Self-assembly and network formation in difunctional and monofunctional associative rheology modifiers

Constantina Sofroniou [1], Karim Mehenaoui [2], Baptiste Quienne [2], Sylvain Caillol [2], Ignacio Martín-Fabiani [1]

1 Department of Materials, Loughborough University, LE11 3TU Loughborough, UK
2 ICGM, University of Montpellier, CNRS, ENSCM, Montpellier, France

c.sofroniou@lboro.ac.uk

Rheology modifiers (RMs) are essential in liquid formulations such as coatings, adhesives, and lubricants. Their concentration-dependent self-assembly into transient associative networks imparts non-Newtonian flow behaviour and governs viscosity and stability. Understanding when and how these networks form is therefore crucial for the rational design and optimisation of commercial formulations. [1]

Telechelic associative RMs based on hydrophobically modified ethoxylated urethanes (HEURs) form flower-like micelles at low concentrations and percolated networks at higher concentrations. [1] Network formation causes macroscopic thickening and is a key performance parameter in applications. However, commercial HEURs are not perfectly telechelic; alongside difunctional chains with two hydrophobic end groups, some chains are monofunctional, possessing only one hydrophobe. These monofunctional chains (mHEURs) cannot bridge micelles and therefore reduce network connectivity and alter rheological behaviour. [2]

Here, we study HEUR:mHEUR mixtures, both based on a 10 kDa PEG backbone with one or two C12 hydrophobes. In earlier work, we studied HEUR network formation using shrinking-gate fluorescence correlation spectroscopy (sgFCS) and the molecular rotor dye Sulfo-Cyanine3.[1] Now we present sgFCS measurements confirming that mHEUR alone produces no slow diffusive component associated with network formation, while in HEUR:mHEUR systems it scales with the fraction of difunctional chains (Figure 1a).

To complement the dynamic information from sgFCS with structural analysis, we performed small-angle X-ray scattering (SAXS) on HEUR:mHEUR mixtures. SAXS reveals systematic steepening of the high-q power-law exponent from ≈2 in mHEUR-rich solutions to ≈4 in HEUR-rich systems, indicating a transition from polymer chain scattering to Porod-like behaviour associated with compact hydrophobic domains (Figure 1b,c). Combined scattering–FCS analysis establishes a direct link between associative dynamics and nanoscale structure in HEUR:mHEUR mixtures.

Keywords:
Rheology modifiers, Associative polymers, Self-assembly, FCS, SAXS

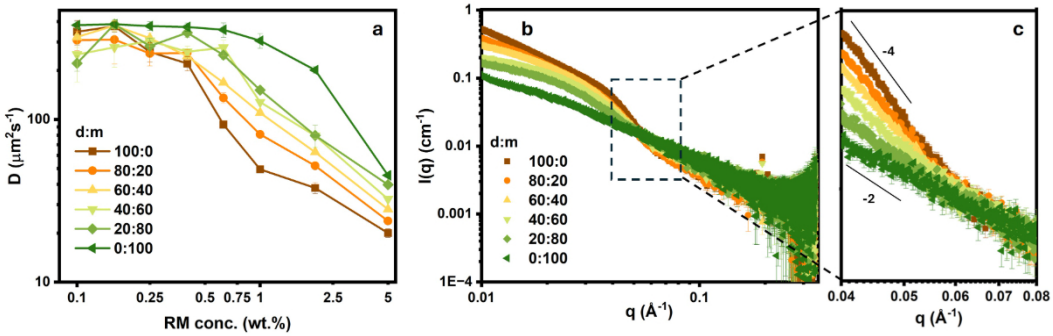

Figure 1: (a) Diffusion coefficients (D) obtained from sgFCS as a function of RM concentration for HEUR:mHEUR mixtures at different difunctional:monofunctional component ratios (d:m). (b) SAXS profiles of the mixtures at 2 wt% RM. (c) Enlarged SAXS curves in the Porod region, offset for clarity.

References:

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