

SYNTHESIS OF POLYURETHANE PARTICLES IN SUPERCRITICAL CARBON DIOXIDE

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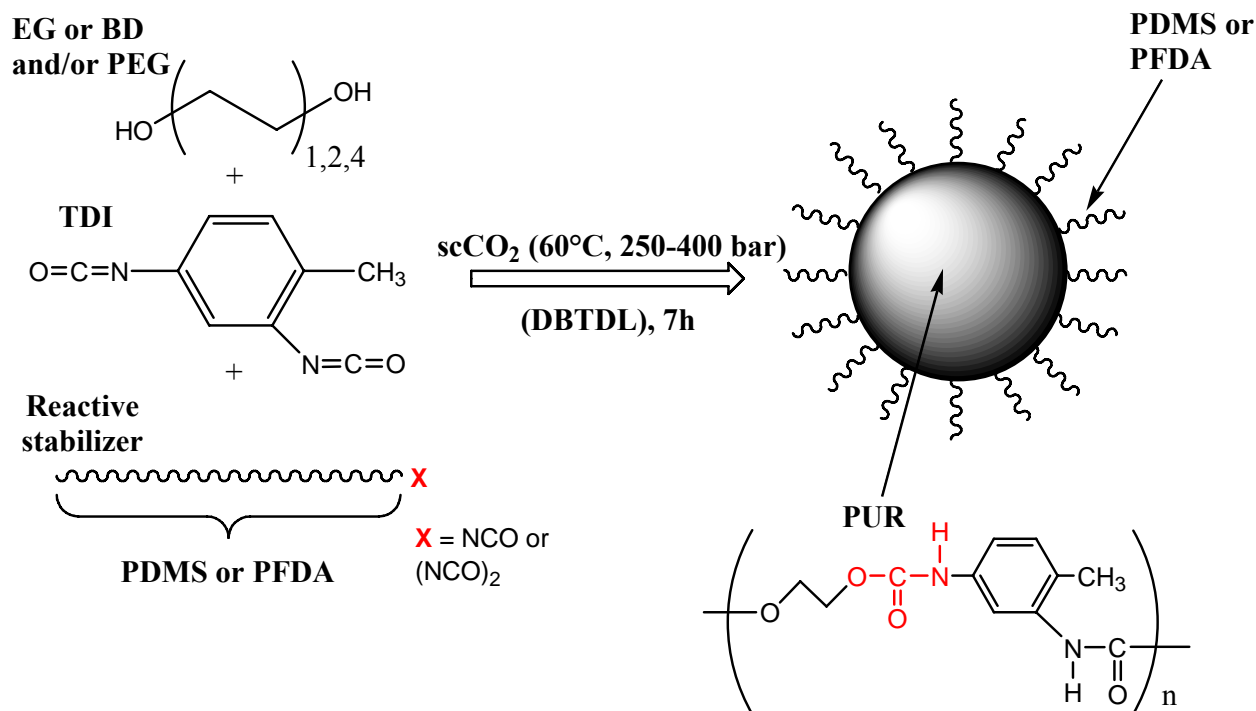
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INTRODUCTION:

Polycondensates such as polyamides, polyesters or polyurethanes are important industrial materials. Their synthesis through "green" and clean synthetic processes is a main challenge. In this context, we investigated the synthesis of polyurethane by dispersion polymerization in cyclohexane and supercritical carbon dioxide (scCO₂) as dispersant media. As indicated below (see Scheme 1), a series of diols and di-isocyanates have been tested in the presence of various reactive stabilizers (surfmers), with respect to the dispersant medium. Depending on specific parameters (nature, functionality, molar mass and concentration of the surfmer, CO₂ pressure, etc.), the polyurethane particle size can be tuned from 100 nm to 5 μm with a low size distribution.



