Supplementary Material

for

Deaminatively-Generated Carbocations as Initiators of Styrene Polymerization.

by

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Materials and methods. Reagents were purchased from the Aldrich Chemical Company; most were used without further purification. Styrene was vacuum distilled prior to use. Hexane was distilled before using.

NMR spectra were recorded on a Bruker AMX 300 MHz, FT instrument; UV-Vis and IR spectra were measured using a Beckman Model 25 UV-Vis Spectrometer and a Perkin Elmer 1600 Series FT-IR spectrometer, respectfully. All syntheses and reactions of the N-nitrosoamide were performed in the dark. The Parr pressure reactor (equipped with a stirrer and temperature regulator) was purged with and then filled with argon prior to use. Clean, vacuum-dried syringe/needle assemblies were flushed 10 times with argon before using.

Stability of the Precursor; Handling and Storage. N-Nitrosopivalamides in addition to being thermolabile are labile in the presence of acids, bases and moisture. As a result, the nitrosoamide was freshly prepared for each run. All manipulations involving the nitrosoamide were performed in the dark. **Caution!** Nitrosoamides should be handled with extreme care because of their possible mutagenicity[1a] and carcinogenicity (local and

systemic).[1b] Efficient fume hoods and appropriate personal protection (chemical-resistant gloves, safety glasses, lab coat, etc.) are recommended when handling these compounds.

N-4-Methoxybenzylpivalamide was prepared from the procedure of Heyns and von Bebenburg.[2] : m.p. 81°-82°C (lit[3] 81°-82°C); IR (KBr) 3309, 1689 1510, 1390, 1375 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (s, 9H), 4.44 (d, 2H, J = 7Hz), 5.90 (bs, 1H), 7.26-7.32 (m, 5H), λ_{max} = 284 (ε = 209).

N-(4-Methoxy)-benzyl-N-nitrosopivalamide (1). A mixture of N-4-methoxybenzyl pivalamide (955 mg, 5 mmol), NaOAc (2.5 g, 30 mmol), and Na_2SO_4 (5 g) was dried at oil pump vacuum. Methylene chloride (30 cm^3) freshly distilled from P_2O_5, was added, under N_2, to the solid material and the suspension was cooled to –78°C A solution of $N_2O_{4(l)}$ (2 cm^3, 31 mmol) in CH_2Cl_2 (10 cm^3) at -78 °C was then added to the stirred suspension at -78°C which was then allowed to warm to -25°C over 20 minutes. After a further 20 minutes at -25°C, the suspension was washed rapidly in turn with saturated solutions of NaCl, $NaHCO_3$ and NaCl at -5°C. The organic phase was dried with stirring over Na_2SO_4 at -30 °C and was evaporated *in vacuo* for ~20 minutes at –30°C to yield a lemon yellow oil (1.1 g, 5 mmol, 100%): IR (Neat) 1720, 16059, 1502, 1390, 1375 cm^{-1}; ^1H NMR (CD_3CN) δ 1.45 (s, 9H), 4.97 (s, 2H), 7.05-7.40 (m, 5H). UV (CH_2Cl_2) λ_{max} 275 nm (ε = 500), 400 nm (ε = 63), 394 nm (sh), 422 nm (ε = 66).

Decomposition of N-(4-methoxy)-benzyl-N-nitrosopivalamide (1) in Styrene. In a typical run, cyclohexane (100 cm^3) and styrene (10 cm^3, 87.2 mmol) were introduced via argon-purged syringes into a 500 cm^3 argon-purged Parr reactor. N-(4-Methoxy)-benzyl-N-nitrosopivalamide (**1**) (0.25 g, 1.2 mmol) in cyclohexane (10 cm^3) was then

introduced via syringe into the reactor; the solution was stirred vigorously and the temperature was maintained at 25°C for 3h. After 3h, the reaction was quenched with 20 cm^3 of isopropyl alcohol and the solution was added dropwise with stirring into 2L of methanol. The resulting suspension was filtered and the residue was air dried to yield a white flaky solid (1.5g, 16.5%). Viscosity average molecular mass 1.25 x 10^6; glass transition temperature (T_g) 148°–155°C; m.p. 165°C. The oligomers were not determined.[4]

References:

1. (a) Lee, K.; Gold, B.; Mirvish, S. *Mutat. Res.* **1977**, *48*, 131. (b) Preussman, R.; Stewart, B. W. *Chemical Carcinogenesis,* Searle, C., Ed., ACS Monograph No. 182, American Chemical Society, Washington, DC, 1984, pp 643-828.
2. Heyns, K.; v. Bebenburg, W. *Chem. Ber.* **1953**, *86*, 278.
3. *Beilstein* Vol. 12, 3rd Suppl. p. 2346.
4. The yield of polystyrene was not optimized and oligomers, though present, were not analyzed for mass range and yields.