

# Synthesis of core-shell polyurethane–polydimethylsiloxane particles in cyclohexane and in supercritical carbon dioxide used as dispersant media: a comparative investigation

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## Abstract

Polyurethane–polydimethylsiloxane particles of tuneable diameter in the range 0.5–5  $\mu\text{m}$ , have been synthesized by step-growth polymerization, both in cyclohexane and in supercritical carbon dioxide ( $\text{scCO}_2$ ) used as dispersant media. The feasibility of the polyaddition between ethylene glycol and tolylene-2,4-diisocyanate, selected as monomers, was first demonstrated in cyclohexane, in the presence of hydroxy- or isocyanate-terminated polydimethylsiloxane used as a surfmer. The polymerizations were then carried out in  $\text{scCO}_2$  at 60 °C and above 200 bar, after the solubility of each reactant has been determined in  $\text{scCO}_2$ , at various pressures and temperatures. Both in cyclohexane and in  $\text{scCO}_2$ , the reaction extent was determined by means of FTIR spectroscopy. The structure and the morphology of the resulting powdery polyurethane–polydimethylsiloxane ‘core-shell’ material were confirmed by NMR, SEC, TEM and SEM techniques.

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## 1. Introduction

In the last decade, the use of supercritical carbon dioxide ( $\text{scCO}_2$ ) as a polymerization medium has been the focus of numerous academic and industrial researches. Indeed,  $\text{scCO}_2$  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,  $\text{scCO}_2$  is non-expensive, non-flammable and its critical point can be easily accessible ( $T_c = 31.1$  °C,  $P_c = 73.8$  bar). Although  $\text{scCO}_2$  has been widely used as a reaction medium for radical [1,2], cationic [3], anionic ring-opening [4], or transition metal-catalyzed polymerizations [5], the literature is rather poor dealing with step-growth polymerizations carried out in this medium [6,7]. Due to the insolubility, in

$\text{scCO}_2$ , of most of the polymers (unless fluoropolymers or silicon-based polymers), the polymerizations conducted in  $\text{scCO}_2$  proceed in heterogeneous conditions. In such conditions, the formation of a stable latex constituted of calibrated particles requires the use of a surfactant (reactive or not). For example, De Simone and Wells described the use of poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) as a steric stabilizer in the free-radical dispersion polymerization of methyl methacrylate in  $\text{scCO}_2$  [8]. Howdle and co-workers have also reported that PMMA particles could be synthesized by dispersion polymerization in  $\text{scCO}_2$  using polydimethylsiloxane monomethacrylate macromonomer as the stabilizer [9,10].

In this paper, we report on the use of PDMS-based reactive stabilizers for the synthesis of novel ‘core-shell’ polyurethane–polydimethylsiloxane particles in  $\text{scCO}_2$ . The objectives of the study are (i) to show that  $\text{scCO}_2$  can be an alternative to organic solvent for the production of polycondensate-based latexes (as long as the obtained particles can be easily re-dispersed) and (ii) to find a new route towards materials that can be applied in biomedicine.

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This study is a continuation of previous investigations devoted to the synthesis of core-shell polyurethane particles by dispersion step-growth polymerization in an organic dispersant phase (cyclohexane), in the presence of well-designed surfmers, such as hydroxy-terminated poly(*n*-butyl acrylate), polystyrene, or polybutadiene [11–13]. These previous investigations pointed out the dual role of the surfmer that not only enables the formation of a stable latex but also gives to the final core-shell particles, specific properties. As an illustration, it is worth mentioning polyurethane particles surrounded by a covalently bonded poly(*n*-butylacrylate) shell and exhibiting specific adhesive properties, when film-coated.

## 2. Experimental

### 2.1. Materials

Toluene-2,4-diisocyanate (Sigma-Aldrich) was purified by distillation under vacuum. Ethylene Glycol (Sigma-Aldrich, 99%), monohydroxy-terminated PDMS  $4670 \text{ g mol}^{-1}$  (Sigma-Aldrich, >99%), monohydroxy-terminated PDMS  $1000 \text{ g mol}^{-1}$  (generously given by The Polymer Technology Group, >99%) and dibutyltin dilaurate (Sigma-Aldrich, 98%) were used as received. Cyclohexane (Baker, 99%) was distilled over  $\text{CaH}_2$ . Liquid  $\text{CO}_2$  (Air Liquide, for supercritical fluids) was cooled with a minichiller and then compressed to the required pressure with a Dosapro Miltonroy pump.

### 2.2. Procedures

#### 2.2.1. Synthesis of isocyanate-terminated polydimethylsiloxane (PDMS-NCO)

A three-neck round bottom flask equipped with a condenser and a nitrogen inlet was loaded with 19 mg of TDI ( $1.04 \times 10^{-4} \text{ mol}$ ) and 5 mL of cyclohexane, heated at  $60^\circ\text{C}$  and stirred at 500 rpm. Then 0.2536 g of monohydroxy-terminated polydimethylsiloxane ( $4670 \text{ g/mol}$ ,  $5.43 \times 10^{-5} \text{ mol}$ ) dissolved in 15 mL of cyclohexane were added drop-wise through an addition funnel and let to react under stirring over a period of 4 h. After evaporation of the cyclohexane, the excess of TDI was removed by precipitation in pentane (three times). The PDMS-NCO in pentane solution was dried under vacuum and characterized by SEC, MALDI-TOF and NMR. Less than 5% of coupled product (i.e. PDMS-TDI-PDMS) could be detected by SEC.

#### 2.2.2. Typical polymerization procedure in cyclohexane

The reactor was loaded with  $x \text{ wt}\%$  ( $x=4.7, 9.1, 13, 16.7$ ) versus the monomers of the reactive stabilizer (either PDMS-OH or PDMS-NCO), dibutyl tin dilaurate (DBTDL) as the catalyst (0.1 g of 1 wt% solution in paraffin) and all the solvent (cyclohexane, 20 g). The temperature and the

stirring speed were, respectively, set-up at  $60^\circ\text{C}$  and 500 rpm. EG (0.6207 g, 0.01 mol) non-soluble in cyclohexane was then added in one lot and the mixture let under stirring for 30 min. Then, TDI (1.9158 g, 0.011 mol) was added drop-wise over 4 h (0.4 mL/h).

After 7 h, the latex was removed by the sampling outlet and then washed three times by centrifugation/re-dispersion in cyclohexane.

After drying under vacuum, the samples were characterized by  $^1\text{H}$  NMR, SEC and TEM or SEM.

