ONE-WAY AND TWO-WAY SHAPE MEMORY STUDY OF CHEMICALLY-CROSS-LINKED STAR POLY(ε-CAPROLACTONE)

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Poly(ε-caprolactone) (PCL), a semi-crystalline polymer, is one of the most widely studied polymers for the development of shape memory materials when chemically cross-linked. PCL presents several advantages such as a melting transition temperature close to human body temperature, a high biocompatibility and (bio)degradability. So, this polymer is highly relevant for both biomedical devices such as stents or resorbable suture wires and also for degradable packaging. However, after cross-linking, the material can not be reprocessed, preventing any reuse/recycling of the material. One of the purposes of this work is to find a solution to this major drawback, which would then allow, for example, to reshape packaging films after use or to recycle trimmings remaining after fabrication. Amongst current trends in the design of new polymer and composite materials, the use of organic reactions that are able to create and reversibly disrupt chemical bonds upon an external stimulus (temperature, irradiation,…) is currently gaining more and more attention as it can lead to applications in various areas such as remendable materials, drug delivery systems, stimulus-degrading materials or recyclable materials.

Amongst all the reversible links described in the literature, thermally (4+2) reversible cycloadditions present interesting features such as the creation of robust bonds and well defined reversibility conditions. As an example, the application of furan/maleimide adducts as covalent link, which cycloreversion is largely favored in the range of temperature (90-120°C), is widely reported. Typically, PCL-based shape memory materials have been prepared by mixing a stoichiometric amount of diene-bearing and maleimide-bearing PCLs in a twin-screw mini-extruder at a temperature at which DA cycloaddition is largely disfavored, followed by the curing of the blend slightly above the melting temperature (65°C) to improve the kinetic of DA adduct formation. The shape memory properties of the materials have been studied by cyclic tensile thermomechanical analysis [1-3]. As cross-linked PCLs are known to exhibit one-way and two-way shape memory properties, a comprehensive study of the shape memory of these materials has been carried out. Unfortunately, creep from shape memory cycle to cycle was observed in DMA for the furan/maleimide sample, certainly due to the reversibility of the adduct. In order to limit this creep effect, the substitution of the furan/maleimide adduct by a more stable adduct is required. The anthracene/maleimide system was then tested because this adduct is more stable under stress than the furan/maleimide one.

This contribution aims at reporting a complete study of one-way and two-way shape memory properties of PCL cross-linked by Diels/Alder adducts of different stabilities. The shape memory properties of these materials have been assessed by DMA experiments while DSC analyses revealed the relationships between PCL crystallinity evolution and their two-way shape memory characteristics.

(1) Defize, T.; Riva, R.; Raquez, J.-M.; Dubois, P. ; Jérôme, C.; Alexandre, M.; *Macromol. Rapid Commun*. **2011**, *32*, 1264.
(2) Defize, T.; Riva, R.; Thomassin, J.-M.; Jérôme, C.; Alexandre, M.; *Macromol. Symp*. **2011**, *309/310,* 154.
(3) Defize, T.; Riva, R.; Jérôme, C.; Alexandre, M.; *Macromol. Chem. Phys.* **2012**, *213,* 187.