

SYNTHESIS OF CORE-SHELL POLYURETHANE-POLYDIMETHYLSILOXANE PARTICLES IN SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

A new route toward the synthesis of polycondensate-based materials under the form of calibrated particles in supercritical carbon dioxide is presented. Core-shell polyurethane-polydimethylsiloxane particles were obtained by polyaddition between ethylene glycol and tolylene-2,4-diisocyanate in supercritical carbon dioxide (scCO₂) in the presence of hydroxy- or isocyanate-terminated polydimethylsiloxane (PDMS) used as the surfmer and dibutyltin dilaurate used as the catalyst. The influences of scCO₂ pressure (200-250 bar) and of PDMS molar mass and weight percentage were investigated with respect to the polymerization feasibility and to the control of the particle formation in scCO₂. Simultaneously, polyadditions were performed in cyclohexane as a reference. The comparison of both dispersed media put forward some advantages in using scCO₂. For example, particles constituted mainly with high molar masses polyurethane-polydimethylsiloxane block copolymers could be obtained in scCO₂.

INTRODUCTION

In the last decade, the use of supercritical carbon dioxide (scCO₂) as a solvent for polymerization reactions has been the focus of great interest both academically and industrially. Indeed, scCO₂ represents an alternative to volatile organic compound and is attractive due to its physical-properties (*i.e.* its viscosity and density) than can be modulated both with the pressure and/or with the temperature. In addition it must be taken into account that scCO₂ is non expensive, non flammable and that its critical point can be easily accessible (T_c = 31,1°C, P_c = 73,8 bar). Although scCO₂ has been widely used as a reaction medium for free-radical [1], cationic [2], anionic ring-opening [3], or transition metal-catalyzed polymerizations [4], the literature is rather poor concerning polyaddition reactions conducted in this medium [5,6]. Due to the insolubility in scCO₂ of most of the polymers (unless fluoropolymers or silicon-based polymers), polymerizations conducted in scCO₂ proceed in heterogeneous conditions. It is well known that dispersion polymerization requires the use of surfactant (reactive or not) that stabilize the particles during the process. De Simone and Wells described the use of poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) as steric stabilizer in the free-radical dispersion polymerization of methyl methacrylate in scCO₂ [7]. Howdle and coworkers have also reported that PMMA particles could be synthesized by dispersion polymerization in scCO₂ using polydimethylsiloxane monomethacrylate macromonomer as the stabilizer [8].

In this paper, we report the use of PDMS-based reactive stabilizers in the synthesis of new core-shell polyurethane-polydimethylsiloxane particles in $scCO_2$. This research wants to achieve two main objectives. First, $scCO_2$ can be an alternative to organic solvent for the production of solvent-free latexes (as long as the obtained particles can be easily re-dispersed). Second, there is a goal to find a new route towards the making of polycondensate-based materials that are of interest in biomedicine. This work is a continuation of previous investigations that allowed us to show the feasibility of the synthesis of polyurethane particles by dispersion polyaddition between tolylene-2,4-diisocyanate and ethylene glycol in an organic medium the cyclohexane [9-11].

I – MATERIALS AND METHODS

Materials. Tolylene-2,4-diisocyanate (Sigma-Aldrich) was purified by distillation under vacuum. Ethylene Glycol (Sigma-Aldrich, 99 %), monohydroxy-terminated PDMS 4670 $g.mole^{-1}$ (Sigma-Aldrich, > 99 %), monohydroxy-terminated PDMS 1000 $g.mole^{-1}$ (generously given by The Polymer Technology Group, > 99 %) and dibutyltin dilaurate (Sigma-Aldrich, 98 %) were used as received. Cyclohexane (Baker, 99 %) was distilled over CaH_2 . Liquid CO_2 (Air Liquide, for supercritical fluids) was cooled with a minichiller and then compressed to the required pressure with a Dosapro Miltonroy pump.

Typical polymerization procedure in cyclohexane. The reactor was charged with 2 eq. of TDI (x moles) with respect to the OH functions of the PDMS stabilizer, dibutyl tin dilaurate (DBTDL) as the catalyst (0.1 g of 1 % solution in paraffin) and all of the solvent (cyclohexane, 20 g). The monohydroxy-terminated PDMS (y wt % vs. monomers ; y = 5, 10, 15, 20) was added dropwise for 2h at 60°C at a stirring speed of 500 rpm. EG (0.01 mole) was then added in one lot and the mixture let for 30 minutes. Then (0.011-x) mole of TDI was added over 6 hours.

After 7 hours the latex was removed by the sampling outlet and then washed three times by centrifugation/re-dispersion in cyclohexane in order to eliminate unreacted compounds.

