Structured (Non-Newtonian) Fluids Studied at the Molecular Level Using Steady–State and Time–Resolved EPR Methods

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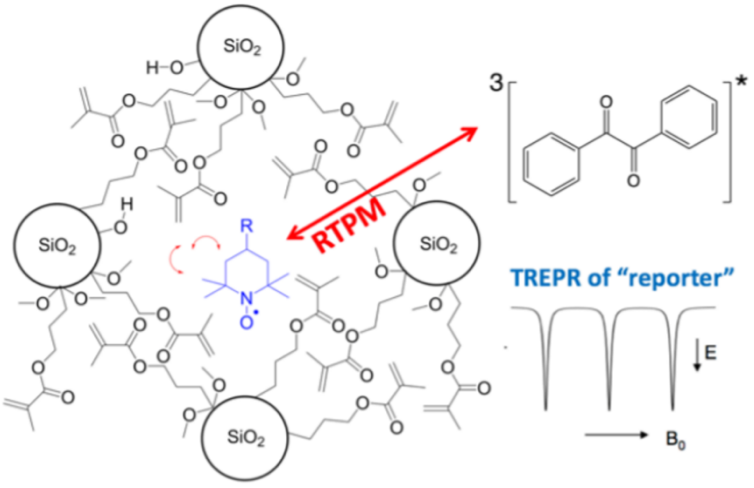
Organic and inorganic photoexcited states often lead to free radicals that have strong chemically induced electron spin polarization (CIDEP), easily detected on the sub-microsecond time scale using time–resolved (CW) electron paramagnetic resonance spectroscopy (TREPR). Of the four known CIDEP mechanisms (radical pair mechanism (RPM), spin–correlated radical pair mechanism (SCRPM), triplet mechanism (TM), and radical–triplet pair mechanism (RTPM), the latter is by far the least understood theoretically but may prove to be the most useful of all of them. Radical-triplet pairs involve electron spin state mixing and sometimes quenching of triplet states by stable doublet state free radicals such as nitroxides. This process can be extended to the study of stable nitroxide biradicals. The RTPM is attractive for investigation of excited state and radical dynamics for reasons: 1) the process is overall non-destructive, i.e., the triplet and the nitroxide eventually return to their electronic ground states with Boltzmann spin state populations, and 2) the resulting spectrum reports spin state information from the unobserved excited triplet state through the nitroxide, the intensity of which can be related to encounters between the two, driven by *translational* motion. Simultaneously, the recorded TREPR spectrum of the nitroxide contains line shape information related to *rotational* motion. The ability to observe and record both types of motion, especially in heterogeneous systems such as micelles, vesicles, bubbles, and emulsions is highly advantageous.



In this talk I will introduce the intricate features of the RTPM, with examples from my laboratory to show how structural, dynamic and mechanistic information can be obtained in a variety of chemical systems. These include micelles, vesicles, structured (non-Newtonian) fluids, polymers, and excited organic triplet states. I will use this talk as a platform to suggest new pathways that can exploit the RTPM for the investigation of more complex systems such as dye-sensitized solar cells, more complex structured fluids, and the dynamic properties of commercially important heteropolymers. The results represent one the first reports of the physical properties on non-Newtonian fluids at the molecular level.