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Kinetics of Mesoglobule Disintegration in Aqueous Poly(N-isopropylacrylamide) Solutions Following Pressure Jumps

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Stimuli-responsive polymers in aqueous solution form mesoglobules in the two-phase region of the temperature-pressure phase diagram. While the formation of mesoglobules has been amply studied [1], their dissolution and associated structural changes are hardly explored. To elucidate the kinetics of chain swelling and mesoglobule disintegration in a semi-dilute aqueous solution of the thermoresponsive polymer poly(N-isopropylacrylamide) (PNIPAM), we use in situ, real-time (50 ms – 1500 s) small-angle neutron scattering (SANS) at instrument D11, ILL. The coexistence line is crossed by applying a fast pressure jump from the two-phase to the one-phase state, and the target pressure is varied. Two limiting mechanisms are identified: 1) The release of single polymers from the surface of the mesoglobules, leading to a semi-dilute solution. 2) Continuous swelling of the mesoglobules due to uptake of water until the entire system is spanned, resulting in a semi-dilute solution. The first mechanism is dominant when the pressure jumps are carried out in the low pressure regime and when the jumps are shallow. The second mechanism is encountered for deep jumps in the low pressure regime and for all target pressures in the high-pressure regime.

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