Synthesis of Core–Shell Polyurethane–Poly(dimethylsiloxane) Particles in Supercritical Carbon Dioxide

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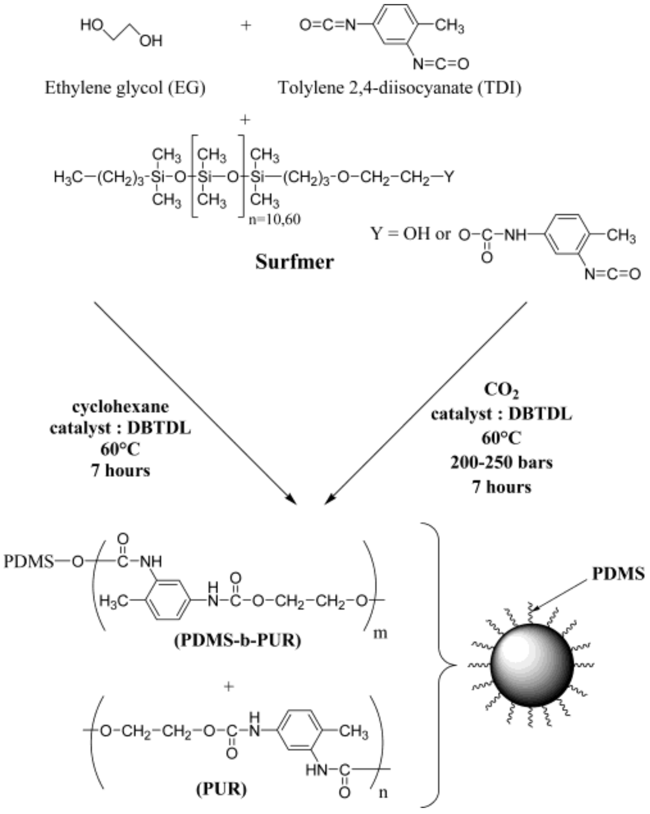
In the field of polymer science, supercritical carbon dioxide ($scCO_2$) has attracted a lot of interest not only for environmental and economical reasons but also as a mean to replace organic solvents.[1,2] The great versatility of CO_2 physicochemical properties—the viscosity and the density can be readily modulated by tuning the pressure and the temperature—as well as its accessible critical point ($T_c = 31.1$ °C and $P_c = 73.8$ bar) explains this interest for $scCO_2$. $scCO_2$ has been mainly used during the past 10 years as a reaction medium for free-radical,[3] cationic,[4] anionic ring-opening,[5] or transition-metal-catalyzed polymerizations.[6] Few data deal with step-growth polymerizations carried out in this medium.[7,8] Because of the insolubility in $scCO_2$ of most of the polymers (unless fluoropolymers or silicon-based polymers), polymerizations conducted in $scCO_2$ proceed in heterogeneous conditions. In this paper, we report on the synthesis in $scCO_2$ of novel core–shell polyurethane–poly(dimethylsiloxane) particles, the latter representing an important family of materials that have applications in many domains such as in biomedicine.[9,10]

We recently investigated step-growth polymerizations between ethylene glycol (EG) and tolylene diisocyanate (TDI) in a dispersant organic medium (i.e., cyclohexane) in the presence of various well-designed surfmers such as hydroxy-terminated polystyrene or hydroxy-terminated poly(*n*-butyl acrylate).[11–13] As a result, original core–shell polyurethane (PUR) materials and exhibiting specific properties according to the shell type could be achieved. These previous studies led us to the conclusion that $scCO_2$ could be advantageously tested as a dispersant medium for the polyaddition reaction between the selected monomers, EG and TDI.

The synthesis of polymeric particles in $scCO_2$ usually requires the use of a steric stabilizer that prevents the coagulation of the growing chains and enables the formation of a stable latex.[14–17] It turned out that commercially available hydroxy-terminated poly(dimethylsiloxane)s, PDMS–OH (e.g., $\bar{M}_n$ of 1000 and 4670 g mol^{-1}), could play the role of surfmers in this investigation. Indeed, PDMS–OH is soluble in $scCO_2$ and bears one hydroxy function (bonded to the silicon backbone through an alkoxy spacer) that may react with the isocyanate function during the polyurethane formation. The participation of PDMS–OH in the process should give to the particles a core–shell structure constituted of a PUR core and a PDMS shell.

