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Deaminatively Generated Carbocations as Initiators of Styrene Polymerization

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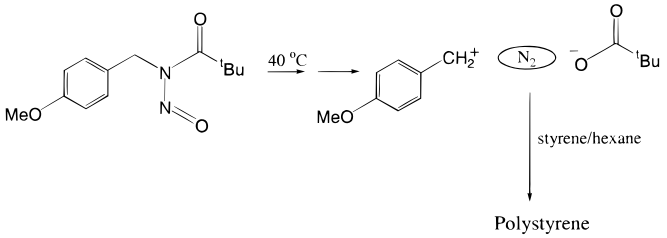
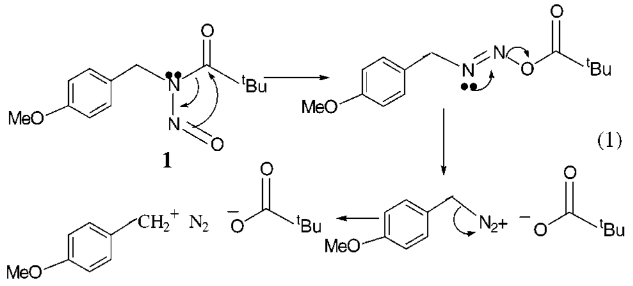
ABSTRACT



Addition polymerization is readily accomplished via free radicals and carbanions but conventional initiations via carbocations are limited principally by low initiator reactivity. Thermolyses of *N*-nitrosamides produce nitrogen-separated ion-pairs (NSIPs) containing exceedingly reactive carbocations. We report here the novel use of this facile mode of carbocation generation in the polymerization of styrene. Polystyrene of viscosity average molecular weight ∼10^6 was obtained.

Thermolyses of *N*-alkyl-*N*-nitrosamides produce nitrogen separated ion pairs (NSIPs) containing exceedingly reactive carbocations (eq 1).[1,2] The high reactivity[1,2] of these deaminatively generated carbocations is due, in part, to the low activation energy required for the loss of nitrogen that allows the cation to be formed with minimal solvent participation.[1,2] Additionally, the temporary screening of the cation from its counterion by the sheer physical presence of the nitrogen molecule results in the maximal positive charge at the electron-deficient center.[1a]



(1)

These exceedingly reactive cations can be chosen so that β-eliminations and rearrangements are not possible and reaction with nucleophiles is their only fate. The nucleophiles available to them are the counterion and the solvent. The cation−solvent reaction must occur before diffusion of nitrogen from between the ions as the latter process leads to internal collapse of the ion pair to form the corresponding ester.

N-Nitrosoamides are favorable sources of carbocations because of the mildness of the conditions required to generate cations, the high reactivity of the unsolvated carbocations formed, the solubility of the precursors in a wide range of solvents, homogeneity of the reactions, wide range of decomposition temperatures possible, straightforward chemistry, and excellent product balance.[2a,b]

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Cation-Initiated Polymerizations. Cationic polymerization represents an important body of techniques for the synthesis of many polymers possessing unique structures and properties.[3b] The cations used to initiate polymerizations include protons,[3c] oxonium ions[3d] and carbocations.[3b] There are two chemical sources of carbocations in current use: (1) *Stable carbocation salts* such as hexafluoroantimonates of trityl[4a,b] and tropylium[4c,d] carbocations—these species are able to initiate polymerizations of reactive monomers such as styrenes[4a,b,d] but they are too stable to initiate polymerizations of less reactive monomers such as ethene and isobutene.[3e] (2) *Haloalkane/Friedel−Crafts (F−C) complexes*—these systems generate carbon-based electrophiles which are not "free" carbocations;[2a,c] they are more reactive than carbocation salts but are still unable to initiate polymerization of monosubstituted alkenes and ethene. Additionally, the utility of this system is compromised by the inability to identify the actual initiating species (polarized haloalkane, carbocation, ion pair, or ion multiplet), extreme moisture sensitivity, and limited catalyst solubility in many of the common solvents. These problems make kinetic assays very difficult.

