

A New PDMS Macromonomer Stabilizer for Dispersion Polymerization of Styrene in Supercritical Carbon Dioxide

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ABSTRACT: Free radical polymerization of styrene in supercritical CO₂ requires addition of a surfactant to produce polystyrene (PS) in high conversion and molecular weight with well-defined particle sizes. In this work, we examined a new stabilizer that can provide effective stabilization for the polymerization of styrene. A commercially available poly(dimethylsiloxane) macromonomer has been employed as a stabilizer for dispersion polymerization of PS in scCO₂. The reactions were conducted in a 225-mL stainless steel autoclave over the temperature range 60–80°C and under

pressures of 1,500 to 3,000 psi. After 2–12 h of polymerization, the conversion determined by gravimetric method was between 20 and 80%. These preliminary results suggest that this macromonomer offers satisfactory stabilization for the styrene system. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 545–549, 2004

Key words: carbon dioxide; dispersion; macromonomer; polystyrene; stabilization; supercritical

INTRODUCTION

Using supercritical carbon dioxide (scCO₂) as a medium for polymer synthesis has been extensively studied in the last decade. Addition to the common features related to supercritical fluids, such as gas-like diffusivities and liquid-like densities, its unique chemical, environmental, and potential economic advantages make scCO₂ a practical and promising alternative to traditional solvents. CO₂ is naturally occurring, abundant, and readily available in high purity from a variety of sources. It has an easily accessible critical point with a T_c of 31.1°C and a P_c of 73.8 bar, and its tunable properties can eliminate large amounts of hazardous organic or aqueous waste that require post-treatment and energy-intensive drying steps for product purification. Furthermore, CO₂ is relatively chemically inert, which will allow a wide variety of polymer synthesis mechanisms.^{1,2}

Free radical polymerization in scCO₂ poses a challenge for the polymer industry. Though it is a good solvent for most monomers, generally CO₂ is a very poor solvent for most high-molecular-weight polymers. The only classes of polymeric materials that have shown high solubility in CO₂ at readily accessible experimental conditions are silicones and fluoropolymers.^{3–5} Therefore, polymerization in scCO₂ will begin as a homogeneous mixture. Once the growing oligomeric radicals reach a critical molecular

weight, the chains are no longer soluble in the continuous phase and phase separation occurs. To prevent coagulation or agglomeration of the particles and to achieve a successful dispersion polymerization in scCO₂, an effective amphiphilic stabilizer must be employed. It should contain a lipophilic backbone that can anchor onto the surface of the growing polymer particles and a CO₂-philic group that will extend into the continuous phase, thus giving rise to steric stabilization and preventing particle flocculation.¹

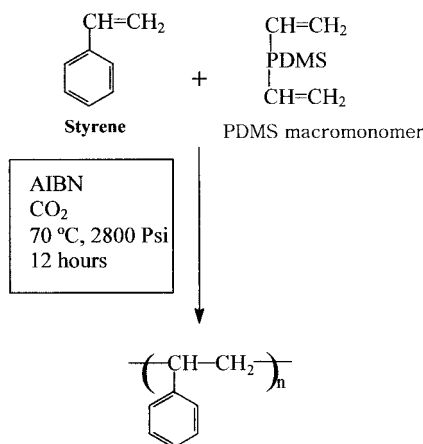
In 1994, DeSimone and coworkers⁶ successfully utilized poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) homopolymer as a steric stabilizer. Since then other fluorinated and siloxane polymers have also been identified as effective stabilizers for free radical dispersion polymerization in scCO₂.^{1,7–9} Alternatively, stabilization can be achieved by copolymerization of a suitable macromonomer containing a “CO₂-philic” moiety. There are several reports of the use of poly(dimethylsiloxane) monomethacrylate (PDMS-mMA) macromonomer to obtain satisfactory results in dispersion polymerizations.^{7,10,11} In this paper, we employed another commercially available macromonomer as surfactant in a styrene polymerization system to examine its possibility as a stabilizer (Scheme 1). The effects of the stabilizer concentration upon conversion, molecular weight, and product morphology have been investigated.

