Supercritical carbon dioxide, a tool for the dispersion ROP of lactone and PCL foaming

Grignard Bruno, Urbanczyk Laetitia, Stassin Fabrice, Calberg Cedric, Detrembleur Christophe, Jérôme Christine,
Centre for Education and Research on Macromolecules (CERM), University of Liège, allée du 6 août, 4000 Liège
e-mail: bruno.grignard@skynet.be

Aliphatic polyesters, namely polylactide (PLA) and poly-ε-caprolactone (PCL) are biodegradable and biocompatible materials that find applications as resorbable suture (PLA) and drugs delivery vectors (PCL) [1,2]. Nevertheless, these polymers were mainly prepared by ring opening polymerization using aluminum alkoxide or tin alkoxide initiators in organic media [3,4]. Recently, the use of supercritical carbon dioxide as polymerization medium was proposed as a potential alternative to the use toxic organic solvents. Nevertheless, due to the non-solubility of PCL in this medium, the growing chains rapidly precipitate during their synthesis leading to the formation of a bulky material that is typical of a precipitation polymerization [5-7]. This work aims at investigating the dispersion ring-opening polymerization (ROP) of ε-caprolactone in the presence of fluoropolymer-based stabilizers, that were prepared by combining the ring opening polymerization of ε-caprolactone and atom transfer radical polymerization of heptadecafluorodecylacrylate (AC8) and so, stabilizing PCL micrometric particles in supercritical carbon dioxide. In practice, the ROP of CL was initiated by dibutyltin dimethoxide in the presence of PCL-b-PAC8 diblock stabilizers of differents molecular weight and composition. After 24h at 40°C, PCL was collected as a powder that consists of small-sized microspheres. Finally, post-polymerization purification of PCL (removal of tin catalyst that may lead to toxicological problems) was demonstrated to be quite feasible by supercritical fluid extraction (SFE) leading to the preparation of PCL with low catalytic residues. The second goal of this work aims at reporting on the use of sc CO_2 for the preparation of foams of poly(ε-caprolactone) (PCL), that could be useful in the packaging sector and/or the biomedical sector as potential scaffolds for tissue engineering but also as substitutes for polystyrene thermoformed trays. The method that consists of saturating a polymer with a compressed or supercritical fluid, such as carbon dioxide followed by depressurization and polymer expansion was investigated. Indeed, no residual product is left in the foam, no toxic gas is produced and no resort to hydrocarbon solvents is required. Moreover, CO_2 is cheap, non-toxic, recyclable, non-flammable and the technology of CO_2-assisted foaming can be used in either a batch mode or in a continuous mode within a high-pressure extruder.

[1] Shogren R.L., Biopolymers from Renewable Resources (Macromolecular systems, Materials approach), 1998, D.L. Kaplan, ED., Springler-Verlag, Berlin Heidelberg, 30
[2] Lecomte Ph., Jerome R., Biodegradable Polymers for Polymer Industrial Application, ED. by R. Smith, Woodhead publishing ltd, 2005, 57-77
[3] Eguiburu J.L., Fernandez-Birridi M.J., San Roman J., Polymer, 2000, 41, 6439
[4] Barakat I., Dubois Ph., Grandfils Ch., Jerome R., J. Polym. Sci., Polym. Chem., 1996, 34, 497-502
[5] Stassin F., Halleux O., Jerome R., Macromolecules, 2001, 34 (4), 775-781.
[6] Bratton D., Brown M. Howdle S. M., Macromolecules, 2005, 38 (4), 1190-1195
[7] Loeker, F.C., Duxbury C.J., Kumar R., Gao W., Gross R.A., Howdle S.M., Macromolecules, 2004, 37 (7), 2450-2453