CHAPTER - VI

Summary and conclusions
6.1 Summary and Conclusions

The thesis has been divided into six chapters. Chapter 1 describes the current literature survey of synthesis of polymeric porous templates using high internal phase emulsion (HIPE) methodology. The detail introduction to HIPE and its physical properties, its formation has been explored. Synthesis of various types of polyHIPEs their structural properties and applications have been covered.

Study of morphological properties of acrylate based polyHIPEs have been investigated. The effect of comonomer type plays an important role in the polyHIPE properties as it significantly contributes to the differentiation in hydrophobic hydrophilic nature of the oil phase affecting the HIPE emulsion stability. Each factor such as initiator type and concentration, salt type and concentration, porogen type and concentration, presence of water soluble monomer in aqueous discontinuous phase plays an important role in designing the architecture of the porous polyHIPE. These preliminary studies help to understand the complexity of HIPE methodology. Increase in salt concentration and presence of water soluble polymers in the aqueous discontinuous phase leads to the formation of soft and elastic polymers. The yield stress of the polymer can be varied with an interplay in composition of the HIPE constituents. For all the polymers synthesized in this study the yield stress was observed in the range of 0.525-1.538 psi depending on the parameter varied.

An attempt was made to investigate the effect of different parameters like initiator concentration, inhibitor concentration, pH and temperature on the rate high internal phase emulsion (HIPE) polymerization. To generate the polymerization kinetics, a synthesis
method was established and kinetics data was generated. It was observed that like emulsion polymerization the rate increases with increase in initiator concentration and temperature. The inhibitor effect was also profoundly observed in case of MEHQ and phenothiazine.

An attempt was made to model the kinetics data by using a phenomenological model. Kinetics experiments using different initiator concentrations and inhibitor concentrations were conducted at three different temperatures viz. 65, 75 and 85°C. The phenomenological model was proposed to evaluate the rate parameters. Activation energy was calculated from the Arrhenius plot. The model was later validated by using Runge Kutta analysis method. The modeled data falls in close resemblance to the experimental data.

As compared to nonionic surfactants to form a stable water in oil HIPE ionic surfactant as Arquad 2HT-75 can be used to generate poly(styrene-divinylbenzene) polymers at oil : water ratios above 1 : 15. Stable water in oil emulsions failed to form in case of nonionic as well as ionic surfactants at low oil : water ratios of 1 : 1 / 2.5 and 5 that was reflected in the morphology of the polymerized HIPEs. The pores generated in HIPE methodology can be used as templates for synthesis of cadmium sulphide particles. Poly (styrene-divinylbenzene) containing cadmium chloride monoliths using high internal phase emulsion methodology were prepared using two different strategies.

a) Before polymerization: In-situ addition of cadmium chloride dissolved in aqueous discontinuous phase during HIPE formation.
\( b) \) \textit{Post polymerization:} Imbibing cadmium chloride solution inside the polymeric matrix synthesized using HIPE methodology.

The cadmium chloride was then converted into cadmium sulphide by treating it with sodium hydroxide followed by sodium sulphide.

Crystal structure was confirmed from X-ray Diffraction studies. XRD patterns showed prominent broad peaks at \( \theta \) values of 26.7, 44.1 and 52.1 that can be indexed to scattering from 111, 220 and 311 crystal planes of cubic CdS respectively. The morphology of the CdS containing polyHIPEs showed presence of CdS particles in the matrix. Studies showed linearity in analysis data in case of in situ incorporation strategy in comparison with external incorporation strategy. In situ incorporation strategy was found to have uniform distribution of particles over the entire polymer matrix as compared to external incorporation strategy. In the external incorporation strategy, the polymer properties such as void diameter, affinity for imbibing \( \text{CdCl}_2 \) solution, accessibility of the reactants for post conversion plays an important role for complete conversion of cadmium chloride (\( \text{CdCl}_2 \)) to cadmium sulphide (CdS).

Functional group present in the polymer is the basic requirement for the polymer to be hydrophobic or hydrophilic in nature. Acrylonitrile containing crosslinked porous polymers were synthesized using high internal phase emulsion HIPE templating. Formation of a stable HIPE using a monomer having water affinity (acrylonitrile) and hydrophobic crosslinker (divinylbenzene) was studied. Several poly (AN-DVB) HIPE emulsions were prepared using various classes of nonionic surfactants i.e. sorbitan esters (Span), polyoxyethylene ethers (Brij) and sorbitan polyoxyethylene fatty acid esters
(Tween). From optical microscopy and visual appearance of the HIPE emulsions, it was found that HIPEs prepared using Span 80 and Span 20 were stable and could be polymerized to obtain an interconnected porous morphology. In case of Span 85 no emulsion was formed at all. This can be attributed to the fact that the HLB value of Span 85 is very low (1.8) and hence it was less soluble in the oil phase. In case of Tween and Brij surfactants emulsions were formed under stirring but on standing they phase separated.

The effect of reaction variants on the HIPE stability of 100% crosslinked acrylonitrile-divinyl benzene polymers like, crosslinker concentration, oil:water ratio, surfactant concentration and porogen were studied. It was observed that the hydrophilicity of acrylonitrile played an important role in formation of stable HIPE and interconnected pore structure formation post polymerization, due to miscibility of the surfactant in the oil phase. The polymerization was carried out at 50°C using redox initiating system (sodium peroxydisulphate : ascorbic acid (1:0.5)) to avoid vaporization of carcinogenic acrylonitrile as well as to maintain the feed concentration. An attempt was made to use porogens in synthesis of AN-DVB polymers using HIPE methodology to obtain polymers having high surface area. During polymerization, in presence of porogen, phase separation is decided by the porogen type used which reflects in the pore dimensions formed and indirectly on the surface area of the polymer formed. Maximum surface area of 329.74 m²/g obtained was in the case of polymer synthesized using toluene as a porogen (1:1) and oil : water ratio 1:20.

The nitrile functionality present on the polymer backbone was post modified to amidoxime functionality. The modification was confirmed by IR spectroscopy showing
the main characteristic peaks at 1653, 1607 and 900 -950 cm⁻¹ for –C=N, -NH₂, and =N-O- groups respectively. The polymers synthesized using porogens were evaluated for its efficiency as a heterogeneous support for Cr(VI) metal ion adsorption. Studies were done at different pH-2, 4, 6, and 8. It was found that the adsorption of Cr(VI) was maximum at pH-2. Maximum adsorption efficiency of 99.8% was found in the case of polymer synthesized using toluene as a porogen (1 : 0.5) and 1 : 10 oil : water ratio.