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Publication date:
2017

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):
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\textsuperscript{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.

While Ferrocene based polymers allow us to introduce Fe$_2$O$_3$ 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.

Sponsoring from the Villum Foundation and the Danish National Research Foundation, Project DNRF103 is gratefully acknowledged.