

Copolymerization of Styrene and Maleic Anhydride in Supercritical Carbon Dioxide

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ABSTRACT: The copolymerization of styrene (St) and maleic anhydride (MA) was carried out in supercritical carbon dioxide (SC CO₂). It was found that St and MA are easy to copolymerize in SC CO₂ and the conversion can reach 97%, and that very fine and dry powders are obtained. The products were characterized using Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). GPC data showed that the molecular weight of the copolymer reach

$3.62 \times 10^4 \text{ g mol}^{-1}$. Scanning electron microphotographs showed the minimum particle size of the product is about 200 nm. DSC measurements indicated that the glass transition temperature (T_g) of the copolymer increases with increasing the MA content in the copolymer. TGA curve showed that the copolymers were decomposed at about 350°C. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3332–3336, 2007

Key words: supercritical carbon dioxide; maleic anhydride; styrene; copolymerization

INTRODUCTION

Supercritical carbon dioxide (SC CO₂) (critical temperature 31.1°C, critical pressure 7.38 MPa) is recognized as an attractive replacement for organic solvents that are traditionally used in chemical industry. SC CO₂ has many advantages as a reaction medium, such as nontoxic, nonflammable, chemical inertia, and inexpensive. Compared with other supercritical fluids, it also has a moderate critical pressure and a low critical temperature. Because of its low viscosity and zero surface tension, the mass-transfer speed in SC CO₂ fluid is much faster than that in conventional liquids.

Many polymerizations using SC CO₂ as a reaction medium have been reported, including solution polymerization,¹ dispersion polymerization,^{2–7} precipitation polymerization,^{8–12} and emulsion polymerization.^{13,14} Especially, using SC CO₂ as a polymerization medium offers an attractive advantage that products are easily obtained as dry powder by just releasing the CO₂ at the end of the reaction. In this work, we synthesized the copolymer of St and MA using SC CO₂ as a reaction medium, and obtained

good results. This study, to our knowledge, may be the first work copolymerizing St and MA in SC CO₂.

EXPERIMENTAL

Materials

Styrene (St) was supplied by Shanghai Chemical Reagent Company and used after distillation. Maleic anhydride (MA), purchased from Beijing Yili Fine Chemical Company, was used after recrystallization in methanol. 2,2'-Azobis(isobutyronitrile) (AIBN), produced by Beijing Chemical Factory, was used after recrystallization from methanol. Methanol (A. R. grade) supplied by Shanghai Chemical Reagent Company was used as received. Carbon dioxide with purity of 99.9% was purchased from Jinan Gas Factory and used as received.

Polymerization

In this work, MA and AIBN were added into a 100-mL stainless steel high-pressure reactor. After the reactor was sealed, the air inside was removed by a vacuum pump. St was injected into the reactor through a special rubber stopper. Liquid CO₂ (about 50 g) was injected into the reactor by a high-pressure injection pump. Then, the reactor was put into a water bath and heated to the desired reaction temperature (65°C) to start the reaction. When the reaction ended, we cooled down the reactor to room temperature, released CO₂ slowly, and collected the product. The product was Soxhlet-extracted using hot methanol for

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TABLE I
Polymerization^a Results at Different Monomer Ratio

Samples	f_{MA}^b	Conversion (%)	$M_n \times 10^{-4}$ (g mol ⁻¹)	Appearance of products
PS	0	41	1.14	Dope
SM5	0.05	73	1.78	Gel
SM10	0.1	96	2.43	White powder
SM20	0.2	97	2.16	White powder
SM30	0.3	97	3.62	White powder

^a Reaction condition: $[M] = 0.5 \text{ mol L}^{-1}$, $[AIBN] = 0.001 \text{ mol L}^{-1}$, $T = 65^\circ\text{C}$, $P = 16 \text{ MPa}$, $t = 10 \text{ h}$.

^b $f_{MA} = [MA]/[M]$ (the mole fraction of [MA]).

8 h to remove the unreacted monomers, and dried to a constant weight to obtain the pure copolymer (SM).

Characterization

FTIR (Perkin–Elmer Spectrum One) was used to characterize the copolymer. GPC (Waters 1525) was used to measure the average molecular weight of the copolymer. DSC (Perkin–Elmer Diamond) and TGA

(Perkin–Elmer Pyris Diamond) were used to analyze the thermobehavior of the copolymer. SEM (Hitachi S-2500) was used to observe the morphologies of the products.

