Cross-reactive poly(ethylene oxide) and poly(ε-caprolactone) stars towards covalent adaptative networks exhibiting water and temperature triggered shape-memory properties.

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Covalent networks of semi-crystalline poly(ε-caprolactone) (PCL) are highly performant shape-memory materials (SMM) i.e. high fixity of the temporary shape and high recovery of the thermally triggered permanent shape. Being in addition biocompatible and degradable, applications in the biomedical field are foreseen. Advantageously, inserting reversible bonds in the network, adaptative materials are obtained which allows reconfiguration of the permanent shape while preserving the shape memory properties at the body temperature [1].
As an answer to the increasingly demanding biomedical field, we aim at providing to such covalent adaptative networks, an additional shape transition triggered by the presence of water at constant temperature. For this purpose, poly(ethylene oxide) has been selected as a hydrophilic component introduced in the PCL networks.

In the present work, a covalent adaptative PEO/PCL hybrid network is formed by Diels-Alder reaction between PCL and PEO stars purposely end-capped by maleimide and furan, respectively. After melt-mixing of these cross-reacting stars and a post-curing, the resulting covalent adaptable hybrid networks shows high crosslinking density, as demonstrated by swelling experiments while preserving enough crystallinity to exhibit high thermal triggered shape-memory performances that remain as good as the ones of PCL covalent networks. Thanks to the insertion of furane-maleimide Diels-Alder adduct in the covalent networks, this material can be recycled by solvent-free hot-melt reprocessing and the permanent shape of this SMM can be reconfigured, e.g. by using mold of a complex shape. In addition, water triggered shape transition was evidenced allowing to achieve medical devices of complex shapes exhibiting in vivo self-deploying properties.

[1] Defize, T.; Riva, R.; Jérôme, C.; Alexandre, M., Multifunctional Poly(ϵ-caprolactone)-Forming Networks by Diels–Alder Cycloaddition: Effect of the Adduct on the Shape-Memory Properties. *Macromolecular Chemistry and Physics* **2012,** *213* (2), 187-197.

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