Highly Stretchable Free Standing Membranes of Poly(acrylic acid)-*b*-Poly(vinyl alcohol) Synthesized via Cobalt Mediated Radical Polymerization

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Abstract

Given by the rapid development of controlled/living radical polymerization (C/LRP) methods, various block copolymers have been synthesized and showed unique properties that are potentially useful in different fields. The block copolymers with poly(vinyl alcohol) (PVA) segment yet have seldom been reported. PVA, which is obtained from the hydrolysis of poly(vinyl acetate) (PVAc), shows the properties of good solvent resistance, strong mechanical properties, high water-containing capacity, and good biocompatibility that lead PVA as one of the most widely used hydrophilic materials adaptable for textile industry, food packaging, and medical devices. However, the difficulty to achieve the controlled/living radical polymerization of vinyl acetate has limited the development of PVA-based block copolymers.

Cobalt mediated radical polymerization (CMRP) is to date one of the most efficient ways to synthesize the controlled polymers of vinyl acetate, and thus controlled poly(vinyl alcohol). We have systematically studied the CMRP and established the mechanism model associated with the thermodynamic and kinetic parameters to correlate the relationship between reduction potential, equilibrium constant of cobalt(II) and organo-cobalt(III), and control mechanism. The control efficiency of different cobalt complexes to the C/LRP and chain extension of vinyl acetate and methyl acrylate has also been compared. With such an in-depth understanding to CMRP technique, cobalt porphyrin complex (Co(TMP)) has been selected as the mediator to prepare the block copolymer of poly(methyl acrylate)-*b*-poly(vinyl acetate), which was hydrolyzed to poly(acrylic acid)-*b*-poly(vinyl alcohol) (PAA-*b*-PVA). The free standing membranes of PAA-*b*-PVA surprisingly own a much higher tensile strain (> 600%) than those made by homopolymers and polymer blends. A series of studies using cross-section SEM images, IR spectrum, and SAXS indicated that the formation of nanostructure in the block copolymers prescribed a considerably larger amount of interface which could enhance the tensile properties drastically.

Keywords: Free-standing membrane, block copolymer, vinyl alcohol, acrylic acid, cobalt mediated radical polymerization.