EXPERIMENTAL

Materials

Styrene (Aldrich) was purified by passage through an alumina column, 2,2'-azobis(2-methylpropionitrile)

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Scheme 1 Dispersion polymerization of styrene in $sc\text{CO}_2$.

(AIBN, Aldrich) was recrystallized twice from methanol, methanol (Aldrich), ethanol (Aldrich), acetone (Aldrich), and polydimethylsiloxane, vinyltrimethylsiloxy (Aldrich) were used as received. Carbon dioxide (SFC/SFE grade) was provided by Praxair and was used as received.

Polymerization of styrene in $sc\text{CO}_2$

The reaction vessel (Parr, 225-mL stainless steel autoclave) was charged with styrene (20 g), AIBN (1 wt % of monomer), and the desired amount of stabilizer, closed, and filled with CO_2 . Temperature was raised to 70°C and pressure was raised to the required level and the system was left to stand with low speed stir for 2–12 h. After that the cooling water was circulated through a coil in the reactor to quench the reaction. The CO_2 then was vented slowly from the reactor at a rate of about 50 psi/min. The polystyrene (PS) product was removed from the cell. The monomer conversion was determined gravimetrically. Samples were retained for further characterization.

Polymer characterization

The molecular weights of the resulting polymers were determined by using a Polymer Laboratories PL-

GPC220 gel permeation chromatograph with a Polymer Laboratories PLGel $5\ \mu\text{m}$ Mixed-D column, using tetrahydrofuran (THF) as the eluent against PS standards (Polymer Laboratories). A differential refractive index detector and Laser Light scattering detector PD2042 from Precision Detector Inc. were used to monitor the column output and the data were processed using Viscotek TriSEC GPC software. Both the sample analysis and the calibration were conducted at a flow rate of 1 mL/min. Scanning electron microscopy (SEM) data were collected using a JEOL 5310 scanning electron microscope. Samples were mounted on an aluminum stub using an adhesive carbon tab and were gold coated. The ^{13}C - and ^1H -NMR data were collected using a Bruker 300 MHz spectrometer.

RESULTS AND DISCUSSION

Stabilizer concentration effect

The concentration of stabilizer controls the morphology of the material produced, with higher concentrations usually leading to smaller particles. To investigate this, a number of polymerizations were performed over a wide range of PDMS macromonomer concentrations.

The results show that increasing the concentration of stabilizer resulted in an increase in the yield and molecular weight of the PS produced. This is indicative of a more efficient stabilization of the dispersed particles. In the absence of stabilizer, PS was produced in low yield and with a low molecular weight (Table I, entry 1). Increasing the concentration of the PDMS macromonomer will increase the yield significantly with a corresponding increase in the molecular weight. Although 0.2 wt % stabilizer gives a significant improvement of the yield and molecular weight (entry 2), the resulting polymer particles were significantly aggregated, forming a white fluffy solid. In contrast, a fine, white powder is formed when using higher stabilizer concentrations.

Upon increasing stabilizer concentration to 1.8% (entry 3), there is further increase in yield and molecular weight, and the SEM reveals that polymer parti-

TABLE I
Polymerization of Styrene in Supercritical Carbon Dioxide using PDMS macromonomer^a

Entry	AIBN ^b (wt %)	PDMS ^b (wt %)	Pressure (mean psi)	Yield (wt %) ^c	M_n ($\times 10^3$) (GPC)	PDI (GPC)
1	1	0	2,470	25	12	4.7
2	1	0.2	2,630	59	21	3.1
3	1	1.8	2,720	61	29	2.7
4	1	2.8	2,650	75	35	2.1
5	1	5.0	2,710	77	45	2.3
6	1	7.8	2,730	82	43	1.9

^a Polymerization was carried out at 70°C for 12 h and 20 g of styrene.

^b Wt % with respect to monomer.

^c Yields were determined gravimetrically.

