

Ultrasound-Assisted Emulsion Polymerization of Methyl Methacrylate and Styrene

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ABSTRACT: In this article, we report on the effect of using ultrasound during emulsion polymerization. This work differs somewhat from that previously reported in that ultrasound is used in conjunction with conventional initiators. The aim is to observe the changes in the nature of polymerization and the synthesized polymer. In this work, reaction conditions and compositions typical of conventional emulsion polymerization are used. Azo-bisisobutyronitrile and potassium persulfate are the initiators used. The initial indication is that the rate of polymerization and the final conversion are higher when ultrasound is introduced into the polymerization system. This effect is more pronounced at lower temperatures (50°C) and low initiator concentrations (0.01%). At higher temperatures (70°C) the polymerization rate is seemingly unaffected by the use of ultrasound. The final product in all the experiments is a latex. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 101–104, 2000

Key words: emulsion polymerization; ultrasound; methyl methacrylate; styrene; sonochemistry

INTRODUCTION

High intensity ultrasound produces cavitation. Such cavitation results in the formation of free radicals.¹ The association of this method of free radical production with free radical polymerization processes is an obvious one. There have been several attempts at synthesizing polymers via this association reported in the literature. Most recently, emulsion polymers of methyl methacrylate (MMA) were synthesized using ultrasound.² A mixture containing MMA, sodium dodecylsulfate (SDS) and water was sonicated. The reported result is that polymerization occurs only when a continuous stream of argon is bubbled through the reaction mixture. Conversions ranging from

21% to 61% are achieved in about 30 min of reaction.

In this study, we explore the effect of using ultrasound on a system containing a monomer, surfactant, water, and initiator. The monomers studied are styrene (ST) and MMA. Three initiators are explored, they are, azo-bisisobutyronitrile (AIBN), potassium persulfate (KPS), and ferrous sulfate.

EXPERIMENTAL

The 700 mL reactor is constructed entirely of stainless steel. Temperature control ($\pm 2^\circ\text{C}$) is achieved via a proportional–integral–differential controller. A heating band and a cooling coil provide the necessary heat input and removal. The reactor has a provision to allow a gas purge of the headspace (≈ 0.4 scfh). A water-cooled reflux condenser prevents loss of volatile components and a sampling

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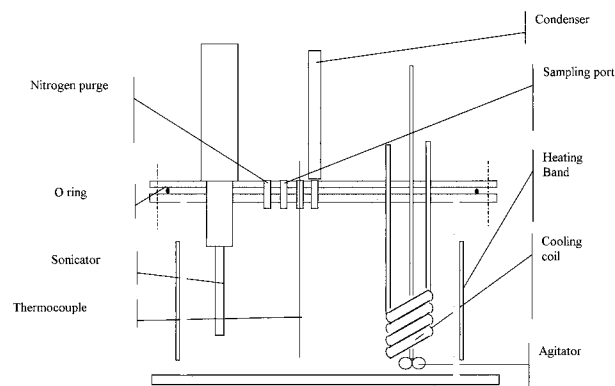


Figure 1 Schematic of batch reactor.

port is also available. A schematic of this reactor is shown in Figure 1.

The monomers (MMA and ST) are used as received without removing the inhibitor. The other ingredients in the recipe, emulsifier (SDS) and initiator, are also used as received. Polymerization temperatures range from 50 to 60°C. Table I shows the recipe used in all experiments.

The emulsifier is dissolved in water and this solution is loaded into the reactor. Nitrogen purge of the headspace, agitation, cooling water, and heater are started. The temperature of the system is allowed to stabilize at a predetermined value. At this point the initiator and monomer are added to the reactor.

Table I Polymerization Recipe

Component	Weight (g)	Percent of Total Weight ^a
Water	540.0	90
Monomer	60.0	10
Emulsifier (SDS)	3.0	0.5
Initiator	0.3–0.03	0.05–0.005

^a Weight percents based on the sum of water and monomer.

In the case of a sonicated polymerization, the agitation rate is turned down low enough (about 75 rpm) to prevent vortex formation. The horn is inserted into the reactor and sonication is started. For the conventional polymerization runs, the agitation is set around 400 rpm. That this provides adequate agitation was confirmed via a series of experiments at various agitation speeds. The total time of each experiment is 120 min and samples are drawn every 15 min. Determination of conversion is by gravimetric analysis.

