Influence of End Groups on the Aggregation of Polymers: A Neutron Scattering Study

Jonathan L. S. Garthe [a], Sylvain Prévost [b], Matthias Karg [a]

[a]Physical Chemistry of Functional Polymers, Martin Luther University Halle-Wittenberg, Halle (Saale), Germany
[b]Large Scale Structures, Institute Laue-Langevin, Grenoble, France

jonathan.garthe@chemie.uni-halle.de

The solution structure of polymers strongly depends on concentration, solvent quality, and molecular weight. Beyond these parameters, chemically distinct end groups can significantly alter phase behavior, with effects strongly dependent on chain length. Previous studies have reported the formation of polymeric micelles in systems bearing hydrophobic end groups. [1] However, a systematic understanding of how micelle formation depends on molecular weight and concentration, particularly in the semi-dilute regime, remains incomplete. Moreover, the possibility that micelle formation is not the dominant state has received little attention.

We investigated the solution behavior and the occurrence of micelle-like structures in (semi)-dilute solutions. Hydrophobically end-functionalized PNIPAM homopolymers were synthesized via controlled reversible addition fragmentation transfer polymerization providing good control over molecular weight and dispersity. The end groups could be selectively cleaved via aminolysis, enabling direct comparison without altering backbone chemistry or molecular weight distribution. Dynamic light scattering (DLS) was used to characterize the dimensions of polymer coils and potential aggregates.

Cloud points in aqueous solution were determined via extinction spectroscopy (see Figure 1, left), providing access to macroscopic phase transitions. These measurements reveal a pronounced dependence on end-group functionality for polymers with molecular weights below 100 kDa, highlighting the increasing relevance of terminal groups at shorter chain lengths. Complementary to this, small-angle neutron scattering (SANS) was used to probe the nanoscale structure of the polymers in solution. From the SANS measurements we were able to determine the ratio between individual polymer chains and the micelles. Our studies demonstrated that a subdominant micelle formation occurs for samples with molecular weights below 100 kDa, indicating a coexistence of free chains and weakly associated micellar structures rather than complete micellization. The aggregation number of these micelles scales inversely with the molecular weight, further suggesting reduced end group association efficiency for longer chains. At low concentrations, these micelles exist as individual structures. Upon increasing the concentration micelles aggregate, leading to pronounced interparticle correlations and a distinct structure factor contribution in the scattering profile (see Figure 1, right).

These results demonstrate that terminal groups have a substantial impact on polymer solution behavior, particularly for shorter chains, and highlight how weak end-group association can drive concentration-dependent self-assembly in otherwise soluble homopolymers.

Keywords:
Small-Angle Neutron Scattering, Thermoresponsive Polymers, End Group Effects

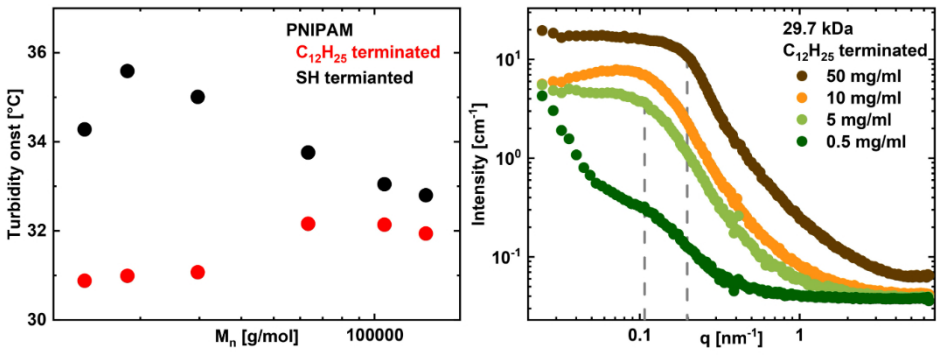

Figure 1: Left: Turbidity onset in dependence of molecular weight with (red) and without (black) hydrophobic end group. Right: Concentration dependent SANS profiles of PNIPAM homopolymers with hydrophobic end group.

References:

[1] Paul A. FitzGerald. Sushen Gupta. Kathleen Wood. Sébastien Perrier. Gregory G. Warr. Langmuir. 2014.