## "APPLICATION OF ATOM TRANSFER RADICAL POLYMERIZATION FOR THE PREPARATION OF MULTIFUNCTIONAL MATERIALS"

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by

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## **Conclusion:**

The present thesis entitled "APPLICATION OF ATOM TRANSFER RADICAL POLYMERIZATION FOR THE PREPARATION OF MULTIFUNCTIONAL MATERIALS" deals with the controlled synthesis and application of different multifunction amphiphilic block and graft copolymers. First chapter is all about study of literature review of ATRP whereas second chapter deals with synthesis of living PDMAEMA carried out in solvent free conditions using CuCl as catalyst and commercially available, relatively cheap ligand PMDETA. In the presence of catalytic amount of AQCl, the catalyst complexes become completely soluble in bulk DMAEMA and hence a controlled polymerization results. Analysis of the kinetics of polymerization confirms that interaction of the monomers with the catalyst complex significantly affects the activity of the catalyst complex, particularly when high molecular weights are targeted with concomitant decrease in catalyst concentration. The conditions have been optimized and synthesis of high molecular weight PDMAEMA has been carried out. Dual stimuli responsive di- and triblock copolymers with thermo responsive PDEGMEM and block copolymers with various other methacrylate systems offering multifunctional properties are synthesized using living PDMAEMA molecules as macroinitiators. The third chapter also summaries the dual stimuli responsive character (pH and temperature) and presence of highly coordinating pendant -NMe<sub>2</sub> groups in the block copolymer (PDMAEMA<sub>10.5k</sub>-b- PDEGMEM<sub>12.5k</sub>-Cl) have been exploited for the synthesis of stimuli responsive PDMAEMA<sub>10.5k</sub>-b-PDEGMEM<sub>12.5k</sub>-Cl/CdS 'Q-particle' hybrid nano structure in aqueous medium. The stabilized CdS quantum dots show shuffling of morphologies between 'core confined' and 'corona embedded' with the change of stimuli. Fourth chapter briefs the synthesis of a couple of PVDF based graft copolymers PVDF-g-(PBMA-alt-PDEGMEM-alt-PFMA)(PVBDF) and PVDF-g-(POEGMA-alt-PFMA)(PVOF) has been successfully carried out by homogeneous solution phase ATRP after being initiated directly from PVDF macroinitiator. In a post polymerization modification step, Diels-Alder reaction of the pendant furan rings with maleimide carried out to prepare PVBDFM and PVOFM membrane materials respectively. The synthesized materials are casted into porous membranes by breath figure (from THF solution of PVBDFM) and immersion-precipitation techniques. A detailed characterization of the polymerization kinetics, molecular weight, structure and morphology of the bulk graft copolymeric materials and membrane surfaces carried out by various spectroscopic, thermal and electron microscopic techniques. The polar/hydrophilic moiety enriched graft copolymer membrane surfaces (as confirmed from Xray photo electron spectroscopy) resulted better anti fouling property than PVDF when tested

with aqueous solution of lysozyme. Relatively higher population of polar residues in the pore wall compared to membrane surface of PVBDFM has been attributed to the dynamic template model of pore generation during breath figure mechanism. This feature is beneficial for having improved anti fouling property as well as affinity based immobilization during convective flow through process. Indeed PVBDFM has exhibited better anti fouling property than PVOFM, which has been attributed to higher graft copolymer concentration in PVBDFM and better aggregation of polar graft chains in the solvent-non solvent interface as THF is a selective solvent where PVDF chains are insoluble. Interestingly, PVBDFM membrane has shown adjustable pore sizes when breath figure casted freshly prepared membranes immersed in water baths having different temperatures. This has been attributed to the temperature dependent aqueous solubility of PDEGMEM block (LCST of 26°C). The graft copolymeric membranes have shown preferential immobilization of adenine and melamine over uracil, which is apparent from their higher binding constant determined from adsorption experiment on PVBDFM surface as well as higher immobilization (adenine > melamine >> uracil) under a competitive situation from aqueous solution of equimolar mixture of these three bases. In a filtration experiment PVBDFM membrane (100 mg) has shown ~ 60% RNA immobilization from 5 ml of its  $5\mu$ M aqueous solution.