Abstract: Photo-induced radical polymerization has been widely utilized as a UV-curing process for inks, paints, adhesives, and photo-resist materials. UV intensity, wavelength, irradiation time and area etc, are easily manipulated, and such simple and rapid (within seconds) UV-curing process is well established in view of industrial processes. However, reaction kinetics, deformation (shrinkage), and phase-separation kinetics associated to polymer network formation are rather complex, and their delicate balance needs to be considered and the precise control the whole process is still challenging.

Controlled (or living) radical polymerization techniques such as atom-transfer controlled radical polymerization (ATRP) have greatly impacted the advancement of polymer synthesis in the last 20 years, allowing well-defined polymers with precise molecular weight distribution and segment blocks. Recently, further temporal (on/off) control of polymerization via external stimuli such as photo-excitation has proposed and gained increased attention. Here we focus on organo-catalyzed iodine-transfer controlled radical polymerization, which allows reversible photo-activation of polymeric dormant without metal catalysts. In this study, we synthesized polymeric dormant with C-I endgroup and utilized to the UV-curing process to challenge the precise control of photo-polymerization and phase-segregation simultaneously. The obtained coatings were optically clear, but internal nanostructure of the coating exhibited unprecedented, bicontinuous nanodomains with gradient size distribution. The domain size was tunable with UV intensity, crosslinker content, and other processing aids. Post-functionalization of the evolved nanostructures will be also discussed.

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