

ORGANIC PHOSPHATES AND PHOSPHONATES AS EFFICIENT CATALYSTS FOR THIOL-CLICK VITRIMERS

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Thermo-activated dynamic networks based on transesterifications are associative in nature and maintain their network connectivity at higher temperatures [1]. Thermally induced bond breakage and reformation reactions occur simultaneously and affect the networks' viscoelastic properties at higher temperatures. Below the topology freezing transition temperature (T_v), the exchange reactions are slow, and the network properties are comparable to thermosets. Above T_v , the exchange reactions are significantly fast, and the rearrangements cause a viscoelastic reflow of the network [2]. This class of dynamic polymer networks is called vitrimers and has unique features such as self-healability, malleability or reprocessability. Although mineral phosphates have been reported for catalyzing transesterification reactions, the catalytic activity of organic compounds in solid polymer networks has not been used as widely. Organic phosphates are promising catalysts for preparing photocurable vitrimers as they do not compromise on shelf-life or cure kinetics. In the present work, organic phosphates and phosphonates were used to catalyze reversible transesterifications in photocurable thiol-click vitrimers. Accordingly, four vitrimeric networks were prepared using selected catalysts including ethylene glycol methacrylate phosphate, bis(2-methacryloyloxy ethyl phosphate, vinyl phosphonic acid and diethyl vinyl phosphonate. FTIR spectrometry was used to study the cure kinetics. Stress relaxation analysis with a moving die rheometer and DMA were carried out to determine the thermo-mechanical properties of the dynamic networks. Results showed that the low- T_g networks were highly mobile at elevated temperatures, and that the exchange rate was highly sensitive to the acidity of the catalysts. The relaxation rate increased with rising pK_a value of the catalysts. In addition, the acidity of the catalysts directly affected the T_v . The organic phosphates and phosphonates under investigation are superior in catalyzing dynamic exchange reactions in vitrimeric photopolymers. Moreover, they enable a convenient tailoring of exchange kinetics and T_v of the vitrimer networks.

[1] C. J. Kloxin, C. N. Bowman, *Chem. Soc. Rev.* 2013, 42, 7161

[2] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science*. 2011, 334, 965