

THERMOREVERSIBLY CROSS-LINKED POLY- ϵ -CAPROLACTONES FOR SHAPE MEMORY MATERIALS

Thomas Defize (1), Raphael Riva (1), Jean-Michel Thomassin (1), Bernard Gilbert (2), Christine Jérôme (1), Michael Alexandre (1)

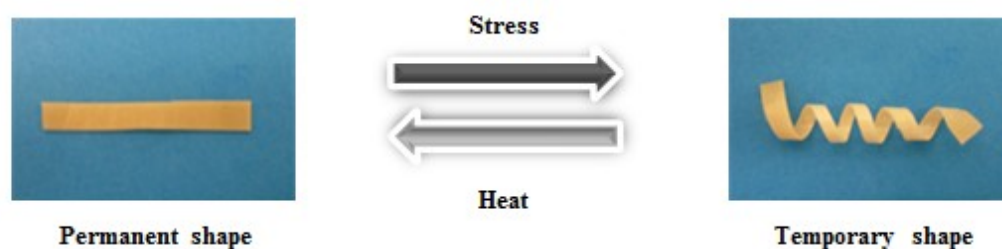
(1) Center for Education and Research on Macromolecules (CERM), University of Liege, Chemistry Department, Building B6a, 4000 Liege, Belgium

(2) Chimie Analytique Inorganique, University of Liege, Chemistry Department, Building B6c, 4000 Liege, Belgium

Properties improvement of existing polymers raises tremendous interest in macromolecular chemistry with the purpose to develop new smart materials. Among them, shape memory polymers (SMPs) are remarkable materials able to switch from a stressed deformed state (temporary shape) to their initial relaxed state (permanent shape) by the simple application of a stimulus, such as heat or light. Typically, the shape memory property is generally observed for chemically or physically cross-linked polymers that exhibit an elastomeric behaviour above a phase transition, e.g. glass or melting transition. Cross-linked semi-crystalline poly(ϵ -caprolactone) (PCL) is already widely studied for the development of SMPs. Indeed, PCL is a (bio)degradable and potentially biosourced polymer, which may advantageously be applied for degradable packaging. Moreover, a high biocompatibility combined to a melting transition temperature close to human body temperature paves the way to the use of PCL for the elaboration of biomedical devices such as resorbable suture wires or stents. However, after classical chemical cross-linking, material reprocessing is impossible preventing any recycling. In order to provide a solution to this major drawback, this work aims at developing a method enabling a cross-linking/cleavage at will, allowing the recycling and the reuse of PCL-based shape memory materials.

In order to generate reversible links, thermally-controlled (4+2) cycloadditions (Diels-Alder reactions), well-known in organic chemistry to create quite robust but reversible bonds with well-defined reversibility conditions, have been selected to cross-link PCL. Moreover, when furan/maleimide adduct is concerned, cycloreversion is largely favored in the range of processing temperatures between 90 and 120°C, which is very well suited in the case of PCL to avoid any degradation.

Linear and multi-arm star shaped PCL precursors have been selectively functionalized at their chain ends either by furan (diene) or maleimide (dienophile). Typically, a stoichiometric amount of furan-bearing and maleimide-bearing PCLs has been blended in a twin-screw mini-extruder at a temperature disfavoring largely the cycloaddition reaction. The temperature of the collected blend has then been decreased to 65°C, so slightly above the PCL melting temperature, with the intention to keep enough chains mobility and favor, this time, the formation of the adducts. The cycloaddition kinetics has been followed by Raman spectroscopy and the PCL cross-linking has been evidenced by both swelling experiments and rheological measurements. The obtained cross-linked PCL was characterized by shape memory properties with excellent fixity and recovery, as determined by cyclic tensile thermomechanical analysis.



Besides, the influence of the nature of the Diels-Alder adduct on the cross-linking rate and on the shape memory properties have been studied by replacing furan by anthracene⁽¹⁻³⁾. When furan is used as diene, the heating of the PCL based SMP at a temperature of 130°C allows the cleavage of the polymer network, which can then be successfully recycled into a new SMP with comparable shape memory properties.

References

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