

# SYNTHESIS OF CORE-SHELL POLYURETHANE PARTICLES IN $scCO_2$ : MICROSCOPIC UNDERSTANDING OF MOLECULAR INTERACTIONS

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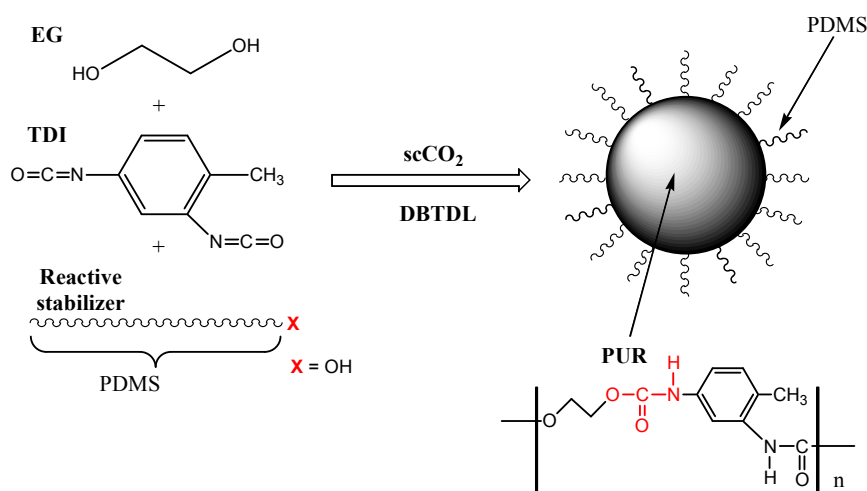
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## INTRODUCTION

Supercritical carbon dioxide ( $scCO_2$ ) has shown great potential as a replacement for conventional aqueous and organic solvents. Not only is carbon dioxide readily available, inexpensive, non-toxic and nonflammable, but also its critical point is also easily accessible ( $T_c = 31.1^\circ C$  and  $P_c = 73.8$  bars) and its physico-chemical properties such as viscosity and density can be readily tuned by pressure and temperature variations. These characteristics make it as the most extensively studied SCF solvent for polymerization reactions [1]. However, to our knowledge, the specific role that  $CO_2$  could play by interacting with the different reactants such as monomers during a polymerization reaction has never been investigated.



**Figure 1:** Step-growth polymerization between EG and TDI in  $scCO_2$

We have previously investigated step-growth polymerization between a diol (ethylene glycol (EG) or 1,4-butanediol) and tolylene-2,4-diisocyanate (TDI) in  $scCO_2$  in the presence of hydroxy-terminated polydimethylsiloxane used as a steric and reactive stabilizer and

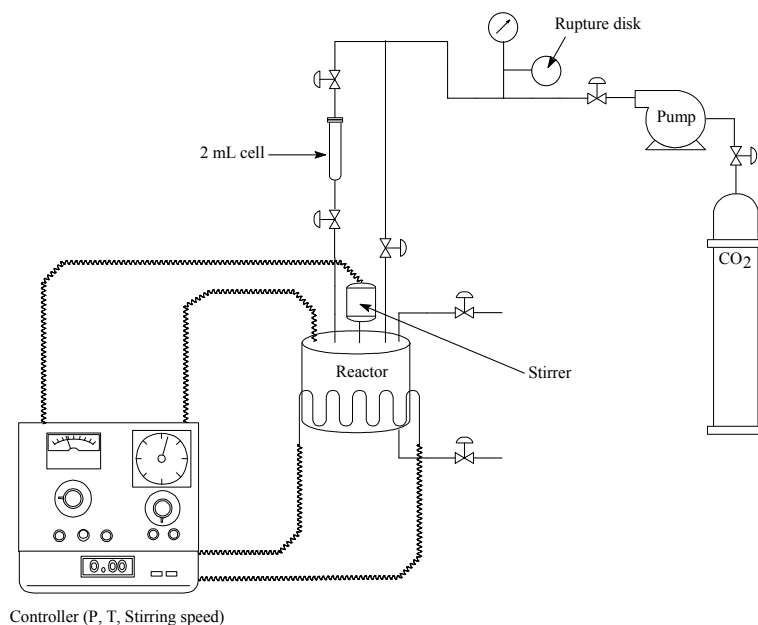
dibutyltin dilaurate (DBTDL) as a catalyst [2, 3]. As a result, original core-shell polyurethane (PUR) particles exhibiting specific surface properties could be obtained (figure 1). More recent studies carried out in our laboratory revealed that such materials could also be achieved at a lower yield with a similar molar mass distribution and a reasonable kinetic without the aid of a catalyst [4].

