, and more specifically the ATRP, TERP and anionic process, has been shown to be a valuable tool for the synthesis of homo and (multi)block copolymers, although some problems were met that are inherent to the ATRP in water-borne medium. These problems, however, can be reduced to a minimum by careful optimization of the polymerization conditions. Keeping all these results and guidelines in mind should allow for the preparation of well-defined materials using such techniques.

I feel confident that with what is already known, there are few limits to what can be produced using (L/CRP) and with the development of new methods, procedures, polymerization techniques that have thus far not been possible will be achieved.