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Alternating Radical Copolymerization of Vinyl Acetate and *tert*-Butyl-2-trifluoromethacrylate

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Abstract: Alternating conventional radical copolymerization of *tert*-butyl-2-trifluoromethacrylate (a non-homopolymerizable fluoromonomer under radical initiation) with vinyl acetate, initiated by 2,2'-azo-bis(4-methoxy-2,4-dimethyl valeronitrile) at 40 °C is presented. The study of the kinetics of the copolymerization using various $[VAc]_0/[MAF-TBE]_0$ feeds showed that an equimolar feed of comonomers led to the highest apparent copolymerization rate ($K_{app} = 4 \times 10^{-4} \text{ s}^{-1}$). The resulting copolymers had a nearly perfect alternating structure over a very wide range of comonomer feed compositions ($f_{MAF-TBE} = 0.05$ to 0.95) until complete consumption of one of the monomers. The reactivity ratios were measured to be: $r_{MAF-TBE} = 0$ and $r_{VAc} = 0.014$ at 40 °C and the Alfrey and Price parameters for MAF-TBE were calculated ($Q_{MAF-TBE} = 1.18$ and $e_{MAF-TBE} = 1.84$).

Keywords: alternating copolymerization; fluoropolymer; radical polymerization; thermal properties; vinyl acetate.

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