

Synthesis of polyurethanes in supercritical CO₂

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ABSTRACT

Metal-catalyzed copolymerization of epoxides and CO₂ to give polycarbonates has been investigated as a potential method for CO₂ fixation. Analogously, aziridines have been reported to react with CO₂ to give cyclic urethanes, and polymers consisting of urethane and amine units.

INTRODUCTION

Synthetic polymers with engineered microstructures are used in a wide variety of applications, including catalysis, chemical separation, and tissue engineering. The synthesis and processing of these materials is frequently solvent intensive. In addition to reducing solvent emissions, supercritical fluids offer a number of specific physical, chemical and toxicological advantages as alternative solvents for the production of functional porous materials. [1]

Besides its established use as a “green” supercritical fluid, the use of CO₂ as an abundant C₁ feedstock is of environmental importance and a synthetic challenge. [2] Chemical fixation of CO₂ in functionalized polymers with long lifetimes is one of the most viable large-scale approaches. [3]

The use of supercritical CO₂ (scCO₂) as reaction medium and reactant offers the opportunity to manipulate the outcome of reactions, including the polymer structure.[4-7] The purpose of this work is to synthesize new polyurethanes in supercritical CO₂, using as monomers the CO₂ and aziridines. Polyurethane elastomers are among the highest performing medical-grade polymers. They have mechanical and biological properties that make them suitable materials for use in a diverse range of implantable medical devices, as they demonstrate a unique combination of toughness, durability, flexibility, biocompatibility and biostability. [8]

Substituted aziridines copolymerize with carbon dioxide to give copolymers of polyurethane in the presence or absence of catalysts. [9] There are detailed studies about the copolymerisation of 2-methylaziridine with supercritical CO₂. [10-12]

The purpose of this work is to study the structure and copolymerisation of the polyurethane synthesized with 1-(2-hydroxyethyl)aziridine.

MATERIAL AND METHODS

Procedure for copolymerisation:

The polymerisation reaction was carried out in an 11 mL stainless steel high-pressure cell. The aziridine (Aldrich) was introduced. Then the vessel was introduced in a thermostated (80 °C) water bath. When the inside temperature of the vessel stabilizes, this one was charged with CO₂ up to a 100 bar. After stirring for 4 h, the reaction was stopped by venting the CO₂ of the vessel. A white foam was obtained. The crude reaction product was then dissolved in methanol. The polymeric product was purified by reprecipitation by adding the methanol solution to diethyl ether to remove low-molecular-weight products and drying in vacuum.

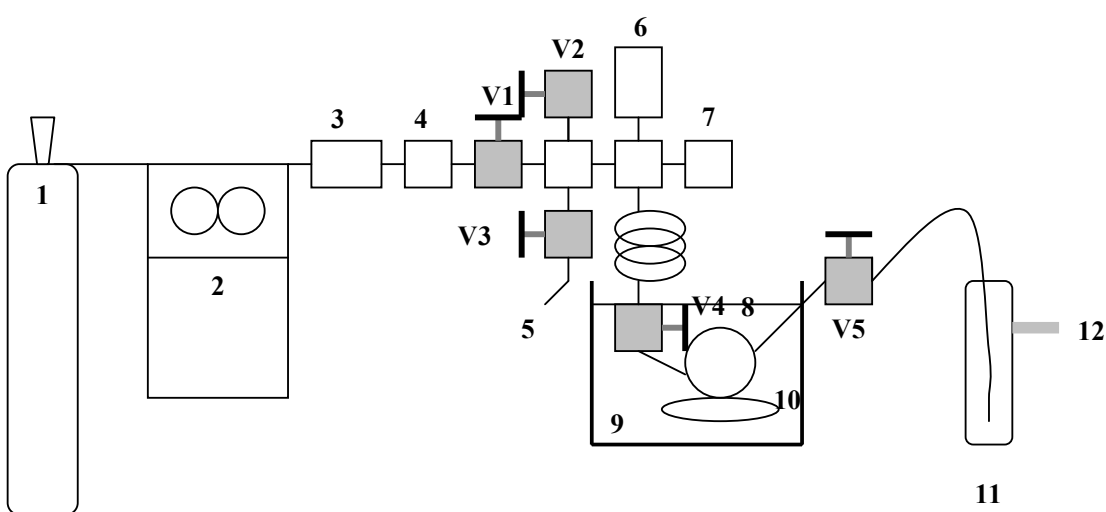


Figure 1. Schematic representation of the apparatus built for the in copolymerisation reactions. 1- CO₂ cylinder; 2- compressor; 3- line filter; 4- check valve; 5- gas entrance (argon or nitrogen) or vacuum exit; 6- high-pressure manometer; 7- rupture disc; 8- high-pressure cell; 9- water bath; 10- immersible stirrer; 11- schlenk; 12- vent; V1 to V5- HIP valves.

Polyurethane analysis:

The composition of the copolymer was determined by elemental analysis in a “Thermo Finnigan Flash EA 1112 Series”. The infrared spectrum was obtained by a microspectrofotometry in a FT-IR “Nicolet Nexus” with a microscope “Continuum” with a diamond cell. The NMR spectrum of a solution in methanol-D₄ was measured by a Burker ARX 400Mz.

RESULTS

In figure 2 it is shown a FT-IR spectrum of the copolymer. It can be observed an absorption peak at 1700 cm⁻¹ that is assigned to a linear urethane linkage (R-O-CO-NH-R), and indicates the insertion of CO₂ in the polymer forming a polyurethane.

