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Functional diblock copolymers and ABC stars: synthesis, properties and potential applicability

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Ferrocene based polymers are attractive due to valuable metallocene-rendered properties as low toxicity, excellent one electron redox reversibility, magnetic susceptibility, photo- and semiconductivity, high plasma etch selectivity, ability to form polymeric charge-transfer complexes, to quench triplet states etc. Narrowly dispersed diblock copolymers containing poly(methyl methacrylate) [PMMA], poly(nonafluorohexyl methacrylate) [PF9MA] or poly(1,4-isoprene) [PI] as the first block and poly(ferrocenylmethyl methacrylate) [PFMMA] as the second block, were prepared by anionic polymerization for the first time[1]. Disordered bulk morphologies in the case of PMMA-b-PFMMA were observed and rationalized in terms of a low Flory-Huggins interaction parameter ($\chi \leq 0.04$) while for the PMMA-b-PI moderate incompatibility ($\chi = 0.12$) accounts for the formation of hexagonally packed cylinder morphology (HEX) in the bulk. The even higher tendency of PF9MA-b-PFMMA to avoid contacts between unlike segments allowed us to achieve the HEX morphology both in the bulk and in thin films on silica substrates.

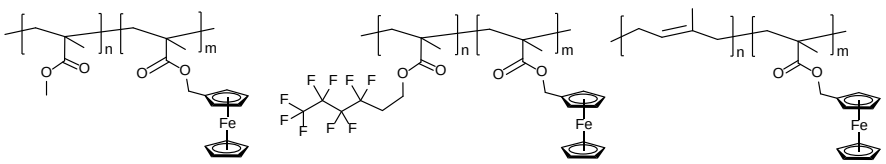

Figure 2: Diblock copolymer sturctures

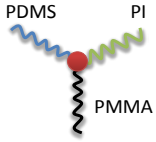

Figure 1 Functional ABC miktoarm star block terpolymers

While Ferrocene based polymers allow us to introduce Fe_2O_3 nanopatterns (after O_2 plasma exposure) on a given substrate, ABC miktoarm terpolymers with poly(dimethyl siloxane) [PDMS] arms could be used to decorate a substrate with a variety of periodic patterns made from SiO_2. Surface structuring via ABC copolymer lithography give rise to principally new morphologies both in the bulk and on the surface unattainable with simple AB diblock copolymers. In a typical example, core-shell structures were produced from PDMS-PI-PMMA ABC miktoarm stars where oxidized PDMS shell is the only component which remains after OR_2 plasma removal of PI and PMMA blocks.

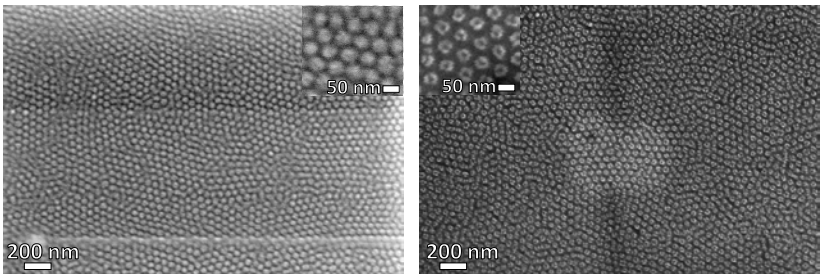

Figure 3 PDMS-PI-PMMA star (relative arm length: 1/1.1/4.9) before (left) and after (right) O_2 plasma etch.

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[1] Sergey Chernyy, Zhongli Wang, Jacob Judas Kain Kirkensgaard, Anders Bakke, Kell Mortensen, Sokol Ndoni, Kristoffer Almdal: *Journal of Polymer Scence. Part A. Polymer Chemistry*, **55**, 495-503 (2017)/doi 10.1002/pola.28435