Silicon-Based and Fluorinated Polymeric Surfactants for Nitroxide Mediated Dispersion Polymerization in Supercritical Carbon Dioxide

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Summary: Block copolymers based on siloxanes and fluorinated block copolymers were synthesized and tested as surfactants for nitroxide mediated polymerizations (NMP) in supercritical carbon dioxide. Styrene was polymerized in the presence of TEMPO at 130 °C using various surfactants. Siloxane-based surfactants were synthesized by a new route based on NMP; the perfluorinated surfactants were also synthesized by NMP. The dispersion polymerizations of styrene in $scCO_2$ reveal conversions of up to 35% in 4 hours at 19.1 MPa. The resulting polydispersity indices lie in the range 1.2–1.4. The best results are obtained using a perfluorinated surfactant. Preliminary copolymerization experiments of the polystyrene macroinitiator in $scCO_2$ have shown successful chain-extension with butyl acrylate (BuA) resulting in the formation of a poly (St-b-BuA) block copolymer.

Keywords: dispersion polymerization; nitroxide mediated polymerization; supercritical carbon dioxide; surfactant

Introduction

In recent years there has been a rising effort to develop clean and environmentally-friendly technologies. Supercritical carbon dioxide ($scCO_2$) is a highly desirable solvent for these purposes because of its favorable characteristics: non-toxic, non-flammable, relatively inert, inexpensive,[1] and easily accessible critical conditions (31.1 °C, 73.8 bar). In addition, it offers a wide range of advantages as reaction media because of the feasibility to remove the solvent after the polymerization, negligible chain transfer to solvent and tunable solvent strength by changing temperature or pressure.[2] Due to the unfavorable solubility behavior of most polymers in $scCO_2$, it is a useful media for precipitation and dispersion polymerizations. In order to perform a dispersion polymerization it is necessary to find a good polymeric stabilizer, molecularly engineered to be interfacially active in $scCO_2$.[3] Block copolymers containing a CO_2-philic block are good candidates as polymeric surfactants in CO_2 medium. Until now CO_2-phillic polymers are limited to fluorinated polymers, silicones and poly(ether-carbonates).[4]

Fluorinated monomers, such as styrenics and meth(acrylates) can be easily polymerized by radical polymerization techniques. Lacroix-Desmazes et al.[4] demonstrated the use of styrene and acrylate based block copolymers as surfactants in CO_2 media. In the present work, poly(2,3,4,5,6-pentafluorostyrene)-block-poly(styrene) (PPFS-b-PS) (Scheme 1) was tested as possible surfactant

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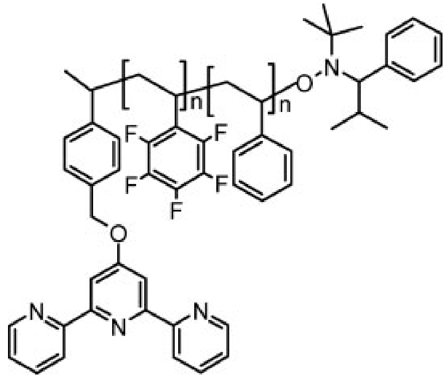


Scheme 1.
Schematic representation of the PPFS-b-PS block copolymer.

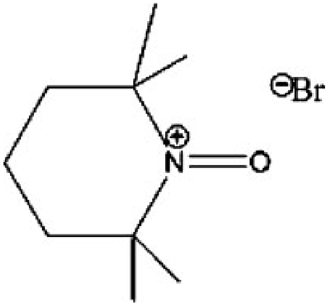
for the controlled radical polymerization of styrene under supercritical conditions.

The PPFS-b-PS block copolymer was synthesized by employing a terpyridine-functionalized nitroxide initiator which was previously reported by Lohmeijer et al.[5] This initiator facilitates good control over the polymerization of a wide variety of monomers and maintains the coordination moiety at the polymer chain end. The tridentate chelating ligand possesses excellent complexation abilities with a large variety of transition metal ions as well as lanthanide ions. The supramolecular moiety can connect different polymer chains with each other resulting in the formation of metallo-supramolecular block copolymers or chain extended polymers in case telechelic macromolecules are present.[6] In this regard, the block copolymer can be utilized as building block for supramolecular structures as well as surfactant for dispersion polymerizations. On the other hand, the silicon-based poly(dimethyl siloxane-block-styrene) has been successfully applied as surfactant for the polymerization of styrene in CO_2 dispersion media.[7] In this contribution a new approach is presented for the preparation of nitroxide-functionalized molecules by reacting a TEMPO bromide salt with a hydroxyl-functionality in order to insert the TEMPO as end-group into the desired macromolecule.