#### 2.2.3. Typical polymerization procedure in $\text{scCO}_2$

The experimental setup is shown in Fig. 1. The reactor (Top Industrie SA, 118 mL) was charged with DBTDL (1.5% with respect to monomers), EG (0.6207 g, 0.01 mol, 1% with respect to  $\text{CO}_2$ ) and the PDMS stabilizer either PDMS-NCO or PDMS-OH ( $y \text{ wt}\%$  vs. monomers;  $y=4.7, 9.1, 13, 16.7$ ). The pressure was increased to 54 bars (the  $\text{CO}_2$  bottle pressure) and the reactor was heated to  $60^\circ\text{C}$  and stirred at 500 rpm. The pressure was then adjusted to 180 bars. After 1 h stirring, a first amount of TDI (0.9484 g,  $5.445 \times 10^{-3} \text{ mol}$ , 1.25% with respect to  $\text{CO}_2$ ) was injected in the reactor by increasing the pressure in a 2 mL cell. The pressure was then adjusted to 250 bars. After 3.5 h reaction, a second addition of TDI (0.9484 g,  $5.445 \times 10^{-3} \text{ mol}$ , 1.25% with respect to  $\text{CO}_2$ ) was realized and the pressure was fixed to 255 bars for 3.5 h. The reactor was then cooled down to room temperature and depressurized to atmospheric pressure. The reaction product (a white powder) was removed, re-dispersed in cyclohexane and washed 3 times by centrifugation/re-dispersion cycles.

After drying under vacuum, the samples were characterized by  $^1\text{H}$  NMR, SEC and TEM or SEM.

### 2.3. Characterization

The molar masses of the polymers were determined by size exclusion chromatography (SEC) in dimethyl formamide (DMF) at room temperature (flow rate 0.7 mL/min) on a Varian apparatus equipped with a refractive index detector and 3 TOSOHAAS TSK gel columns in series calibrated by means of narrow polystyrene standards.  $^1\text{H}$  NMR spectra were recorded using a Bruker AC-200 NMR spectrometer. Infrared (FTIR) spectroscopy experiments of polyurethane samples were performed on a Bruker Tensor 27 apparatus using ATR technique. Mid-infrared absorption spectroscopic investigation in  $\text{scCO}_2$  of the polymerization between EG and TDI was performed in situ on a FTIR (Bio-Rad: FTS-60A) spectrometer using the cell shown in Fig. 2. Scanning electronic microscopy (SEM) analysis were carried out on a JEOL JSM 2500 apparatus and transmission electronic microscopy (TEM) was performed on a JOEL JEM-100S electronic microscope.

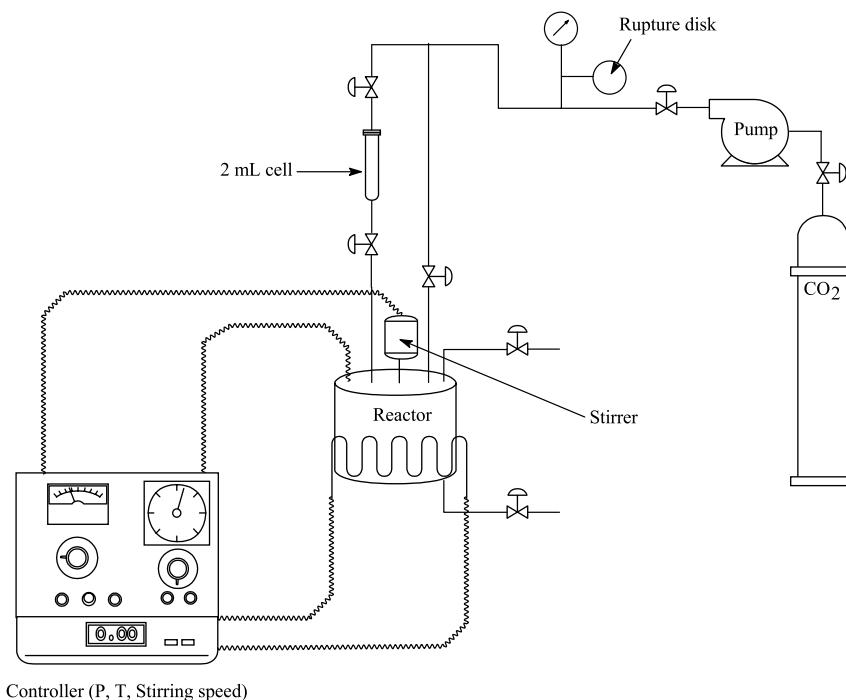


Fig. 1. Experimental set-up for the polymerizations carried out in supercritical carbon dioxide.

### 3. Results

#### 3.1. Synthesis of polyurethane particles in cyclohexane

Step-growth polymerizations between ethylene glycol (EG) and tolylene-2,4-diisocyanate (TDI) were implemented in cyclohexane (at 60 °C and 500 rpm) in the presence of either hydroxy- or isocyanate-terminated polydimethylsiloxane, respectively, noted PDMS-OH or PDMS-NCO-, used as a steric reactive stabilizer (or surfmer). On the grounds of previous investigations which demonstrate the dramatic effect of the experimental procedure on the resulting latex, we follow the addition mode which consists in the drop-wise addition of TDI over a

cyclohexane solution containing the reactive polydimethylsiloxane stabilizer and dispersed EG droplets [11–13]. The general synthetic pathway is given in Scheme 1.

The influence of the polydimethylsiloxane molar mass, weight concentration and type of functionality (OH or NCO) on the resulting latex has been investigated. Data are collected in Table 1.

Except the cases where no stabilizer was added (entry c1) or when the monomer addition mode was reversed (i.e. drop-wise addition of EG over a mixture of PDMS-NCO + TDI + DBTDL) (entry c6), stable latexes constituted of calibrated particles have been generally obtained, as illustrated by Scanning Electron Microscopy (SEM) pictures shown in Fig. 3.

