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## Phase separation in vitrimeric networks

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Vitrimeric polymers have recently been proposed as a reprocessable alternative to thermoset plastics [1]. Their potential recyclability stems from the dynamic covalent bonds forming the polymeric network: they are solid-like at low temperatures, but flow when heated. An obstacle to the production of homogeneous vitrimeric plastics is the onset of phase separation during synthesis [2]. Two possible mechanisms exist for the separation into different phases: one is enthalpic, stemming from the interaction between species; the other is entropic, if the network-forming components prefer to form clusters and leave the rest of the sample free to flow.

We propose to investigate this phenomenon using existing theories for associative polymeric networks [3,4] to predict the regimes in which phase separation is favourable, with the goal of providing hints for the experimental design of vitrimeric plastics. Our study focuses on systems with four species: (i) non-reactive homopolymer such as polystyrene, (ii) the same polymer with equally-spaced function sites, binding to either (iii) a dyfunctional 'cross-linker' moiety or (iv) a monofunctional 'stopper' for the function sites. We aim to identify regimes in which phase separation is stymied, in order to facilitate industrial production.

## References:

- [1] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, Science 334, 965–968 (2011).
- [2] R. Ricarte, F. Tournilhac, L. Leibler, Macromolecules 52, 432-443 (2019)
- [3] M. Rubinstein, A. Semenov, Macromolecules **31**, 1386–1397 (1998).
- [4] A. Dobrynin, Macromolecules **37**, 3881–3893 (2004).