Both block copolymers, PPFS-b-PS and PDMS-b-PS, were used as surfactants for nitroxide-mediated dispersion polymerization (NMP) of styrene. In addition, first results are shown towards the block copolymerization by sequential addition of butyl acrylate under supercritical conditions.

Materials and Methods

Styrene and butyl acrylate (Aldrich, 99%) were purified by vacuum distillation over CaH_2 after inhibitor removal. 2,2′-Azo(i-sobutyronitrile) (AIBN, Akzo Nobel) was recrystallized from ethanol and chloroform. 2,2,6,6-tretramethylpiperidine 1-oxyl (TEMPO, Aldrich), molecular bromine (Sigma-Aldrich, 99.5%), poly(dimethylsiloxane), hydroxy terminated (PDMS1, Sigma-Aldrich, 90–150 cSt, $M_n = 3{,}900$ g/mol, PDI = 1.87 measured by GPC (PS calibration) and PDMS2, Sigma-Aldrich, ($M_n = 5{,}600$ g/mol reported) $M_n = 6{,}000$ g/mol, PDI = 1.48 measured by GPC with PS calibration), 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 as reported by Ott et al.[8] 1-oxo 2,2,6,6-tetramethylpiperidinium bromide salt (TEMPO bromide salt or Br-T, Scheme 2) was synthesized according to literature.[9] Briefly, in a typical experiment, bromine (0.032 mol) was added slowly to a solution of TEMPO (0.032 mol TEMPO in 100 ml of



Scheme 2.
1-oxo, 2,2,6,6-tetramethylpiperidinium bromide or TEMPO bromide salt.

CCl_4). A brown solid was formed instantaneously which was separated from the solution by filtration. The filtrate was intensely washed with CCl_4 until the filtered solution showed no color. The salt was dried over vacuum at 40 °C for 24 h.

PDMS-TEMPO (PDMS-T) Functionalization

In order to functionalize PDMS with TEMPO, triethylamine (Et_3N, 0.02 mol) was added to PDMS (0.0025 mol). After a few minutes, an excess of a solution of Br-TEMPO (0.015 mol in CH_2Cl_2, 10 mL) was added dropwise to the polymer. Temperature was raised to 40 °C and the mixture was stirred for 24 h. The reaction procedure, which is based in a previous publication of our group,[9] is schematically shown in Scheme 3. Et_3N was used as an intermediate species which allows trapping the hydrogen bromide (HBr) formed during the reaction. The amount of Et_3N and Br-TEMPO (excess) were calculated assuming the presence of two OH groups per PDMS polymer chain according to the number average molecular weight (M_n) determined by SEC. The final solution was evaporated and then dissolved in THF in order 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 solvent was evaporated in vacuo, the product was dried under vacuum for 8 h at room temperature and subsequently characterized by ^1H NMR and SEC.

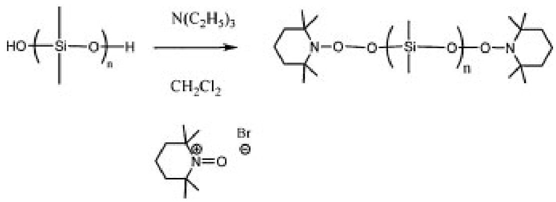
Synthesis of Copolymer PDMS-b-PS/PS-b-PDMS-b-PS

PDMS-T (5 g, 0.0012 mol) was dissolved in styrene (15 g, 0.0480 mol) and transferred to a sealed glass reactor where the oxygen is displaced by a flow of argon (see Scheme 4). The mixture is heated to 130 °C and stirred for 48 h. Styrene was added stepwise to the reaction mixture in order to minimize autoinitiation of styrene. The resulting product contains PS and PDMS homopolymers as well as the desired PDMS-b-PS (diblock and/or triblock) copolymers. The reaction mixture was precipitated in methanol, filtered and dried under vacuum for 8 h.

