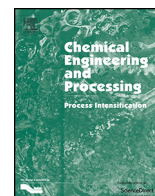




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Kinetic studies of semibatch emulsion copolymerization of methyl methacrylate and styrene in the presence of high intensity ultrasound and initiator



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ABSTRACT

The present work deals with kinetic studies of copolymerization of methyl methacrylate and styrene using ultrasound assisted semibatch emulsion copolymerization in the presence of sodium dodecyl sulfate (emulsifier) and potassium persulfate (external initiator). The effect of temperature, acoustic intensity, initiator loading, surfactant concentration and monomer concentration on the extent of conversion has been investigated. The extent of polymerization was observed to increase with an increase in the temperature, and concentrations of initiator, monomer and surfactant. Further, the initial polymerization rate increased with an increase in the acoustic intensity from 11.2 to 23.1 W cm⁻² and then it was found to decrease with a further increase to 33.80 W cm⁻². The novelty of this work lies in the fact that there have been only limited kinetic studies for the approach of ultrasound assisted emulsion copolymerization. It has been also established in the present work that the formation of fine and stable monomer droplets, due to the cavitation activity at/near the interface of immiscible monomer phase and subsequent disruption by micro jets, leads to the smaller final polymer particle size and under optimized conditions, it was found to be about 40 nm.

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1. Introduction

Emulsion polymerization is an important industrial approach used for the production of polymer latex suitable for multiple applications such as paints, adhesives, coatings, varnishes etc. Emulsion polymerization offers significant advantages such as controlled reaction conditions and narrow particle size distribution as compared to the bulk and solution polymerization processes, attributed to the fact that reaction occurs in small droplets dispersed in a continuous phase leading to controlled polymerization rates, controlled molecular weights of polymer, no emulsifier migration during film formation, and excellent shear stability [1]. However, the multiphase nature of the system (water, monomer droplet and polymer particle phase) and nonlinear behavior at different stages makes an emulsion polymerization system complicated for the

kinetic analysis. Also the mass transfer resistances due to the multiphase nature can lower the polymerization rates. These aspects encourage a detailed study related to the kinetic analysis of emulsion polymerization and possible use of ultrasonic irradiations for process intensification [2].

Copolymerization is one of the promising techniques to achieve engineered properties desirable for the commercial applications [3–8] based on the use of two different monomers with complimentary properties. The present work deals with copolymerization based on the use of methyl methacrylate and styrene as the monomers. Polymethyl methacrylate (PMMA) has excellent properties such as transparency and high modulus though its melt viscosity is high and mechanical properties such as abrasion and wear are relatively low. On the other hand, polystyrene (PS) has a relatively low modulus [9] and high abrasion resistance, load bearing capacity, and greater tensile strength [10]. The use of a combination of two or more monomers for the formation of a copolymer can compensate their disadvantages and the resulting copolymer can significantly improve the desired properties as compared to the neat polymers.

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The semibatch mode of emulsion polymerization and the use of ultrasound can give distinct advantages over the conventional emulsion polymerization process such as improved polymerization rate, controlled particle size distribution, and higher monomer conversion at small loading of initiator [11–13]. When ultrasound is passed through a liquid medium, a large number of microbubbles are formed which grow under the influence of fluctuating pressure fields and finally collapse in a very short time span (a few microseconds) releasing large magnitudes of energy. The adiabatic cavity collapse results in generation of very high local temperatures ($>10,000$ K) and pressures (>1000 atm) [14] and also results in the formation of radicals by decomposition of water ($\bullet\text{OH}$ and $\bullet\text{H}$), surfactant, monomer and/or oligomer molecules, which help in initiating and propagating the polymerization reactions. It has been reported that an emulsion polymerization initiated by only ultrasound generates a very small quantity of radicals ($\bullet\text{OH}$ and $\bullet\text{H}$) and most of the radicals recombine to give water and H_2O_2 [15–17]. Therefore, it is required to add a small quantity of initiator during the ultrasound assisted emulsion polymerization for an industrially viable process in terms of rates of polymerization. Several researchers have studied the ultrasound assisted emulsion polymerization of various monomers such as methyl methacrylate, butyl acrylate, styrene etc. [11,15,18–34]. In particular, Teo et al. [11] have presented a comparison of ultrasound initiated emulsion polymerization of methyl methacrylate (MMA), *n*-butyl methacrylate (BMA) and 2-ethylhexyl methacrylate (2EHMA) in the presence of sodium dodecyl sulfate as a stabilizer. The obtained latex particles were in the size range of 70–110 nm with molecular weights of the order of $2\text{--}6 \times 10^6 \text{ g mol}^{-1}$. It has been also reported that the rates of polymerization of the methacrylate monomers are dependent on the physicochemical properties of the monomers. Ooi and Biggs [20] synthesized polystyrene latex by ultrasonically initiated emulsion polymerization and reported the effect of ultrasonic intensity on the monomer conversion rate. Yin and Chen [27] have also used ultrasound as a polymerization initiating mechanism for the emulsion copolymerization process.

