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Understanding How the Presence of Uniform Electric Fields Can Shift the Miscibility of Polystyrene / Poly(vinyl methyl ether) Blends

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Techniques which can externally control and manipulate the phase behavior of polymeric systems, without altering chemistry on a molecular level, have great practical benefits. One such possible mechanism is the use of electric fields, shown to cause interfacial instabilities, orientation of morphologies, and phase transitions in polymer blends and block copolymers. We have recently demonstrated that the presence of uniform electric fields can also strongly enhance the miscibility of polystyrene (PS) / poly(vinyl methyl ether) (PVME) blends [J. Chem. Phys. 2014, 141, 134908]. Using fluorescence to measure the phase separation temperature T_s of PS/PVME blends with and without electric fields, we show that T_s can be reproducibly and reversibly increased by 13.5 +/- 1.4 K for electric fields of 17 kV/mm for this lower critical solution temperature (LCST) blend. This increase in blend miscibility with electric fields represents some of the largest absolute shifts in Ts ever recorded, well outside of experimental error. The best theoretical prediction for the expected shift in T_s with electric field for this system is still two orders of magnitude smaller than that observed experimentally. We discuss the limitations of this theoretical prediction and consider possible factors affecting miscibility that may need to be also included.

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