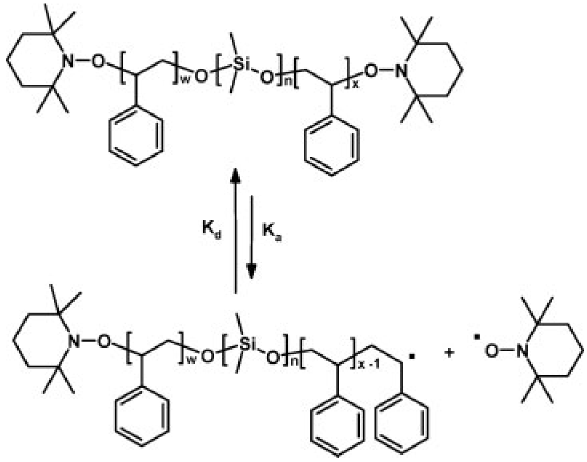
In order to separate the PDMS homopolymer (see Figure 1) from the product, the polymer was dissolved in n-hexane (50%-wt. solution), and stirred for 2 h and then filtered. The soluble phase (composed of PDMS and PS oligomers) is evaporated in vacuum and dried under vacuum for 12 h. In order to separate the PS homopolymer, the insoluble phase was dissolved in a cyclohexane: n-hexane (25:1.2) mixture, centrifuged at 12000 rpm and cooled to 0 °C for 15 min. The phases resulting from the ultracentrifugation were separated, precipitated in methanol and dried under vacuum. The liquid (soluble) phase contains the desired PDMS-b-PS diblock and/or the PS-b-PDMS-b-PS triblock copolymer. All products were analyzed by ^1H NMR and SEC.

Dispersion Polymerization of Styrene

Dispersion polymerizations of styrene were conducted in a 25 mL stainless steel reactor. The polymerization were carried out as follows: styrene (5 mL, 4.7 g, 0.045 mol), TEMPO (0.0705 g, 4.51×10^{-4} mol), AIBN (0.047 g, 2.86×10^{-4} mol), surfactant^b (0.2820 g) and a magnetic stirrer were added to the reactor. Subsequently, the reactor was pressurized with CO_2 up to 17.0 MPa. Afterwards, the reactor temperature was raised to 130 °C using a heating mantle. The pressure



Scheme 3.
Schematic representation of the functionalization of PDMS using a TEMPO bromide salt.



Scheme 4.
Schematic representation of the chain extension of PDMS-T with styrene using the nitroxide-mediated polymerization process.

increased up to 19.1 MPa during that time. After several hours of reaction, the polymerization was stopped by cooling the reactor with iced water, consequently the CO_2 slowly evaporated. The polymer was precipitated in methanol in order to remove remaining monomer and dried under vacuum for 24 h. In one case, the resulting polystyrene (2 g) was copolymerized using the same conditions as stated above. A mixture of butyl acrylate/styrene (2 g/0.6 g) was added to the reactor and the reaction was performed for 1 h at 130 °C.

Characterization

^{1}H NMR spectroscopy was performed on a FT-NMR Jeol Eclipse 300 MHz spectrometer at room temperature using $CDCl_3$. Size Exclusion Chromatography (SEC) was performed using an Alliance 2695 gel permeation chromatograph (GPC) coupled to a Waters 2414 IR detector and a Waters 996 UV detector. Standard 10^5 and 10^6 Å columns were used. THF, HPLC grade was used as eluent at a flow rate of 1 mL/min at 30 °C.

