

## Troponoid-mediated radical polymerization of vinyl acetate and acrylates

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A series of tropone derivatives, including the natural product of hinokitiol, has been utilized as new organic mediators in controlling the radical polymerization of vinyl acetate (VAc), methyl acrylate (MA), and *N*-vinyl pyrrolidone (NVP) with the predictable molecular weight and formation of block copolymers. The mechanism of this troponoid-mediated radical polymerization (TPRP) was investigated through control studies, DFT calculations, and chain-end characterization. The tropone derivatives deactivated the propagating radicals by forming a C-C bond at the  $\alpha$ -carbon of tropone, thus generating the dormant species. The dynamic equilibrium between the dormant species and the tropones with radicals leads to the control of polymerization. The equilibrium constants ( $K_{eq}$ ) for polymerizations of vinyl monomers with various troponoids have been calculated using the Eyring equation, rationalizing the control efficiency of different tropones in VAc, NVP and MA polymerizations.