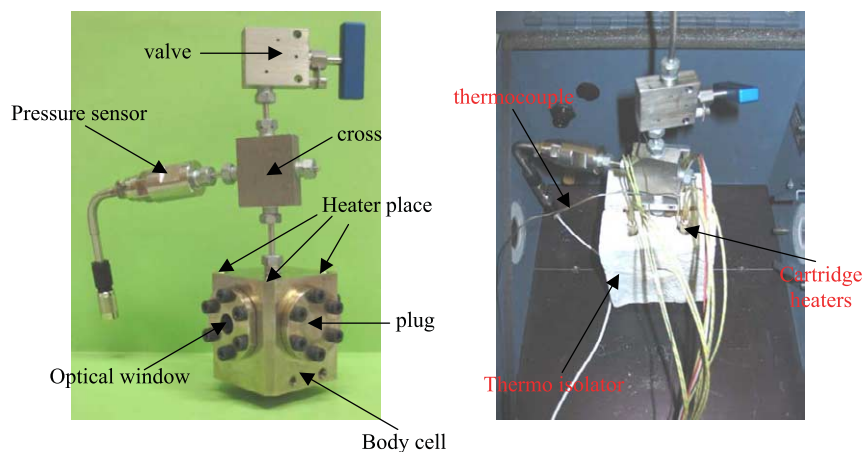
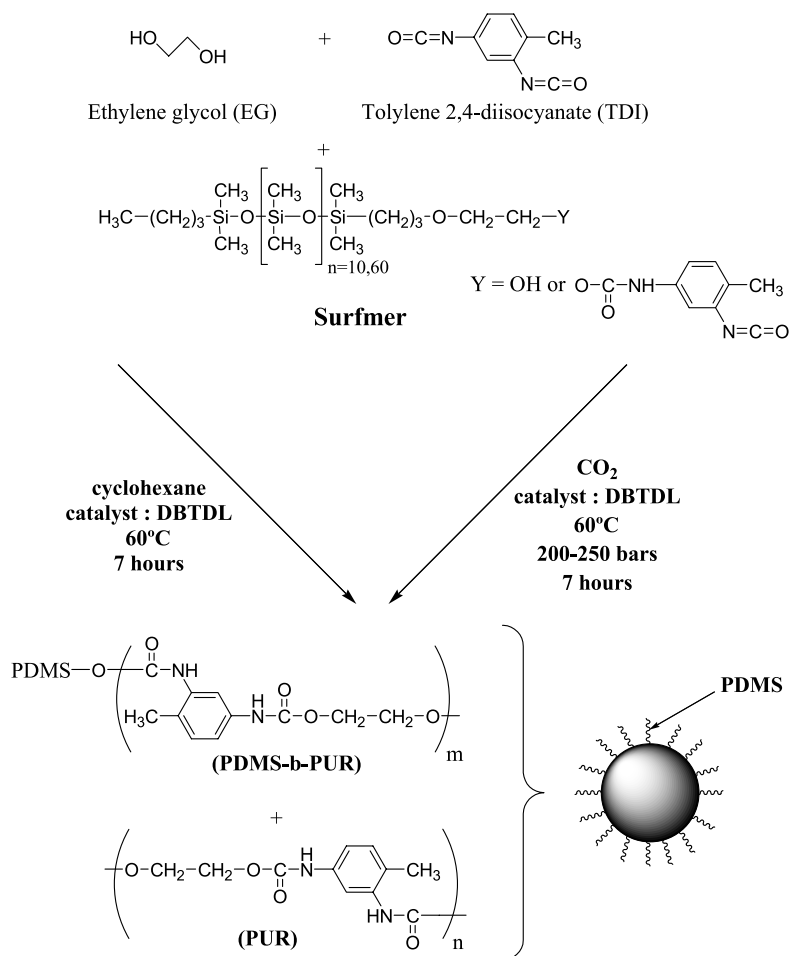


Fig. 2. Experimental set-up for FTIR measurements in  $scCO_2$  at 60 °C and 250 bar (for the stirring, a magnetic stirrer is placed under the cell equipped with a stirrer bar).



A first analysis of the latexes reveals that dispersions implemented in the presence of PDMS-OH (entries c10–c13) yield bigger particles (2–5  $\mu\text{m}$ ) than dispersions (entries c2–c9) carried out in the presence of PDMS-NCO (0.4–1.2  $\mu\text{m}$ ). A decrease of the average particle size and size distribution with respect to an increase of PDMS-OH weight concentration was logically observed until a plateau is reached (entries c10–c12). Such a trend was surprisingly not obtained when using PDMS-NCO as a surfmer. Indeed, the average size of the particles was found constant and equal to 0.4  $\mu\text{m}$  (entries c2–c5) with PDMS of  $\bar{M}_n = 4670$  g/mol and to 1  $\mu\text{m}$  (entries c7–c9) with PDMS of  $\bar{M}_n = 1000$  g/mol, respectively, whatever the surfmer concentration. However, in both cases, the higher the surfmer (PDMS-OH or PDMS-NCO) molar mass, the lower the particle size, in agreement with a better surrounding of the particles when increasing the surfmer molar mass.

In order to explain the differences observed and to quantify the participation of the PDMS surfmer in the step-growth polymerization, the latexes were analysed by  $^1\text{H}$  NMR spectroscopy and SEC. A typical  $^1\text{H}$  NMR spectrum of the dissolved particles in DMF  $d_7$  is shown in Fig. 4.

The integration of the signals corresponding to the

dimethylsiloxane and to the urethane units, respectively, at 0.1 ppm ( $\text{CH}_3$  groups of the PDMS) and at 7–8 ppm (aromatic protons of TDI units) allowed us to calculate the ratio of PDMS incorporated in the final recovered core-shell PUR particles. As given in Table 1, the weight percentage of PDMS finally found in the material, after the washing/centrifugation treatment, was generally lower than the weight percentage of PDMS introduced at the beginning of the reaction. It may be anticipated that the first PDMS chains chemically grafted onto the growing particles act as a steric barrier for remaining unreacted PDMS surfmer (PDMS-NCO or PDMS-OH). The latter, can only adsorbed at the surface of the particles and therefore be easily removed during the washing process.

The SEC characterization of the samples could be realized in DMF. As expected, the SEC traces exhibit a multi-modal distribution, in agreement with the formation of oligo-urethanes embedded within the particles, together with PDMS-PUR block copolymer. The different chromatograms shown in Fig. 5 and corresponding to dispersions carried out in the presence or in the absence of PDMS surfmer, allowed us to discriminate the two families constituting the samples. It is important to specify that

Table 1

Data of dispersion step-growth polymerization between tolylene-2,4-diisocyanate and ethylene glycol carried out in cyclohexane (20 g) in the presence of functional PDMS surfmer, at 60 °C and for 7 h (cat. DBTDL, 500 rpm, [NCO]/[OH] = 1.1)

