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Gradient Architecture as Means of Phase Diagram Manipulation in Copolymers: Accessing Both LCOT and UCOT in High Molecular Weight Styrene/n-Butyl Acrylate Systems MICHELLE MOK, WESLEY BURGHARDT, Northwestern University, CHRISTOPHER ELLISON, University of Texas at Austin, JOHN TORKELSON, Northwestern University — Traditionally, phase transitions of block copolymers could only be tuned through molecular weight and relative block length. Here, we introduce comonomer sequence design through gradient compositions as a means of further manipulating phase diagram boundaries. In such gradient copolymers, the reduced repulsion between chain segments allows access to phase transitions even at high molecular weights (MW). Rheological and x-ray scattering studies were performed to study the impact of comonomer sequence on phase behavior in styrene/n-butyl acrylate (S/nBA) systems. In S/nBA block copolymers, only upper critical ordering behavior was observed. In contrast, by using a gradient architecture of higher MW we observed both upper and lower ordering transitions similar to those seen in very weakly segregating S/n-butyl methacrylate block copolymers, where such dual ordering transitions were first detected by Russell et al. This is the first study to access a miscibility gap in gradient copolymers. Access to such behavior is very rare in blends and block copolymers, limited to low MW and/or very weakly segregating systems.

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