After drying under vacuum, the samples were characterized by 1H and ^{13}C NMR, SEC, TEM, DSC, etc...

Typical polymerization procedure in $scCO_2$. The experimental setup is shown in figure 1. The reactor (Top Industrie SA, 118 mL) was charged with DBTDL, EG (0.01 mole) and the PDMS-NCO stabilizer (y wt % vs. monomers ; y = 5, 10, 15, 20). The pressure was increased to 54 bars (the CO_2 bottle pressure) and the reactor was heated to 60°C and stirred at 500 rpm. Then the pressure was adjusted to 120 bars.

After 1h of stirring a first amount of TDI was injected in the reactor by increasing the pressure in a 2 mL cell and then the pressure was adjusted to 200 bars. After 3.5 h reaction the same addition of TDI was realized and then the pressure was fixed to 210 bars for 3.5 h. After the reactor had been cooled to room temperature and depressurized to atmospheric pressure, the product (a white powder) was removed and then re-dispersed in cyclohexane so as to be washed 3 times by centrifugation/re-dispersion cycles.

After drying under vacuum, the samples were characterized by 1H and ^{13}C NMR, SEC, TEM, DSC, etc...

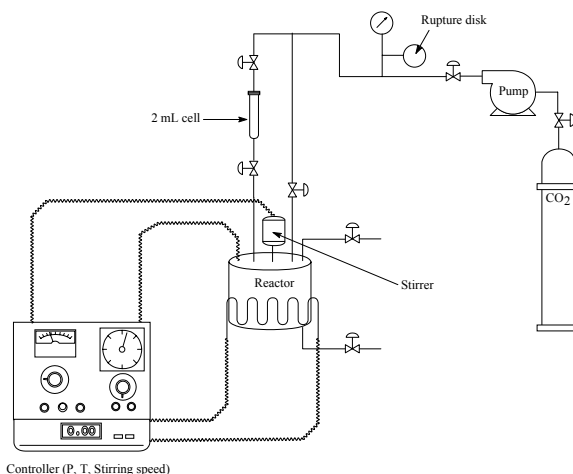
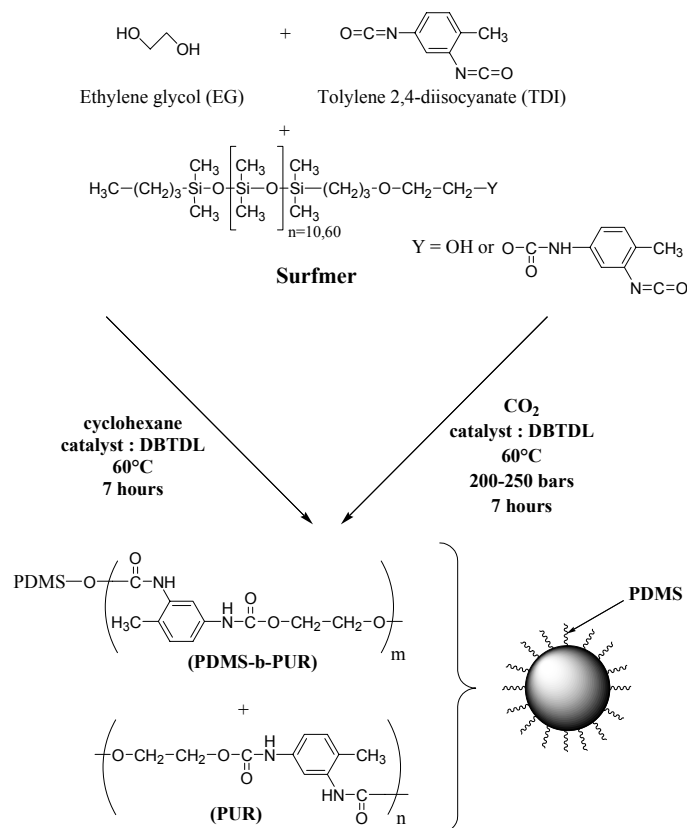


Figure 1 : Experimental set-up for the polymerizations carried out in supercritical carbon dioxide.