Entry	Precursor	$\bar{M}_n$ of PDMS-OH (g/mol)	wt% of PDMS introduced	wt% of PDMS incorporated <sup>a</sup>	Yield (%) <sup>b</sup>	Particle average size (μm) <sup>c</sup>	Span (μm–μm)	$\bar{M}_w$ (g/mol) <sup>d</sup>	$\bar{M}_w/\bar{M}_n$
c1	PDMS-NCO	–	–	–	90	No particle	–	–	–
c2	PDMS-NCO	4670	4.8	–	86	0.45	0.35–0.55	2800	1.9
c3	PDMS-NCO	4670	9	3.5	89	0.5	0.4–0.6	4100	1.4
c4	PDMS-NCO	4670	13	5.3	85	0.37	0.35–0.4	4200	2.7
c5	PDMS-NCO	4670	16.7	8.7	80	0.4	0.35–0.45	3400	2.1
c6 <sup>e</sup>	PDMS-NCO	4670	9	7.1	80	No particle	–	1080	1.3
c7	PDMS-NCO	1000	4.8	4.2	88	0.9	0.8–1.0	5600	2.4
c8	PDMS-NCO	1000	9	2.8	91	1.1	1.0–1.2	3200	2.8
c9	PDMS-NCO	1000	16.7	2.2	82	1.0	0.8–1.2	2070	1.6
c10	PDMS-OH	4670	4.8	5	65	4.2	3.0–5.0	1700	1.7
c11	PDMS-OH	4670	9	6	68	2.5	2.2–2.8	2400	2.0
c12	PDMS-OH	4670	16.7	6.5	73	2.2	2.0–2.4	1750	1.7
c13	PDMS-OH	1000	9	8.5	67	3.5	2.0–4.0	1800	1.7

<sup>a</sup> Determined by <sup>1</sup>H NMR relative integration from the final particles (i.e. after three centrifugation/re-dispersion cycles in cyclohexane).

<sup>b</sup> PUR particles recovered after three centrifugation/re-dispersion cycles in cyclohexane (yield = weight of washed product vs weight of monomers + surfmer).

<sup>c</sup> Determined by SEM and TEM analysis; average values estimated over 100 particles.

<sup>d</sup>  $\bar{M}_w$  Values of the chains constituting the PUR-PDMS particles (i.e. after three centrifugation/re-dispersion cycles in cyclohexane); SEC in DMF (0.7 mL/min; calibration PS).

<sup>e</sup> ‘Reversed process’: PDMS-NCO + TDI (1 lot), then addition of EG drop-wise (5 h addition).

‘apparent’ values, listed in Table 1, were calculated on the basis of a polystyrene calibration. Such experimental molar masses are slightly lower than the theoretical ones (theoretical  $\bar{D}P_n$  close to 19, taking into account the OH/NCO ratio ( $r=0.91$ ), the presence of mono-functional surfmer ( $q=(\text{OH}_{\text{mono-functional}}/\text{OH})=0.0054$ ) and the reaction extent  $p$  equal to 1,  $\bar{D}P_n=(1+r+2q)/(1+r+2q-2rp)$ ). The growth of the polymer chains with time was followed by sampling out aliquots for SEC characterizations. As indicated in Fig. 6, values reach a plateau after 7–8 h reaction time and the polydispersity index  $\text{PDI}=\bar{M}_w/\bar{M}_n$  grows up to 2.

The polymerization kinetic was also determined by means of FTIR analysis using an ATR technique. Indeed, the increase with time of the signal characteristic of the –N–H vibration mode located at  $3300\text{ cm}^{-1}$  which corresponds to the formation of urethane linkages, allowed us to determine the reaction extent,  $p$ , against time (we consider that  $p$  is equal to 1 when there is no more evolution of the –N–H signal intensity). The kinetic curves given in Fig. 7 for dispersions carried out in the presence of PDMS-OH or PDMS-NCO as a surfmer are comparable and argue for a complete formation of urethane units after 7–8 h. It is worth noting that the curves exhibit a plateau between 3 and 5 h that corresponds to the end of the drop-wise TDI addition.

### 3.2. Synthesis of polyurethane particles in $sc\text{CO}_2$

Prior to any polymerization, the solubility in  $sc\text{CO}_2$  of the monomers (EG, TDI) and of the surfmers (PDMS-OH and PDMS-NCO) at the concentration used during the

polymerizations was checked by using an optical cell set-up that allowed us to determine the demixing pressure of each compound [14]. It was found that, at 60 °C, EG (1 wt% with respect to  $\text{CO}_2$ ), TDI (2.5 wt%), PDMS-OH (0.35 wt%) and PDMS-NCO (0.35 wt%) were totally soluble above 140, 170, 180 and 190 bar, respectively. According to these

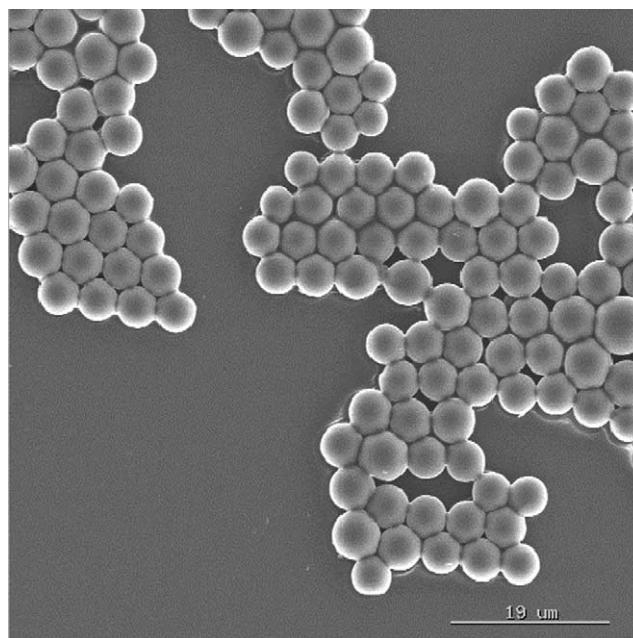


Fig. 3. Scanning electron microscopy (SEM) picture of polyurethane-polydimethylsiloxane particles obtained in cyclohexane at 60 °C (500 rpm) using TDI and EG as monomers and PDMS-OH (4.8 wt%) as reactive stabilizer (entry c10).