Results and Discussion

PDMS Functionalized with TEMPO

Figure 2 represents a ^{1}H NMR spectrum of the TEMPO-functionalized PDMS. The zoom in clearly shows the presence of two signals in the range between 1.0 and 1.6 ppm corresponding to the hydrogen

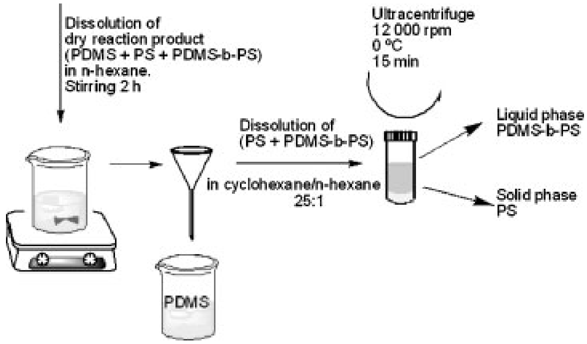


Figure 1.
Schematic representation of the separation process of the PDMS-b-PS copolymer.

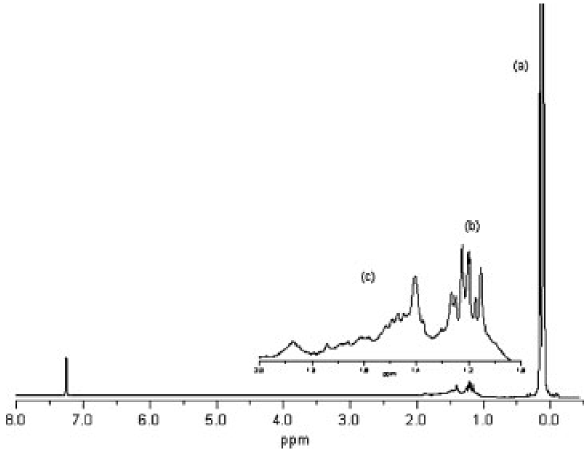


Figure 2.
^{1}H NMR spectrum of PDMS-T in $CDCl_3$.

atoms of the methyl (b) and methylene groups (c) of the TEMPO moiety, indicating the successful functionalization as it was reported in a similar way by Cho et al.[10]

PDMS-b-PS

As mentioned before, the product resulting from the chain extension reaction contains PS and PDMS homopolymers, as well as PDMS-b-PS copolymers. After the separation, the different fractions were analyzed by SEC. Some illustrative results of the DMS-S-0 block copolymer are shown in Figure 3 and the characteristics are summarized in Table 1.

The PDI values of DMS-S-0 and the PS homopolymer suggest that the polymerization did not proceed in a controlled fashion. A reason for this could be that TEMPO-derivatives possess a decreased rate of C-O bond dissociation in comparison to second-generation nitroxides (SG1, TIPNO).

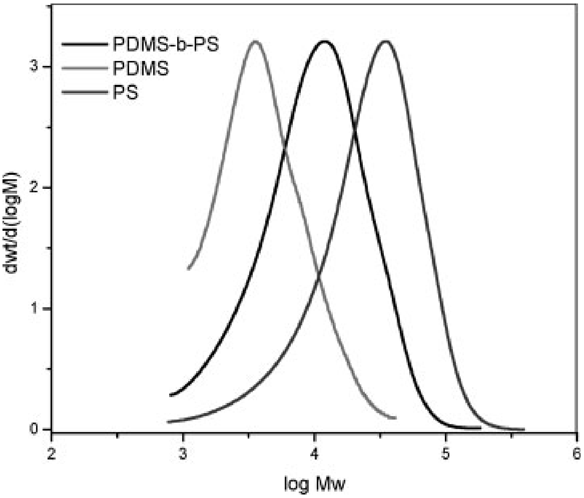


Figure 3.
SEC chromatograms of the block copolymer DMS-S-0 reveals (after separation) the presence of PS and PDMS homopolymers besides the desired PDMS-b-PS copolymer.

Table 1.
M_n and PDI by SEC of source polymers and separated fractions after synthesis of surfactant DMS-S-0.