In order to better understand the role of CO<sub>2</sub> in this polymerization, we investigated by means of infrared spectroscopy interactions occurring in the system between monomers and carbon dioxide. Indeed, vibrational spectroscopy is a powerful tool for probing such questions about solute-solvent interactions, since both intensity and frequency associated with any vibrational mode of the solute depends upon the potential of mean force existing between the solvent and the solute.

## I. MATERIALS AND METHOD

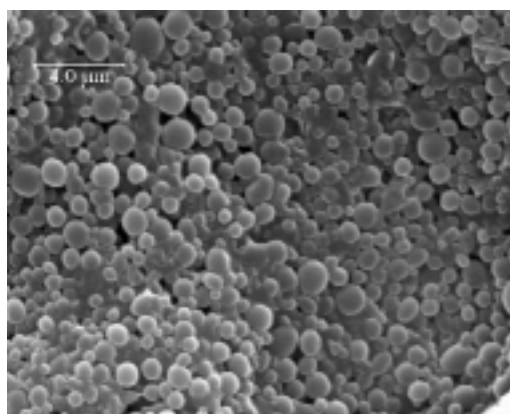
*Materials.* Toluene-2,4-diisocyanate (Sigma-Aldrich) was purified by distillation under vacuum. EG (Sigma-Aldrich, 99 %), monohydroxy-terminated PDMS 4670 g.mole<sup>-1</sup> (Sigma-Aldrich, > 99 %), monohydroxy-terminated PDMS 1000 g.mole<sup>-1</sup> (generously given by The Polymer Technology Group, > 99 %) and dibutyltin dilaurate (Sigma-Aldrich, 98 %) were used as received. Deuterated EG (DOCH<sub>2</sub>CH<sub>2</sub>OD, 98 % purity) was purchased from Sigma-Aldrich. CO<sub>2</sub> (purity 99.9%) and Argon (purity 99.9%) was supplied by Air liquide.

*Typical polymerization procedure in scCO<sub>2</sub>.* The experimental setup is shown in figure 2. 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<sub>2</sub> bottle pressure) and the reactor was heated to 60°C and stirred at 500 rpm. Then the pressure was adjusted to 200 bars.



**Figure 2:** Experimental set-up for the polymerizations carried out in supercritical carbon dioxide.

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 300 bars. After 3.5 h reaction the same addition of TDI was realized and then the pressure was fixed to 350 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  $^1\text{H}$  and  $^{13}\text{C}$  NMR, SEC, DSC, SEM (figure 3), etc...



**Figure 3:** Scanning electronic micrograph of core-shell polyurethane-polydimethylsiloxane particles synthesized in  $\text{scCO}_2$  (@ 250 bar and  $60\text{ }^\circ\text{C}$ ) from the system TDI/EG/DBTDL with 10 wt % of PDMS-NCO surfmer ( $[\text{NCO}]/[\text{OH}]=1.1$ )

