

Silicon-based and fluorinated polymeric surfactants for copolymerization in dispersion in supercritical carbon dioxide

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Abstract

Copolymers based on siloxanes or fluorinated polymers have been proposed as surfactants for nitroxide mediated free radical polymerizations in supercritical carbon dioxide. Styrene was polymerized in the presence of TEMPO at 130° C. A siloxane-based surfactant was synthesized by a new route based on NMP. Dispersion polymerizations in scCO₂ using surfactants show conversions of 35% in 4 hours. Initial copolymerization experiments were made with BuA.

Keywords: Surfactants, supercritical carbon dioxide, controlled radical polymerization.

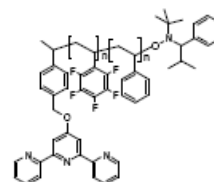
1. Introduction

In recent years a rising effort has emerged to develop clean technologies. Supercritical carbon dioxide (scCO₂) is a highly desirable solvent for environmental benign processing. It is non-toxic, non-flammable, relatively inert, inexpensive^[1], and its critical conditions are easily accessible (31.1° C, 73.8bar). In addition, it offers a wide range of advantages as reaction media due to the easy removal of solvent after polymerization, negligible chain transfer to solvent and tunable solvent strength by changing temperature or pressure^[2]. However, scCO₂ is a bad solvent for most polymers and consequently, is a useful solvent for precipitation and dispersion polymerizations. In order to achieve dispersion polymerization it is necessary to find a good polymeric stabilizer, molecularly engineered to be interfacially active in scCO₂^[3].

Block copolymers containing a CO₂-philic block are good candidates as polymeric surfactants in CO₂ medium. CO₂-philic polymers are limited until now to some

fluorinated polymers, silicones and some poly(ether-carbonates)^[4].

Fluorinated monomers, specially styrenics and meth(acrylates) can be easily synthesized by radical polymerization. Lacroix-Desmazes et al. demonstrated the use of block copolymers based on styrene and acrylates as surfactants in CO₂ media. In the present work, poly (2,3,4,5,6-pentafluorostyrene)-block-poly(styrene) that was synthesized by nitroxide mediated polymerization (NMP) is suggested as a possible CO₂ surfactant.



Scheme 1. PPFS-b-PS

In the other hand, the family of silicones, specifically, the poly(dimethylsiloxane-block-styrene) has been successfully proved as surfactant in the polymerization of styrene for CO₂^[5] dispersion media by Aldabbagh et

al. This work presents a new way to obtain the same copolymer with a different bromide salt.

Both copolymers, fluorinated and silicones, were used as surfactants in the dispersion polymerization by NMP of styrene and the sequential addition of butyl acrylate to make block copolymers.

II. Materials and Methods

Styrene and butyl acrylate (Aldrich, 99%) were purified by vacuum distillation over CaH_2 after inhibitor removal. Reagent grade 2,2'-azo(isobutyronitrile) (AIBN, Akzo Nobel) was recrystallized from ethanol and chloroform. 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, Aldrich), Molecular Bromide (Sigma-Aldrich, 99.5%), Poly(dimethylsiloxane), hydroxy terminated (Sigma-Aldrich, 90-150cSt), dichloromethane (Aldrich, 99%), methanol (C.J.Baker, 95%), n-hexane (Rye, 95%), cyclohexane (Rye, 95%), tetrahydrofuran (Sigma-Aldrich, 99%) were used as received.

