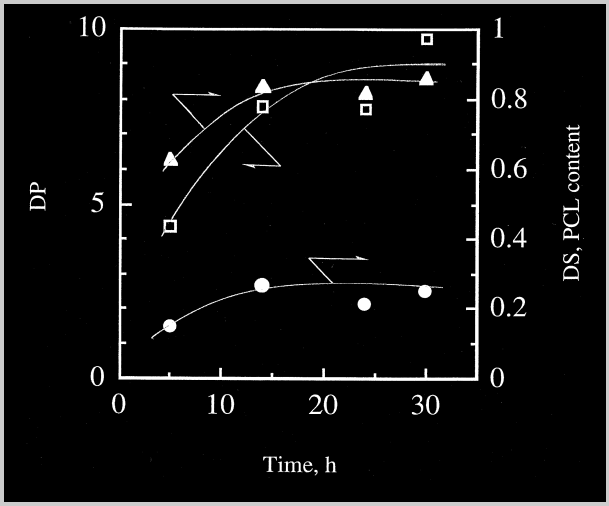
Full Paper: Poly(vinyl alcohol)-*graft*-poly(ε-caprolactone) (PVA-g-PCL) was synthesized by ring-opening polymerization of ε-caprolactone with poly(vinyl alcohol) in the presence of tin(II) 2-ethylhexanoate as a catalyst in dimethyl sulfoxide. The relationship between the reaction conditions of the solution 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.



Relationship between polymerization time and *DS* (●) and *DP* (□) of poly(ε-caprolactone) (PCL) side chain, and PCL content (▲) of product poly(vinyl alcohol)-*graft*-poly(ε-caprolactone) (PVA-g-PCL). PVA, 0.075 g (1.7 mmol of repeating units, $\bar{M}_n$ = 15 300); CL, 0.97 g (8.5 mmol); tin(II) 2-ethylhexanoate, 38 mg (0.094 mmol); dimethyl sulfoxide, 0.5 mL; temp., 100 °C; under nitrogen.

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

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