Scheme 1: Route to polyurethane particles in scCO₂

MATERIALS AND METHODS

Tetrahydrofuran (THF) (J. T. Baker, 99%), was first distilled over CaH₂ and then distilled over sodium-benzophenone. Cyclohexanone (Aldrich) was distilled over sodium sulphate. α,α,α -Trifluorotoluene (TFT – Aldrich 99%) and 1,1,2-trichlorotrifluoroethane (F113 – Aldrich 99%) were used as received. 1,1,2,2-tetrahydroperfluorodecyl acrylate (FDA - Atochem) was distilled under reduced pressure and passed through a column of neutral alumina to remove inhibitor. Ethylene glycol, 1,4-butanediol, α,ω -dihydroxy-terminated polyethylene oxide (PEO, $M_n = 200$ g/mol), tolylene-2,4-diisocyanate, dibutyltin dilaurate (DBTDL) and monohydroxy-terminated polydimethylsiloxane (PDMS – $M_n = 4670$ g mol⁻¹) were purchased from Sigma-Aldrich and used as received. ω,ω' -dihydroxy-terminated PDMS ($M_n = 3200$ g mol⁻¹) was generously supplied by Shin-Etsu Chemical Co. Ltd.. Liquid CO₂ (Air Liquide, for supercritical fluids) was cooled with a Minichiller and then compressed to the required pressure with a Dosapro Miltonroy pump.

Syntheses of reactive stabilizers for dispersion polymerization in scCO₂ have been reported elsewhere.^{[2],[3]}

Typical polymerization procedure in scCO₂

The reactor (Top Industrie SA, 118 mL) is charged with the diol (0.01 mol) and DBTDL (1.5% with respect to monomers) if used. The pressure is increased to the CO₂ bottle pressure and the reactor is heated to 60 °C and stirred at 250 rpm. The pressure is then adjusted to 25 MPa. After 30 min stirring, the PDMS stabilizer (10 wt% vs. monomers) is injected in the reactor by over pressurizing a 12 mL cell. The pressure is then adjusted to 30 MPa. In the same manner, TDI (0.011 mol) is added after 30 mn and the pressure is fixed to 40 MPa for 7 h. The reactor is then cooled down to room temperature and slowly depressurized to atmospheric pressure. Then, the reaction product is removed, re-dispersed in cyclohexane and washed 2 times by centrifugation/re-dispersion cycles. The general synthetic pathway is given in Scheme 1.

Characterizations

The molar masses of the polymers were determined by size exclusion chromatography (SEC) in dimethyl formamide (DMF) at 60°C (flow rate 0.7 mL/min) with lithium bromide as a chaotropic salt (1g/L) on a Varian apparatus equipped with a refractive index detector and three TOSOHAAS TSK gel columns in series calibrated by means of narrow polystyrene standards. The molar masses of the surfactants were determined by SEC in pure tetrahydrofuran at room temperature using the same apparatus.

¹H NMR spectra were recorded using a Bruker AC-400 NMR spectrometer.

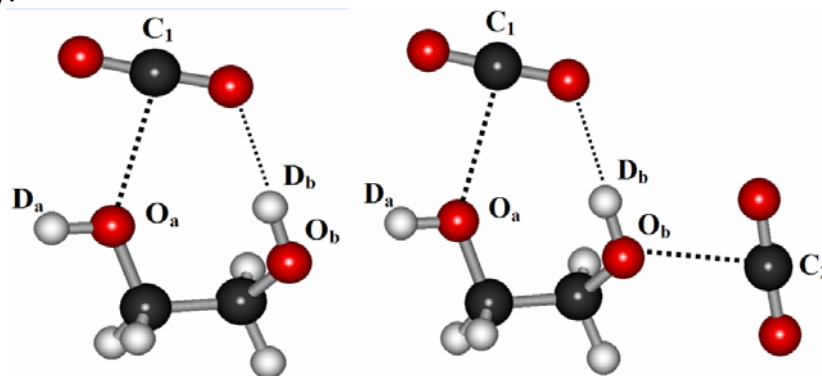
Scanning electronic microscopy (SEM) analyses were carried out on a JEOL JSM 2500 apparatus.