Poly(pentafluorostyrene-block-styrene), PPFS-b-PS was synthesized by Cristina Ott in Technische Universiteit Eindhoven

a. Bromide salt

Bromide salt was synthesized according to the reported procedure.^[6] Briefly, in a typical experiment bromine (0.032mol) was added slowly to a solution of TEMPO (0.032mol TEMPO in 100ml of CCl_4). A brown solid was formed instantaneously and was separated from the solution by filtration. The filtrate was exhaustively washed with CCl_4 until the filtered solution showed no more color. The salt was dried over vacuum at 40° C for 24 h.

b. PDMS-TEMPO functionalization

To functionalize poly(dimethylsiloxane) with TEMPO, triethylamine was used as an intermediate species that helps trapping the hydrogen bromide (HBr) formed during the reaction. Et_3N (0.0200mol) was added to PDMS-OH (0.0025mol) and after a little while, a solution of Br-T (0.0100mol in CH_2Cl_2 , 10mL) in excess was added

dropwise. Temperature was raised to 40° C and the mixture was stirred by 5 h. The reaction excess was calculated with respect to the two OH groups present per chain in the PDMS-OH according to the Number Average Molecular weight (M_n) determined by SEC. The final solution was evaporated and then dissolved in THF to eliminate HBr. Functionalized and "free" polymers were passed through a silica column with CH_2Cl_2 to completely remove the HBr and humidity. The product was dried by roto-evaporation and then treated with vacuum during 8h at room temperature before ^1H RMN and SEC characterization.

Scheme 2 PDMS-OH Functionalization

c. Copolymer PDMS-b-PS

In a typical run, PDMS-T (0.0012 mol) is dissolved in styrene (0.0720mol) and charged in a sealed glass reactor where the oxygen is displaced by Argon flux. The mixture is heated to 130° C and stirred by 36 h. The resulting product contains PS homopolymers, PDMS homopolymers and PDMS-b-PS copolymers. It is then precipitated in methanol, filtered and dried over vacuum per 8h.

Scheme 3 Copolymerization by NMP

In order to separate the PDMS homopolymers, the product is dissolved in n-hexane (solution 50%w), stirred during 2 h and then filtered. Soluble phase (composed by PDMS and PS oligomers) is roto-evaporated and dried over vacuum 12 h. To separate PS homopolymers, the insoluble phase is dissolved in a ciclohexane: n-hexane (25:1.2) mixture and centrifuged at 12000 RPM and 0° C during 15 min. Both phases are precipitated in methanol and dried under vacuum (the liquid phase is PDMS-b-PS). The purity of all products and their chemical structure was analyzed by ^1H NMR and SEC.

d. Dispersion polymerization of styrene

Dispersion polymerizations of styrene were conducted in a 25 ml stainless steel reactor. A typical polymerization was carried out as follows: S (5 mL, 4.7 g, 0.0450 mol), TEMPO (0.0470 g, 0.0003 mol), AIBN (0.0705 g, 0.0004 mol), surfactant* (0.3290 g) and a magnetic stirrer were added to the reactor. Subsequently, the reactor was pressurized with CO_2 to 17.0 MPa. The reactor temperature was then raised to 130° C with a heating mantle, during which the pressure increased up to 19.1 MPa and the stirring started. The polymerization was stopped by cooling the reactor with iced water and the CO_2 was vented slowly. The polymer is most of the times dissolved in styrene, so it's precipitated in methanol to remove the remaining monomer and dried over vacuum 24 h.

The resulting polystyrene (2g) was then copolymerized by sequential addition of Butyl Acrylate (2g) in a second charge to the stainless steel reactor under the same conditions of the first reaction.

e. Characterization

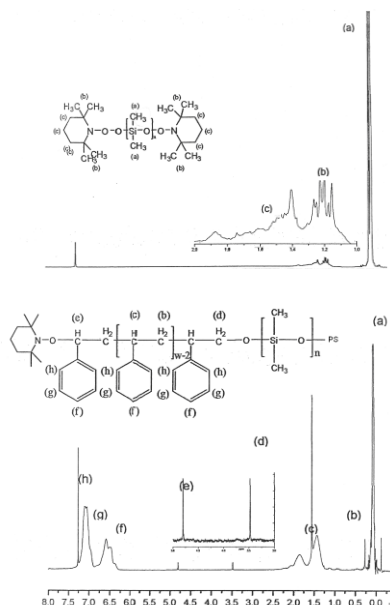
^1H NMR spectroscopy was performed on a FT-NMR Jeol Eclipse 300 MHz Spectrometer at room temperature using CDCl_3 . Size Exclusion Chromatography (SEC) was measured in an Alliance 2695 coupled to a Waters 2414

IR detector, a Waters 996 UV detector with standard 10^5 and 10^6 Å columns, using THF, HPLC grade as the eluent with a flux of 1 mL/min at 30° C.