RESULTS AND DISCUSSION

The copolymerization of St and MA in SC CO₂ is precipitation polymerization. The reaction can be

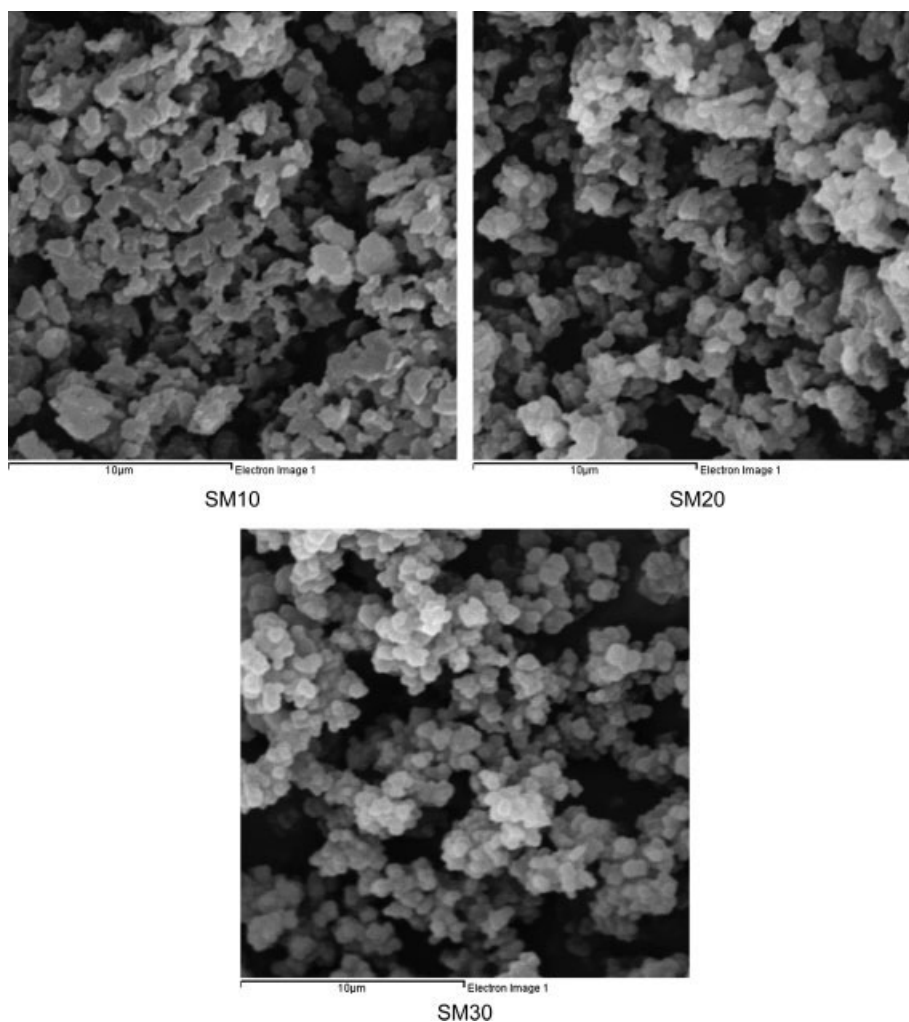


Figure 1 Scanning electron micrographs of the products prepared at 16 MPa.

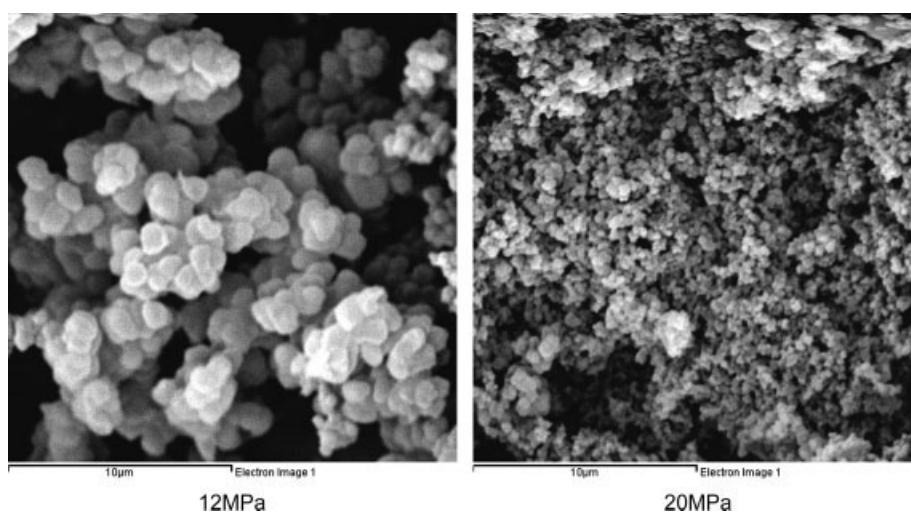


Figure 2 Scanning electron micrographs of SM30 prepared at different pressure. (Reaction condition: $[St] = 0.35 \text{ mol L}^{-1}$, $[MA] = 0.15 \text{ mol L}^{-1}$, $[AIBN] = 0.001 \text{ mol L}^{-1}$, $T = 65^\circ\text{C}$, $t = 10 \text{ h}$.)

observed through the glass windows of the reactor. At the beginning of the polymerization, the reaction system of CO_2 , initiator and monomers is a single phase, indicating that all the monomers and AIBN in the system are dissolved in SC CO_2 . After about 10 min, the reaction mixture become cloudy, and then more and more white particles of solid precipitate appear. When the polymerization finish and open the reactor, it can be seen that the whole reactor is filled with white precipitation. The product is very fine and dry powder, and easy to collect.

