

Stereoselective Alternating Copolymerization of Aliphatic Acetylenes with Sulphur dioxide

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ABSTRACT

Purified terminal aliph. acetylenic hydrocarbons were copolymerized with liquid SO₂ in the presence of tert-BuOOH [75-91-2] at low temperature. Neither SO₂ nor tert-BuOOH alone was capable of polymerizing pure alkynes. Aged (impure) alkynes were copolymerized with SO₂ in the absence of tert-BuOOH. All resulting alkyne-SO₂ copolymers were alternating with 100% trans configuration regardless of the nature of the alkyne, the solvent, or temperature. A mechanism was proposed in which SO₂ homolytically decomposed the organic hydroperoxide into free radicals which initiate the polymerization. The alkyne-SO₂ charge transfer complex was formed in solution, and the initiation and propagation steps probably involved this complex in equilibrium with its monomers.