

SUPERCritical CARBON DIOXIDE ASSISTED SYNTHESIS OF AMPHIPHILIC GRAFT COPOLYMERS BASED ON POLY(STYRENE-*CO*-MALEIC ANHYDRIDE) WITH METHOXYL POLY(ETHYLENE GLYCOL) SIDE CHAINS*

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Abstract Supercritical carbon dioxide (scCO₂) was used as a reaction medium in synthesizing amphiphilic graft copolymers composed of poly(styrene-*co*-maleic anhydride) (SMA) backbones and methoxyl poly(ethylene glycol) (MPEG) side chains via esterification. The synthesized copolymers were characterized by Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), ¹H-NMR, thermo-gravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC). The gelation phenomenon was suppressed effectively by tuning reaction conditions. The influences of scCO₂ temperature and pressure on the conversion of anhydride were investigated. It was found that the highest conversion ratio occurred at 80°C under a constant pressure of 14 MPa or 26 MPa. With the increase of scCO₂ pressure, the conversion ratio increased first, and then leveled off. The conversion ratio of anhydride could be controlled by regulating the reaction conditions. It was also revealed that using low molecular weight MPEG brought a high conversion ratio of anhydride.

Keywords: Supercritical carbon dioxide; Poly(styrene-*co*-maleic anhydride); Poly(ethylene glycol); Amphiphilic graft copolymer.

INTRODUCTION

Amphiphilic graft copolymers consisting of hydrophobic backbones and hydrophilic side chains exhibit many unique characteristics and have drawn more and more attention in recent years. These copolymers are often employed as battery polyelectrolytes^[1–4], drug carriers^[5–7], membranes additives^[8–10] and so on.

Amphiphilic graft copolymer based on poly(styrene-*co*-maleic anhydride) (SMA) with methoxyl poly(ethylene glycol) side chains (SMA-*g*-PEG) has been investigated increasingly due to its specific properties and convenient synthesis process^[11–14]. SMA is a quasi-amphiphilic and commercially available copolymer containing abundant reactive anhydride groups, which is easy to react with hydrophilic agents to obtain amphiphilic graft copolymers. The grafting reactions between SMA and methoxypolyethylene glycol (MPEG) in organic solvents have been reported recently^[3, 4, 8, 14]. The major obstacle for the popularity of these available synthetic strategies is the formation of gel during reaction process, leading to the insolubility of the products in most organic solvents^[14]. Secondly, a great number of organic solvents and precipitators often have to be used,

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which is not favorable in green chemistry. Additionally, a large amount of methanol was required to endcap the unreacted carboxyl group to gain soluble product, which might cause crosslinking in subsequent treatment^[15].

Using supercritical carbon dioxide (scCO₂) as reaction medium may be a feasible approach that can overcome the above-mentioned drawbacks in the synthesis of SMA-g-PEG. Practically, scCO₂ had been widely applied in polymerization and polymer processing, which had been reviewed by Kendall and Nalawade^[16, 17]. It possesses many advantages such as nonflammable, nontoxic, relatively inexpensive and easy reaching a supercritical state^[18, 19]. Moreover, it is very easy to remove the solvent from the final product since CO₂ is a gas at ambient condition^[20–22]. In the meanwhile, the unreacted molecules can be extracted from the polymer matrix to result in a purified product. To the best of our knowledge, it has not been investigated in scCO₂ by undergoing esterification between SMA and MPEG to synthesize amphiphilic graft copolymers so far.

The objective of the present work is to develop a novel approach to synthesize SMA-g-PEG copolymers without using any organic solvent. The opening ring esterification between anhydride in SMA with hydroxyl in MPEG was carried out in scCO₂ medium. In synthesis process, scCO₂ acted as solvent, swelling agent and carrier simultaneously. The chemical structure of the products was characterized in detail. The influences of scCO₂ temperature and pressure on the conversion of anhydride were investigated also. The resulted amphiphilic SMA-g-PEG copolymers are favorable as additive in the blend modification of polymer membranes.

EXPERIMENTAL

Materials and Reagents

SMA (2021p, the unit ratio of styrene to maleic anhydride is 2:1, Table 1) was purchased from Sartomer and dried in vacuum at 40°C for 12 h prior to use. Methoxyl poly(ethylene glycol)s (MPEGs) (abbreviated as MPEG350 and MPEG750, Table 1) were obtained from Aldrich. *p*-Toluenesulfonic acid (PTSA), diethyl ether and other chemicals were analytical grade and used as received.