Effect of MA dosage on polymerization

The copolymerization results are summarized in Table I. One can find that the conversion increases with increasing the MA dosage. The conversion of

pure St ($f_{MA} = 0$) is only 41%, and the product is dope. However, even when $f_{MA} = 0.05$, the conversion is increased to 73%, the product also becomes a gel. When f_{MA} is increased to 0.1, 0.2, 0.3, respectively, the conversions reaches or exceeds 96%, and the products are very fine dry powder. This phenomenon can be explained as following: in terms of the Alfrey-Price $Q-e$ scheme, where Q describes the reactivity of monomer; e describes the polarity of monomer.¹⁵ $Q_{St} = 1.0$, $e_{St} = -0.8$; $Q_{MA} = 0.23$, $e_{MA} = 2.25$.¹⁶ The polarity difference between St and MA is so large that they are easy to attract each other and to copolymerize. The reactivity of the copolymerization between St and MA is much greater than that of homopolymerization of St.¹⁷ Therefore, the conversion of the copolymerization increases with increasing the MA dosage.

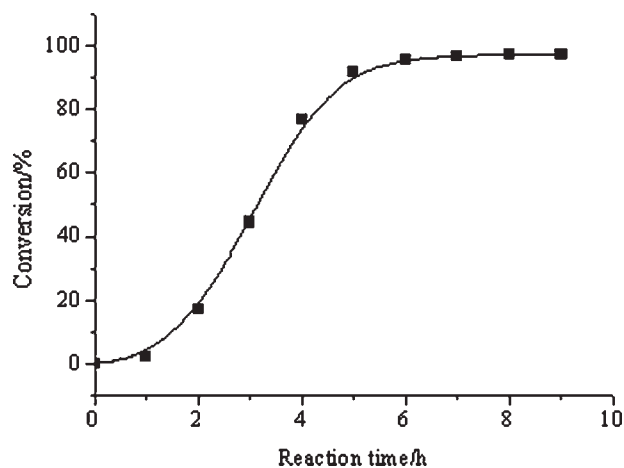


Figure 3 Effect of reaction time on conversion. (Reaction condition: $[St] = 0.35 \text{ mol L}^{-1}$, $[MA] = 0.15 \text{ mol L}^{-1}$, $[AIBN] = 0.001 \text{ mol L}^{-1}$, $T = 65^\circ\text{C}$, $P = 16 \text{ MPa}$.)

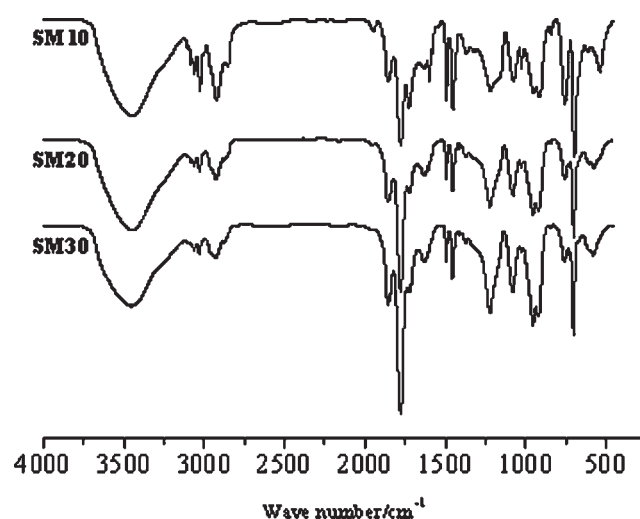


Figure 4 FTIR spectra of SM.

Morphology of the products

From scanning electron photomicrographs, one can find that the particle size of the products prepared in SC CO₂ is very fine, and is influenced by the SC CO₂ pressure. The average size is about 500 nm when the SO CO₂ pressure is 16 MPa (Fig. 1). However, the particle sizes of SM30 are decreased from 1000 to 200 nm when SC CO₂ pressure is changed from 12 to 20 MPa (Fig. 2). The main reason may be that, with increasing the SC CO₂ pressure, the concentration of the monomers decreases, consequently the average size of precipitated particles decreases.

