

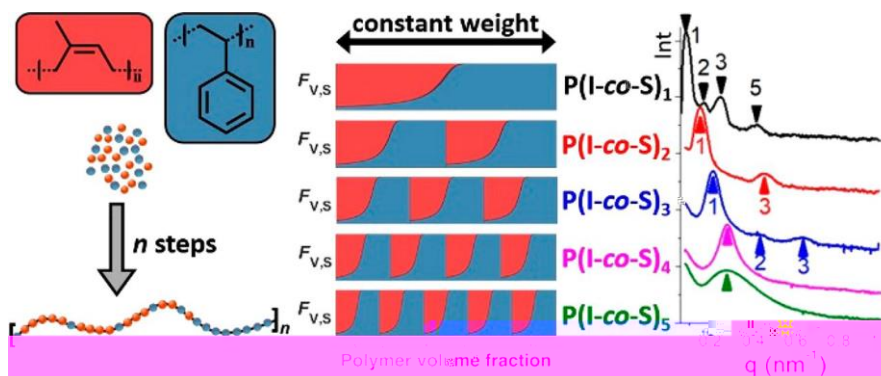
Multiblock Copolymers with up to 18 Blocks: Synthesis, Morphology and Consequences for Materials Science

Holger Frey, Johannes Gutenberg-University Mainz, Germany

The multiblock structure plays a key role in natural scleroproteins showing extraordinary mechanical properties, such as silk fibroin and collagen. They consist of alternating flexible and rigid, crystalline chain segments in repetitive sequences [1], which leads to high tensile strength. In contrast, only few cases of synthetic polymers consisting of well-controlled flexible and rigid chain segments are known that additionally show low dispersity.

The living anionic copolymerization of isoprene and styrene in cyclohexane affords tapered block copolymers due to the highly disparate reactivity ratios of $r_I = 12.8$ and $r_S = 0.051$. Repeated addition of a mixture of these monomers was exploited to generate tapered multiblock copolymer architectures of the $(AB)_n$ type with up to 10 blocks ($1 \leq n \leq 5$), thereby subdividing the polymer chains in alternating flexible polyisoprene (PI) and rigid polystyrene (PS) segments. Three series of well-defined tapered multiblock copolymers with approximate molecular weights of 80 kg/mol, 240 kg/mol and 400 kg/mol were prepared on the 100 g scale. Via this synthetic strategy polymer chains are divided in di-, tetra-, hexa-, octa-, and decablock tapered multiblock structures, respectively. Due to the living nature of the polymerization, low dispersities in the range of 1.06 to 1.28 (decablock) were obtained. In order to ensure full monomer conversion prior to the addition of the isoprene/styrene mixture, kinetic Monte Carlo simulation was employed, permitting to simulate chain growth *in silico* by employing the known polymerization rates and rate constants k_p [2].

The question is addressed, to which extent the multiblock copolymers are capable of forming ordered nano-segregated morphologies. Detailed thermal, structural and rheological investigations showed that the tapered multiblock copolymers with a molecular weight of 240 kg/mol formed ordered phases with the expected lamellar morphology. However, X-ray scattering data and transmission electron microscopy (TEM) images of the octablock and decablock copolymers reflect weakly ordered structures at ambient temperature. The domain spacing, d , was found to scale as $d \sim N^{0.62}$, where N is the total degree of polymerization, suggesting stretching of chains and non-ideal configurations. The viscoelastic response of the tapered copolymers is controlled by the nanodomain structure, the degree of segregation, nanodomain-bridging configurations of blocks.



References

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- [2] E. Grune, T. Johann, M. Appold, C. Wahlen, J. Blankenburg, D. Leibig, A. H. E. Müller, M. Gallei, H. Frey *Macromolecules* **2018**, 51, 3527.