# Fine-tuning of solid-state thermoresponsive behaviour of various LCST showing organic-inorganic hybrid systems

## Abstract

Stimuli responsive properties of smart polymers have gained much attention in the recent past. Over the top, thermosensitive materials have already rendered much applications in the field of biomedical and chemistry with highly importance projected in the future than it has ever been in the past. Nowadays, environmentally benign "green" solvents ionic liquids with their enormous database of distinguished cationic and anionic counterparts have enabled the researchers over the globe to invest more time into their future applications. There have been reports about ionic liquids showing thermoresponsive properties as well, in addition to polymers. Considering the vitality of these smart materials, the present research will be addressing synthesis and study of thermoresponsive properties of various polymer-based/ ionic liquid based/ and their copolymer based materials and their tunability over critical solution temperatures.

The primary aim of this thesis work is to focus on the thermosensitivity and tunability of various polymer and ionic liquid system. In the present thesis, thermoresponsive property is examined on three kinds of states: (1) Solid-supported LCST showing materials, (2) LCST showing hydrogels and (3) LCST in liquid-liquid equilibria-Phase transitions of imidazolium based ionic liquids in water. LCST showing hydrogels- Further, dimensionally controlled plasmonic nanoparticles will be embedded into thermoresponsive PNIPAM copolymerized with polymerizable ionic liquids. Au and Ag both acts as tuning agents for phase transitions of these hydrogels. **Chapter 1** opens up to the introduction of thermoresponsive property with respect to polymers and ionic liquids in detail. With a brief introduction about thermoresponsive phase transitions and its types, mechanism to critical solution temperature (CST) and applications corresponding to CST have been discussed.

In **Chapter 2**, the research is directed towards improving the tuning of LCST behaviour of oxazoline based thermoresponsive copolymer and creating a solid-supported hybrid material from it. The chapter describes the synthesis of novel sol-gel hybrids using thermoresponsive copolymer of 2-ethyl-2-oxaoline and 2-isoporopyl-2-oxazoline with tetramethylorthosilicate as the silicate compound. It also reports the method to fine-tune the thermoresponsive property of these hybrids.

**Chapter 3** describes another method to form solid-supported LCST showing materials utilizing silicon wafers and polyoxazoline as the thermoresponsive material. In this work, silicon wafers were exposed to extreme acidic conditions to covalently bind with the thermosensitive polymer of 2-ethyl-

2-oxazoline. The system works as a solid-supported phase gradient.

Next, focus was made to target the applications shown by the formation of hydrogels and nanoparticles along with the thermosensitivity due to polymers. Hence, PNIPAM was copolymerized with different imidazolium based ionic liquids such as 1-allyl-3-octylimidazolium bromide and 1-hexyl-3-methyl imidazolium acrylate with tunable properties in **chapter 4** and the corresponding in-situ polymerization was done using Ag and Au nanoparticles. How the size of nanoparticles and structure of IL play a major role in LCST tunability was investigated.

Further, attention was made to study liquid-liquid phase systems in **chapter 5**. Hence, room temperature imidazolium-based ionic liquids was found to exhibit LCST and UCST properties. A more advance, superior and informative technique which is electrochemical impedance spectroscopy was used as the diagnostic tool to evaluate the phase transition temperature as clear visualization of the separation cannot be observed optically. Factors affecting the CST in ionic liquids and its mechanism was scrutinized using Kamlet-Taft parameter studies. Also, COSMO-RS simulations were carried out which suggested a procedure to predict the occurrence of phase transitions, and if so, what type in ILs

Lastly, **chapter 6** chapter summarized the findings of each chapter. It also gave an outlook towards future for the utilization of these materials.

**Keywords:** Thermoresponsive polymers, Lower Critical Solution Temperature (LCST), Ionic Liquids (ILs), sol-gel materials, plasmonic nanoparticles, nanoparticles, organic-inorganic hybrids, ionic liquids