Preparation of Syndiotacticity-Rich High Molecular Weight Poly(vinyl Alcohol) by Low Temperature Bulk Polymerization of Vinyl Pivalate Using 2,2'-Azobis(2,4-Dimethylvaleronitrile)

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Vinyl pivalate (VPi) was bulk-polymerized at 30, 40, and 50°C using a low temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN), and the effects of polymerization temperature and initiator concentration were investigated in terms of the polymerization behavior and molecular structures of poly(vinyl pivalate) (PVPi) and resultant poly(vinyl alcohol) (PVA) obtained by saponifying it with potassium hydroxide/water/methanol. The lowering of polymerizartion temperature and conversion actualized by using ADMVN proved to be successful in obtaining syndiotacticity-rich ultrahigh molecular weight PVA. PVPi having number-average degree of polymerization (P_n) of 15,000-2,8000 was obtained, and the degree of branching for pivaloyl group was 0.75-1.00 at conversion of below 25%. By saponifying the prepared PVPi PVA having maximum P_n of over 15,500, and maximum syndiotactic diad (S-diad) content of 61% was obtained. The syndiotactic triad and diad contents, and crystal melting temperature were higher than those of PVA prepared from PVPi polymerized at lower temperatures. It was found that high strength microfibrillar PVA fibers could be prepared by saponifying PVPi (S-diad content of 58-61%) as well as PVPi prepared by photo-bulk polymerization at polymerization temperature of 0-10°C (S-diad content of 63-64.5%).