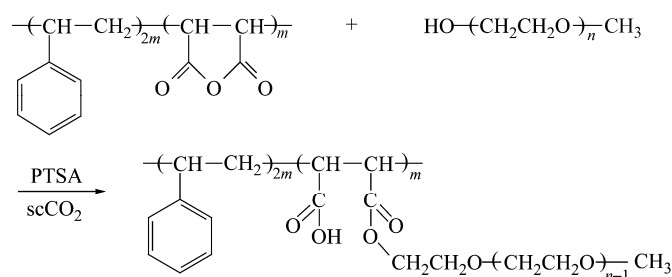
Table 1. Characteristics of the starting SMA and MPEG

Materials	[Styrene]/[Maleic anhydride]	<i>M_n</i> by GPC	Polydispersity	Average no. of anhydride group per molecule ^a
SMA2021p	2:1	12100	1.90	39.6
MPEG350	—	320	1.15	—
MPEG750	—	619	1.23	—

^a Calculated from the GPC

Synthesis of Amphiphilic Graft Copolymers

The grafting reaction, as shown in Scheme 1, was carried out in a 1 L high pressure cylinder reactor equipped with thermostated water bath and mechanical stirrer and pressure sensor. In a typical procedure, 20.0 g of SMA powder, a given amount of MPEG and 0.2 g of PTSA were put into the tank. After sealing, the tank was poured with gaseous CO₂ three times to remove air at a designed temperature. An ISCO model no.500D automatic syringe pump was used to pressurize the tank to a given pressure. After reaching the desired pressure and temperature, the reaction was allowed to proceed under mechanical stirring for 24 h. At the end of the reaction,



Scheme 1 The synthesis route of SMA-g-MPEGs in scCO₂

the tank was cooled, and the CO₂ was slowly vented. The product was fully dried in a vacuum oven at 60°C for use. A small amount of the product was refined by repetitious dissolution/precipitation for characterization.

Characterizations of SMA-g-MPEG

¹H-NMR spectra were recorded with a Bruker Advance DMX 500 MHz instrument using DMSO-*d*₆ as solvent and tetramethylsilane as the internal standard.

FTIR spectra of the copolymers were recorded on a Bruker Vector22 FTIR spectrophotometer.

The molecular weight and its distribution were determined by a Waters 150/C-AL gel permeation chromatograph (GPC) with three 950 mm MixB columns of linear, 10.3 nm and 10.4 nm porosities and a 410 differential refractometer at 30°C. THF was used as the mobile phase with a flow rate of 1.0 mL/min, and the instrument was calibrated using PS standards (narrow standard).

TGA experiments were performed using a Dupont TGA 910 with a heating rate of 20 K/min under nitrogen atmosphere. The heating temperature ranged from 50°C to 600°C. DSC measurements were performed on a TA® DSC Q100 calorimeter. The samples were quenched to -80°C, and then heated at the rate of 10 K/min.

RESULTS AND DISCUSSION

Characterization of SMA-g-MPEG

As reported previously^[14], it was difficult to gain SMA-g-PEG copolymers with high grafting percentage due to the occurrence of gelation. As a result, the products were difficult to dissolve in most organic solvents, and could only swell in a few polar organic solvents or water.

In this work, SMA2021 was chosen as backbone of the graft copolymers because of its high content of anhydride groups in polymer chains (Table 1) and water insolubility, which makes the corresponding graft copolymers suitable as amphiphilic additives in membrane preparation. ScCO₂ is a solvent of MPEG which can also swell and plasticize SMA well because of the specific intermolecular interactions between carbon dioxide and carbonyl groups^[23]. Meanwhile, the free volume and segment mobility of SMA are largely increased^[24–27] in scCO₂. The low viscosity of scCO₂ allows MPEG and PTSA to diffuse rapidly into the swollen SMA and react with anhydride groups. By regulating the reaction conditions, the gelation can be controlled during the synthesis process, and the products obtained can dissolve well in some polar organic solvents such as DMF, DMAc, THF and so on.