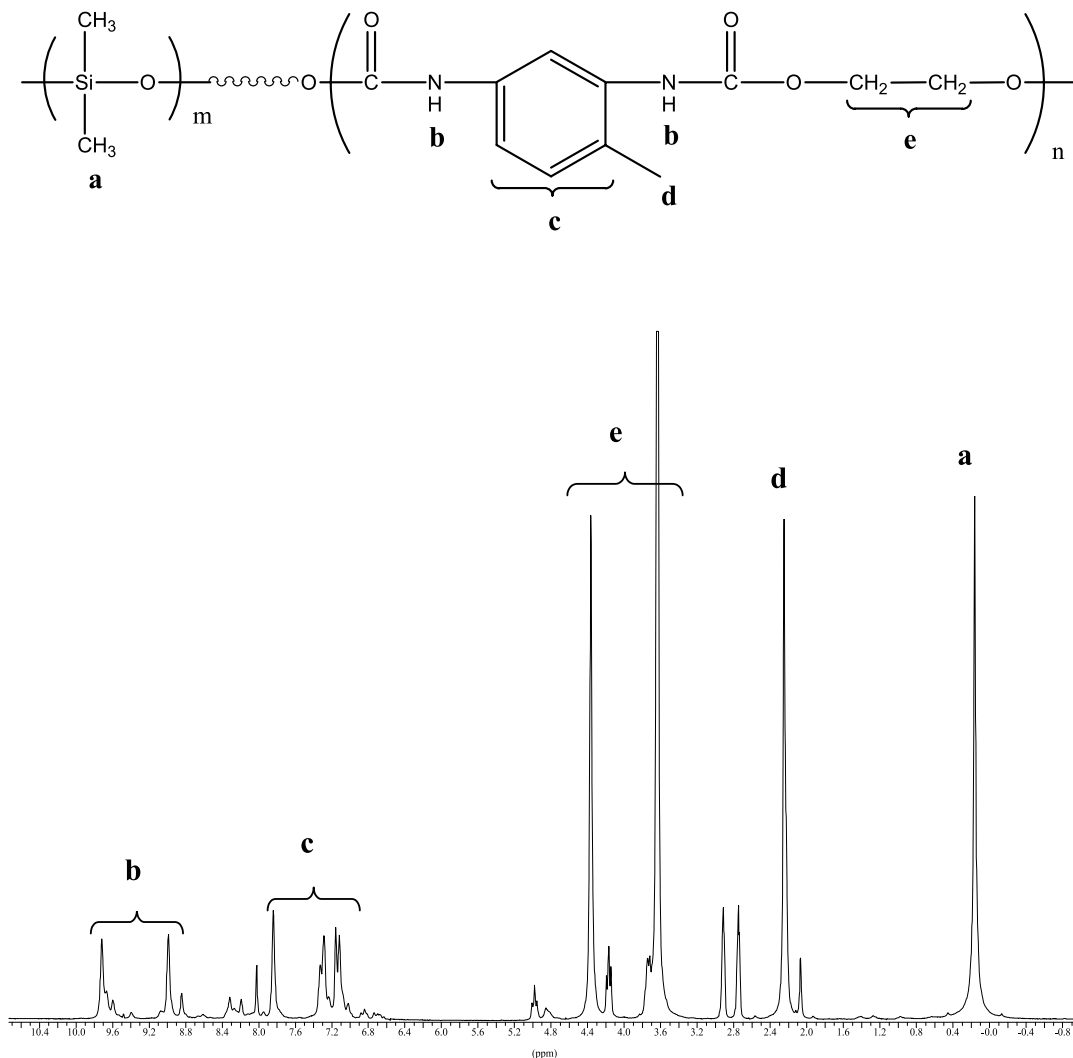


Fig. 4.  $^1\text{H}$  NMR spectrum (200 MHz, DMF  $d_7$ ) of PUR particles obtained in supercritical carbon dioxide ( $T=60^\circ\text{C}$ ,  $P=200$  bar) from the system EG/TDI/PDMS-NCO (1000 g/mol).

results, polymerizations conducted in  $\text{scCO}_2$  were carried out at  $60^\circ\text{C}$  and at a pressure above 200 bar to ensure a one-phase system at the beginning of the reaction. In such conditions, the density of the  $\text{scCO}_2$  is close to the one of cyclohexane (i.e. 0.74). The polymerizations were carried out in the stainless steel reactor. The latter is linked to a small 2 mL stainless steel cell which enables the addition of TDI with time (see experimental set-up in Fig. 1). In the procedure, the PDMS surfmer, EG and DBTDL were first introduced all together in the reactor, followed by a first addition of TDI (50%) then a second TDI batch after 3.5 h. It is worth noting that unlike DeSimone report [15], we did not observe any pressure change along the reaction. This can be explained by the large volume of  $\text{CO}_2$  used in the experiments (i.e. 1 wt% EG and 2.5 wt% TDI vs.  $\text{CO}_2$ ). The powdery-like PUR samples were recovered by depressurization and washed by a series of re-dispersion/centrifugation cycles in cyclohexane. Data corresponding to the

polymerizations implemented in  $\text{scCO}_2$  are collected in Table 2.

As expected, no particles are formed in absence of PDMS surfmer (entry sc1). Conversely to data obtained in cyclohexane, the polymerizations carried out in the presence of PDMS-OH ( $\bar{M}_n=4670$  g/mol) used as a reactive stabilizer did not yield particles (entry sc9). Such a behavior is comparable to the one observed for dispersions carried out in cyclohexane in the presence of PS-OH or PnBuA-OH used as surfmers, for which a coagulation phenomenon was observed [12,13]. On the other hand, the use of PDMS-NCO enabled the formation of stable PUR latexes (entries sc2–sc7). Unlike experiments in cyclohexane, the particle size distribution (span) was found rather large for dispersions conducted in  $\text{scCO}_2$  at 200 bar (entries sc2–sc5). However, an increase of the pressure (250 bar) leads to a narrowing of the particle size (entries sc6–sc7). This pressure effect can be explained by a better solubility

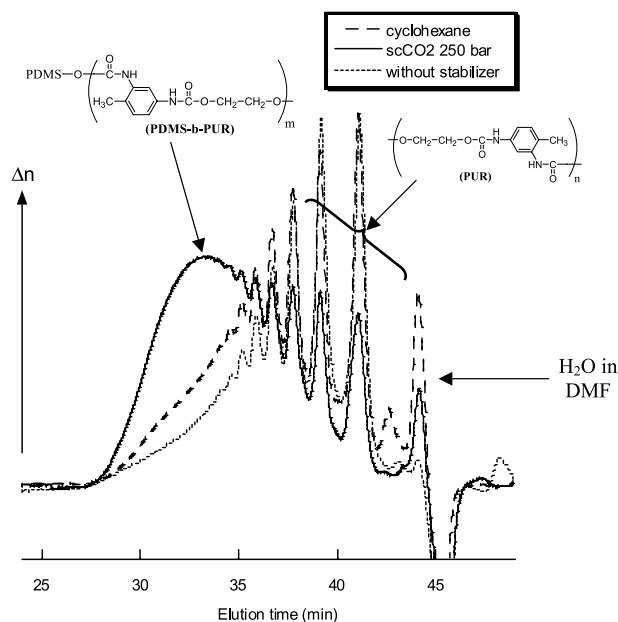


Fig. 5. SEC traces of PUR samples obtained in  $scCO_2$  (at  $60^\circ C$  and 250 bar, plain line), in cyclohexane (at  $60^\circ C$ , dashed line) and without stabilizer (in  $scCO_2$  at  $60^\circ C$  and 250 bar, dotted line) from the system: EG/TDI/PDMS (10 wt%) over 7 h.

of the surfmer and therefore avoiding an agglomeration phenomenon [16]. A SEM picture of PUR-PDMS particles obtained in  $scCO_2$  at 250 bar is given in Fig. 8.

