Thermoresponsive polymers and host-guest chemistry: a win-win combination

Patrice Woisel

Thermoresponsive polymers and host-guest chemistry: a win-win combination

Patrice Woisel

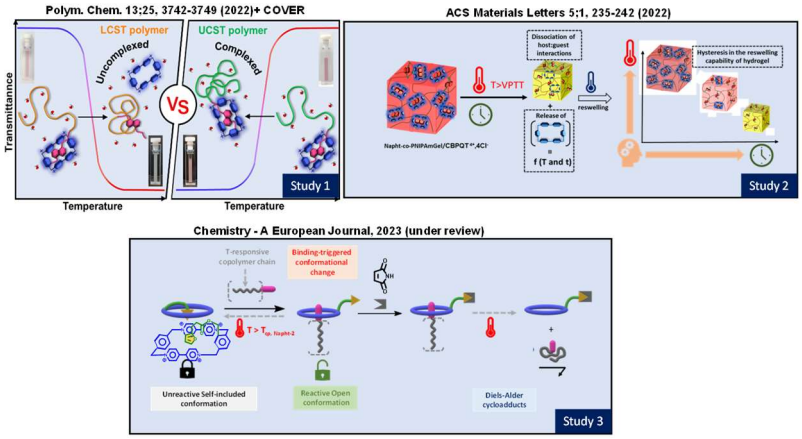
[a] *Univ. Lille, CNRS, Centrale Lille, INRAE, UMR 8207 - UMET - Unité Matériaux Et Transformations*

Keywords: Thermoresponsive polymers, Host-guest complexation, memory function, synergistic control of host reactivity

Abstract:

The combination of heat-sensitive polymers and supramolecular chemistry has recently led to the development of fascinating adaptive materials. In this context, most studies have focused on exploiting host-guest interactions to control the physicochemical properties of polymeric materials.[1] This approach has notably enabled the creation of materials with programmable thermosensitivity and sensor properties.[2] In contrast, the exploitation of polymer thermoresponsiveness to control the recognition properties of host-guest systems at the molecular level is much less developed, and a perfect understanding of the mechanisms triggering thermo-induced decomplexation or complexation is still elusive.

In this communication, we will illustrate through three studies how the host-guest chemistry and the thermo-induced phase separation mechanisms can "talk together" to synergistically tune the coil↔globule transition and the complexation state of polymeric systems. The first example[3] will concern a comparative analysis of the behaviour of complexes formed from different naphthalene end-functionalized LCST or UCST polymers and the electron-deficient cyclobis(paraquat-p-phenylene) tetrachloride (**$CBPQT^{4+}$, $4Cl^-$**)[3] host when subjected to heat treatment. This study provided an understanding of the mechanisms triggering the thermo-induced (de)complexation of such complexes. The second study will report a supramolecular approach for developing an intelligent thermoresponsive polymeric hydrogel featuring a dual temperature and time memory function based on a kinetic control of the material's (de)complexation and (re) swelling behaviours. The last study will illustrate how a thermo-induced phase separation mechanism can regulate on demand the Diels-alder reactivity of a synthetic self-complexing host-guest molecular switch **$CBPQT^{4+}$-Fu**, consisting of an electron-rich furan unit covalently attached to the electron-deficient $CBPQT^{4+}$host, with maleimide in water. Thanks to a supramolecular control over the topology of **$CBPQT^{4+}$-Fu** combined with a thermoresponsive supramolecular regulator, we reported a rare example of decreased reactivity upon increasing temperature.



References :

1) V. R. de la Rosa and coll., Mater. Today, 2016, 19, 44-55; 2) N. Herzer and coll. J. Am. Chem. Soc. 2012, 134, 7608–7611; 3) H. Guo and coll. Polym. Chem. 2022,13;25, 3742-3749, 4) P. R. Ashton and coll. Angew. Chem., 1988, 27, 1550-1553; 5) L. De Smet and coll. ACS Materials Letters, 2022,5;1, 235-242; 6) C. Ribeiro and coll. submitted