Surprisingly, no efforts have yet been made to explore the use of deaminatively generated carbocations in polymerization. We report here the novel use of this facile mode of carbocationation in the polymerization of styrene.

Polymerization via Deamination. *N*-4-Substituted benzyl-*N*-nitrosopivalamides were chosen for these studies because the steric bulk of the *tert*-butyl and substituted benzyl groups around the *N*-nitroso moiety results in a low half-life,[5] and because the reactivity of the benzyl cation generated could be readily modified by appropriate substitution at the 2, 4, and 6 positions. The half-life of *N*-benzyl-*N*-nitrosopivalamide at 40 °C is $\sim$7 min,[2a] consequently a reaction time of 3 h (= 12 half-lives) was chosen for the runs. A moderate temperature was chosen to minimize the thermally induced free-radical pathway but to still allow relatively rapid carbocationation. Hexane was chosen as the cosolvent because it is inert to the cation under consideration, it is relatively volatile, and readily dissolves both the monomer and the nitrosoamide.

Freshly distilled styrene in dry hexane was polymerized through decomposition of *N*-4-methoxybenzyl-*N*-nitrosopivalamide (**1**) at 40 °C for 3 h. The resultant yellow solution was then treated with 2-propanol to quench any trace electrophiles and poured into methanol to precipitate the polystyrene. A 16.5% yield (*nonoptimized*) of polystyrene of viscosity average molecular mass $= 1.25 \times 10^6$ and mp $= 165$ °C was obtained. The polystyrene obtained is higher melting and of higher mass than commercially available material.[6a]

Ostensibly the highly reactive,[1,2] first-formed 4-methoxybenzyl cations generated on thermolysis of **1** react with styrene monomers to generate a hierarchy of daughter ions that are themselves of sufficient reactivity to extend propagation of the chain. Additionally, the pivalate anion is both bulky and poorly nucleophilic ($n \sim 2.7$);[6b] consequently it is both sterically and electronically inept at capturing the growing polymer chain. Thus the high reactivity[1,2] of the parent ion, the low nucleophilicity,[6b] and the steric bulk of the pivalate ion apparently lead to expansive chain growth. The resultant large mass and concomitant high melting point observed for the deaminatively generated polystyrene are consistent with the NSIP model.[1,2]

Conclusions. It has been demonstrated for the first time, that deaminatively generated carbocations are successful initiators of addition polymerization. It is to be noted that despite its ability to polymerize styrene, the 4-methoxybenzyl cation generated in the present study is among the least reactive of the simple 4-R-substituted benzyl cations due to the electron-releasing ability of the methoxy group. Although the yields are low, the system has not been optimized, even for the 4-methoxybenzyl cation. Presumably, however, tandem use of more highly reactive substituted-benzyl carbocations (e.g., those containing nitro groups in the 2, 4, and/or 6 positions) and less nucleophilic counterions (e.g., triflate) would lead to larger yields of more massive polymer.

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Supporting Information Available: Experimental data for *N*-4-methoxybenzylpivalamide, *N*-4-methoxybenzyl-*N*-nitrosopivalamide (**1**), and *N*-4-methoxybenzyl-*N*-nitrosopivalamide (**1**) in styrene. This material is available free of charge via the Internet at http://pubs.acs.org.

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[5] The thermal stability of *N*-nitrosamides falls with steric bulk in the alkyl and acyl groups. White, E. H.; Stuber, J. E. *J. Am. Chem. Soc.* **1963**, *85*, 2168.

[6] (a) Commercial polystyrene (e.g., from Sigma-Aldrich Chemical Co.) typically has an average molecular mass of the order of 10^5 and a T_g of 100 °C. (b) The nucleophilicity, n, of a reagent is defined by $\log(k/k_o) = sn$, where k is the rate constant for the S_N2 reaction of MeI at 25 °C.; k_o is the corresponding rate constant with water. The term s gauges the sensitivity of the substrate toward variation in the nucleophiles. Swain, C. G.; Scott, C. B. *J. Am. Chem. Soc.* **1953**, *75*, 141.