



POLYELECTROLYTE BEHAVIOR OF IONIZED ARBORESCENT POLYSTYRENE-GRAFT-POLY(2-VINYLPYRIDINE) COPOLYMERS

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A method was developed for the 100-g scale synthesis of arborescent (dendrigraft) copolymers with poly(2-vinylpyridine) (P2VP) segments. The branched polyelectrolyte precursors were obtained in up to 96 % yield by coupling 'living' P2VP macroanions with acetylated linear and arborescent polystyrene substrates of generations G0 or G1. Copolymers with $M_n \approx 5000$ or 30000 side chains and containing 87-98 mol % P2VP were thus synthesized. These materials are characterized by a very compact structure, a narrow molecular weight distribution ($M_w/M_n = 1.08-1.10$), and roughly geometric increases in branching functionality and molecular weight over successive generations. The copolymers are freely soluble in water and in polar organic solvents such as methanol and N,N-dimethylformamide (DMF) upon protonation by a strong acid. The viscosity of the copolymers was investigated using capillary viscosity measurements as a function of their concentration and their protonation level in different solvents (water, N,N-dimethylformamide, and methanol). Properties typical of polyelectrolytes were observed, including strong curvature in plots of the reduced viscosity (η_{sp}/C) versus concentration (C) at both low and high concentrations. The curvature was more pronounced in methanol (polar protic solvent) than in DMF (polar aprotic solvent), and the expansion of the branched molecules apparently varied in the order $G1 > G0 > G2$. The reduced viscosity of arborescent polyelectrolyte solutions was nonetheless much lower than for linear P2VP samples of comparable molecular weights, due to the smaller dimensions and increased structural rigidity of the molecules. The addition of salts to the solutions decreased their viscosity and suppressed the curvature of the reduced viscosity plots, presumably due to charge screening.