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Photochemical Crosslinking of Preformed Glassy and Amorphous Polymers Through bis-Benzophenone Mediated Covalent Bridging[1]

NICHOLAS CARBONE, MARY DICKSON, JEFFREY LANCASTER, Columbia University, GREG CARROLL, University of Groningen, JEFFREY KOBERSTEIN, Columbia University — We show that bis-benzophenone (bis-BP) is an effective method to photochemically crosslink essentially any solvent-free glassy or amorphous preformed polymer system that contains abstractable hydrogen atoms. When bis-BP is mixed into a polymer and exposed to UV radiation, it abstracts hydrogen atoms from any chains in proximity, thereby initiating a cascade of free radical reactions that include several mechanisms that can lead to covalent polymer crosslinking. Herein we study the early stages of branching reactions that precede gelation by following molecular weight changes in bis-BP modified glassy polystyrene (PS) and amorphous poly(n-butyl acrylate) (PnBA) thin films on silicon wafers by Gel Permeation Chromatography. Quantitative molecular weight changes in PS:bis-BP and PnBA:bis-BP thin films are studied as a function of irradiation time, polymer:bis-BP molar ratio, and film height. Increases in molecular weight and polydispersity are quantified and model equations are developed.

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