The influence of block polydispersity on phase separation of diblock copolymers

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Polydisperse block copolymers have attracted much interest in recent years as the ability to tolerate block dispersity could considerably lower the manufacturing cost of block copolymers. While polydisperse block copolymers are capable of microphase separation, the increase in block dispersity is known to have significant influence on block copolymer phase behavior and domain morphologies. The published studies thus far are focused on asymmetric systems where at least one of the blocks is kept to be monodisperse. In this study, we synthesized and characterized a series of polystyrene-b-poly(methyl methacrylate) (PS-PMMA) diblocks where polydispersity index (PDI) of both blocks were varied. The PS-PMMA diblock copolymers were synthesized by sequential atom transfer radical polymerization (ATRP). PDI of the first block was controlled by temporal regulation of initiator feed rate, while the second block PDI was controlled by the addition of phenylhydrazine modifier. The domain morphologies of the resulting diblocks were examined using small-angle X-ray scattering (SAXS). At the same volume fraction of the PS block, PDI dictated phase transition was observed.