

Ultrasound assisted polymerization of MMA and styrene in near critical CO₂

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Abstract

It has been shown that ultrasonic irradiation can induce the formation of free radicals in liquid carbon dioxide. In this work, ultrasonically induced polymerization of MMA or styrene in liquid CO₂ was successfully performed. With ultrasound irradiation for 2–6 h and the absence of any form of stabilizer, discrete polymer particles have been generated and the resulting polymer formed as a fine powder. The results also show that the irradiation period and CO₂:MMA ratio have a significant effect on both the molecular weight and molecular weight distribution for the resulting polymer.

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1. Introduction

Due to tightening environmental restrictions, the uses of clean and low emission technologies are attracting great interest and may be of increasing economic importance. Polymerizations carried out in supercritical carbon dioxide are a convergence of the polymer industry and the clean technologies of the 21st century. Among the supercritical fluids being studied, carbon dioxide has attracted much attention because of its unique physical and chemical properties. It has an easily accessible critical point with a T_c of 31.1 °C and a P_c of 73.8 bar. CO₂ represents a more environmentally friendly alternative to traditional solvents and may eliminate large amounts of hazardous organic or aqueous waste that require post-treatment and energy intensive drying steps for product purification [1,2].

Free radical polymerization in supercritical CO₂ poses a challenge. Though it is a good solvent for many monomers, CO₂ is a very poor solvent for most high molecular weight polymers. Therefore, in order to prevent coagulation or agglomeration of the particles, an appropriate stabilizer is

needed to produce a stable dispersion. The stabilization mechanism in dispersion polymerization is usually steric in nature, whereby a layer of stabilizer, which contains a lipophilic backbone and a CO₂-philic group, adsorbs to or becomes chemically attached to the polymer colloid-solvent interface and imparts long-range steric repulsion between particles. The only class of polymeric materials, which have shown high solubility in CO₂ at readily accessible experimental conditions, are silicones and fluoropolymers [3–5]. Another approach is to use a compound containing a silicone or fluoro-group as a co-surfactant or co-monomer. Thereby achieving in situ stabilization or homopolymerization as opposed to dispersion polymerization. Until now, most stabilizers used for dispersion polymerization contained either silicon or fluorine group, whose high cost make them unfavorable for large-scale industrial applications [6–9]. In the process of searching for new stabilization mechanism for scCO₂ polymerization, ultrasound irradiation appears to be a new route with considerable potential.

Ultrasound is sound waves with frequencies ranging from 16 kHz to a few megahertz, which are above those within the hearing range of the average person. When ultrasound of sufficient amplitude passes through a liquid medium, a large number of microbubbles form, grow and collapse in

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a very short time because of the acoustic pressure changes during its compression and rarefaction cycle. This cavitation phenomenon provides a primary mechanism for the sonochemistry effect. During cavitation, bubble collapse produces intense local heating, high pressures, and very short lifetimes; these transient, localized hot spots drive high-energy chemical reactions. These hot spots have temperatures of more than 5000 °C, pressures of about 1000 atm, and heating and cooling rates above 1000 K/s [10]. The harsh conditions generated by cavitation are capable of producing excited states, able to break chemical bonds and generate free radicals [11]. Recent efforts have been devoted to the ultrasonically induced free radical polymerizations [12–15]. In addition, ultrasound also has intense dispersing, stirring and emulsifying effects, which provides a new route to stabilize the dispersion latex. Recently, Okudaira et al. reported that a successful suspension polymerization of styrene was achieved without the use of any emulsifier and initiator under sonication [16].

Before we are able to combine and take advantage of the two advanced methods, one largest and most important question need to be answered, how to induce the cavitation in the high-pressure medium? A reference for the occurrence of cavitation is the Blake threshold, where stabilized microbubbles are presumably expanded beyond the surface tension limit at large negative pressures. According to the literature, during pressurization of a liquid, the Blake threshold pressure increases, which implies that higher acoustic pressures are needed to produce cavitation. The equation for the Blake threshold pressure is [17]:

$$P_B = P_0 - P_V + \frac{4}{3}\sigma \times \sqrt{\frac{2}{3} \times \frac{\sigma}{(P_0 + 2 \times (\sigma/R_0) - P_V) \times R_0^3}}$$

where P_B is the Blake threshold pressure, P_0 is the external pressure, P_V is the vapor pressure, and σ is the surface tension, and the R_0 is the equilibrium radius of the bubble, usually assuming $R_0 = 10^{-5}$ m. From the equation, it is very clear that for the low volatility liquid, the threshold pressure is mainly determined by the static pressure and the surface tension. Unlike the ordinary liquids, dense-phase fluid, which is usually a gas at ambient conditions, has a high vapor pressure, thus its vapor pressure will have a substantial influence on the Blake threshold pressure. It is shown that at 58.2 atm and 293 K, the threshold pressure for liquid CO₂ equals that of water at 1 atm and 293 K [18]. So, it is much easier to generate enough acoustic pressure to exceed the Blake threshold, thereby initiating cavitation in the high-pressure dense-phase medium.

In fact, Keurentjes et al. already proved that ultrasound irradiation can induce cavitation inside high-pressure liquid CO₂, as long as CO₂ stays in a subcritical state [18]. In the present study, ultrasonic irradiation has been employed to induce the polymerization of MMA or styrene in a high pressure CO₂ system. The effects of irradiation period and monomer

ratio on the molecular weight (MW) and MW distribution have been studied systematically.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, Aldrich, 99%) and styrene (Aldrich, 99%) were purified by passage through the inhibitor remover columns (Aldrich) to remove the inhibitor each contained. 2,2-Diphenyl-1-picrylhydrazyl (DPPH, Aldrich, 95%) was used as received and worked as a radical scavenger. Tetrahydrofuran (THF, Aldrich, HPLC grade) was used as received. Carbon dioxide (SFC/SFE grade) was provided by Praxair and was used as received.

2.2. Apparatus

The reactor used for the research scheme was made in house. It is a cylindrical reactor with a volumetric capacity of 45 ml, made of 316 stainless steel. A schematic of the experimental apparatus is shown in Fig. 1. The cell was also equipped with two tempered steam gauge glass windows in order to observe the cavitation phenomena directly.

A Misonix sonicator XL-2020 system (Misonix, Farmingdale, NY) was used to generate the ultrasound at a fixed frequency of 20 kHz. It has a standard 1/2" titanium-tapped horn with replaceable titanium flat tip and an adjustable power supply, which goes up to 550 W.

In this work, we developed a fiber-optic-based reactor connected directly to a charge-coupled device (CCD) array ultraviolet UV–visible spectrometer for in situ determination of the radical formation rate in the high-pressure reaction system. The design of the fiber-optic cell is similar to that described previously in the literature [19]. The cell has a single optical path formed by the ends of two fiber optic cables. The path length was 5 mm. The optical fibers (Polymicro Technologies, Phoenix, AZ) used for this study were 600 μm high OH-silica core, and connected to a CCD array UV–vis Spectrophotometer model SI-420 (Spectral Instruments, Inc. Tucson, AZ). The instrument consists of a tungsten and deuterium light source providing a full spectra range from 190 to 980 nm. The SI 400 control software is used to control the spectrometer and analyze the spectral data collected from the probe.

2.3. Radical formation confirmation

Radical formation was measured in the reaction system using a radical scavenger. DPPH has been reported to be effective for determining radical formation kinetics. This chemical rapidly reacts with a variety of radicals along with undergoing a significant color change. It was found that the difference in molecular absorption coefficients of the active and inactive radical scavenger has a maximum at 519 nm [20]. The

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