II – RESULTS AND DISCUSSION

The same synthetic procedure, shown in Scheme 1, was implemented both in cyclohexane and in $scCO_2$ on the basis of preliminary reported investigations [9-11]. On these grounds, PDMS-OH was first derivatized by reaction with TDI added in slight excess (2 mol eq. TDI) into isocyanate-terminated stabilizer PDMS-NCO, in the presence of dibutyl tin dilaurate (DBTDL) as a catalyst, in cyclohexane at $60^\circ C$ [11]. 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 : Polyaddition reaction between ethylene glycol and toluene-2,4-diisocyanate carried out both in cyclohexane and in $scCO_2$ as the dispersant media

Polyadditions were first monitored in cyclohexane, as a dispersant medium. PDMS-NCO was first added, followed by EG and TDI (added drop-wise over a period of 6 hours) 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. At the end of the polyaddition, the resulting latex was washed several times by a series of centrifugation/re-dispersion cycles in cyclohexane in order to remove the soluble fraction (serum) constituted of chains not trapped within the particles. The effects of PDMS stabilizer weight concentration and molar mass ($\overline{M}_n=1000$ or 4670 g/mole) on the PUR particle size were investigated. Results are gathered in Table 1 (entries 1 to 8). While no effect of the stabilizer concentration (varied from 5 to 20 wt %) on the particle size could be observed, PDMS molar mass affect it. Indeed, bigger PUR particles ($\sim 1 \mu\text{m}$) are respectively obtained with PDMS of $\overline{M}_n = 1000$ g/mole and smaller ones (~ 500 nm) with PDMS of $\overline{M}_n = 4670$ g/mole. This result argues for a better surrounding of the growing particle when increasing the size of the stabilizer. The TEM micrographs clearly show a narrow size distribution of the particles. This underlines the remarkable steric stabilizing efficiency of the PDMS surfmer in the dispersion process.

Entry	Dispersed media	Pressure (bar)	\overline{M}_n of PDMS-OH (g/mole)	Wt % of PDMS-NCO introduced	Wt % of PDMS incorporated ^c	Yield (%) ^d	Particle average size (nm) ^e	Span (nm-nm)	\overline{M}_w (g/mole) ^f	$\frac{\overline{M}_w}{\overline{M}_n}$
1	cyclohexane ^(a)	-	-	-	-	90	No particle		3900	1.4
2	cyclohexane ^(a)	-	4670	4.8	-	86	450	400-500	5000	1.5
3	cyclohexane ^(a)	-	4670	9	3.5	89	500	450-550	4050	1.4
4	cyclohexane ^(a)	-	4670	13	5.3	85	370	350-390	5100	1.5
5	cyclohexane ^(a)	-	4670	16.7	8.7	80	400	380-420	5600	1.7
6	cyclohexane ^(a)	-	1000	4.8	4.2	88	900	800-1000	3400	1.4
7	cyclohexane ^(a)	-	1000	9	2.8	91	1100	1000-1200	4500	1.6
8	cyclohexane ^(a)	-	1000	16.7	2.2	82	1000	950-1050	3100	1.6
9	scCO ₂ ^(b)	200	-	-	-	52	No particle		4400	1.9
10	scCO ₂ ^(b)	200	4670	4.8	9	55	900	300-1500	4500	1.9
11	scCO ₂ ^(b)	200	4670	9	11	70	900	"	4200	1.9
12	scCO ₂ ^(b)	200	4670	16.7	30	67	900	"	4800	1.9
13	scCO ₂ ^(b)	200	1000	9	17	60	1000	"	3500	1.8
14	scCO ₂ ^(b)	250	4670	9	21	50	700	500-1000	6500	1.9
15 ^g	scCO ₂ ^(b)	250	4670	9	13	50	700	500-1000	6700	1.9

^(a) EG = 0.62 g, TDI = 1.91 g, cyclohexane = 20 g

^(b) EG = 0.62 g, TDI = 1.91 g, CO₂ = 80-95 g

^(c) Determined by ¹H NMR titration from the final particles (*i.e.* after 3 centrifugation/re-dispersion cycles in cyclohexane)

^(d) PUR particles recovered after 3 centrifugation/re-dispersion cycles in cyclohexane

^(e) Determined by SEM and TEM analysis

^(f) \overline{M}_w values of the chains constituting the PUR-PDMS particles (*i.e.* after 3 centrifugation/re-dispersion cycles in cyclohexane); SEC in DMF (0.7 mL/min; calibration PS)

^(g) 20 hours experiment

Table 1 : Dispersion polyaddition between tolylene-2,4-diisocyanate and ethylene glycol carried out both in cyclohexane and in scCO₂ (at 60°C, cat. DBTDL, 7 hours, $[\text{NCO}]/[\text{OH}] = 1.1$)