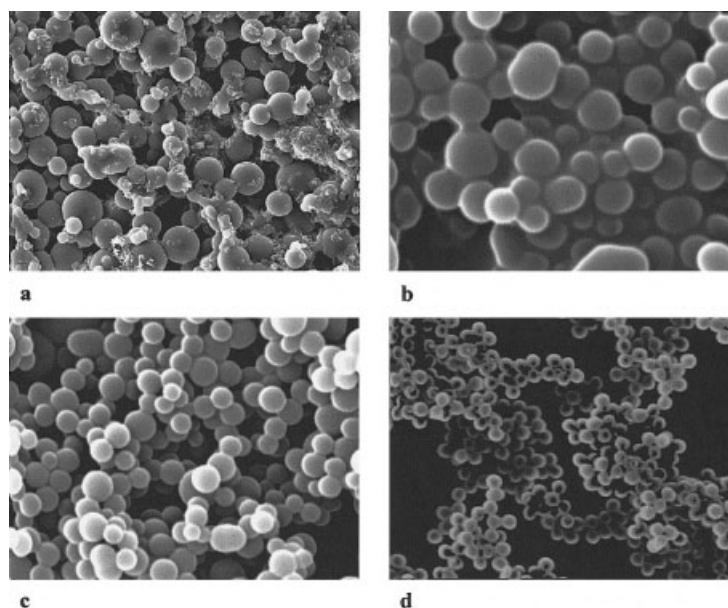


Figure 1 SEM micrograph of PS formed using (a) 1.8 wt %, (b) 2.8 wt %, (c) 5 wt %, (d) 7.8 wt % of polydimethylsiloxane, vinyltrimethylsiloxy macromonomer as stabilizer (Table I, entries 3–6).

cles aggregated with each other and a mixture of discrete particles and “strings” are formed [Fig. 1(a)]. As there is a fairly wide distribution of the particle size, this suggests that the dispersion is still not completely stabilized with insufficient steric stabilizer to achieve coverage of the particle surface. As the stabilizer concentration reaches 2.8% (entry 4), the particle size distribution has been narrowed down notably. But without enough stabilizer to stabilize the dispersion, a “partial strings and partial separated particles” state was formed due to aggregation, therefore not many discrete particles are found in the SEM microscopy [Fig.1(b)]. At even higher stabilizer concentrations (entry 5 and 6), discrete particles are produced and have a fairly narrow size distribution. The diameter of the particles decreases from 3.4 to 2.3 μm upon increasing the stabilizer concentration from 5 to 7.8%. Such trends in particle size have been observed for a

number of stabilizer systems in scCO_2 and in conventional solvents.^{7,11–13} The yield and molecular weight will keep increasing until the concentration of stabilizer reaches around 8 wt %. After that, further increasing the stabilizer shows no significant effect on either yield or SEM morphology, probably because complete coverage of the particle surfaces had already been achieved at this concentration [Figs. 1(c) and (d)]. At 7.8 wt % (entry 6), the dispersion polymerization provides a moderate monodispersity where the polydispersity index (PDI) is 1.9.

Pressure effect

A primary advantage of employing scCO_2 lies in the ability to tune the solvent density and dielectric constant by simply changing either the temperature or the pressure. Therefore we can explore the solvent effects of a St polymerization without adding a cosolvent.

TABLE II
Effect of Pressure on Dispersion Polymerization of Styrene^a

Pressure(psi)	Yield (wt %) ^b	$M_n (\times 10^3)$	PDI
1,640	68	37	4.9
1,830	73	41	3.6
2,350	75	39	2.4
2,680	81	42	2.0
2,810	80	40	2.3

^a Polymerization was carried out at 70°C for 12 h and 20 g of styrene, using 1 wt % AIBN and 7.5 wt % with respect to monomer.

^b Yields were determined gravimetrically.

TABLE III
Conversion of Styrene as Function of Time^a

Reaction Time (h)	Pressure(psi)	Yield (wt %) ^b	$M_n (\times 10^3)$	PDI
4	2,670	38	14	3.0
7	2,720	58	28	2.5
9	2,680	73	36	2.7
12	2,750	81	43	1.9
16	2,710	82	45	2.1

^a Polymerization was carried out at 70°C and 20 g of styrene, using 1 wt % AIBN and 7.5 wt % PDMS (both with respect to monomer).