The final yields in PUR particles were found lower in  $scCO_2$  than in cyclohexane. Besides, the weight fraction of incorporated PDMS in the particles, estimated from  $^1H$  NMR analysis, was found apparently higher than the theoretical value (equal to the weight percent of stabilizer introduced). Two hypothesis can be postulated to explain this observation: (i) a fraction of oligourethanes non-captured in the particles are eliminated in the serum during

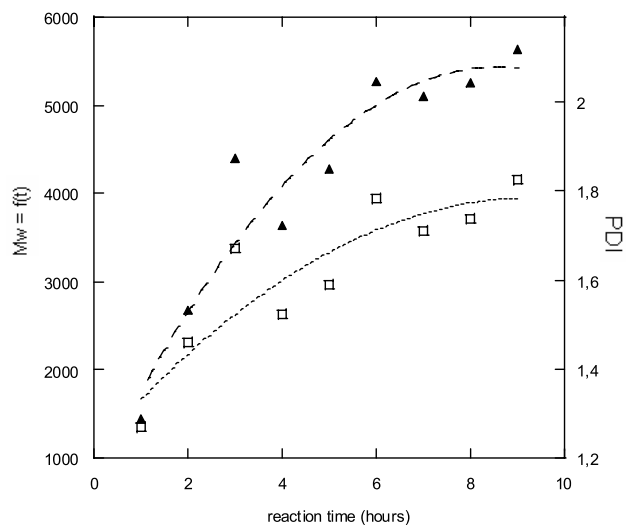


Fig. 6.  $\bar{M}_w$  and PDI ( $\blacktriangle$ ) evolution versus time of PUR-PDMS samples obtained from the system TDI/EG/PDMS-OH (9.1 wt%) in cyclohexane  $60^\circ C$  (results obtained before centrifugation).

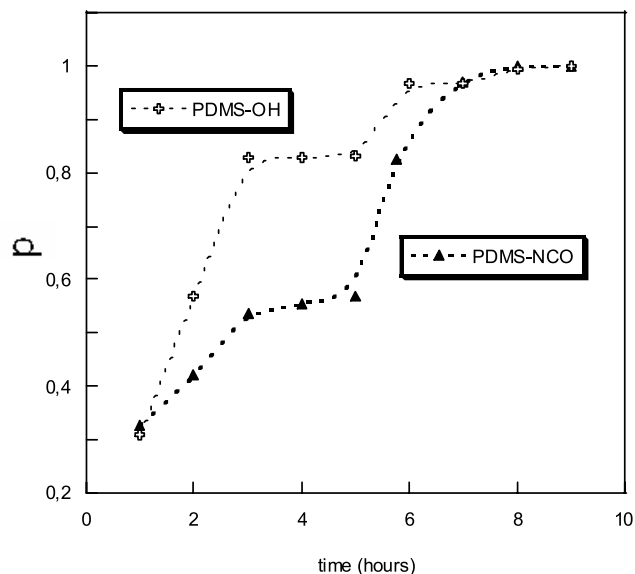


Fig. 7. Reaction extent,  $p$ , versus polymerization time for step-growth polymerizations between EG and TDI in the presence of PDMS-OH or PDMS-NCO (9.1 wt%) as a surfmer carried out in cyclohexane at  $60^\circ C$ .

the recovering treatment procedure—hypothesis in accord with the final lower particle yield and/or (ii) a fraction of PDMS chains remain trapped within the particle due to the swelling ability of  $scCO_2$ . At the stage of our investigations, none of these hypothesis can be ruled out. The SEC characterizations of the materials prepared in  $scCO_2$  are in agreement with NMR data and show a more important content of higher molar mass polymer (see Fig. 5 and data in Table 2). It is clearly noticeable on the SEC traces that less oligourethanes are present in the particles prepared in  $scCO_2$  compared to samples issued from dispersions in cyclohexane. It could be also speculated that the procedure optimized in cyclohexane was not totally effective in  $scCO_2$ . Therefore

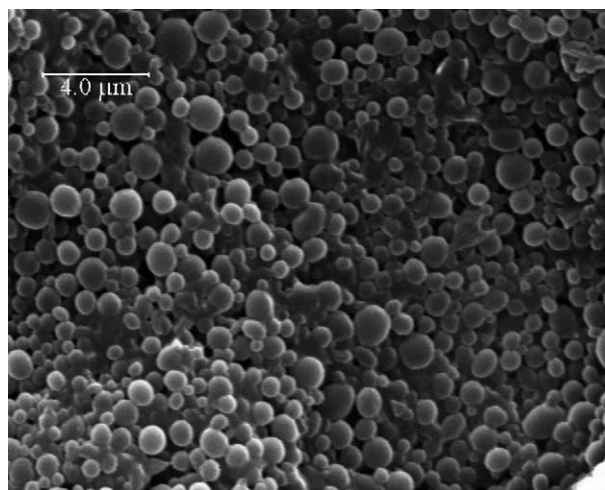


Fig. 8. Scanning electronic micrograph of polyurethane-polydimethylsiloxane particles synthesized in  $scCO_2$  at 250 bar and  $60^\circ C$  from the system TDI/EG/DBTDL with 9.1 wt% of PDMS-NCO (4670 g/mol) surfmer (entry sc6).

Table 2

Data of dispersion step-growth polymerization between tolylene-2,4-diisocyanate and ethylene glycol carried out in  $\text{scCO}_2$  (80 g) in the presence of functional PDMS surfmer, at 60 °C and for 7 h (cat. DBTDL, 500 rpm,  $[\text{NCO}]/[\text{OH}] = 1.1$ )

Entry and pressure (bar)	Precursor	$\bar{M}_n$ of PDMS-OH (g/mol)	wt% of PDMS-NCO introduced	wt% of PDMS incorporated <sup>a</sup>	Yield (%) <sup>b</sup>	Particle average size ( $\mu\text{m}$ ) <sup>c</sup>	Span ( $\mu\text{m}$ – $\mu\text{m}$ )	$\bar{M}_w$ (g/mol) <sup>d</sup>	$\bar{M}_w/\bar{M}_n$
sc1 (200)	PDMS-NCO	–	–	–	52	No particle		3400	2.2
sc2 (200)	PDMS-NCO	4670	4.8	9	55	0.9	0.3–1.5	4500	2.3
sc3 (200)	PDMS-NCO	4670	9	11	70	0.9	0.3–1.5	4200	2.3
sc4 (200)	PDMS-NCO	4670	16.7	30	67	0.9	0.3–1.5	4800	2.6
sc5 (200)	PDMS-NCO	1000	9	17	60	1.0	0.3–1.5	5500	2.9
sc6 (250)	PDMS-NCO	4670	9	21	50	0.7	0.5–1.0	6500	2.0
sc7 (250) <sup>e</sup>	PDMS-NCO	4670	9	13	50	0.7	0.5–1.0	6700	2.3
sc8 (250) <sup>f</sup>	PDMS-NCO	4670	9	13	59	No particle		5300	2.7
sc9 (250)	PDMS-OH	4670	9	5.8	45	No particle		2800	1.8

<sup>a</sup> Determined by  $^1\text{H}$  NMR relative integration from the final particles (i.e. after three centrifugation/re-dispersion cycles in cyclohexane).