The same synthetic procedure, shown in Scheme 1, was followed both in cyclohexane and in $scCO_2$ on the basis of preliminary reported investigations.[11–13] On these grounds, PDMS–OH was first derivatized by reaction with TDI added in excess (TDI/PDMS–OH = 2) into isocyanate-terminated poly(dimethylsiloxane), noted PDMS–NCO, in the presence of dibutyltin dilaurate (DBTDL) as a catalyst, in cyclohexane at 60 °C.[13] The structure of PDMS–NCO was checked by NMR and SEC (see Figures a and b in the Supporting Information). Despite the addition mode, the formation of coupled byproduct PDMS–TDI–PDMS was observed by SEC, at a low concentration (less than 5 wt %), and was considered negligible. In the case of polymerizations conducted in $scCO_2$, PDMS–NCO was preliminary synthesized in a side glass reactor, prior to the polymerizations.

Scheme 1



Polyadditions were first monitored in cyclohexane as a dispersant medium. PDMS–NCO was first added in cyclohexane, followed by EG, as dispersed monomer droplets due to the insolubility of EG in this solvent. The reaction mixture was stirred for about 30 min before TDI addition. It could be checked by SEC analysis that coupling reaction between PDMS–NCO and EG, leading to PDMS–EG–PDMS, was not detectable (see Figure b, Supporting Information). TDI (soluble in cyclohexane) was then added dropwise over a period of 4 h to ensure both the control of the particle size and the completion of the polyaddition. A measurement of the reaction extent, *p*, was carried out by means of FTIR analysis which allowed us to follow the growth with time of the N–H vibration band at 3300 cm^{-1} (see Figure c in the Supporting Information). At the end of the polymerization, the resulting latex was washed several times by a series of centrifugation/redispersion cycles in cyclohexane in order to remove the soluble fraction

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Table 1. Dispersion Polyaddition of TDI with EG Respectively in Cyclohexane and in $scCO_2$ (at 60 °C, Cat. DBTDL, 7 h, [NCO]/[OH] = 1.1)

entry	dispersed medium	press. (bar)	$\bar{M}_n$ of PDMS−OH (g/mol)	wt % of PDMS−NCO introduced	wt % of PDMS incorporated[c]	yield (%)[d]	particle average size (μm)[e]	$\bar{M}_w$ (g/mol)[f]	$\bar{M}_w/\bar{M}_n$
1	cyclohexane[a]	1				90	i		
2	cyclohexane[a]	1	4670	4.8		86	0.45 ± 0.1	2800	1.9
3	cyclohexane[a]	1	4670	9	3.5	89	0.5 ± 0.1	4100	1.4
4	cyclohexane[a]	1	4670	13	5.3	85	0.37 ± 0.05	4200	2.7
5	cyclohexane[a]	1	4670	16.7	8.7	80	0.4 ± 0.05	3400	2.1
6	cyclohexane[a,h]	1	4670	9	7.1	80	i	1080	1.3
7	cyclohexane[a]	1	1000	4.8	4.2	88	0.9 ± 0.1	5600	2.4
8	cyclohexane[a]	1	1000	9	2.8	91	1.1 ± 0.1	3200	2.8
9	cyclohexane[a]	1	1000	16.7	2.2	82	1.0 ± 0.2	2070	1.6
10	$scCO_2$[b]	200				52	i	3400	2.2
11	$scCO_2$[b]	200	4670	4.8	9	55	0.9 ± 0.6	4500	2.3
12	$scCO_2$[b]	200	4670	9	11	70	0.9 ± 0.6	4200	2.3
13	$scCO_2$[b]	200	4670	16.7	30	67	0.9 ± 0.6	4800	2.6
14	$scCO_2$[b]	200	1000	9	17	60	1.0 ± 0.6	5500	2.9
15	$scCO_2$[b]	250	4670	9	21	50	0.7 ± 0.3	6500	2.0
16	$scCO_2$[b,g]	250	4670	9	13	50	0.7 ± 0.3	6700	2.3
17	$scCO_2$[b,h]	250	4670	9	13	59	i	5300	2.7