Effect of reaction time on conversion

As shown in Figure 3, the conversion increases with increasing of reaction time initially, and reaches a plateau in 6 h. The reason is that the concentration of the monomers is high at the beginning, so the reaction speed increases rapidly after the induction period. As the reaction goes on, the concentration of the monomers is decreasing, and the reaction speed is also decreasing. Gradually, the conversion tends to saturation.

FTIR analysis of the polymers

Figure 4 is the FTIR spectrum of SM. one can find that there are stretching bands at 1779 and 1858 cm⁻¹ for the carbonyl group (—C=O), C—C bands in the phenyl at 1454, 1494, and 1630 cm⁻¹, —CH₂ at 2927 cm⁻¹, and =CH at 3028 cm⁻¹. The peaks at 3445, 1727, and 956 cm⁻¹ indicate that some anhydride in SM have become acid because anhydride is easy to absorb water from air.

Comparing the FTIR spectra of SM10 and SM30, one can also find that the absorb peaks of carbonyl group (—C=O) (at 1779 cm⁻¹ and 1858 cm⁻¹) in the spectrum of SM30 are more prominent than that in the spectrum of SM10. However, the absorb peaks of

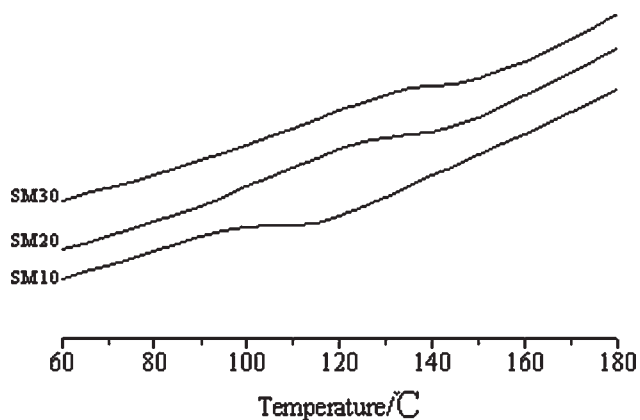


Figure 5 DSC thermographs of SM.

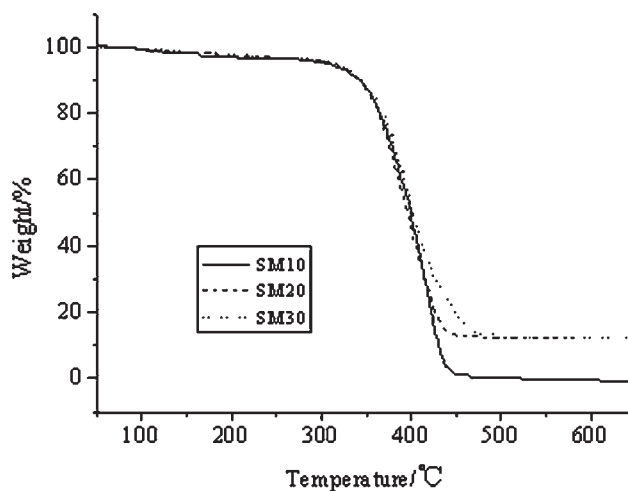


Figure 6 TGA thermographs of SM.

polystyrene (at 3104, 3084, 3062, 3028, and 3004 cm⁻¹) in the spectra of SM30 are weaker than those in the spectra of SM10. The reason is that there are more MAs in SM30 structure and more polystyrene chain in SM10 structure.

DSC analysis of the polymers

DSC results are shown in Figure 5. It can be seen that the glass transition temperatures (T_g) of SM10, SM20, and SM30 are 107, 133, and 145°C, respectively, indicating that the T_g of SM increases with increasing the content of MA in the copolymer due to the rigidity of the MA molecular structure (pentaring shape). So more the copolymer contains MA units, more rigid is the polymer chain and higher is T_g .

TGA thermographs of the polymers

Figure 6 shows the TGA curves of SM10, SM20, and SM30. It can be seen that the copolymers lose weight slightly from 89.4 to 206.9°C. The reason is that water absorbed by SM is vaporized and water combined with anhydride decomposed. The copolymers lose weight heavily from 353.4 to 438.6°C because the polymer chain is decomposed. One can also find that SM10 lose its weight completely at 500°C. However, SM20 and SM30 retain some weight until 600°C. The reason may be that the copolymers containing more MA can produce certain heat-resistant compound during the decomposing process.

CONCLUSIONS

SC CO₂ can be used as a good medium for copolymerization of St and MA. High conversion can be obtained using this method. The copolymers are

very fine and dry powders, and their size is influenced by SC CO₂ pressure.

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