RESULTS

In this section some of the results obtained this far are presented. Shown in Figure 2 are the MMA conversion profiles at 50°C for various

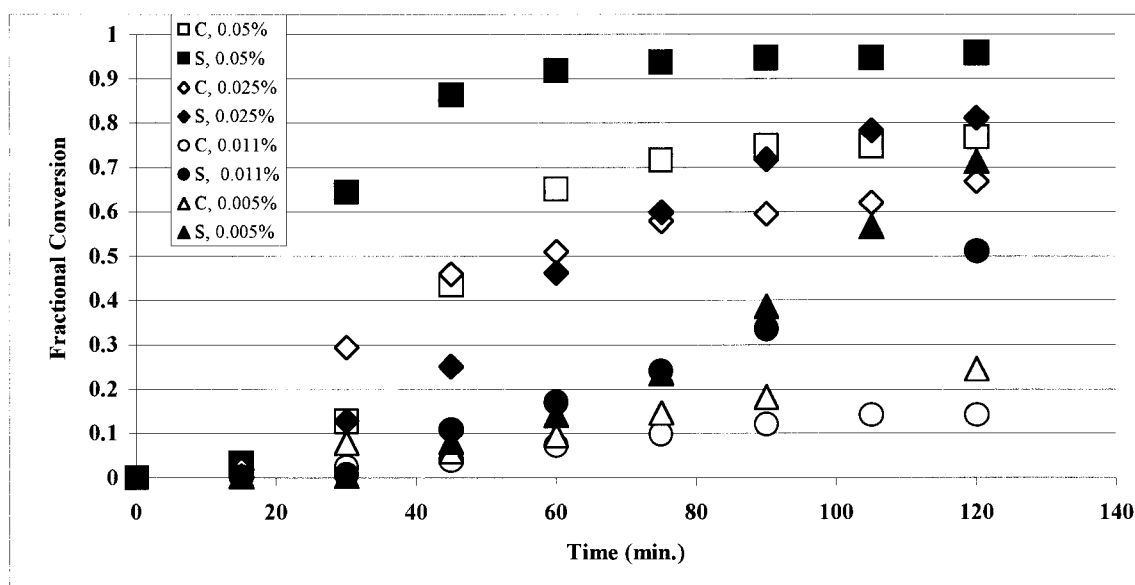


Figure 2 Fractional conversion of MMA versus time at various AIBN concentrations. ($T = 50^\circ\text{C}$, S = sonicated, C = conventional).