[a] EG = 0.62 g, TDI = 1.91 g, cyclohexane = 20 g. [b] EG = 0.62 g, TDI = 1.91 g, CO_2 = 80−95 g. [c] Determined by ^{1}H NMR titration from the final particles (i.e., after three centrifugation/redispersion cycles in cyclohexane). [d] PUR particles recovered after 3 centrifugation/redispersion cycles in cyclohexane. [e] Determined by SEM and TEM analysis; average values estimated over 100 particles. [f] $\bar{M}_w$ values of the chains constituting the PUR−PDMS particles (i.e., after three centrifugation/redispersion cycles in cyclohexane); SEC in DMF (0.7 mL/min; calibration PS). [g] 20 h experiment. [h] "Reversed process": PDMS−NCO + TDI, then fractionated addition of EG. [i] No particle.

(serum) constituted of chains not trapped within the particles. The effects of PDMS stabilizer weight concentration and molar mass ($\bar{M}_n$ = 1000 or 4670 g/mol) on the PUR particle size were investigated. Results are gathered in Table 1 (entries 1−9). Except the cases where no PDMS was added (entry 1) or when the monomer addition procedure was reversed (entry 6; dropwise addition of EG onto a cyclohexane solution containing PDMS−NCO and TDI), calibrated core−shell particles have been generally obtained, as illustrated by TEM (Figure 1a). While no significant effect of the stabilizer concentration (varied from 5 to 20 wt %) on the particle size could be observed, the PDMS molar mass was found to affect the particle size. Indeed, bigger PUR particles (~1 μm) are obtained with PDMS of $\bar{M}_n$= 1000 g/mol and smaller ones (~500 nm) with PDMS of $\bar{M}_n$= 4670 g/mol. This observation argues for a better surrounding of the growing particle when increasing the size of the stabilizer. The TEM pictures (see Table a in the Supporting Information) clearly show a narrow size distribution of the particles, stressing the steric stabilizing efficiency of the PDMS surfmer in the dispersion process. It is noteworthy that such calibrated "core−shell" PUR−PDMS particles tend to aggregate under the form of hexagonal structures during a film-casting procedure.

The preparation of PUR−PDMS core−shell particles was then investigated in $scCO_2$. For that purpose, a 120 mL high-pressure stainless steel vessel equipped with a magnetic stirrer was used (see Scheme a in the Supporting Information). The polymerization temperature was maintained at 60 °C, and the "gauge" pressure was varied from 200 to 250 bar. In such conditions, the density of the medium is close to the one of cyclohexane (i.e., 0.74).

The solubility in $scCO_2$ of the monomers (EG, TDI) and of PDMS−NCO at the concentration used during the polymerizations was first checked by using an optical cell setup that determines the demixing pressure of each compound (see Schemes b and c in the Supporting Information). At 60 °C, EG (1 wt % with respect to CO_2), TDI (2.5 wt %), and PDMS−NCO (0.35 wt %) were found totally soluble above 140, 170, and 190 bar, respectively. In the polymerization process, PDMS−NCO, EG, and DBTDL were first introduced all together in the reactor, and the pressure was maintained at 120 bar. A first addition of TDI (50% of the all content) was then realized, and the pressure increased to 200 bar. A second batch of TDI was then added after 3.5 h polymerization time. Similarly to the experiments carried out in cyclohexane, the polymerizations in $scCO_2$ were allowed to go for 7 h. The powdery-like reaction product (recovered by simple depressurization) was then washed by cycles of redispersion/centrifugation in cyclohexane. Data from the polymerizations are collected in Table 1. As already observed in cyclohexane, no particles are formed in absence of PDMS−NCO surfmer (entry 10, see SEM picture Figure 1c). The average size of the PUR particles prepared in $scCO_2$ does not change significantly with a variation of PDMS ($\bar{M}_n$ = 4670 g/mol) weight concentration (from 5 to 20 wt %, entries 11−13). Nevertheless, in identical experimental conditions, the PUR particle size is larger in $scCO_2$ than in cyclohexane (0.9 μm vs 0.5 μm), and the particle size distribution is much broader too (see Table b in the Supporting Information). Similar behavior was observed with PDMS ($\bar{M}_n$ = 1000 g/mol, entry 14). Better results in terms of particle size distribution could be obtained by increasing the pressure of the reactor to 250 bar (entries 15 and 16), as illustrated in Figure 1b. This result may be linked to a better solubility of PDMS−NCO surfmer at higher pressure, in agreement with the relationship between solvation and CO_2 pressure increase. Besides, it is worth noting that, similarly to experiment carried out in cyclohexane (entry 6), the "reversed" dropwise addition of EG onto PDMS−NCO and all the TDI (entry 17) does not yield particles, in $scCO_2$ too.