The preparation of PUR-PDMS core-shell particles was then investigated in scCO₂. For that purpose, a 118 mL high-pressure stainless steel vessel equipped with a magnetic stirrer was used (see Figure 1). The polymerization temperature was maintained at 60 °C and the 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 scCO₂ of monomers (EG, TDI) and of PDMS-NCO at the concentration used during the polymerisations was first checked by using an optical cell set-up that determines the demixing pressure of each compound. At 60 °C, EG (1 wt % with respect to CO₂), TDI (2.5 wt %) and PDMS-NCO (0.35 wt %) were found totally soluble above 140 bar, 170 bar and 190 bar respectively. In the process, PDMS-NCO, EG and DBTDL were first introduced all together in the reactor, followed by a first addition of TDI and a second one after 3.5 hours. Similarly to the experiments carried out in cyclohexane, the polymerizations in scCO₂ were allowed to go for 7 hours. The powdery-like reaction product (recovered by simple depressurization) was then washed by cycles of re-dispersion/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 (entries 1 and 9). The yields in PUR particles were found lower in scCO₂ than in cyclohexane even after longer reaction time (entry 15). This observation can be explained by a loss of polymer during the recovering-washing procedure. Moreover, the average size of the PUR particles prepared in scCO₂ does not change significantly with a variation of PDMS ($\overline{M}_n=4670$ g/mole) weight concentration (from 5 to 20 wt %, entries 10 to 12). However, in identical experimental conditions, the particle size distribution is much broader in scCO₂ than in cyclohexane and it seems that the PUR particle size is larger (0.9 μm vs. 0.5 μm). Similar behaviour was observed with PDMS of $\overline{M}_n=1000$ g/mole (entry 13) when using 10 wt % of stabilizer. Better results in terms of particle size distribution could be obtained by increasing the pressure of the reaction to 250 bar (entries 14-15). As illustrated in Figure 2, smaller and more homogeneous in size PUR particles could be obtained at 250 bar. This result may be linked to a better solubility of PDMS-NCO at higher pressure, in agreement with the relationship between solvation and CO₂ pressure increase.

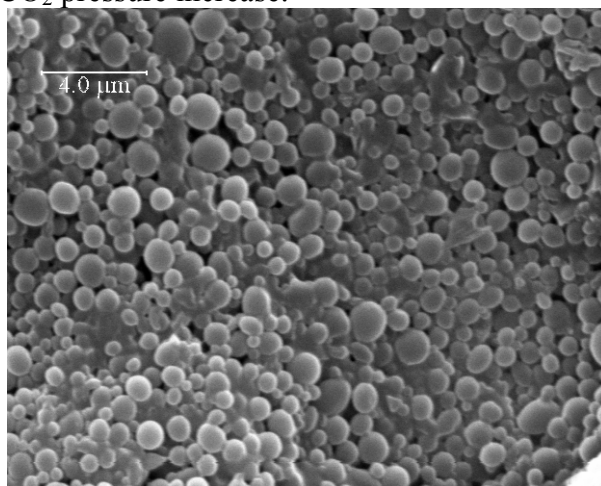


Figure 2 : Scanning electronic micrograph of core-shell polyurethane-polydimethylsiloxane particles synthesized in scCO₂ (@ 250 bar and 60 °C) from the system TDI/EG/DBTDL with 10 wt % of PDMS-NCO surfmer ([NCO]/[OH]=1.1).

The PUR particles formed in both reaction media (cyclohexane or scCO₂) were characterized by ¹H NMR and SEC in DMF with the objective to quantify the participation of PDMS-NCO surfmer in the polyaddition reaction. For instance, by ¹H NMR characterization, the titration of the signals due to the PDMS and to the polyurethane units, at 0.1 ppm (CH₃ groups of the PDMS) and at 7-8 ppm (aromatic protons of TDI units) respectively, enabled 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 is very much dependent of the reaction medium. In cyclohexane, the efficiency of PDMS-NCO as surfmer is rather low since less than 40 wt % of introduced PDMS is finally incorporated in the particle (entries 3-8). Conversely, the weight fraction of incorporated PDMS in the PUR particles elaborated in scCO₂ is, apparently higher than the theoretical value. This observation must be correlated to the lower yield obtained in scCO₂ compared to cyclohexane. The SEC traces (in DMF) of PUR samples elaborated both in cyclohexane and in scCO₂ show a multimodal distribution. We observed that PUR particles elaborated in scCO₂ contain less oligourethane chains and proportionally higher PDMS-richened fraction in agreement with NMR data.

CONCLUSION

To sum up, supercritical carbon dioxide has been shown to replace efficiently cyclohexane as the dispersant medium for the synthesis of core-shell polyurethane-polydimethylsiloxane particles. The latter were found to be mainly constituted of PUR-PDMS block copolymers when they were synthesized in scCO₂ while they were mostly composed of oligourethanes when prepared in cyclohexane. Moreover, we have shown an influence of the pressure on the particle size distribution. Indeed, the higher the pressure (*i.e.* 250 bar) the more calibrated the PUR particles. Such materials are quite promising in terms of their potential application as biomaterials.

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