	Mn	PDI
PDMS-OH	3,900	1.87
PDMS-T	5,100	1.43
DMS-S-0 (IR detector)	6,200	2.31
PDMS homopolymer*	3,200	1.67
PS homopolymer*	14,500	2.47
Mn for DMS-S-0 calculated by eq (1)	7,190	

*after separation

Consequently, the equilibrium is shifted to the dormant species side and the probability to create radicals by autoinitiation of styrene is higher, which results in the formation of polystyrene by free radical polymerization. Moreover, the fact has to be considered that maybe not both chain-ends were functionalized with the TEMPO end-group, affording a mixture of diblock and triblock copolymers at the same time which results in an increased polydispersity index. The chemical nature of the different fractions as it is shown in Figure 3 was confirmed by ^{1}H NMR spectroscopy. However, some contamination of the PDMS-b-PS block copolymer with low molecular weight PS cannot be excluded by using the described separation method. Figure 4 represents the SEC chromatograms of PDMS, PDMS-T as well as PDMS-b-PS (top: DMS-S-0; bottom: DSM-S-2) proving a successful chain extension. The ^{1}H NMR spectra of both block copolymers, DMS-S-0 and DMS-S-2, reveal the typical signals at 4 ppm associated to the C-O bond between the styrenic segment and TEMPO.[11] The molar ratio PS/PDMS of the block copolymers was determined by integrating the corresponding signals of the ^{1}H NMR spectra. It is reported in literature that a suitable surfactant block ratio (PS/PDMS) should be between 3:1 and 1:3.[12]

In addition, it is possible to get a gross estimation of the absolute M_n of the block copolymer by using the molar ratio PS/PDMS obtained by ^{1}H NMR analysis of the final polymer, together with an estimation of the absolute M_n of the initial PDMS segment. The absolute M_n of the PDMS segment can be approximately estimated by measuring its apparent M_n (based on polystyrene standards) by SEC analysis with IR detector, and correcting this value by the intrinsic viscosities of the PDMS and PS polymers, using the principle which is the base for the construction of the universal calibration curve in SEC analysis. This approximation is reasonable as long as the a exponent in the Mark-Houwink equation for the calculation of the intrinsic viscosity is similar for both polymers. In our case $a = 0.725$ for PS[13] and $a = 0.77$ for PDMS[14] in THF, so the approximation is valid. Once the M_n of the PDMS block is known the total molecular weight can be calculated by the formula:[15]

$$M_n{}^* = (M_n\ PDMS\ block) \times \left(1 + 1\Big/2\left(molar\ ratio\,\frac{styrene}{siloxane}\right)\cdot\frac{104.15}{74.13}\right) \tag{1}$$

Table 2 summarizes the characteristics of the PDMS-b-PS surfactants prepared. Although there is some increase in polydispersity (PDI) with respect to the base PDMS, the obtained polydispersity indices are reasonable considering that there are maybe diblock and triblock species present.

Fluorinated Surfactants

Table 3 shows the characteristics of the two synthesized PPFS-b-PS block copolymers which were tested as potential surfactants.

The synthesis of another fluorinated block copolymer, poly(styrene-b-3,3,4,4,5,5,6,6,7,8,8,8-dodecafluoro-7-(trifluoromethyl) octyl methacrylate), was also attempted in order to test it as surfactant in $scCO_2$ polymerization. The synthesis strategy consisted of heating a polystyrene macroalkoxyamine having a 2nd generation nitroxide-capped end in the presence of the fluorinated methacrylate monomer in cyclohexanone as solvent. Although some precipitate was formed during the reaction, presumably the desired block copolymer, it was not possible to dissolve it in any standard solvent for characterization, so this route was not pursued further.

