



Synergetic effect of multi-site phase transfer catalysis system mediated free radical polymerization of acrylonitrile – a kinetic study

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ABSTRACT

In this work, the kinetics and mechanism of free radical polymerization of acrylonitrile (AN) using potassium peroxydisulphate (PDS-K₂S₂O₈) as a water soluble initiator in the presence of synthesized 4,4'-dihexadecyl-1,1'-bipyridine diiumdichloride (DHPDDC) as multi-site phase-transfer catalyst (MPTC) has been investigated. The polymerization reaction were carried out under nitrogen atmosphere and unstirred condition at constant temperature 60±1°C in ethyl acetate/water biphasic medium. The effects of variation of monomer (AN), initiator (PDS) and catalyst (MPTC) solvent polarity and temperature on the rate of polymerisation (R_p) were ascertained. The order with respect to monomer (acrylonitrile) was found to be unity. The order with respect to initiator and catalyst was found to be 0.51, 0.48 respectively. However, an increase in the polarity of the solvent has slightly increased the rate of polymerization value (R_p). Based on the results obtained, a suitable kinetic mechanism scheme has been proposed to account for the experimental observations and its significance was discussed. The other thermodynamic parameters such as entropy of activation ((ΔS[#]), enthalpy of activation (ΔH[#]) and free energy of activation (ΔG[#]) have been calculated.

1. Introduction

The phase – transfer catalysts usually as quaternary onium salts, crown ethers, cryptands etc., can be applied to give a high change and products selectivity. Phase-transfer catalysis is considered to be one of most well-organized tools in all branches of chemistry because of its ease, high conversion, under very mild reaction condition and environmental concern [1-4]. It is widely used for manufacturing pharmaceuticals, agricultural chemicals, perfumes, flavours, dyes, polymers and environmental applications. The reaction between mutually immiscible reactants was usually difficult to conduct strongly even under severe operating. Such problems as low reaction rate, low conversion of reactants and low of products can be overcome by phase-transfer catalysis (PTC) [5–8]. Many authors reported the single-site PTC assisted radical polymerization of hydrophobic vinyl monomers in aqueous-organic two phase system [9-12]. Recently, the

catalytic behaviour of multi-site phase-transfer catalysts has been attracted much attention, due to the fact that multiple molecules of the aqueous reactant can be carried into the reaction phase once a reaction cycle. The catalytic competence is thus better [13-16]. The first report published on multisite PTC (MPTC) was by Idoux et al., and they have synthesized phosphonium and quaternary onium ions containing more than one site per molecule [17]. Vajjiravel et al [18-19] reported the kinetics of free radical polymerization of vinyl monomers using multisite PTC-PDS system in organic-water two phase medium. The phase-transfer catalyzed free-radical polymerization of vinyl monomers with water-soluble initiators like potassium peroxydisulphate (PDS) and ammonium perdisulphate (ADS) is a relatively new area of research [20]. It has been found that such water soluble initiators have been used efficiently for bulk or solution polymerization with phase-transfer catalysts [21-23]. A several authors reported the use of single site-PTC for free radical

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