

Abstract:

The self-assembly of poly(ferrocenyldimethylsilane-*b*-methyl methacrylate) block copolymers, with PFDMS contents of 9-61 wt % (block ratios 1:23-1:1.5), is described. PFDMS-*b*-PMMA block copolymers form remarkable cylindrical micelles with very narrow diameter distributions at block ratios in the range of 1:10-1:6 (18-26 wt % PFDMS) in the block-selective solvent acetone, which is a good solvent for PMMA and a nonsolvent for PFDMS. The micelles, with a PFDMS core and a PMMA corona, were studied in solution by means of dynamic light scattering, ¹H NMR spectroscopy, and cryo-transmission electron microscopy. Micelles were also deposited on silicon substrates by dip-coating and characterized with atomic force microscopy and scanning electron microscopy. The micelles were over 3 μm long and had an overall diameter of around 22 nm. Dynamic light scattering experiments confirmed the formation of rodlike micellar aggregates in acetone. The cylindrical micelles exhibited a rod-to-sphere transition around 60 °C. When cooled below this transition temperature, the micelles reassembled back to their original aggregation state. Depolarized DLS experiments showed no rotational contribution to the measured decays of the autocorrelation functions. We ascribe this to the extreme length of the micelles, which arrests rotational movement. ¹H NMR spectra recorded in acetone-*d*₆ showed PFDMS signals, indicating that these blocks in the micellar cores have some mobility. This suggests that the cores are not in a crystalline state and that crystallization is not a driving force in the formation of these PFDMS-*b*-PMMA cylindrical micelles, but rather the contrast in solvophilicity between the blocks, which in the bulk are in the strong segregation limit.