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Block Copolymers and Ionic Liquids: A New Class of Functional Nanocomposites[1]

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Block copolymers provide a remarkably versatile platform for achieving desired nanostructures by self-assembly, with lengthscales varying from a few nanometers up to several hundred nanometers. Ionic liquids are an emerging class of solvents, with an appealing set of physical attributes. These include negligible vapor pressure, high chemical and thermal stability, tunable solvation properties, high ionic conductivity, and wide electrochemical windows. For various applications it will be necessary to solidify the ionic liquid into particular spatial arrangements, such as membranes or gels, or to partition the ionic liquid in coexisting phases, such as microemulsions and micelles. One example includes formation of spherical, cylindrical, and vesicular micelles by poly(butadiene-*b*-ethylene oxide) and poly(styrene-*b*-methylmethacrylate) in the common hydrophobic ionic liquids [BMI][PF_6] and [EMI][TFSI]. This work has been extended to the formation of reversible micelle shuttles between ionic liquids and water, whereby entire micelles transfer from one phase to the other, reversibly, depending on temperature and solvent quality. Formation of ion gels has been achieved by self-assembly of poly(styrene-*b*-ethylene oxide-*b*-styrene) triblocks in ionic liquids, and by the thermoreversible system poly(N-isopropylacrylamide-*b*-ethylene oxide-*b*-N-isopropylacrylamide), using as little as 4% copolymer. Further, these gels have been shown to be remarkably effective as gate dielectrics in organic thin film transistors. The remarkably high capacitance of the ion gels ($> 10\ \mu F/cm^2$) supports a very high carrier density in an organic semiconductor such as poly(3-hexylthiophene), leading to milliamp currents for low applied voltages. Furthermore, the rapid mobility of the ions enables switching speeds approaching 10 kHz, orders of magnitude higher than achievable with other polymer-based dielectrics such as PEO/$LiClO_4$. Finally, we have shown that ordered nanostructures of block copolymers plus ionic liquids show the characteristic self-assembly properties of strongly-segregated systems. Prospects for anisotropic ionic conductivity are also being explored.

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