Living atom transfer radical polymerization of 4-acetoxystyrene

Living atom transfer radical polymerization (ATRP) of 4-acetoxystyrene (1), a protected 4-vinylphenol, leading to poly(4-acetoxystyrene) with well-defined molecular weight and narrow molecular weight distribution was carried out in bulk with a,a'-dibromoxylene(2)/CuBr/2,2'-bipyridine(bpy) as initiating system. A linear $<M_n>\text{ versus monomer conversion}$ plot was found in good accordance with the theoretical line, indicating 100% initiating efficiency. The polymerization is first order in respect to monomer up to about 70% monomer conversion. Deviations from linearity at higher conversion in the first order plot are due to physical effects, i.e., to the increase of the viscosity of the reaction medium. The resulting 1-bromo-1-phenylethyl-telechelic poly(4-acetoxystyrene) (3) is a precursor of the hydrophilic poly(4-vinylphenol) and a potential new macroinitiator.