The PUR particles formed in both reaction media (cyclohexane or $scCO_2$) were characterized by ^{1}H NMR and SEC in DMF with the objective to quantify the participation of PDMS−NCO surfmer in the polyaddition reaction. By means of ^{1}H NMR characterization (see Figure d in the Supporting Information), the relative

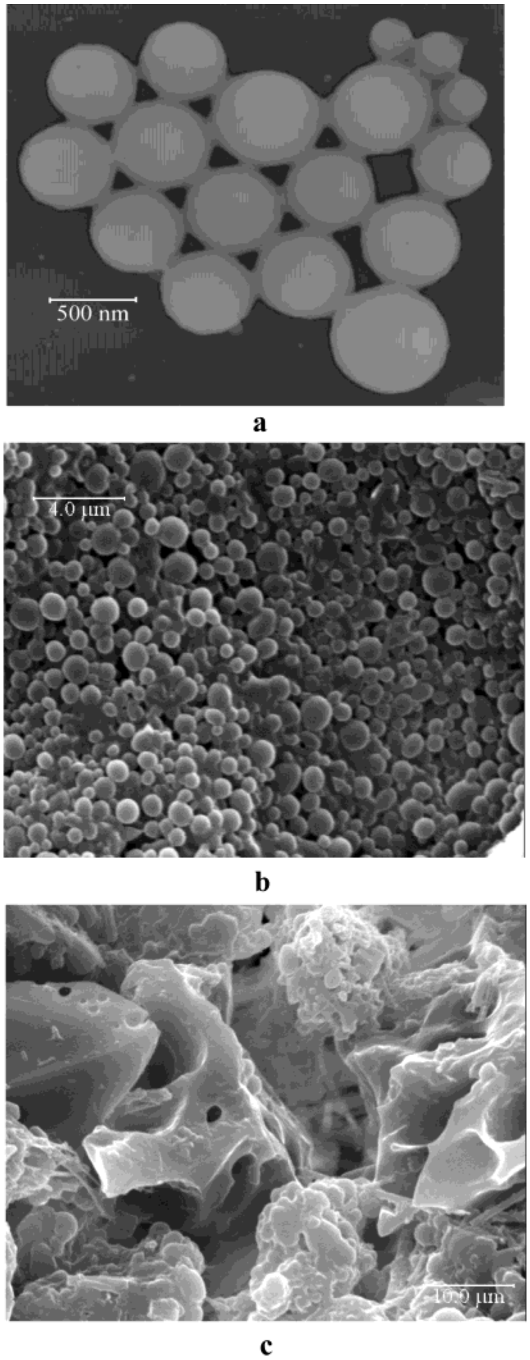

Figure 1. (a) Transmission electron microscopy (TEM) picture of PUR particles synthesized in cyclohexane at 60 °C from the EG/TDI/PDMS−NCO (10 wt %) system. (b) Scanning electron microscopy (SEM) pictures of PUR particles synthesized in supercritical CO_2 (at 250 bar and 60 °C). (c) SEM picture of the reaction product obtained without stabilizer in $scCO_2$ (at 200 bar and 60 °C).