In the present work, it was found that the gelation easily occurred for MPEG350 when the temperature was above 80°C, the pressure > 21 MPa and the OH/Mah (mol/mol) was 0.85–1.0, and for MPEG750 when the temperature > 90°C, the pressure > 21 MPa and the OH/Mah (mol/mol) was 0.9–1.0. The presence of dihydroxylic PEG in MPEG was thought to be responsible for the gelation^[12]. The formation of gel would lead to the insolubility of the products in most organic solvents. In the other reaction conditions, even though cross-linking may take place due to the dihydroxylic PEG, the degree of cross-linking maybe too low and the gained copolymers is soluble.

The FTIR spectra of SMA, SMA-g-MPEG350 (SgM350) and SMA-g-MPEG750 (SgM750) are shown in Fig. 1. For SgM350, both the absorptions at 1855 and 1777 cm⁻¹ are nearly absent, and the strong absorption at 1731 cm⁻¹ implies the forming of carboxyl or ester bond, which results from the reaction of anhydride groups (SMA) and hydroxyl groups (MPEG). The successful reaction is further confirmed by the absorption at 1105 cm⁻¹ that is attributed to the ether group of PEG. For products with MPEG750 as side chains, anhydride absorption is still visible, indicating the lower conversion of anhydride when MPEG750 was used as an esterification reagent compared to MPEG350. The FTIR spectra indicate that the conversion of anhydride groups is not complete. This phenomenon may be attributed to the following reasons. First, the reactivity of MPEG350 is higher than that of MPEG750. Secondly, the solubility of MPEG350 in scCO₂ is better than that of MPEG750, and MPEG350 is easier to diffuse into the swollen SMA and then react with the anhydride groups. Finally, the steric hindrance of MPEG350 to react with anhydride is lower than that of MPEG750.

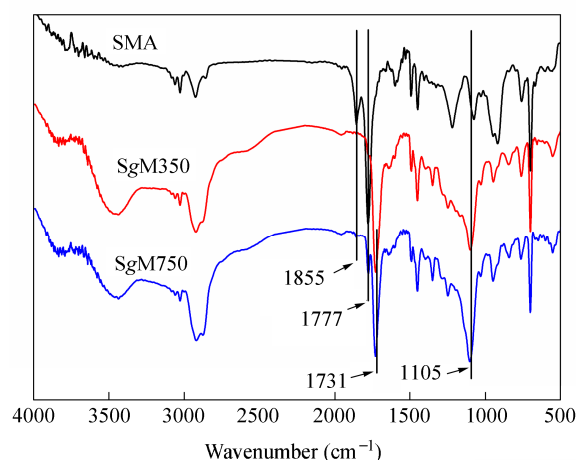


Fig. 1 FTIR spectra of SMA, SgM350 prepared at 80°C, 14 MPa and SgM750 prepared at 80°C, 26 MPa

A typical ^1H -NMR spectrum of SMA-g-MPEG copolymer and the attribution of the peaks are presented in Fig. 2. The broad peak at $\delta = 7.1$ is assigned to the resonance peak of the phenyl protons of the styrene units in SMA, the peak at $\delta = 3.5$ corresponds to the ethylene protons of MPEG, and the peak at $\delta = 3.2$ is the resonance peak of the terminal methoxyl protons on MPEG. The peaks between $\delta = 3.3$ and 3.4 are the protons of SMA backbone and the peak at $\delta = 2.5$ is the solvent residual peak. In addition, the broad peak at $\delta = 4.0$ is attributed to the methylene protons attached to the ester group formed in the opening reaction^[8, 14], indicating the covalent linking of MPEG chains with SMA backbones. From the results, it can be deduced that the grafting reaction between SMA and MPEG has been successfully conducted in scCO_2 .

