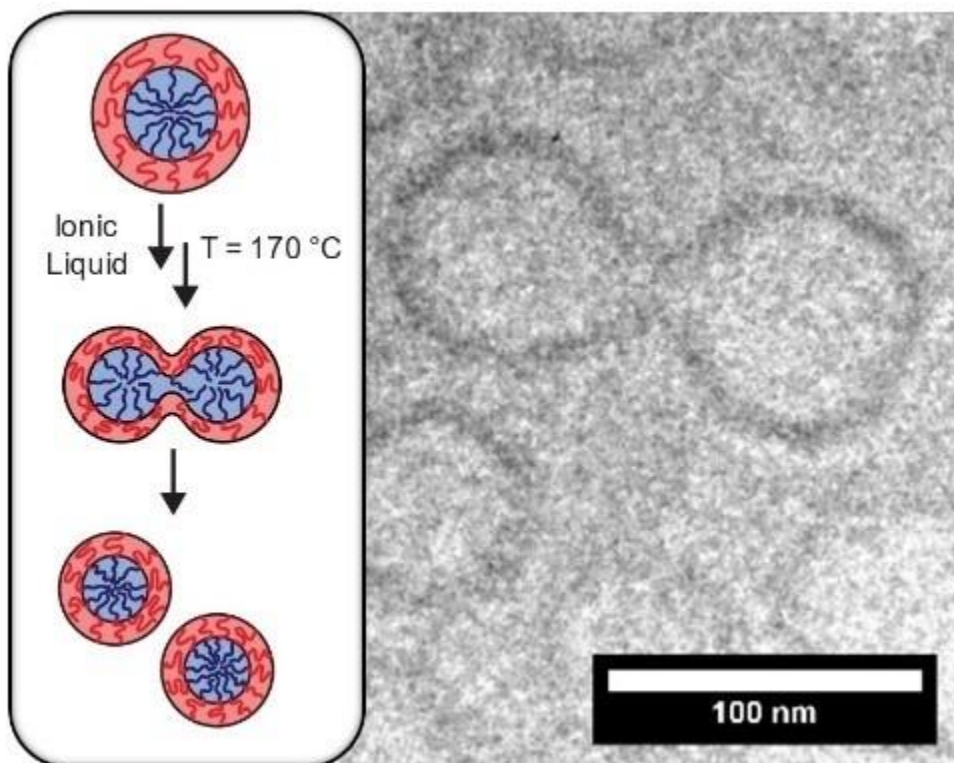


Spontaneous fragmentation of block copolymer micelles

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Block copolymers (BCPs) self-assemble into various micellar nanostructures in selective solvents, and can be applied in a host of diverse technologies including drug delivery, viscosity modification, and nanoreactor design. To fully realize these practical uses, the mechanisms for micellization and equilibration must be elucidated. Micelle fragmentation, fusion, and chain exchange are all possible relaxation mechanisms. To date, fragmentation has not been studied in any detail. We use temperature-jump dynamic light scattering (*T*-jump DLS), synchrotron small-angle X-ray scattering (SAXS), and liquid-phase transmission electron microscopy (LP-TEM) to develop a quantitative understanding of micelle fragmentation kinetics in ionic liquids (ILs). The use of non-volatile IL solvents enables high-temperature annealing and direct use of TEM. Fragmentation of one molecular weight of 1,2-polybutadiene-*b*-poly(ethylene oxide) (BO) was studied in five ILs to determine the effect of solvent selectivity. Then, fragmentation of BO was visualized for six molecular weights in one IL using LP-TEM. The fragmentation kinetics were also quantified by time-resolved SAXS and *T*-jump DLS. By combining these experimental techniques, a detailed analysis of micelle fragmentation kinetics, along with the direct observation of intermediate structures during fragmentation events, was achieved.



Transmission electron micrograph of BO micelle (light region) fragmenting in an IL (dark region) solvent. Fragmentation is illustrated schematically on the left.