Dynamic light scattering (DLS) experiments were performed using ALV Laser Goniometer, which consists in a 22 mW HeNe linear polarized laser with 632.8 nm wavelength and an ALV-5000/EPP Multiple Tau Digital Correlator with 125 ns initial sampling time. The samples were kept at constant temperature (25°C) during all the experiments. The solutions were introduced into 10 mm diameter glass cells. Experiments were carried out with a PUR-PDMS sample (entry S9) diluted in DMF at concentrations of 2, 10 and 20 mg/ml at 40° and 90°. The data acquisition was done with the ALV-Correlator Control Software, and the counting time was 150 s for each sample. The analysis of the autocorrelation functions $C(q,t)$ where q is the scattering vector and t the time was carried out following the cumulant method. The thermal phase behaviour of PUR materials was investigated using a TA instruments Q100 differential scanning calorimeter operating at a heating and cooling rate of 10°C.min⁻¹. Polymer samples were subjected to two heating and cooling cycles between 20 and 250°C. Glass transitions were recorded from the second heating scan using the midpoint inflection method.

Mid-infrared absorption spectroscopic investigation in $scCO_2$ of the polymerizations between EG and TDI in the presence of PDMS-NCO at $60^\circ C$ were performed in situ on a FTIR (Bio-Rad: FTS-60A) spectrometer using a titanium cell previously described.

RESULTS:

In the specific case of dispersions in $scCO_2$, we have studied the role played by this dispersant in the synthesis of polyurethane particles.^{[1],[4]} High temperature-high pressure *in situ* infrared spectroscopic measurements combined with *ab initio* calculations were performed to investigate the hydroxyl stretching vibrations of ethylene glycol (EG) and 1,4-butanediol (BD), the two diols commonly used. Specific interactions between the diols and CO_2 have been put in evidence. While the structural characteristics of EG and BD are very similar - both diols have a gauche conformation due to an internal H-bond between the two hydroxyl functions - they behave differently in the presence of dense CO_2 . In the case of EG, this internal H-bond is broken, allowing the diol and CO_2 to form a complex through the conjunction of a Lewis acid-Lewis base (LA-LB) interaction and a new H-bond. When BD complexes to CO_2 , internal H-bond remains and is even reinforced indirectly by the LA-LB interaction occurring between the two moieties. In both cases, such a complex formation induces a polarization of the hydroxyl groups and consequently an increase of their nucleophilicity.



Scheme 2: Specific interactions between one or two molecules of CO_2 and ethylene glycol (EG)

Among the various key parameters that have been tuned emphasis was placed on both the **reactive stabilizer** (*i. e.* its nature, functionality, size, amount, etc.) and the nature of the **diol** monomer used (see Scheme 1).

On the one hand, two types of reactive stabilizers have been investigated either based on silicon or fluorinated derivatives (*i.e.* isocyanate-terminated polydimethylsiloxane (PDMS-NCO_x with $x=1$ or 2) and isocyanate-terminated poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) (PFDA-NCO)).^{[2],[3]}

