

Probing Soft Matter Interfaces on the Nanoscale with Radicals

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Magnetic resonance methods such as nuclear magnetic resonance (NMR) or electron paramagnetic resonance (EPR) can give valuable insights into materials that show long range disorder and some short range or intermediate range order, e.g. synthetic and biological soft matter.

In particular, EPR spectroscopy with its high sensitivity and selectivity is complementary to the well-established methods of soft matter characterization (e.g. light-, X-ray, neutron scattering) and delivers information that is otherwise not accessible. While conventional continuous-wave (CW) EPR allows studying rotational dynamics in the microsecond to picosecond regime, EPR methods that measure the dipolar (through-space) interaction of individual electron spins can be used to gain information on the spatial distribution of paramagnetic probe molecules up to ~8 nm.

Here, I will show that methods of EPR spectroscopy can help illuminating – on the molecular scale – the interfaces of synthetic and biological macromolecules with mainly solvent on the molecular scale. Further, although EPR spectroscopy is a local method that has its greatest versatility in the range of several nm, it is possible to obtain insight into fundamental interactions on the short length scales and into macroscopically observable function on much longer length scales.^[1]

These features will be highlighted through recent examples of synthetic polymers studied in my lab. The main part will be on synthetic polymers that exhibit environmentally responsive behavior. These polymers are a very interesting class of materials envisioned for a multitude of applications. With simple CW EPR on amphiphilic spin probes, mainly simple TEMPO, we could show that thermoresponsive polymeric systems show nanoinhomogeneities in structure and reactivity. These nanoinhomogeneities can be static on an EPR timescale ($> \sim 1$ ns), or dynamic ($< \sim 1$ ns). Such, the thermal transition of thermoresponsive dendronized polymers,^[1] of PNIPAAm hydrogels^[2] as well as commercially available Pluronic triblock-copolymers (PEO-PPO-PEO)^[3] is characterized on a molecular scale by CW EPR spectroscopy, performed on a low-cost, easy-to-use benchtop EPR spectrometer. While all processes are macroscopically sharp phase transitions as seen by turbidimetry, we in general find that dehydration processes proceed over a temperature interval of at least 30°C.

Combining our molecular scale information from CW EPR spectroscopy and meso-/macroscopic information from various other characterization techniques, we could further explain the formation of mesoglobules of thermoresponsive dendronized polymers.^[4] Using CW EPR, the formation of a dense polymeric layer at the periphery of the mesoglobule, a skin barrier, is formed in a narrow temperature range of ~4 K above T_C and prohibits the release of molecules that are incorporated in the polymer aggregate. In large mesoglobules, formed at low heating rates and at high polymer concentrations, a considerable amount of water is entrapped that micro phase separates from the collapsed polymer chains at high temperatures. This results in aggregates possessing an aqueous core and a corona consisting of collapsed polymer chains and may bear consequences for the design and use of thermoresponsive polymeric systems in the fast growing field of drug delivery.

[1] a) M. J. N. Junk, et al., **EPR Spectroscopic Characterization of Local Nanoscopic Heterogeneities during the Thermal Collapse of Thermoresponsive Dendronized Polymers**, *Angew. Chem.*, **122**, 5818-5823 (2010); *Angew. Chem. Int. Ed.*, **49**, 5683-5687 (2010). b) M. J. N. Junk, et al., **EPR Spectroscopy Provides a Molecular View on Thermoresponsive Dendronized Polymers below the Critical Temperature**, *Macromol. Chem. Phys.*, **212**, 1229-1235 (2011).

[2] M. J. N. Junk, U. Jonas, D. Hinderberger, **EPR Spectroscopy Reveals Nanoinhomogeneities in The Structure and Reactivity of Thermoresponsive Hydrogels**, *Small* **4**, 1485-1493 (2008)

[3] D. Kurzbach, M. N. Reh, D. Hinderberger, **Nanoscale Inhomogeneities in Thermoresponsive Tri-Block Copolymers**, *ChemPhysChem*, DOI:10.1002/cphc.201100474

[4] M. J. N. Junk, et al., **Formation of a Mesoscopic Skin Barrier in Mesoglobules of Thermoresponsive Polymers**, *J. Am. Chem. Soc.*, **133**, 10832-10838 (2011)