PC 92

SELF-ASSEMBLY PROCESS OF DIFFERENT POLY(OXYSTYRENE)-POLY(OXYETHYLENE) BLOCK COPOLYMERS: SPONTANEOUS FORMATION OF VESICULAR STRUCTURES AND ELONGATED MICELLES

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We have investigated the micellization, gelation and structure of the aggregates of three polyethylene oxide-polystyrene oxide block copolymers ($E_{12}S_{10}$, $E_{10}S_{10}E_{10}$ and $E_{137}S_{18}E_{137}$, where E denotes ethylene oxide and S styrene oxide, and the subscripts the block length) in solution. For the first time, the spontaneous formation of vesicles by this class of block copolymers is reported. These vesicular structures are present when copolymer $E_{12}S_{10}$ self-assembles in aqueous solution in coexistence with spherical micelles, as confirmed the size distribution obtained by dynamic light scattering and pictures obtained by polarized optical microscopy (POM), transmission and cryo-scanning electron microscopies (TEM and cryo-SEM, respectively). Vesicle sizes vary between 60 to 500 nm. On the other hand, for copolymers $E_{10}S_{10}E_{10}$ and $E_{137}S_{18}E_{137}$ only one species is found in solution, which are assigned to elongated and spherical micelles, respectively. If we compare the high aggregation number derived by SLS for the triblock block copolymer micelles with the maximum theoretical micellar dimensions compatible with a spherical geometry, the micellar geometry cannot be spherical but elongated.¹ This is corroborated by TEM images. On the other hand, tube inversion was used to define the mobile-immobile phase boundaries. To refine the phase diagram and observe the existence of additional phases, rheological measurements of copolymer $E_{137}S_{18}E_{137}$ were done. In contrast, copolymers $E_{12}S_{10}$, $E_{10}S_{10}E_{10}$ did not gel in the concentration range analyzed. Only certain concentrations of copolymer $E_{10}S_{10}E_{10}$ were analyzed by rheometry, for which an upturn in the low-frequency range of the stress moduli is observed denoting an evidence of an emerging slow process, which we assign to the first stages of formation of an elastic network.

References

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