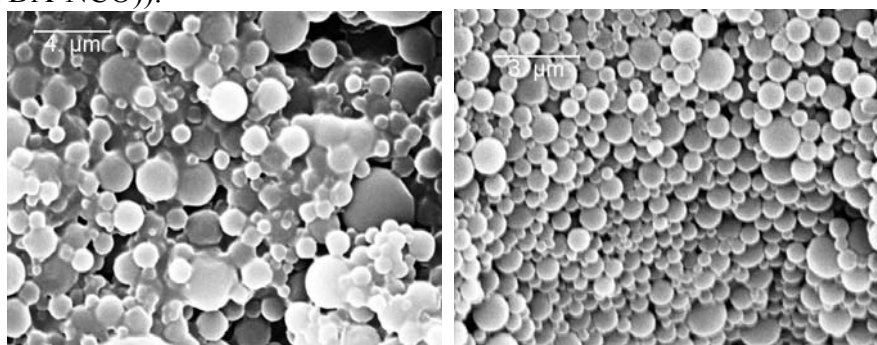


Figure 1: Scanning electronic micrographs of polyurethane-polydimethylsiloxane particles synthesized in $scCO_2$ at 40 MPa and $60^\circ C$ from the system TDI/EG/DBTDL with 10% of PDMS-NCO (left) and PDMS-(NCO)₂ (right) as surfmers.

It is noteworthy that it is necessary to end-functionalize the stabilizer with an isocyanate moiety in order to form stable polyurethane latexes. In the case of PDMS-NCO used as the reactive stabilizer doubling the functionality of the reactive stabilizer (*i.e.* using PDMS-NCO₂) significantly enhances the ability of the PDMS to anchor to the growing chains and improvement of the morphology in the resulting polymer product was thus observed (Fig. 1).^[2] PFDA's were not only shown interesting as reactive stabilizers but also because they can give rise to super-hydrophobic materials once PUR-PFDA particles are deposited onto a silica plate. Contact angles of a 4 μ L water droplet as high as 154° have been measured (Fig. 2).^[3]

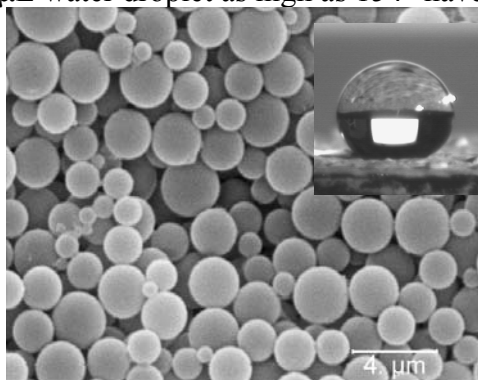


Figure 2: Scanning electronic micrograph of PUR-PFDA particles synthesized in scCO₂ at 40 MPa and 60°C from the system TDI/BD/DBTDL with 10% of PFDA-NCO as reactive stabilizer. Insert image shows a 4 μ L water droplet on a silica sheet surface covered with the corresponding PUR-PFDA particles.

On the other hand, as carbon dioxide is a mediocre solvent for macrodiols, only short aliphatic diols were investigated as monomers in this study: EG, BD and PEO (M_n = 200 g.mol⁻¹). The effect of the diol on the molar mass and morphology of the obtained PUR materials was investigated. The SEC traces of some of the samples are shown in Figure 3. Molar masses of PUR materials obtained in scCO₂ were comprised between 16000 and 28000 g.mol⁻¹.

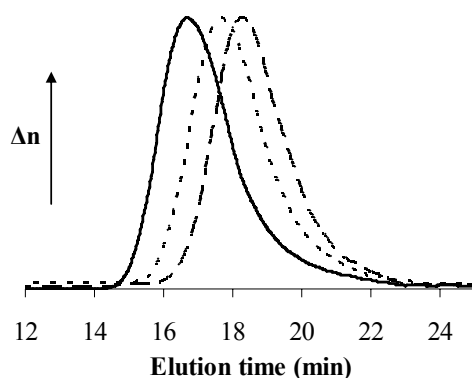


Figure 3: SEC traces of PUR samples obtained in scCO₂ at 60 °C and 40 MPa (BD - plain line, EG - dashed line, PEO - dotted line) in DMF at 60°C.

