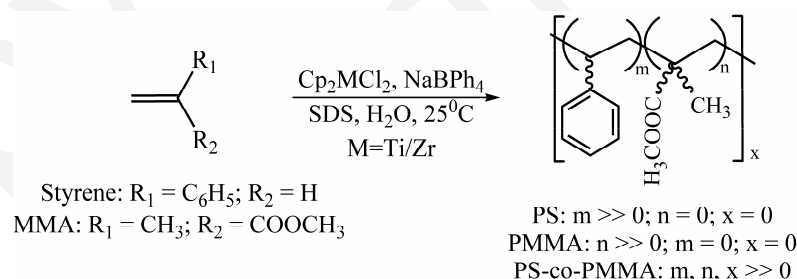


Catalytic aqueous polymerization has gained immense importance in recent years due to increasing environmental concern regarding the detrimental effect of volatile organic solvents. A number of catalytic systems capable of polymerization in aqueous medium involving mainly late transition metal catalysts have been developed, as these catalysts are functional group tolerant and less oxophilic in nature. However, in these cases, due to the ease of β -hydride elimination, usually low molecular weight polymers are obtained. Manders et al. have reported the first use of an early transition metal catalyst $[(C_5Me_5)Ti(OMe)_3]$ in aqueous emulsion polymerization of styrene. Recently we found that in presence of anionic surfactant (SDS), $[Cp_2MCl_2]$ $[M = Ti, Zr, V]$ can polymerize olefins in an aqueous medium. However, in these reactions longer reaction time, typically 6 to 16 hours, as well as higher temperature (50 to 90 °C) was required. Also, the catalytic activity and stereoselectivity was found to be poor. This thesis presents the successful efforts in overcoming these drawbacks by suitable choice of a cocatalyst and the consequent development of some early transition metal based catalytic systems for polymerizations of polar and non-polar olefins at room temperature in aqueous emulsion.

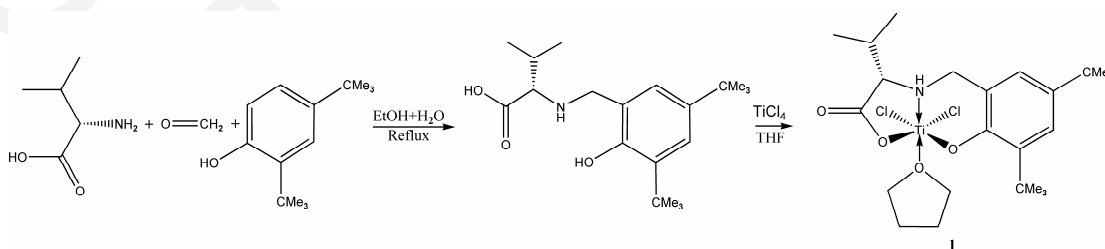


Scheme 1

Polymerizations in presence of common large, soft and weakly coordinating anions have revealed that Cp_2MCl_2 ($M=Ti/Zr$) in presence of $NaBPh_4$ and sodium n-dodecyl sulfate act as an effective precatalyst for room temperature aqueous homo- and copolymerization of methyl methacrylate and styrene to the corresponding high molecular weight syndiotactic rich homopolymers as well as the copolymerization of styrene and MMA to a cosyndiospecific rich random sequence macromolecule (Scheme 1). Various control experiments, including end group analysis by in-situ derivatization with trichloroacetyl isocyanate method, suggest that the polymerization

proceeds through a coordination insertion mechanism involving a 14 electron cationic active species $[\text{Cp}_2\text{MOH}]^+$. The activity of the catalytic system, defined as the grams of polymer obtained per mole of catalyst per hour, has been found to be high (up to 8.8×10^4) with considerably good yield (up to 90%). NMR spectral analysis show that (a) the homopolymers are syndiotactic rich (~63-68%), (b) the syndioselectivity is chain end controlled and (c) the copolymers contain cosyndiospecifically enchaind MMA units (up to 77%) with MMA incorporation as high as 81%. Gel Permeation Chromatography shows that the polymers have very high molecular weights [$M_n = (1 \text{ to } 11) \times 10^5$] with considerably low polydispersity index (1.6 to 2.6). Moreover in the case of zirconium catalyzed reaction, the composition of the resulting copolymer could be controlled precisely by changing the feed ratio.

Recently, there has been a growing interest in developing new nonmetallocene catalysts. An important family of such catalysts developed is based on tridentate ONO type ligands. However most of them work only in non-aqueous medium. In this regard a new water soluble titanium(IV) complex bearing amino acid based ONO-type ligand has been synthesized (Scheme 2). In the presence of sodium tetraphenyl borate, this complex also successfully catalyzes homo- and co-polymerization of polar (MMA) and non-polar (styrene) olefins at room temperature in aqueous emulsion with moderate to high activity (up to 37×10^3) and afford ultra high molecular weight polymers (M_n in the order of 10^6) with narrow polydispersity (1.6-1.8). The system behaves in a living manner and block copolymers could be synthesized by sequential addition of monomers. Moreover the polymerization recipe allows the formation of highly stable, nearly monodisperse polymer latex with particle diameter less than 50 nm at comparatively lower surfactant levels.



Scheme 2

Keywords: Aqueous polymerization; Early Transition metal; Polystyrene; Poly(methyl methacrylate); Poly(styrene-co-methylmethacrylate)