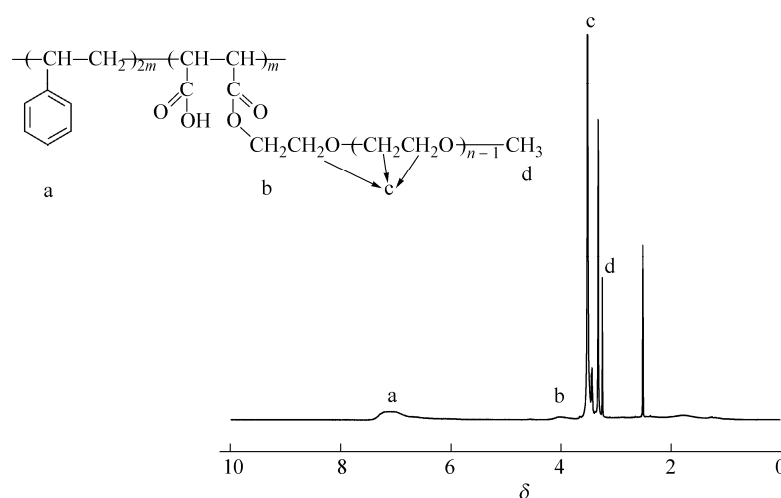


Fig. 2 Typical ^1H -NMR spectrum of SgM350 copolymer prepared at 80°C, 14 MPa

Figure 3 shows the GPC curves of SMA and the graft copolymers. Only an elution peak appeared for all these polymers, suggesting the unreacted MPEG has been almost completely removed by the repetitious dissolution/precipitation process. Moreover, the synthesized graft copolymers have larger polydispersity than SMA. The conversion of anhydride can be calculated from GPC results according to the following equation,

$$\text{Conversion of anhydride (\%)} = \frac{(M_n \text{ of SgM} - M_n \text{ of SMA}) / M_n \text{ of MPEG}}{\text{Average no. of anhydride group per molecule}} \times 100\% \quad (1)$$

where M_n is obtained from GPC analysis.

From the ¹H-NMR data, the conversion of anhydride groups can also be calculated by comparing the area of the proton peak at $\delta = 4.0$ to that of the reference peak at $\delta = 7.1$. The corresponding equation is:

$$\text{Conversion (\%)} = \frac{A_b/2}{A_a/10} \times 100 \quad (2)$$

where A_b and A_a are the areas of the peak b and a, respectively.

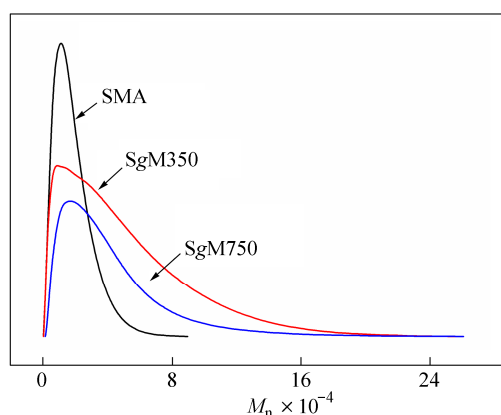


Fig. 3 GPC chromatograms of SMA and graft copolymers
SgM350 was prepared at 80°C, 14 MPa and SgM750 was prepared at 80°C, 26 MPa.

The results are listed in Table 2. The calculated M_n from ¹H-NMR is lower than that calculated from GPC. Similar results have also been reported in other literature^[14]. The molecular weights reported by GPC depend on the hydrodynamic volume of polymers in the mobile phase rather than their actual molecular weights. And amphiphilic graft copolymers elute at volumes close to, or greater than, those obtained for the corresponding backbone polymers because of the adsorption of graft copolymer on the packing material in the analytical columns or because of conformational effects. All of these may cause that the calculated conversion and M_n based on ¹H-NMR is remarkably different from those based on GPC. The conversions of anhydride of SgM350 and SgM750 are 46.5% and 20.7%, respectively (Table 2). And the conversions in the study are lower than those reported in literatures^[13, 14]. This may be that the grafting reaction between SMA and MPEG is difficult due to the high viscosity of SMA, for SMA can only be plasticized rather than be dissolved in scCO₂.

Table 2. Results of the grafted SMA-g-MPEG copolymers

Samples	Conversion of anhydride (%) ^a	Polydispersity ^a	Conversion of anhydride (%) ^b	MPEG incorporation (wt%) ^b	MPEG grafted per molecule ^b	M_n^a	M_n^b	T_g (°C)
SgM350	86.8	3.01	46.5	32.7	18.4	23100	18000	-34.8 / 57.6
SgM750	55.1	2.90	20.7	29.5	8.2	25600	17200	-34.6 / 11.0

^a Determined by GPC; ^b Calculated from the ¹H-NMR results;

Samples: SgM350 was prepared at 80°C, 14 MPa and SgM750 was prepared at 80°C, 26 MPa.