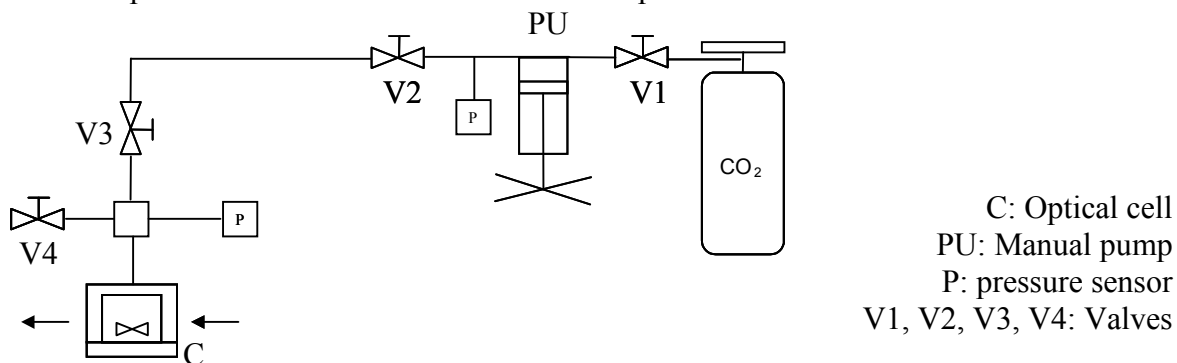
*Spectroscopic measurements.* The measurements were performed on a Biorad interferometer (type FTS-60A) equipped with a globar source, a KBr beam splitter and a DTGS detector. Single beam spectra recorded in the spectral range  $400\text{-}6000\text{ cm}^{-1}$  with a  $2\text{ cm}^{-1}$  resolution were obtained by Fourier transformation of 50 accumulated interferograms.

We used a special titanium cell, which has four cylindrical windows, two silicium windows for the infrared absorption measurements with a path length of 25 mm (which can be varied from 3 to 25 mm) and two sapphire windows for direct observation of the solution to ensure that there is no demixing in the sample. In order to be sure that the solution was at the equilibrium, mixing was performed with a magnetic stirrer put into the cell. The complete experimental set-up is shown in figure 4.

Different steps were performed for obtaining the spectra:

- 1) The vacuum was attained inside the variable volume cell by connecting a vacuum pump to the purge valve V4. The working temperature was selected in the temperature controller. The agitation was switched on. A first spectrum was recorded to ensure the cell is free of any polluting product.
- 2) Once the valve V4 was closed,  $\text{CO}_2$  was slowly added through the valves V2 and V3 up to the atmospheric pressure in order to minimize the insertion of impurities (especially atmospheric water) during the injection of monomer. The cell was then disconnected and the monomer was injected.
- 3) The cell was filled up with  $\text{CO}_2$  to the working pressure. The stabilization of the operating conditions has been controlled by recording consecutive spectra. Since it is known that a variation of the density of an interactive SCF solvent induces strong variations in the intensity and frequency of the normal mode of the solute, spectra of monomers diluted in  $\text{CO}_2$  have

been collected at a constant temperature ( $T=60^{\circ}\text{C}$ ) and at different pressures (9MPa, 11MPa, 13MPa, 16MPa, 20MPa, 25MPa and 30MPa) in order to point out the interactions between the two moieties. The diol hydroxyl stretching band and the TDI isocyanate symmetrical stretching band have been obtained respectively by removing from the spectrum of the binary mixture the spectrum of the neat solvent at the same pressure.



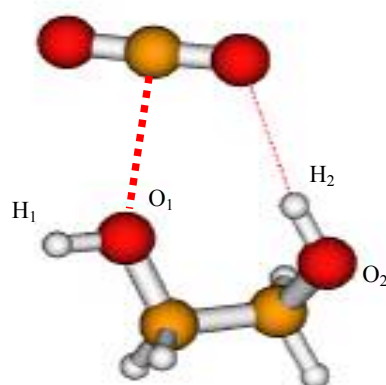
**Figure 4:** High-pressure spectroscopic set-up.

