Toward photo-tunable thin film morphology using block copolymer via reversible-deactivation radical polymerizations

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*4-Methacryloyloxyazobenzene (MOAB) and a polystyrene-\(b\)-poly(\(n\)-butyl methacrylate) (PS-\(b\)-PnBMA) block copolymer with the azobenzene moiety in the PnBMA segment were prepared. The purpose for synthesis of this material is to adjust the lower disorder-to-order transition (LDOT) behavior by UV/Vis light by slight changes in the volume resulting from isomerization. A P(nBMA-co-MOAB)-X macroinitiator was prepared by activators regenerated by electron transfer (ARGET) ATRP. The macroinitiator was chain extended with styrene by normal ATRP. An acceleration in reaction rate in the presence of a reducing agent was observed. The low polydispersity P(nBMA-co-MOAB)-b-PS diblock copolymers were obtained. The first-order kinetic plots were observed. The molar masses were in good agreement with the calculated values and the polydispersity was in the range of 1.16-1.31, indicating a well-controlled synthesis of the photo-responsive block copolymer. Preliminarily, photoisomerization phenomenon was observed in solution and film states. Block copolymer film with higher azobenzene content has a significant change in the in-situ X-ray reflectivity measurement (Fig. 1), implying that phase transition occurred after UV exposure.

Fig. 1. Variation of X-ray reflectivity on BCP thin film (15.4 mol% azobenzene).