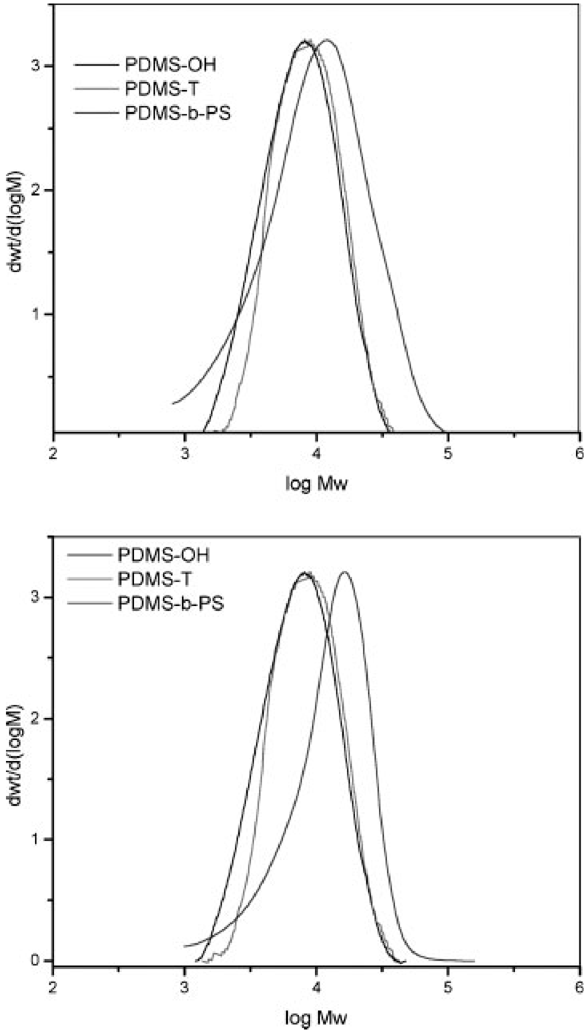


Figure 4.
GPC traces of PDMS, nitroxide-functionalized PDMS (PDMS-T) and the PDMS-b-PS block copolymer: DMS-S-0 (top) and DMS-S-2 (bottom).

Dispersion Polymerizations

Table 4 summarizes the results of the dispersion polymerizations carried out in $scCO_2$ using different surfactants. All polymerizations were performed for 4 h at 130 °C using 5 mL of styrene, 1.5 wt.-% of TEMPO, 1 wt.-% of AIBN and 6 wt.-% of surfactant, all with respect to the monomer.

Table 2.
Characteristics of the synthesized PDMS-based surfactants.

Code	PDMS/PS molar ratio ^1H NMR	M_n PDMS block	M_n	PDI$^+$	wt.-% styrene
DMS-S-0	0.9 [a]	3,900	6,900	2.3	39
DMS-S-1	1.4 [a]	3,900	8,400	1.7	50
DMS-S-2	2.0 [b]	6,000	15,600	1.7	57
DMS-S-3	3.1 [a]	3,900	13,500	1.9	69

$^+$From GPC, IR detector

Table 3.
Molecular weights of PPFS-B-PS block copolymers by SEC.

Tag	M_n (S)	M_n	M_w	PDI
PFS-S-0	4,300	11,600	13,400	1.16
PFS-S-1	3,400	10,600	12,100	1.14

Table 4.
Dispersion polymerization of styrene using different surfactants. Conditions are 4 h reaction, 130 °C, [TEMPO]/[I] = 1.58.

Surfactant	Conversion %	PDI	M_n	M_n (Th)
None	24.8	1.6	1700	–
DMS-S-0	25.5	1.4	2400	3670
DMS-S-1	27.8	3.6	7400	3670
DMS-S-2	32.7	1.4	3200	3670
DMS-S-3	35.2	1.5	4100	3670
PFS-S-0	35.6	1.2	3500	3706

High conversions could not be achieved by applying this rather short polymerization time; however, it provides a measurement to compare the efficiency of the polymerizations using different surfactants. For comparison, consider that Canelas et. al.[16] previously published the use of a PS-PDMS surfactant which revealed conversions of 8.5% in 4 h (PDI = 1.9) and 93% in 24 h (PDI = 3.1) for the free radical polymerization of styrene. Recently, the dispersion polymerization of styrene mediated by nitroxides was reported.[17] The polymerization was performed using a PDMS-b-PS block copolymer as surfactant and SG1 as control agent for 72 h at 110 °C resulting in conversions of 60%.

In a control experiment, which was performed without any surfactant, the polymerization resulted in the formation of low molecular weight polymer chains due to the limited solubility of polystyrene in the CO_2-media. The best control is observed for DMS-S-2 among the silicon-based surfactants and, in general, for surfactants with a higher PDMS/PS ratio (more CO_2 philic). However, the best results are obtained using the perfluorinated surfactant. These findings are in accordance with a previously published paper and with the expected performance of the two surfactant families.[4]

