

**TITLE:** Thermo-reversible reactions for the preparation of smart materials : recyclable covalently-crosslinked shape memory polymers

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**INTRODUCTION:** Semi-crystalline shape memory polymers (SMPs) used for the preparation of advanced stents or smart surgical sutures may be obtained either from the chemical crosslinking of semi-crystalline polymers or from physically crosslinked (multi)block copolymers where hard blocks (with high softening point) insure the physical network formation. Chemically crosslinked SMPs usually shows excellent shape memory properties but cannot be reprocessed or recycled while the fully recyclable physically-crosslinked SMPs may display less accurate shape memory properties due to their sensitivity towards processing conditions, especially as far as phase segregation is concerned. This work aims at preparing well defined chemically crosslinked SMPs through formation of thermally reversible Diels-Alder cycloadducts that allows their re-processing/recycling upon thermal treatment, therefore coupling the advantages of both type of classical SMP materials.

**EXPERIMENTAL:** Polymer functionalization: a hydroxyl-ended 4-arm star-shaped poly( $\epsilon$ -caprolactone) (PCL) was functionalized by esterification successively with succinic anhydride and furfuryl alcohol or 9-anthracene methanol (as dienes) or a protected 2-hydroxyethyl maleimide that can be thermally unprotected (as dienophile). Network formation : tetra-diene PCL and tetra-maleimide PCL were melt blended at 65°C in a mini-extruder, cured for three days at 65°C and aged for min 7 days before characterization by DMA (stress-controlled cyclic tensile testing between 65°C and 0°C) and rheology.

**RESULT AND DISCUSSION:** 4-arm star shaped PCLs bearing either furan or anthracene moieties as diene or maleimide end groups as dienophile can be prepared with a high degree of functionalization (above 90%) by a two-esterification process . When melt blended, cured and aged, an equal mixture of diene-functionalized and maleimide functionalized PCL gives rise to the formation of a crosslinked semi-crystalline materials that exhibits excellent shape memory properties (fixity above 99% and recovery above 99% after only 1 training cycle). The material prepared using the furan-maleimide Diels-Alder couple exhibits thermally-activated network disruption when heated at 105°C as demonstrated by rheological experiment. The material based on the anthracene-maleimide couple is more thermally stable and shows network disruption above 250°C. Recycling tests of the chemically-crosslinked SMP based on the furan-maleimide couple show the ability to recover a processable material if the sample is heated at 130°C for 15 min. The reprocessed and re-shaped material exhibits similar shape memory properties when cured and aged under identical conditions as those used for the initial material.

**CONCLUSIONS:** A new concept to build shape memory polymers (SMP) combining outstanding fixity and recovery ratios (both above 99% after only one training cycle) typical of chemically-crosslinked SMPs with reprocessability restricted to physically-crosslinked SMPs is demonstrated by covalently bonding, through thermoreversible Diels-Alder (DA) adducts, star-shaped poly( $\epsilon$ -caprolactones) (PCL) end-functionalized by furan and maleimide moieties. A PCL network is easily prepared by melt-blending complementary end-functional star polymers, curing at 65°C and ageing to favour the DA cycloaddition. Such covalent network can be reprocessed when heated at a temperature favouring the retro Diels-Alder reaction. The resulting reprocessed SMP shows still excellent shape memory properties attesting for its good recyclability.

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