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AGGREGATION BEHAVIOR OF HIGHLY ASYMMETRIC TRIBLOCK COPOLYMERS ACCESSED BY SCATTERING MEASUREMENTS

F.C. Giacomelli[a,b], I.C Riegel[b], C.L. Petzhold[b], N.P. da Silveira[b], J. Pleštil[a], P. Štěpánek[a]

[a]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského nám. 2, CZ-162 06 Praha 6, Czech Republic*

[b]*Institute of Chemistry, Universidade Federal do Rio Grande do Sul, Av. Bento Goncalves 9500, 91501-970 Porto Alegre, Brazil*

5-(*N*,*N*-dialkylamino) isoprenes constitute a new class of polar monomers that can be attached to apolar monomers via anionic polymerization to form interesting block copolymers with specific architectures and well-defined molecular weight distributions. Previously, we verified that 5-(*N*,*N*-diethylamino)isoprene (PAI) short blocks can be quaternized leading the formation of crew-cut aggregates in water[1]. Herein, we describe their ability in the non-quaternized version to form self-assembled aggregates in DMF, a selective solvent for polystyrene (PS) middle block, as studied by Dynamic (DLS) and Static (SLS) Light Scattering linked to Small Angle X-ray Scattering (SAXS) measurements.

We discovered by means of DLS and SLS that there is a minimum amount of PAI needed in the block copolymer chains for appearance of self-assembly ($w_{AI} \sim 0.08$) independently of the block copolymer molecular weight (from 14 to 76 kDa). Above $w_{AI} \sim 0.08$, the triblock copolymers tend to aggregate in narrow spherical particles with number of aggregation (N_{agg} = 22-40 chains/micelle) and size (R = 14-43 nm) depending on the molecular weight.

The analytical expression for the form factor of block copolymer micelles proposed by Pedersen and Gerstenberg[2] fitted very well the X-ray scattering profiles of the micellar solutions, providing the dimension of the PAI core and PS shell of the particles. Scattering profiles of samples that did not undergo aggregation could be described using the Debye function, which is the structure factor of an ideal random walk Gaussian coil.

1. Reigel, I.C.; Eisenberg, A.; Petzhold, C.L.; Samios, D. *Langmuir* (18), 3358-3363, **2002.**

2. Pedersen, J.S.; Gerstenberg, M.C. *Macromolecules* (29), 1363-1365, **1996**.

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