*Computational details.* *Ab initio* calculations have been carried out using the Gaussian 2003 program suite [5]. Preliminary geometry optimizations were carried out at the Hartree-Fock (HF) level using 6-31G\*\* basis sets for both hydrogenated and deuterated EG ( $\text{C}_2\text{H}_4\text{O}_2\text{D}_2$ ) and 6-31+G\*\* for 1,4-butanediol. More exact calculations of geometry, energies, and vibrational frequencies were performed at the second-order Moller-Plesset (MP2) [6] level to include the effects of electron correlation. The geometry optimization calculations have been achieved using the augmented correlation-consistent polarized Valence Double basis sets (aug-cc-VDZ) proposed by *Dunning and co-workers* [7-10]. The initial configuration used for EG was the lowest energy conformer previously reported by several authors who investigated the conformational properties of EG using *ab initio* and Density Functional Theory (DFT) [11-13]. Stabilization energy of the EG- $\text{CO}_2$  complex investigated here was calculated using the “supermolecule” method as the difference in energy between each complex and the sum of the isolated monomers. The basis set superposition errors (BSSE) were calculated using the full counter-poise method of Boys and Bernardi. [14]. Finally, vibrational analysis were carried out within the standard Wilson FG matrix formalism [15] from the appropriate optimized structures of the complex and their corresponding individual moieties using the MP2/aug-cc-VDZ level of calculations.

## II. RESULTS AND DISCUSSION

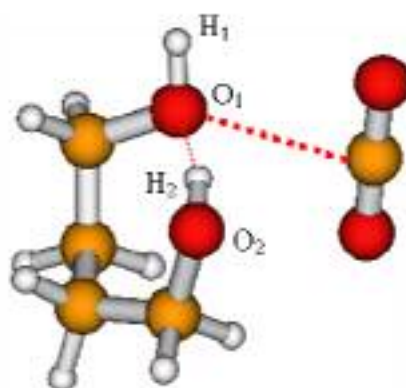
From the analysis of the IR spectra of EG solutions diluted in  $\text{CO}_2$  combined with *ab-initio* calculations, we have put in evidence the existence of molecular interactions between the two moieties. This study resulting in the optimized geometry displayed in figure 5 points out the existence of an  $\text{O}-\text{H}\cdots\text{O}$  interaction between the  $\text{H}_2$  hydroxyl proton of the EG moiety and one of the oxygen atoms of  $\text{CO}_2$ . This additional weaker H-bond acts cooperatively with the Lewis acid-base interaction occurring between the  $\text{O}_1$  atom of EG and the carbon atom of  $\text{CO}_2$ . The *ab initio* binding energy of the complex relative to the infinitely separated molecules for the geometry optimized at the MP2/aug-cc-pVDZ level is -3.46 kcal/mol, including the Lewis acid- base and H-bond interactions. Although it is difficult to assign separate energies to individual interactions, we may compare the interaction energy of the EG- $\text{CO}_2$  pair with that obtained for the ethanol- $\text{CO}_2$  dimer at the same level of calculation. An

Electron-Donnor-Acceptor (EDA) interaction takes place [16]. Therefore, we can estimate the contribution due to the cooperative hydrogen bond to be about -0.5 kcal/mol. Interestingly, this complex formation leads to a relevant increase in the partial positive charge at the hydrogen atoms and in the partial negative charge at the oxygen atoms of EG. Binding of the oxygen atom  $O_2$  with a second molecule of  $CO_2$  further accentuates the polarization of the whole hydroxyl  $O_2-H_2$ . This significant increase in the partial charges of the reactive functions of the monomer when it is complexed with  $CO_2$  induces an enhancement of its reactivity. This promoting effect may be quite general with respect to Lewis base group that can interact with  $CO_2$ . In addition, cooperative interactions such as hydrogen bonding will enhance this effect, allowing the synthesis of polyurethane nanoparticles without the help of a catalyst.



**Figure 5:** Optimized structure (MP2/aug-cc-pVDZ level) of the  $CO_2$ -EG complex

In the case of 1,4-butanediol, several studies showed evidence for internal hydrogen bonding involving the hydroxyl groups regarding the isolated molecule [17, 18]. According to the IR spectra of the monomer highly diluted in  $CO_2$  combined with *ab initio* calculations, a Lewis acid-base interaction occurs between the  $O_1$  atom of the diol and the carbon atom of  $CO_2$  (figure 6).