^b Yields were determined gravimetrically.

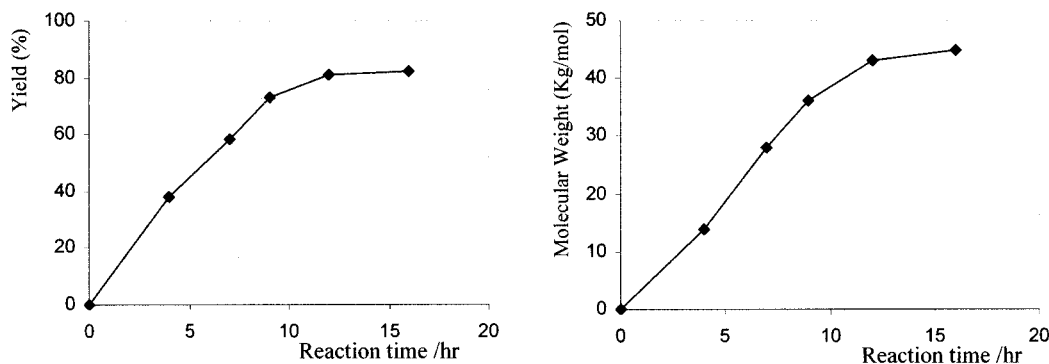


Figure 2 PS yield and molecular weight as a function of reaction time.

The effects of pressure on the polymerization are summarized in Table II. At low pressure under 2000 psi, the yield can still reach up to 70%. But since the solubility of the PDMS group is considerably decreased under lower pressure, polymer particles appear to be stuck together. No spherical particles were obtained and the PDI was larger than that obtained from higher pressure. Under the lower pressure situation, at the beginning of the polymerization, the stabilizer is still soluble in the monomer with a high concentration. That is, the monomer acts like a cosolvent. As the polymerization proceeds, the monomer is consumed and the solubility of the stabilizer in scCO_2 is decreased. The polymer colloid becomes more and more unstable even though the stabilizer already covered the whole polymer surface.

Time effect

In an effort to gain insight into the reaction progress as a function of time, samples were obtained by stopping the reactions at various intervals. Table III and Figure 2 depict the results from this study. The plots show a fairly linear increase in both conversion and molecular weight as time increases until around 10 h. After that, further increases in the reaction time only improve the conversion and molecular weight slightly.

The preliminary NMR results suggest that the macromonomer stabilizer is incorporated into the product polymers even after being washed repeatedly with hexane, which indicates that the copolymerization with styrene occurred during the PS polymerization. This is consistent with other polymerization results using a siloxane-based macromonomer.^{10-12,14} Further NMR and DSC experiments should be able to give us more detailed information about how the stabilizer behaves during the dispersion polymerization process.

It is clear that the new PDMS macromonomer we are using here provides fairly effective stabilization to the polystyrene dispersion system in scCO_2 . It may also have an advantage in terms of cost and industrial

manufacturing. Silicone polymers are considerably less expensive to produce than their fluorinated counterparts, making silicone polymers more economically attractive as stabilizers.¹ Compared with the most studied silicon-based stabilizer, another commercially available PDMS macromonomer: PDMS-mMA, our new stabilizer is much cheaper. With a similar ability to stabilize the dispersion system, this new PDMS macromonomer makes more effective use of the expensive siloxane component and may be a more cost effective approach for polymerization on an industrial scale.

CONCLUSION

This work has shown that polydimethylsiloxane, vinyl dimethylsiloxane is a successful stabilizer for the dispersion polymerization of styrene in scCO_2 ; high conversion of high-molecular-weight PS can be produced using the PDMS macromonomer. The particle size of the product polymer was controlled by the amount of stabilizer added. It is also interesting to note there is no suggestion of crosslinking or branching of the polymer product, as one might expect since the macromonomer has two reactive vinyl groups.

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