Full Paper: Poly(vinyl alcohol)-graft-poly(e-caprolactone) (PVA-g-PCL) was synthesized by ring-opening polymerization of e-caprolactone with poly(vinyl alcohol) in the presence of tin(II) 2-ethylhexanoate as a catalyst in dimethyl sulfoxide. The relationship between the reaction conditions of the solution polymerization and the chemical structure of the graft copolymer was investigated. The degree of substitution (DS) and degree of polymerization (DP) of the PCL side chains were roughly controlled by varying the reaction periods and feed molar ratios of the monomer and the catalyst to the backbone. PVA-g-PCL with a PCL content of 97 wt.-% (DP = 22.8, DS = 0.54) was obtained in 56 wt.-% yield. The graft copolymer was soluble in a number of organic solvents, including toluene, tetrahydrofuran, chloroform, and acetonitrile, which are solvents of PCL. The molecular motion of the graft copolymer from $^1$H NMR measurements appears to be restricted to some extent at 27–50°C, however the $^1$H NMR signal intensities measured at temperatures higher than ca. 50°C reflect the actual chemical structure of the graft copolymer as determined by elemental analysis. The graft copolymer having a short PCL side chain (DP = 4.4, DS = 0.15) was amorphous. The melting temperature of a sample with relatively high PCL content (DP = 22.8, DS = 0.54) was observed at 39°C. Thermogravimetric analysis revealed that the thermal stability of PVA was improved by introducing PCL side chains. The surface free energies of the air-side of a graft copolymer film, as calculated by Owens’ equation using contact angles, were comparable to that of PCL homopolymer.

Synthesis of a Poly(vinyl alcohol)-Based Graft Copolymer Having Poly(e-caprolactone) Side Chains by Solution Polymerization

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Keywords: biodegradable polymer; graft polymer; poly(e-caprolactone); poly(vinyl alcohol); ring-opening polymerization