Effect of Temperature on the Graft Reaction

The influences of temperature on the reactions were investigated, and the results are presented in Fig. 4. During the reactions, the anhydrides are ring opened with the simultaneous formation of an ester group and a carboxylic acid group. Generally, the reaction temperature has great effect upon the reactivity of esterification reactions in

scCO₂ as that is usually found in solvents. There is an additional effect on the degree of swelling (plasticization) of SMA and the solubility of MPEG in scCO₂. When temperature arises, the free volume and segment mobility of SMA increase, while the solubility of MPEG decreases in scCO₂^[28, 29]. As a result, the MPEGs are much more easier to diffuse into SMA and react with anhydrides, and the conversion of anhydrides is improved. As shown in Fig. 4, the optimum temperature is found at 80°C, and below or above that temperature the conversion decreases.

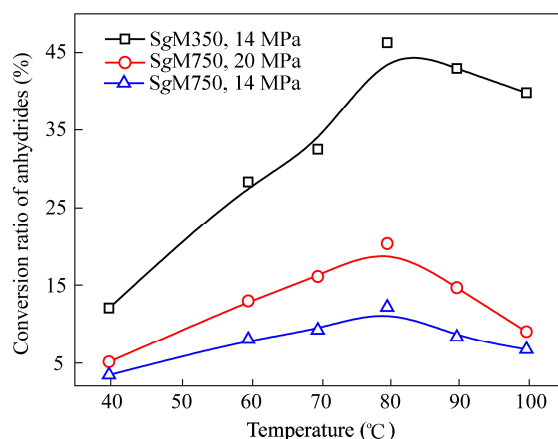


Fig. 4 Effect of temperature on the conversion of the anhydrides (calculated from the ¹H-NMR results)

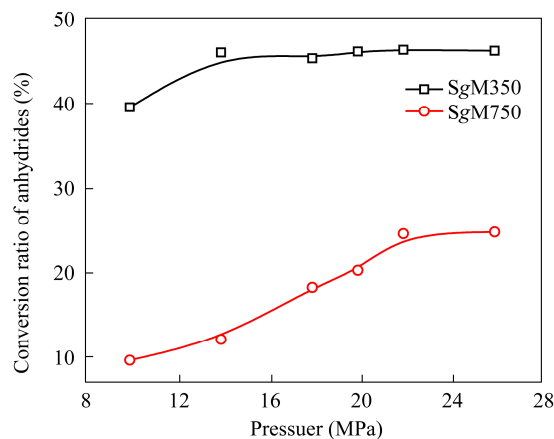


Fig. 5 Effect of the CO₂ pressure on the conversion of the anhydrides at 80°C (calculated from the ¹H-NMR results)

Effect of the CO₂ Pressure on the Graft Reaction

The CO₂ pressure is another parameter that influences the conversion of anhydrides since the remarkable difference of scCO₂ solvency at different pressures. Figure 5 shows the effect of the pressure on the graft reaction. At a given temperature, the conversion of anhydride increases with the pressure, and the maximum conversion is obtained at 14 MPa for MPEG350 and at 26 MPa (or higher) for MPEG750. Further increasing the pressure shows little influence on the conversion. At low pressures, the density of supercritical fluid is low and cannot provide enough solubility of MPEG and the swelling of SMA is also insufficient, which reduce the diffusion of MPEG into SMA. At higher pressures, scCO₂ has stronger solubility of MPEG and much better swelling of SMA, which are favorable for the grafting reaction. Further increasing the pressure to a very high level, MPEG will intend to dissolve into scCO₂ phase rather than into SMA which is unfavorable for the grafting reaction. However, in our study, with increasing pressure, the conversion shows an optimum value rather than decreases. The reasons may be that only esterification reaction is conducted, for MPEG can not self-polymerize. This is different for the free radical grafting in solid-state in scCO₂ that always goes with some secondary reactions, such as homopolymerization, and the graft degree decreased with increasing pressure^[22, 26].