Interestingly, high molar mass polymers were obtained using BD as a diol monomer. Indeed, as explained above in terms on specific interactions between diols and CO₂, one can suppose that the activation of the diol by CO₂ enables the oligomeric chains formed in the early stages of the reaction to reach relatively high degrees of polymerization before they precipitate. When EG is used as a monomer, it results in highly cohesive materials due to high contents in urethane linkages. Using BD would decrease the density of urethanes linkages within the polymer. It thus would allow a more significant swelling of the particles by CO₂ and so a better diffusion of the monomer within the polymer. Conversely, despite this swelling should be even more pronounced as PEO is used as a diol, diffusion of the monomer into the particle

might be hindered by the relatively high molar mass of the monomer itself. Thus, when compared to the use of EG or PEO as monomers, polymerizations with BD allow a relevant increase of the molar mass of the resulting PUR materials

The effect of the diol on the thermal behaviour of the resulting PUR particles was also investigated by differential scanning calorimetry (DSC). All samples exhibit only one T_g and do not show crystallization or melting temperature, indicating the totally amorphous nature of the polymer. Glass transition temperature peculiar to PDMS (i. e. $T_g = -123^\circ\text{C}$) could not be observed in agreement with the low amount of stabilizer finally found in the material. Polyurethanes are highly cohesive due to the formation of intermolecular hydrogen bonding and a logical decrease of the T_g was observed (from 146°C to 49°C using EG and PEO respectively) as the length of the diol incorporated increased, i. e., as the density of urethane linkages decreased. In order to tune the thermal properties of the obtained PUR particles, the molar ratio of PEO/EG introduced at the beginning of the reaction was varied. Whatever the value of the ratio, only one T_g was observed, confirming that there is no phase segregation within the particles. A quasi-linear decrease of the glass transition temperature is shown as the concentration of PEO increases (Figure 4).

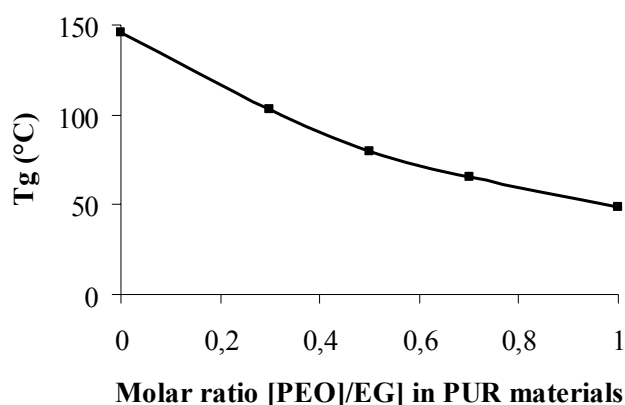


Figure 4: Evolution of the T_g of PUR samples depending on the PEO/EG molar ratio.

CONCLUSION:

Series of PUR-PDMS and of PUR-PFDA copolymers under the form of particles were prepared in scCO_2 varying several parameters such as the pressure, the stabilizer amount and functionality and the nature of the diol. The pressure was found to have little influence on the final product. On the contrary, the functionality of the stabilizer as well as the nature of the diol introduced had a dramatic effect on the resulting material. For instance, the use of BD as a monomer and a gemini type PDMS as a reactive stabilizer enabled the formation of high molar mass amorphous PUR particles. scCO_2 was efficiently shown as a neat medium for dispersion polyaddition and preparation of various interesting polyurethane-based materials of high molar masses and of well-defined spherical morphologies.

REFERENCES:

1. Renault, B.; Cloutet, E.; Cramail, H.; Tassaing, T.; Besnard, M. *J. Phys. Chem. A*, 111(20), **2007**, 4181-4187.
2. Renault, B.; Tassaing, T.; Cloutet, E.; Cramail, H. *J. Polym. Sci.:Part A, Polym. Chem.*, 45, **2007**, 5649-5661.
3. Renault, B.; Cloutet, E.; Lacroix-Desmazes, P.; Cramail, H. *Macromol. Chem. Phys.*, 209(5), **2008**, 535-543.
4. Renault, B.; Cloutet, E.; Cramail, H.; Hannachi, Y.; Tassaing, T. *J. Phys. Chem. A*, 112(36), **2008**, 8379-8386.