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Index No. : 158/18/Chem./26

Title of the thesis: POLY(IONIC LIQUID)S: SYNTHESIS, STIMULI-RESPONSIVE PROPERTIES AND THEIR MATERIAL APPLICATIONS

ABSTRACT

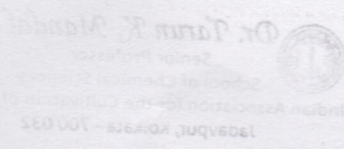
The present thesis describes the design and synthesis of new types of ionic liquids (ILs) and/or poly (ionic liquids) (PILs), their stimuli-responsive behaviours and explores the role of macromolecular engineering in the development of novel polymer materials for advanced applications. The main aim of this thesis is to synthesize a series of new stimuli-responsive ionic liquid-based random copolymers of different architectures via RAFT polymerization of an ILM with a variety of hydrophilic or hydrophobic monomers followed by the investigation of these PILs with regards to their stimuli-responsiveness, particularly in solution under different external stimuli such as temperature and ionic strength. This follows by the polymerization of an ionic liquid monomer into nonionic-ionic type random copolymers with varying composition of monomers followed by the investigation of their ionic conductivities as a function of different parameters. Further development of new type of photoinitiating ILs along with the detailed study of the photoinitiation mechanism and comparative photoinitiating abilities in aqueous medium are described along with exploration of PIL as macromolecular photoinitiator towards the development of different types of thermoresponsive graft copolymers. Finally, new cross-linkable ILMs and their successive use to fabricate hydrogel adsorbents for the removal of dyes are described.

Chapter 1 provides a quick overview on the general aspects of ILs and PILs and the design and synthetic strategies for different types of ILs, ionic liquid monomers (ILMs) in particular, PILs via conventional free radical or controlled radical polymerization (e.g. RAFT) of ILMs. The different properties of ILs/PILs, particularly in connection with their ionic conductivity and stimuli-responsiveness are described in detail. This section also concentrates on the recent developments on water-soluble photoinitiators and fabrication of polymeric hydrogel adsorbents which are potential for advanced applications. Finally, the chapter ends with precise descriptions of various potential applications of ILs/PILs.

Chapter 2 describes the synthesis of a series of PIL, P[VBTP][Cl]- based random copolymers containing conventional polymer segments namely, P[VBTP][Cl]-ran-PMMA, P[VBTP][Cl]-ran-PS, P[VBTP][Cl]-ran-PHEMA and P[VBTP][Cl]-ran-PNIPAM of varying compositions via RAFT polymerization technique. The copolymeric solutions in the presence of externally added halide ions experience UCST-type phase behaviours due to the insertion of PIL (P[VBTP][Cl]) segment. The cloud point of UCST transitions in these copolymers are tunable with respect to various parameters such as content of ionic segment as well as concentrations of added halide anions. On the other hand, P[VBTP][Cl]-ran-PNIPAM copolymers show a composition dependent dual thermo- and ion-responsive phase behaviour. The copolymers with low ionic PIL contents show only inherent LCST behaviour of PNIPAM with tunable cloud points by the addition of varying amount of Cl⁻ anion. However, the copolymer with moderately high ionic PIL content exhibits both LCST-type behaviour, inherent to PNIPAM segment as well as UCST-type behaviour arising from PIL (P[VBTP][Cl]) segment simultaneously in the presence of halide anion.

Chapter 3 describes the polymerization of an ionic liquid monomer [VBTP][Cl] with a hydrophobic monomer MMA using both free radical polymerization as well as reversible addition-fragmentation chain-transfer (RAFT) polymerization methods to synthesize a series of random copolymers (namely P[VBTP][Cl]-ran-PMMA). The influence of copolymer

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compositions, counter anions (Cl⁻ and TFSI⁻) and molecular weight as well as physical mixing of copolymer segments on the ion transport and relaxation of these random copolymers are investigated. The free ion diffusivity and ion number density of these random copolymers are also investigated. The temperature dependence of ionic conductivity, relaxation time and ion diffusivity exhibit VFT behavior in these copolymers indicating ion transport controlled by segmental motion of polymer chains. In comparison with other reported system, the applicability of these PIL copolymers as energy storage materials is relatively higher because of their less moisture sensitivity due to incorporation of hydrophobic PMMA segment.

Chapter 4 describes synthesis of a series of phosphonium and imidazolium ionic liquids (ILs) followed by their utilization as efficient photoinitiators (PIs) for the polymerization of vinyl monomers such as N-isopropylacrylamide (NIPAM) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) upon UV irradiation ($\lambda_{\text{max}} = 310 \text{ nm}$) in aqueous medium. The photopolymerization proceeds through a free radical pathway systematically established by EPR and ¹H-NMR spectroscopy, MALDI-TOF-MS, SEC analysis, and other control experiments. Control experiments show that these IL-based PIs have high water solubility and capability of producing high-molecular-weight polymers compared to those obtained by other commercially available water-based PIs. Additionally, poly(NIPAM) and poly(DMAEMA) are grafted from the photoactive pendent IL moiety of the poly(ionic liquid), poly(triphenyl-4-vinylbenzylphosphonium chloride) (P[VBTP][Cl]) backbone by the grafting-from copolymerization. The presence of either poly(NIPAM) or poly(DMAEMA) graft segment induces thermo-responsiveness to their P[VBTP][Cl]-based copolymers.

Chapter 5 describes the syntheses of two different types of cross-linkable ionic liquid monomers (ILMs) followed by their utilization as cross-linkers for the fabrication of acrylamide and 2-hydroxyethyl methacrylate-based hydrogels. Investigation of the thermal stability of the hydrogels by TGA and DTG analyses shows that these hydrogels are thermally stable at high temperature. Swelling performance and diffusion mechanism of water within the hydrogels are investigated. The dye adsorption abilities of these hydrogels are investigated using Eosin B and Alizarin Red S as model dyes. The dye adsorption data of representative hydrogels fitted well with pseudo second-order kinetic model indicating chemisorption to be the rate controlling step. To explain the dye adsorption mechanism, intra-particle diffusion model is further used which show multi-linearity behaviour confirming that the adsorption occurred through different steps. Further fitting the experimental data to Boyd kinetic model it shows straight lines, which did not pass through the origin. This indicates that both liquid film diffusion and intra-particle diffusion jointly control the removal of anionic dyes from aqueous solution by the macroporous cationic hydrogels.

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17.10.2022

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