Thermal Analyses of the Graft Copolymers

Thermal stability is very important for materials in application. The graft copolymers will be used as filler in membrane preparation, and their thermal stability were investigated. Thermo-gravimetric analysis (TGA) was used to evaluate the thermal stability of the SMA, SgM350 and SgM750. Figure 6 plots typical TGA curves for the copolymers. The pure SMA has only one degradation step and the decomposition begins at about 350°C^[4]. But two degradation stages are observed in the curves for the graft copolymers. The first step starting from 200°C to 314°C can be attributed to the decomposition of PEG side chains. The second step, beginning at about 314°C, corresponds to the degradation of SMA backbones. From the weight loss percentage in the first decomposition step, the content of PEG side chains in the graft copolymers can be evaluated approximately. According to the TGA curves, the PEG content in graft copolymers is about 32.9 wt% for SgM350 and 28.9 wt% for SgM750, which are in good agreement with the data calculated from ¹H-NMR spectra.

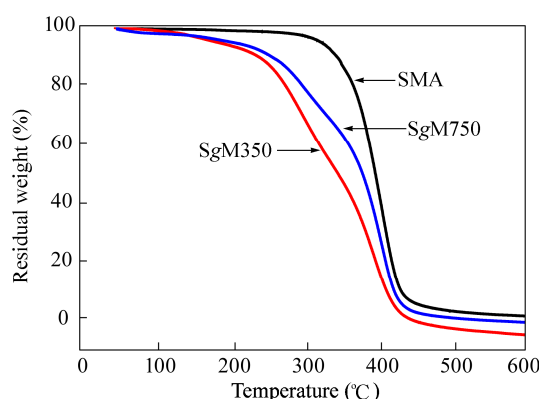


Fig. 6 Thermal stability of SMA and SMA-g-MPEG copolymers
SgM350 was prepared at 80°C, 14 MPa and SgM750 was prepared at 80°C, 26 MPa.

DSC analyses were performed to evaluate the glass transition temperatures (T_g) of SMA, SgM350 and SgM750, and the results are shown in Fig. 7. Just as shown, there appear two T_g s for both SgM350 (−34.8°C and 57.8°C) and SgM750 (−34.6°C and 11.0°C), and the T_g s are much lower than the T_g of SMAs (155.1°C). According to the literature^[14], this indicates that the graft chains MPEG and backbone SMA may form different phases because of the incompatibility of PEG side chains and SMA.

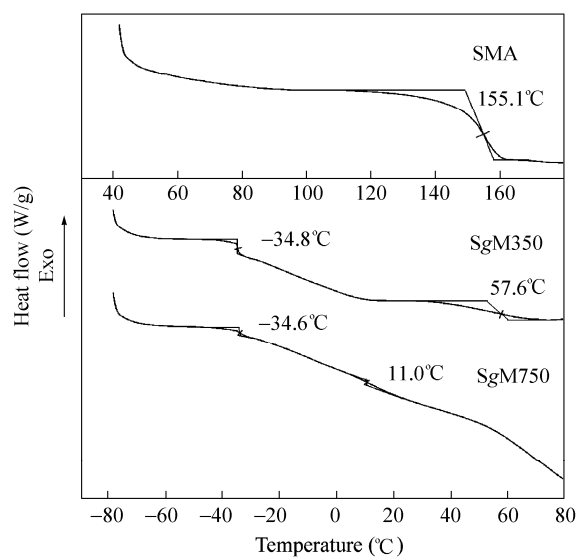


Fig. 7 DSC curves of SMA and SMA-g-MPEG copolymers
SgM350 was prepared at 80°C, 14 MPa and SgM750 was prepared at 80°C, 26 MPa.

CONCLUSIONS

Amphiphilic graft copolymers with SMA as backbones and MPEG as side chains were successfully synthesized in scCO₂ via the esterification between anhydride groups and hydroxyl groups. The synthetic graft copolymers are dissolvable in some polar organic solvents. There is an optimum reaction temperature and a maximum pressure to achieve the highest grafting yield of amphiphilic copolymers containing MPEG. The highest conversion ratio occurred at 80°C under a constant pressure of 14 MPa and 26 MPa for MPEG350 and MPEG750, respectively. The reactivity of MPEG350 is much higher than that of MPEG750, and it is more appropriate to prepare amphiphilic graft copolymer in scCO₂ when SMA is used as an anhydride source.

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