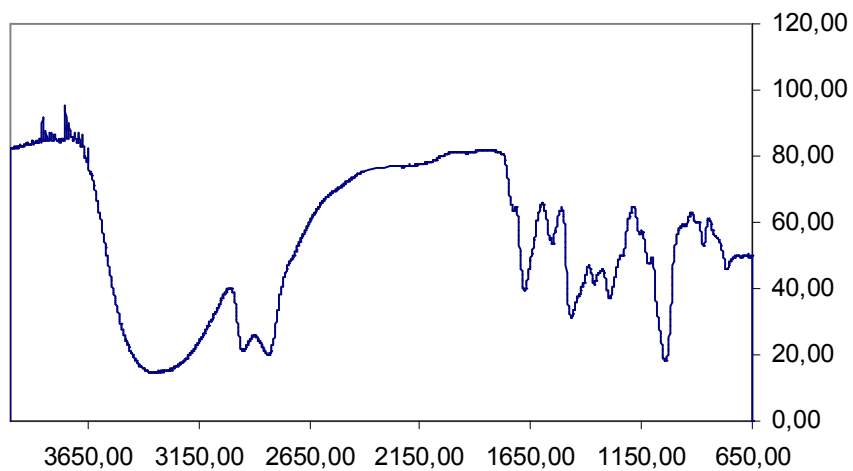


Figure 2. FT-IR spectrum of the copolymer

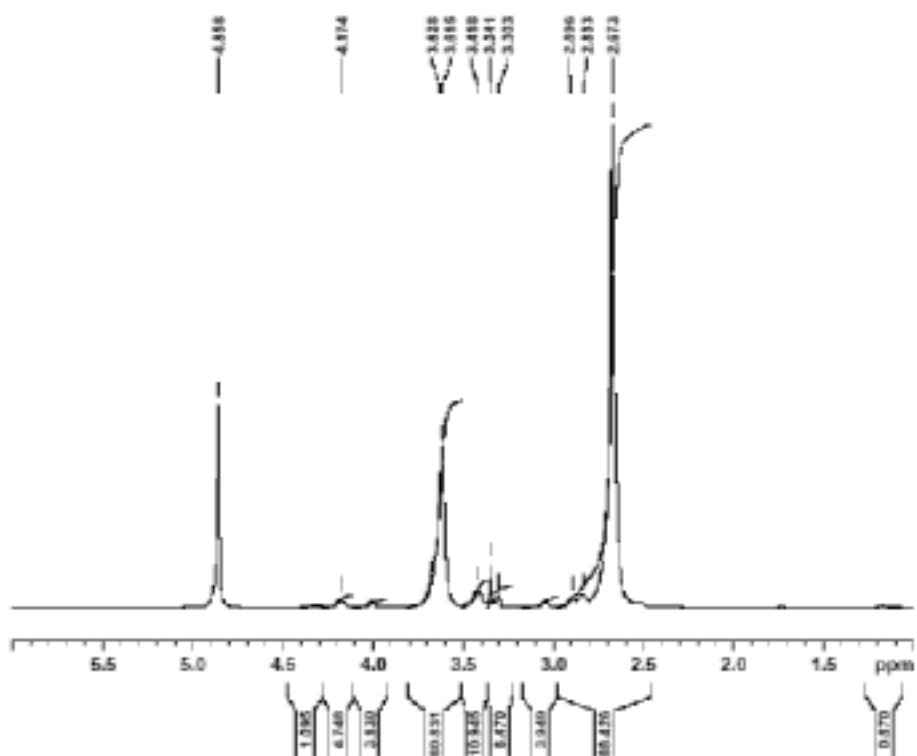
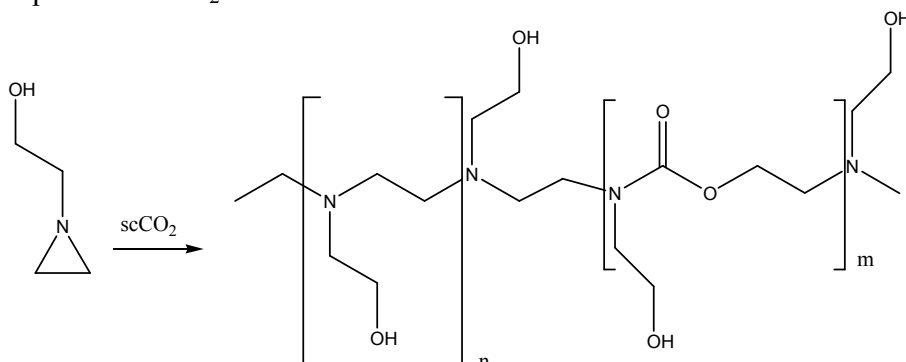


Figure 3. $^1\text{H-NMR}$ spectrum of the copolymer

In figure 3 it can be seen a typical copolymer $^1\text{H-NMR}$ spectrum [13] of the synthesized polyurethane.

The urethane unit content was determined through elemental analysis (0,16 urethane unit content). The combination of this data and the previous analysis information proved that

the synthesis of a poly[1-(2-hydroxyethyl) aziridine-co-CO₂] was successful in supercritical CO₂.



Scheme 1. Copolymerization of 1-aziridineethanol with scCO₂

CONCLUSION

Carbon dioxide and 1-(2-hydroxyethyl)aziridine were allowed to copolymerize without using any catalyst to give polyurethane with a urethane unit content of 16 %. In future work it will be studied new copolymerisations with different aziridines.

ACKNOWLEDGMENT

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