**Figure 6.** Optimized structure (MP2/aug-cc-pVDZ level) of the  $CO_2$ -1,4-butanediol complex

The stable intramolecular H-bond mentioned above precludes intermolecular additional interactions between the  $H_2$  atom of 1,4-butanediol and one of the oxygen atoms of  $CO_2$ . However, the high intrinsic reactivity of the diol combined with the promoting effect of carbon dioxide due to the EDA interaction between the two moieties allow the catalyst free synthesis of well-defined core-shell PUR particles.

The IR spectra of TDI highly diluted in scCO<sub>2</sub> do not show any signatures of specific interaction between the monomer and CO<sub>2</sub>. However, some frequency shifts of the vibrational modes of TDI on going from the neat liquid to the solution suggest that scCO<sub>2</sub> does not interact with TDI but acts as a structural breaker of the highly cohesive neat liquid.

## CONCLUSION

Original core-shell PUR materials exhibiting specific properties have been obtained by step growth polymerization between a diol (EG or 1,4-butanediol) and tolylene-2,4-diisocyanate in scCO<sub>2</sub> in the presence of hydroxy-terminated polydimethylsiloxane as a steric and reactive stabilizer. In order to better understand the role of CO<sub>2</sub> in this process, we investigated by means of infrared spectroscopy interactions occurring in the system. Experimental measurements combined with *ab initio* calculations pointed out particular interactions between carbon dioxide and the diols, leading to an enhancement of the reactivity of the latter. Further investigations, especially in terms of kinetic, molar mass, and yield, are in progress to find out to which extent this relevant promoting effect might be turned to advantage in step growth polymerization synthesis in accordance with green chemistry.

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## REFERENCES

- [1] J. L. Kendall, D. A. Canelas, J. L. Young, D. J. M., *Chem. Rev.* **1999**, *99*, 543.
- [2] P. Chambon, E. Cloutet, H. Cramail, T. Tassaing, M. Besnard, *Polymer* **2005**, *46*, 1057.
- [3] P. Chambon, E. Cloutet, H. Cramail, *Macromolecules* **2004**, *37*, 5856.
- [4] B. Renault, T. Tassaing, M. Besnard, E. Cloutet, H. Cramail, **Submitted**.
- [5] M. J. Frisch, *et al.*, Gaussian 03, Revision C.02 ed., **2004**.
- [6] C. Moller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618.
- [7] T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 551.
- [8] A. K. Wilson, T. V. Mourik, T. H. Dunning, *J. Mol. Struct.* **1996**, *388*, 339.
- [9] H. Tatewaki, S. Huzinaga, *J. Comp. Chem.* **1980**, *3*, 205.
- [10] R. A. Kendall, T. H. Dunning, R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796.
- [11] M. A. Murcko, R. A. DiPaola, *J. Am. Chem. Soc.* **1990**, 10010.
- [12] P. Bultinck, A. Goeminne, D. Van de Vondel, *Theochem* **1995**, *357*, 19.
- [13] T. Oie, I. A. Topol, S. K. Burt, *Journal of Physical Chemistry* **1994**, *98*, 1121.
- [14] S. F. Boys, F. Bernardi, *Mol. Phys* **1970**, *19*, 553.
- [15] E. B. Wilson, J. C. Decius, P. C. Cross, *Molecular Vibrations*, Mc Graw-Hill, New York ed., **1955**.
- [16] P. Lalanne, T. Tassaing, Y. Danten, F. Cansell, S. C. Tucker, M. Besnard, *J. Phys. Chem. A* **2004**, 2617.
- [17] A. J. Lopes Jesus, M. T. S. Rosado, M. L. P. Leitao, J. S. Redinha, *J. Phys. Chem. A* **2003**, *107*, 3891.
- [18] M. Traetteberg, K. Hedberg, *J. Am. Chem. Soc.* **1994**, *116*, 1382.