III. Results and Discussion

^1H RMN spectra for PDMS-T and the copolymer PDMS-b-PS can be found in the Figure 1. Multiple signals δ : 1.12-1.56 ppm show that functionalization occurred in similar way to that reported by Cho et al.^[7]

For the copolymer there is a typical displacement at δ 4.7 ppm associated to the bond C-O between the styrenic segment and TEMPO.



Scheme 4 ^1H NMR Spectra (i) PDMS-T, (ii) PDMS-b-PS

According to the integration of signals in NMR spectra of styrene (δ 6.2-7.3) and PDMS (δ 0.12-0.14), the molar relation PS/PDMS was found. For a good surfactant it is recommended that the relation PS/PDMS must be between 3:1 and 1:3^[8]; in this case it was 3.2.

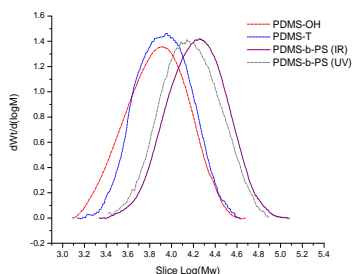
By the results of SEC we can appreciate the evolution of molecular weight.

The SEC analysis of the copolymer by IR and UV detectors indicate the weight fraction of styrene in the copolymer and its molar relation by the formula:

* PDMS-b-PS or PS-b-PPFS

$$(PS / PDMS)^{-1} = 2 \left(\frac{M_n(IR)}{M_n(UV)} - 1 \right) \left(\frac{104.13}{74.13} \right)$$

The molar relation was found to be 3.1 and the weight fraction of styrene: 70%.



Scheme 5 Mw's from PDMS-OH to PDMS-b-PS

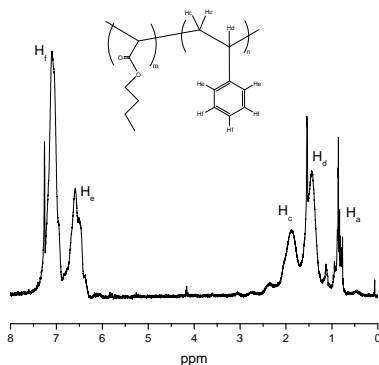
Dispersion polymerizations

Table 1 summarizes the most successful reactions in dispersion polymerizations in scCO₂ with each surfactant. All the polymerizations were made with 5 ml of styrene (4.7 g), 1.5% weight of TEMPO with respect to the monomer, 1% of AIBN, 6% of surfactant. The reaction time was 4 h for all runs. The theoretical Mn was calculated on the basis of the amount of TEMPO.

Table 1 Homopolymerization Results

Surfactant	X	Ip	Mn	Mn (Th)
None	24.81	1.6	1728	
PDMS-b-PS	35.23	1.5	4102	3670
PS-b-PPFS	35.56	1.2	3541	3706

For copolymerization only the fluorinated surfactant has been tested.



Scheme 6 ¹H RMN of PS-b-PBuA

By ¹H NMR analysis the composition obtained was 20% poly(butyl acrylate) and 80% polystyrene.

IV. Conclusions

Surfactant PDMS-b-PS can be synthesized from PDMS-OH by NMRP with a bromide salt using Et₃N as an intermediate species.

PS-b-PPFS is suggested as a good surfactant in spite of the fact that fluor atoms are not in the main chain.

Low polydispersity indexes and similarity between Mn values and their theoretical prediction is one characteristic of controlled radical polymerizations. These results encourage us to improve the conversions and look for a more extended study of copolymerization.

V. References

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