<sup>b</sup> PUR particles recovered after three centrifugation/re-dispersion cycles in cyclohexane (yield=weight of washed product vs weight of monomers+surfmer).

<sup>c</sup> Determined by SEM and TEM analysis; average values estimated over 100 particles.

<sup>d</sup>  $\bar{M}_w$  values of the chains constituting the PUR-PDMS particles (i.e. after three centrifugation/re-dispersion cycles in cyclohexane); SEC in DMF (0.7 mL/min; calibration PS).

<sup>e</sup> Twenty hours experiment.

<sup>f</sup> ‘Reversed process’: PDMS-NCO+TDI (1 lot), then addition of EG (in 2 lots).

the reversed monomer addition was tested (entry sc8), i.e. PDMS-NCO and TDI were first mixed together and EG was then added in two stages. This novel procedure was found not effective since the reaction product was not observed under the shape of particles.

Similarly to the experiments carried out in cyclohexane, the polymerizations monitored in  $\text{scCO}_2$  were followed by means of in situ FTIR spectroscopy. This kinetic study could be achieved through the use of a stainless steel cell equipped with two sapphire windows with a pathlength of 4.5 mm, which allowed us to follow the growth of the broad band centred at  $3300\text{ cm}^{-1}$  associated with the N–H stretching vibration, resulting from the increasing formation

of urethane linkages (see Fig. 9). In this kinetic study, only one injection of TDI was realized at the beginning of the reaction. It is noteworthy that 5 min after the injection of TDI, the infrared spectrum in the wavenumber range  $3150\text{--}3500\text{ cm}^{-1}$  is mainly composed of three narrow peaks centred at  $3450$ ,  $3350$  and  $3180\text{ cm}^{-1}$  superimposed over a broad component centred at about  $3325\text{ cm}^{-1}$ . All these bands can be assigned to the NH stretching mode of the urethane functional group [17]. The narrow bands are associated with NH groups which are ‘free’ from hydrogen bonds with surrounding molecules whereas the broad component can be assigned to NH groups interacting with other urethane functional group of the same or another

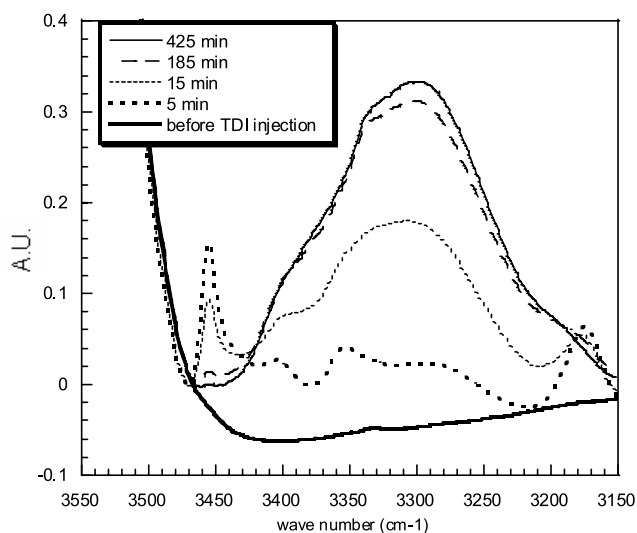


Fig. 9. FTIR spectra recorded in  $\text{scCO}_2$  during the step-growth polymerization between EG and TDI in the presence of PDMS-NCO as the surfmer ( $T=60\text{ }^\circ\text{C}$ ,  $P=250\text{ bar}$ , under magnetic stirring).

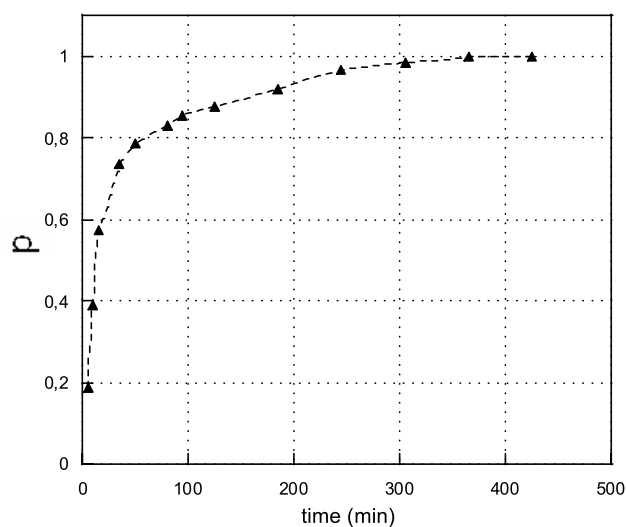


Fig. 10. Kinetic curve for step-growth polymerization between TDI and EG carried out in supercritical carbon dioxide at 250 bar and 60 °C in the presence of PDMS-NCO as the surfmer.