Preliminary Copolymerization in $scCO_2$

The growth of a second block of different chemical nature in $scCO_2$ is a challenging endeavor. A surfactant that is effective for the stabilization of the polymer during the polymerization of the first block may not be appropriate for the growth of the second block and, most likely, a different surfactant or a mixture of surfactants may be needed for the stabilization of the second block. In this work, only the fluorinated surfactants (PPFS-b-PS) were used for preliminary copolymerization experiments. In this regard, 1 h test reactions were performed by adding a mixture of styrene and butyl acrylate (0.6 g/2 g) to the preformed polystyrene. The product was analyzed by ^1H NMR spectroscopy proving the presence of a small amount of butyl acrylate (estimated as 1 wt.-%). The SEC chromatogram of the copolymer is shown in Figure 5 and the results are presented in Table 5. In general, the SEC-trace shifted slightly to higher molecular weights, indicating an effective polymerization. Nevertheless, in order to confirm these results, additional experiments are required. After the polymerization, the corresponding SEC-trace shows tailing to lower molecular weights suggesting the formation of smaller polymer chains. These new chains may have been formed by autoinitiation of styrene as well as chain-transfer reactions through highly reactive propagating radicals. Acrylates are susceptible for side reactions including branching and termination reactions especially at high temperatures.[18,19]

In order to increase the level of control during the polymerization by reducing the radical polymerization a small amount of styrene was added, since it is well known that TEMPO is a very poor controller for pure BuA polymerization. Additionally, the Mayo Lewis copolymerization equation predicts that the initial copolymer formed for the monomer composition in the charge (23/77 wt. for St/BuA) should have a composition of only 57 wt.-% BuA using $r_1 = 0.8$, $r_2 = 0.15$ (St = 1, BuA = 2).[13] The amount of BuA detected in the final copolymer is consistent with the small

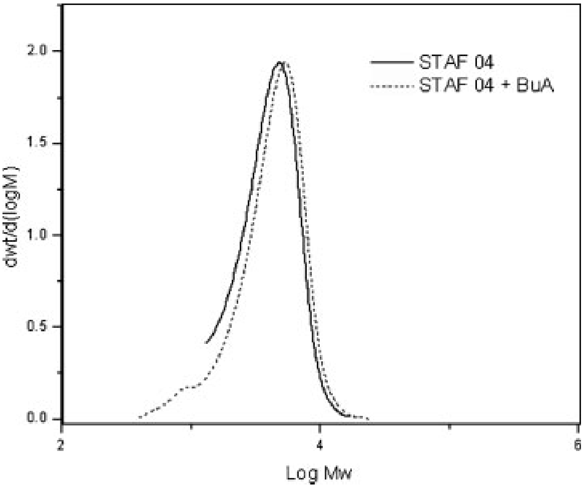


Figure 5.
GPC traces of PS block and PS-b-PBuA copolymer prepared in $scCO_2$ with PPFS-b-PS as surfactant.

Table 5.
Characteristics of the prepolymer (PS block, STAF-04) and the copolymer (STAF-b-BuA) after chain extension with BuA.

	STAF 04	STAF-b-BuA
M_n	3,540	3,280
M_w	4,470	4,770
M_p	4,630	5,150
PDI	1.26	1.45

Note: PFS-S-0 was used for the synthesis of STAF 04 and PFS-S-1 for the synthesis of STAF-b-BuA.

increase observed in the molecular weight. Most likely further incorporation of BuA requires another type of surfactant in order to avoid precipitation.

Conclusions

Surfactants of the type PDMS-b-PS can be synthesized starting from PDMS by NMP using an oxoammonium bromide salt. These surfactants reveal a good performance for stabilizing the nitroxide-mediated polymerization of styrene in $scCO_2$. The best result was obtained by surfactants possessing a higher ratio of PDMS to PS (more CO_2-philic). Moreover, PS-b-PPFS block copolymers were tested for the same purpose showing a very good performance as surfactants for the polymerization of styrene in $scCO_2$.

Relatively low polydispersity indexes and a good agreement between theoretical and experimental M_n values indicate the feasibility of performing nitroxide-mediated radical polymerizations in $scCO_2$. Future studies include the improvement of polymerization parameters. Longer reaction times will be applied in the future and the goal is to achieve higher conversions while keeping control over the polymer structure. In addition, strategies for the synthesis of block copolymers in $scCO_2$ are being tested after preliminary experiments show promising results.

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