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TRIMETHYLSILYL TRIFLATE AS INITIATOR FOR THE CATIONIC POLYMERIZATION OF HETEROCYCLICS AND ALKENES. MODEL REACTIONS FOR THE CATIONIC GRAFTING FROM POLYSILANES.

by

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March 23, 1989

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Trimethylsilyl trifluoromethanesulfonate is one of the strongest silylating reagents. It reacts with a variety of nucleophiles including alcohols, amines, ethers, and esters. Reaction with cyclic ethers, iminoethers, and esters leads to silyl onium ions which initiate polymerization of strained heterocyclic monomers. The reactivity of the first silyl onium ions is lower than that of the subsequent alkyl onium ions. Therefore initiation rate constant (k_i) is lower than propagation rate constant (k_p). Reaction of poly(phenylmethylsilylene) with triflic acid leads to dearylation of polysilane and formation of very reactive silyl triflate groups along the chain of polysilane. These sites were used to initiate cationic polymerization of various monomers from polysilanes, and to prepare new graft copolymers based on polysilanes.

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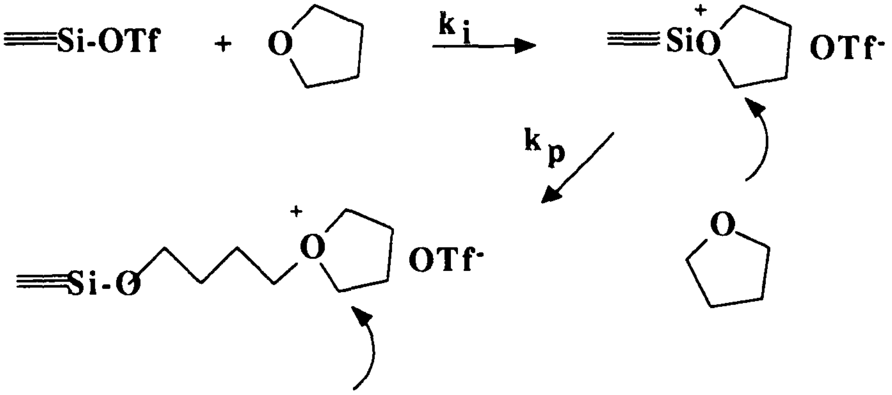

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Trimethylsilyl triflate reacts directly only with the most nuceophilic alkenes (N-vinylcarbazole). Polymerization of less reactive styrene is initiated by traces of triflic acid, which is a decomposition product of silyl triflate.

Reaction of poly(phenylmethylsilylene) with triflic acid leads to dearylation of polysilane and formation of very reactive silyl triflate groups along the chain of polysilane. These sites were used to initiate cationic polymerization of various monomers from polysilanes, and to prepare new graft copolymers based on polysilanes.

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