

Catalyst-free transesterification vitrimers: the remarkable activating effect of Fluorine.

D. Berne^a, F. Cuminet^a, S. Lemouzy^a, C. Joly-Duhamel^a, R. Poli^{b,c}, S. Caillol^a, E. Leclerc^a, <u>V.</u> <u>Ladmiral</u>^{a*}

^a ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France ^b CNRS, LCC (Laboratoire de Chimie de Coordination), Université de Toulouse, UPS, INPT, 205 Route de Narbonne, BP 44099, F-31077, Toulouse Cedex 4, France ^c Institut Universitaire de France, 1 rue Descartes, 75231 Paris Cedex 05, France.

Contact : vincent.ladmiral@enscm.fr

Vitrimers¹ are polymer networks in which associative exchange reactions can take place under specific conditions, and confer reprocessability to the insoluble materials.² Recently, catalyst-free vitrimers have emerged as a new generation of vitrimers able to overcome potential leaching, ageing and sintering issues of catalysts and to ensure the preservation of the vitrimer properties after numerous reshaping processes.³

Here, we present a novel approach to prepare catalyst-free transesterification vitrimer. The transesterification reactions usually catalyzed using an organometallic complex or a nucleophile, are, in our materials, activated by the presence of fluorinated groups located at the alpha or beta position of the ester groups (Figure 1). Due to the high electron-withdrawing effect of fluorine, these activating groups not only vastly accelerate the network formation (acid ring opening reaction of epoxydes) but also strongly promote the transesterification reactions at relatively low temperaure (150°C), thus allowing easy reshaping of polymer networks. This original approach, very efficient for transesterification vitrimers, is likely also applicable to other Covalent Adaptable Networks relying on other exchange reactions.



Figure 1: Reshaping of crosslinked epoxy-acid network via transesterification activated by Fluorine atoms.

Références :

- [2] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, L. Science 334, 965–968, 2011.
- [3] F. Cuminet, S.Caillol, E. Dantras, E.. Leclerc, V. Ladmiral, Macromolecules 54, 3927–3961, 2021.

^[1] N. J. Van Zee, R. Nicolaÿ, Prog. Polym. Sci. <u>696 104</u>, No. 101233, **2020**.