RAFT Polymerization of Acrylates and Acrylamides in Ionic Liquids; An Accelerated and Potentially Sustainable Process

Abstract: Ionic liquids (ILs) are organic salts having asymmetric cations and anions that remain as liquid below 100 °C. ILs have emerged as a new class of sustainable solvents for polymerisation processes because of their unique combination of properties such as low vapour pressure, high thermal and chemical stability, high conductivity, wide electrochemical window, ability to dissolve organic and inorganic solutes, low volatile organic content (VOC), and have tuneable solvent properties such as miscibility, melting point, viscosity, and hydrophilicity depending on the constituting cations and anions. The use of ILs as polymerization media not only increases the sustainability of the process but also increases the rate of polymerization. However, the role of IL and its influence on the polymerisation rate are still subject of investigation. This thesis addresses these issues by designing experiments to study the kinetics of RAFT polymerisation in different ILs, IL-organic binary solvents, and using different monomers and RAFT agents. The kinetics study revealed that the [BMIM][PF_6] IL enhances the rate of RAFT polymerization of *n*-butyl methacrylate almost 10 times irrespective of its miscibility with the polymerization system. It is also revealed that only a small amount of IL is enough to increase the rate of polymerization. Deep eutectic solvent (DES), a subclass of ILs, made of choline chloride/urea was studied as a polymerization media for RAFT polymerization of 2-hydroxyethyl methacrylate and its copolymerization with methyl methacrylate. The kinetics of polymerisation was studied using a novel DSC methodology, which allowed the polymerisation to be monitored in real time. The data showed that the DES accelerated polymerisation as fast as bulk polymerisation but with more than 90% monomer conversion. The block copolymerisation yielded a spherical and a vesicular morphology of the copolymers demonstrating polymerisation-induced self-assembly in DES. Photoiniferter RAFT polymerisation is a slow but unique process to produce high chain-end fidelity polymers. [EMIM][$EtSO_4$] IL was studied to accelerate the RAFT polymerization of *N*,*N*dimethyl acrylamide under photoiniferter condition achieving more than 90% monomer conversion in less than 5 h. Synthesis of different polymer architecture such as chain extension and block copolymerization demonstrated the versatility and robustness of the process. A comparison was made with thermal initiated RAFT polymerisation which showed the high chain-end fidelity of photoiniferter RAFT polymerisation process in ILs.

Keywords: Ionic Liquids, RAFT Polymerization, Sustainability, Recyclable, Polymerization Induced Self-Assembly (PISA), Deep Eutectic Solvents (DES), Photoiniferter.