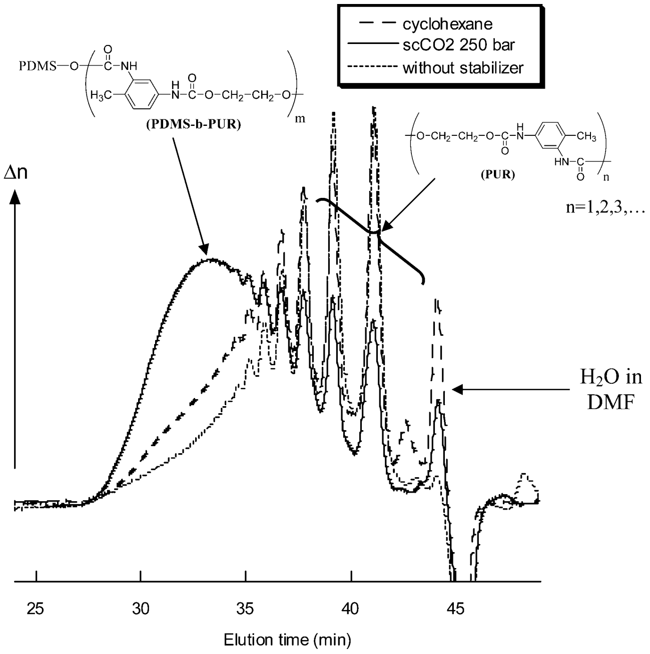

Figure 2. SEC traces of PUR samples obtained in $scCO_2$ (at 60 °C and 250 bar, plain line), in cyclohexane (at 60 °C, dashed line), and without stabilizer (in $scCO_2$ at 60 °C and 250 bar, dotted line) from the system EG/TDI/PDMS (10 wt %) over 7 h.

integrations of the signals corresponding to siloxane and to urethane units respectively at 0.1 ppm (CH_3 groups of the PDMS) and at 7−8 ppm (aromatic protons of TDI units) allowed us to determine the ratio of PDMS incorporated in the final recovered core−shell PUR particles (data are gathered in Table 1).

The weight fraction of PDMS incorporated in the PUR particles was found variable with respect to the dispersion medium. In cyclohexane, the ratio of PDMS incorporated in the recovered particles does not exceed 50% (entries 2−9), the rest of PDMS units being eliminated in the serum. Conversely, the weight fraction of incorporated PDMS in the PUR particles synthesized in $scCO_2$ is, apparently, higher than the theoretical value (entries 11−17). This observation must be correlated to the lower yield obtained in $scCO_2$ compared to cyclohexane. Indeed, it may be anticipated that (i) a fraction of PUR oligomers are noncaptured within the particles and are therefore eliminated during the recovery procedure of the calibrated particles and (ii) a fraction of PDMS remains trapped within the particles due to the swelling ability of $scCO_2$. The SEC traces (in DMF) of PUR samples prepared both in cyclohexane and in $scCO_2$ in the presence or absence of PDMS−NCO surfmer are given in Figure 2 and show a multimodal distribution. As may be observed, PUR particles synthesized in $scCO_2$ contain less oligourethane chains and proportionally higher PDMS-rich fraction, in agreement with NMR data. In all cases, the $\bar{M}_w$ values were found in the range 3000−7000 g/mol. Although these values are determined with respect to a calibration with PS standards, they are in agreement with the initial isocyanate vs alcohol functions ratio [NCO]/[OH] = 1.1 (i.e., theoretical value of $\overline{DP}_n$ is equal to 19) and with the use of monofunctional PDMS−NCO surfmer that can be seen as a chain stopper with respect to the polyaddition mechanism (see Scheme 1).

This study is the first report concerning step-growth polymerization carried out in $scCO_2$ and yielding core−shell polyurethane particles. It was shown that both cyclohexane and $scCO_2$ are effective dispersant media for the production of such materials. The latter are promising in terms of their potential application in biomedicine. Further investigations are currently in progress.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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