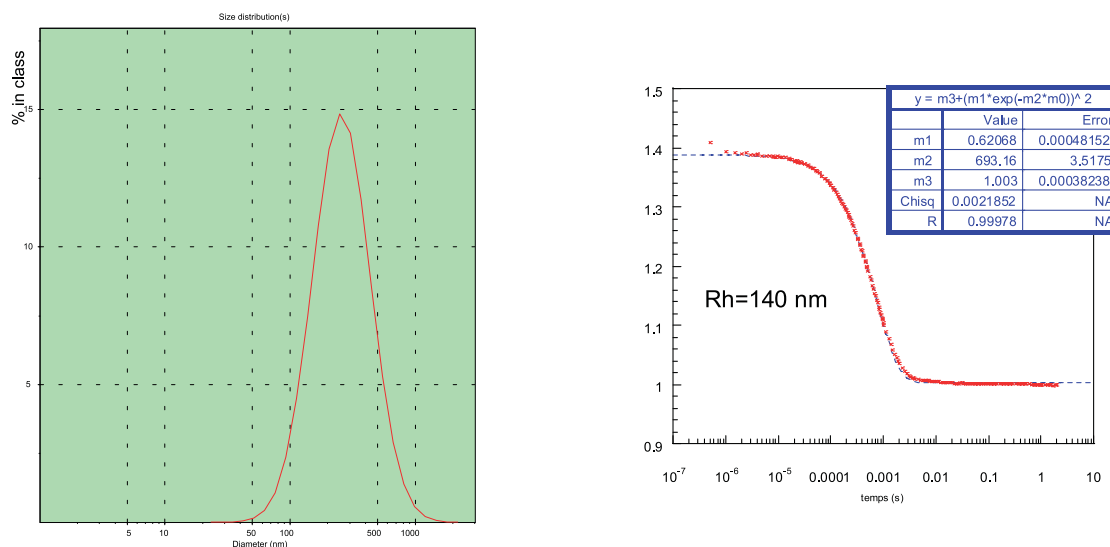


Fig. 11. Dynamic light scattering measurements and autocorrelation curve obtained from the system PDMS-NCO (4670 g/mol) + 1 equiv TDI in solution in cyclohexane (10 mg/mL) at 25 °C.

polyurethane chain through hydrogen bonds with the carboxyl group. Therefore, at the beginning of the reaction, only small oligomers of polyurethane are formed leading to the observation in the infrared spectrum of only free NH groups. However, at longer reaction time, the concentration and the size of polyurethane chains increases allowing the formation of intra and/or inter chain hydrogen bonds which lead to the increase of the intensity of the broad component centred at about  $3325\text{ cm}^{-1}$ . Thus, the reaction extent was determined from the evolution of the intensity of this broad component. Similarly to results obtained in cyclohexane, the plot given in Fig. 10 shows that a plateau is reached after 7–8 h.

#### 4. Discussion

The use of hydroxy- and isocyanate-terminated polydimethylsiloxane (PDMS-OH and PDMS-NCO, respectively) as surfmers for the step-growth polymerization between ethylene glycol and tolylene-2,4-diisocyanate carried out in dispersant media such as cyclohexane or supercritical carbon dioxide ( $\text{scCO}_2$ ), allowed us to synthesize new polyurethane-based materials under the shape of calibrated particles. These investigations have clearly underlined that the dispersant medium nature (cyclohexane or  $\text{scCO}_2$ ) as well as the affinity of the 'so-called surfmer' towards the dispersant medium are important parameters to tune, for the production of calibrated particles.

Indeed, while PDMS-OH ( $M_n = 4670\text{ g/mol}$ ) enables the preparation of monodispersed particles in cyclohexane, it is not effective in  $\text{scCO}_2$ . Reversibly, PDMS-NCO plays effectively its surfmer role in both dispersant media.

The fact that PDMS-NCO leads, in cyclohexane, to

smaller particles than PDMS-OH does, can be logically explained by a better affinity of PDMS-NCO (compared to its homolog PDMS-OH) with the growing particles. To further discriminate between the two reactive PDMS, we carried out a series of dynamic light scattering (DLS) measurements of cyclohexane solutions at 25 °C containing either PDMS-OH or PDMS-NCO ( $M_n = 4670\text{ g/mol}$ ) at various weight concentrations (1 equiv of TDI was present within the PDMS-NCO solution in order to mimic the synthetic procedure). After several hours under stirring at 25 °C, no specific organization of the surfmer, either PDMS-OH or PDMS-NCO, could be detected. This observation allows us to rule out a micellar nucleation mechanism.

Nevertheless, after longer time (several days) under stirring, while no specific self-assembly of PDMS-OH could be again detected in cyclohexane, large aggregates of PDMS-NCO with a hydrodynamic radius  $R_H = 140\text{ nm}$  formed in cyclohexane, as shown in Fig. 11. The formation of such aggregates in cyclohexane highlights the poor affinity of PDMS-NCO towards this solvent. Interestingly, it could be checked that dispersions performed with such 'aged PDMS-NCO' solution do not yield any calibrated polyurethane particles. This fact demonstrates that PDMS-NCO chains, once aggregated, are no more available to stabilize the growing polyurethane particles and a coagulation phenomenon occurs.

The effect of PDMS weight percentage has also a very little effect on the particle size whatever the dispersion medium (cyclohexane or  $\text{scCO}_2$ ). This fact is not in agreement with our previous investigations, which demonstrated the sensitive effect of the surfmer concentration onto the PUR particle size [12,13]. Indeed, in the case of PS-OH and PnBuA-OH used as surfmers, an increase of the surfmer weight concentration yields a decrease of the particle average diameter, in agreement with a higher particle

surface coverage. In addition and conversely to findings with PDMS-OH, the derivatization of PS-OH and PnBuA-OH into PS-NCO and PnBuA-NCO, respectively, was found required, prior to the dispersion, to ensure the formation of calibrated core-shell particles. These different behaviors according to the surfmer nature can be correlated to the solubility parameter differences between the surfmers—PDMS ( $\delta = 14.9 \text{ MPa}^{1/2}$ ), PS ( $\delta = 18.2 \text{ MPa}^{1/2}$ ), PnBuA ( $\delta = 20.4 \text{ MPa}^{1/2}$ )—and cyclohexane ( $\delta = 16.8 \text{ MPa}^{1/2}$ ). In the case of experiments carried out in the presence of PDMS, due to the poor solubility of PDMS in cyclohexane ( $\Delta\delta = \delta_{\text{cyclohexane}} - \delta_{\text{PDMS}}$ ), the higher particle surface coverage is reached for a critical concentration of surfmer (i.e. between 4.8 and 9 wt% in the case of PDMS-OH and below 5 wt% for PDMS-NCO).

In the specific case of dispersions carried out in  $\text{scCO}_2$ , it was clearly shown that high pressures ( $> 200 \text{ bar}$ ) are required to control the average particle size and its distribution, highlighting the relationship between the pressure and the solvation effect. The order of monomer addition was also found crucial to avoid coagulation phenomenon. Indeed, a control of the particle formation was only obtained when the di-isocyanate (TDI) was added last, drop-wise in cyclohexane and in two lots in  $\text{scCO}_2$ . One can speculate that a slow addition of TDI in  $\text{scCO}_2$  (not possible with our set-up) could also lead to the formation of calibrated particles while using PDMS-OH as a surfmer.

As a conclusion, it is worth noting that  $\text{scCO}_2$  was found quite attractive not only as a substitute of organic media for dispersion polymerizations but also as an effective mean to produce polyurethane-*b*-polydimethylsiloxane block copolymers under the form of spherical core-shell particles. Such materials have potential applications as biomaterials. Further investigations will be discussed in forthcoming papers.

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