A brief overview of the earlier studies related to the use of ultrasound in polymerization reveals that most of the work has dealt with emulsion polymerization of neat polymers and concentrated on the mechanistic aspects and the effect of ultrasound on the size of droplets based on the Ostwald ripening. There have been very few reports on the use of ultrasound for emulsion copolymerization process. Bradley et al. [30] studied the ultrasonically initiated batch miniemulsion copolymerization of methyl methacrylate (MMA) and butyl acrylate (BA) at different MMA:BA ratios and investigated the physical properties and chemical composition of the formed polymers. The reported molecular weight for the copolymer was $2.1 \times 10^6 \text{ g mol}^{-1}$ and particle size was in the range of 40–100 nm. Also, there have been no reports for the use of ultrasound for intensifying semibatch microemulsion copolymerization involving the use of initiator. It is expected that the polymerization rate and other polymer properties can be controlled by the semibatch addition of monomer and/or initiator. Also, under monomer starved conditions achieved by the semibatch operation, particles do not undergo an appreciable growth during polymerization and as a result a large number of smaller and uniform size polymer particles can be obtained [31]. The present work reports a novel study related to the use of ultrasound for the intensification of copolymerization of styrene and MMA operated in semibatch mode. The effect of presence of ultrasound and initiator concentration on the monomer conversion and the polymerization rate has been investigated. Also the influence of acoustic intensity, reaction temperature, and concentrations of initiator, monomer and surfactant on the extent of conversion and polymerization rate has been reported.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, Aldrich, 99%, A.R. grade) and styrene (Aldrich, 99%, A.R. grade) were procured from Sigma-Aldrich and used after the removal of inhibitors. The inhibitor was removed by washing monomer with 5% aqueous NaOH and water, followed by drying over Na_2SO_4 and distillation under reduced pressure. Analytical grade chemicals such as sodium dodecyl sulfate (SDS, $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$) as surfactant and potassium persulfate (KPS, $\text{K}_2\text{S}_2\text{O}_8$) as initiator were procured from S.D. Fine Chem Pvt., Ltd., Mumbai and were used without any purification. Deionized water obtained using Millipore apparatus was used as a medium during the synthesis of poly(styrene-co-methyl methacrylate) [P(MMA-co-St)] and for preparation of any aqueous solutions required in the work.

2.2. Semibatch emulsion copolymerization of MMA and styrene

Synthesis of P(MMA-co-St) nanoparticles was performed using semibatch emulsion copolymerization in a jacketed glass reactor (500 mL) equipped with a 13 mm stainless steel sonic probe connected to an ultrasonic generator (Sonics Vibra-cell, USA) operating at a frequency of 22 kHz. The selected output power of the sonicator was 375 W at 50% amplitude (maximum rated power of sonicator = 750 W). The actual power dissipated by the probe sonicator was measured using a calorimetric method and was found to be 44.86 W giving a calorimetric energy efficiency of around 12%. Surfactant solution containing 1.076 g SDS (5% of total monomer quantity of 21.52 g) in 100 mL of distilled water was then added to the reactor. In all the cases, styrene monomer was added entirely (10.76 g) to the reactor and then continuous addition of MMA (10.76 g) was accomplished over a period of 30 min after increasing the reactor temperature to 60°C in the presence of ultrasonic irradiations. Initiator solution containing 0.86 g KPS (4% of total monomer quantity) in 20 mL of water was also added continuously to the reactor in 30 min time along with MMA monomer in the presence of ultrasonic irradiations. The reaction temperature was maintained at 60°C (± 1) throughout the experimental run. Reaction vessel was continuously purged with nitrogen gas along with feed addition to avoid the contact of the monomers with oxygen. Dissociation of initiator KPS at the reaction temperature generates sufficient radicals (very small amount of radicals is generated through acoustic cavitation only) resulting in the initiation of the copolymerization reaction. The MMA monomer addition process was completed within the first 30 min of the total reaction time of 1 h. After the complete reaction time i.e., 60 min, entire reaction mass was dried in an oven at 150°C for 2 h. The dried samples were weighed and characterized using XRD and TEM.

2.3. Analysis and characterization

Monomer conversion was determined by gravimetric method, after collection of a representative sample at definite time interval during polymerization, using the following equation:

$$\text{Conversion} = \frac{(M_4 - M_3 - M_2)}{M_1} \quad (1)$$

where M_1 = total amount of monomer (styrene and MMA) in wet sample,

M_2 = mass of surfactant in wet sample,

M_3 = mass of initiator in wet sample,

M_4 = mass of dried sample.

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