Miktoarm Star Polymers as Functional and Responsive Materials

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Polymers with narrow molecular weight and composition dispersity are essential for establishing the structure/property relationships that are necessary for achieving one of the most sought after goals in polymer chemistry: designing molecules with predetermined properties. In particular, the synthesis of star polymers with molecular weight or chemical asymmetry has gained much interest in recent years because of the striking influence of structure on morphology. The compact multifunctional structure and globular shape of miktoarm star polymers provides them with a set of unique properties and a wide variety of potential applications.^{1,2}

The first general procedure for synthesizing non-linear polymers was in 1948 by Schaefgen and Flory,³ where condensation polymerization of ε caprolactam in the presence of cyclohexanone propionic acids gave four and eight arm starshaped polyamides for the first experimental investigation of star polymer viscosities. It wasn't until the development of living polymerization in 1956⁴ that other synthetic methods began to emerge. Two general strategies were developed for the synthesis of star polymers: the first uses multifunctional substitution reactions on chlorosilane linking agents and the second is based on divinyl compounds. In 1962, Morton utilized living polystyryllithium to synthesize four arm polystyrenes by reaction with tetra-chlorosilane.⁵ Then in 1972, Rempp used *p*-divinylbenzene to create a densely crosslinked nuclei of poly-divinylbenzene with several pendant polystyrene chains.⁶ Around this same time, there was a remarkable increase in the interest in the microphase separation of block copolymers and star polymers began to be seen in new light. The first star copolymer of $A_n B_n$ type was synthesized by Burchard and Eschwey by growing a second type of polymer chain off the living nuclei in Rempp's DVB polymers.⁷ These materials have gained popularity over the years and many other methods of synthesis have been developed. In 1992, the term miktoarm stars (coming from the Greek word μικτός, meaning mixed) was adopted for stars with chemical asymmetry.8



Figure 1. Equilibrium morphologies of (a) AB diblock copolymers^{9,10} (b) an aperiodic "bricks and mortar" mesophase^{11,12} and (c) an asymmetric lamellar structure.¹³

Thermopastic elastomers have gained much attention in industry due to their excellent processability at high temperature and their elastic mechanical properties at room temperature. Of the several varieties of thermoplastic elastomers (TPEs), one of the best known and widely used is block copolymers consisting of a hard and rigid thermoplastic (commonly styrene) that alternates with block segments of a soft and flexible elastic material (often butadiene or isoprene).⁹ Polymer structure and the volume fraction of PS (f_{PS}) are critical factors in controlling morphology (Figure 1a).^{10,11} To exemplify the utility of star copolymers as thermoplastic elastomers, Avgeropoulos and coworkers studied PS_1 -b-(PI-b-PS₂)_n miktoarm copolymer systems. They found that the discrete cylindrical or spherical PS domains can be achieved with high PS volume fractions in these materials due to shifted phase boundaries. The f_{PS} is a key factor that relates to the elastic recovery and ultimate strain at break of the TPE.¹² Thus, asymmetric architectures have considerable potential in improving the mechanical performances in standard TPEs as well as creating new families of tougher, stronger, and elastic materials. This is further demonstrated by their discovery of a new aperiodic "bricks and mortar" mesophase structure in PS_1 -b-(PI-b-PS₂)_n miktoarm copolymer and PS homopolymer blends (Figure 1b). The extreme domain volume fractions and lack of positional order in this material imparts high stiffness while the PI matrix sustains recoverable elasticity in this new hard-tough-strong thermoplastic elastomer.¹³ Utilizing the same shifted

(a)



Figure 2. Miktoarm polymers that respond to (a) pH,¹⁶ (b) temperature,¹⁷ (c) and to UV light.¹⁸

equilibrium, lamellar microphases with unprecedented compositional asymmetry were created due to the exceptionally large polystyrene weight fractions needed to achieve lamellar structure (Figure 1c). Lamellae with tunable domain periods have attracted considerable interest in a range of emerging applications, including photonic crystals and transfer printing techniques.¹⁴

Because the micellar structures that are formed from linear AB systems are limited to only an "inside" and "outside" component, the use of miktoarm copolymers for self-assembly applications allows for the development of responsive morphologies that utilize several complementary components at once.¹⁵ Common examples of responsive miktoarm polymer micelles include those with pH sensitive side chains that expand or contract due to changes in solubility (Figure 2a),¹⁶ temperature responsive side chains that transition from spherical micelles to short nano-rods at temperatures higher than the lower critical solution temperature (LCST) (Figure 2b),¹⁷ or photoresponsive polymers that degrade upon exposure to UV light (Figure 2c).¹⁸ The use of responsive miktoarm polymers shows particular promise for applications in pharmaceuticals. For example, wormlike micelles can persist for a longer time in the circulation following intravenous injection when compared with spherical micelles and pH sensitive micelles allow for targeted drug administration along the gastrointestinal tract.

In summary, miktoarm star polymer architectures impart many new and intriguing properties that were never thought possible for linear polymers, such as unique microdomain morphologies and responsive self-assemblies. The microdomain and core shell architectures enable a wide variety of potential applications, from thermoplastic elastomers to drug delivery.

References

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