Spin Probe Approach for Studying Inhomogeneities in Solutions of Thermoresponsive Polymers

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Thermoresponsive polymers are of great interest because they undergo coil-to-globule transitions of single polymer chains in polar solvents near the lower critical solution temperature (LCST). This peculiarity makes them perspective for biomedical and pharmaceutical applications such as drug and gene delivery, tissue engineering, and cell expansion. Macroscopic methods (turbidimetry, DSC, etc.) usually fix sharp and reversible changes of aqueous solutions or wet films of thermoresponsive polymers in the vicinity of LCST. Besides this, the formation of small, even nanoscopic inhomogeneities of polymer gels in different solvents before LCST is proved by continuous-wave electron paramagnetic resonance spectroscopy (CW EPR) [1–3].

In the present report, we discuss the features of the formation and structure of inhomogeneities of aqueous solutions of poly-N-isopropylacrylamide (PNIPAM) as one of the most applied and studied thermoresponsive polymers using spin

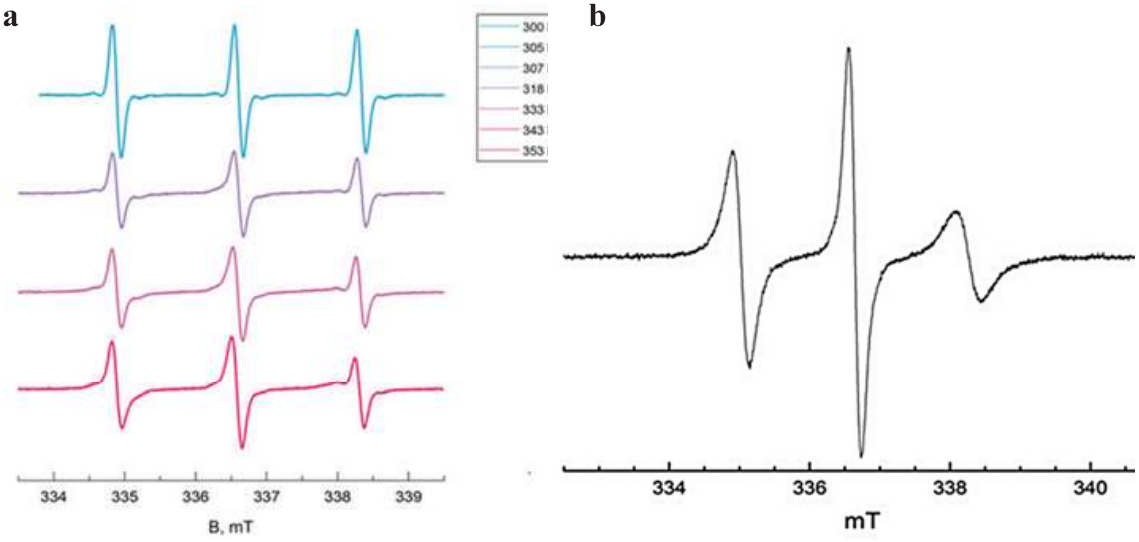

Fig. 1. a EPR spectra of TEMPO in 10wt% PNIPAM aqueous solutions at 300–353 K. **b** EPR spectrum of TEMPO in 10wt% PNIPAM aqueous solutions at 353 K in the presence of Cu(II) ions.

probe CW EPR. The effect is based on the greater affinity of TEMPO radical to hydrophobic media of the polymer associates. It manifests itself by appearing of the more broadened and hence less intensive signal of TEMPO radicals while heating compared to their water solutions at low temperatures (see Fig. 1). Using Cu(II) ions as "quencher" for fast-moving radicals in the liquid phase allowed us to obtain individual spectra of TEMPO in polymer globules and observe inhomogeneities in solutions before globule collapsing. Spin-Hamiltonian parameters of TEMPO in PNIPAM globules were obtained by modeling the spectra. The spectra simulations confirm the formation of molten globule at the first step with its further shrinkage due to coming out of water molecules, making it denser and more hydrophobic.

1. Antheunis H., van der Meer J.-C., de Geus M., Heise A., Koning C.E.: Biomacromolecules **11**, 1118 (2010)
2. Kurzbach D., Junk M.J.N., Hinderberger D.: Macromol. Rapid Commun. **34**, 119 (2013)
3. Winnik F.M., Ottaviani M.F., Bossmann S.H., Garcia-Garibay M., Turro N.J.: Macromolecules **25** (1992) 6007.