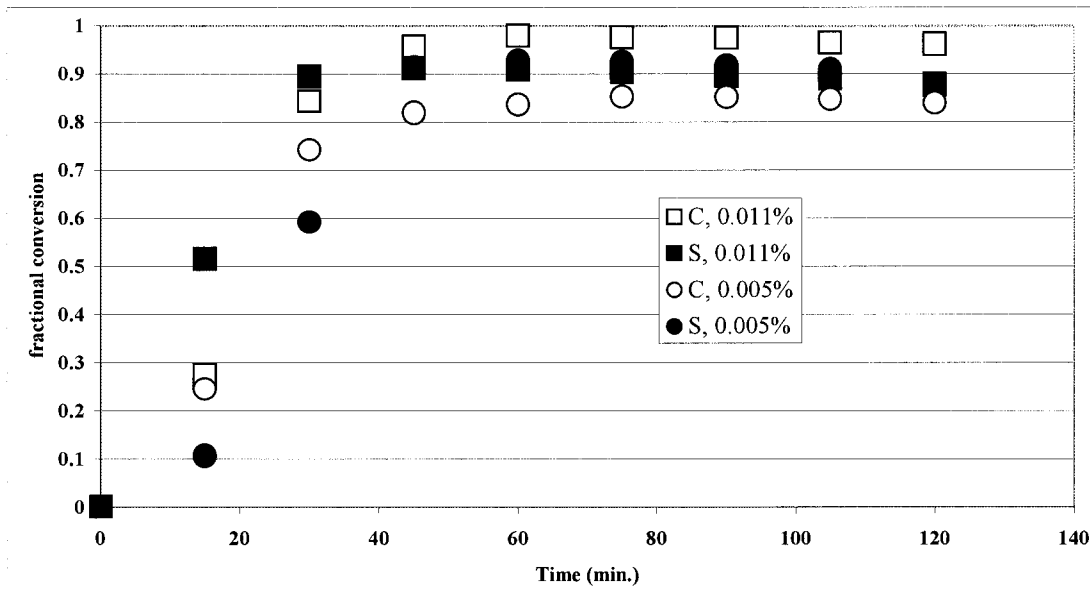


Figure 3 Fractional conversion of MMA versus time at various AIBN concentrations. ($T = 70^{\circ}\text{C}$, S = sonicated, C = conventional).

AIBN concentrations. From the plot it can be seen that the conversion obtained from the sonicated runs is higher.

Shown in Figure 3 are MMA conversion profiles at 70°C for two AIBN concentrations. At this temperature there is little difference between the conversion obtained via sonication and conventional polymerization.

Once again, from Figure 4 it can be seen that sonication yields a higher conversion when the concentration of the initiator is at the lower end. At higher concentrations (0.05%) of initiator, there is no obvious advantage to using ultrasound.

The polymer formed in these experiments is in the form of a latex. Analysis of the latex and the latex particles is under way.

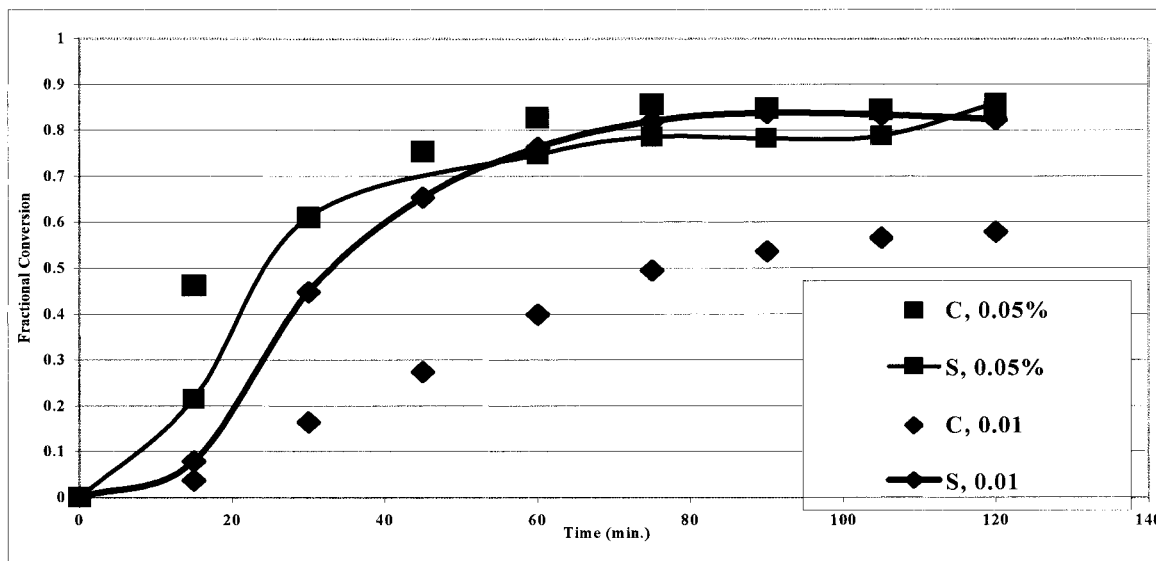


Figure 4 Fractional conversion of ST versus time at various KPS concentrations. ($T = 70^{\circ}\text{C}$, S = sonicated, C = conventional).

DISCUSSION

Currently, experiments are underway to further characterize the polymers produced in this work. It is believed the improvement in conversion is either due to increased production of free radicals or due to better mixing induced by cavitation. Molecular weights, particle size, and size distributions are expected to provide some clues to facilitate a better explanation of these effects.

In an ultrasonic field, it is possible to do the following:

1. abstract atoms off the polymer backbone, thus reactivating a dead chain;
2. reactivate chains when scission occurs; and

3. form free radicals of other chemical species that make up the reactant mixture.

This opens the door to interesting possibilities. Experiments are also underway to explore the introduction of various moieties into the polymer chain.

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