Notes

New Alkoxyamines from the Addition of Free Radicals to Nitrones or Nitroso Compounds as Initiators for Living Free Radical Polymerization[1]

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Introduction

Nitroxide-mediated living free radical polymerization, first mentioned in the seminal work[2] of Solomon and co-workers, has been the object of intensive academic and industrial research during the past years. The control of this polymerization originates from the reversible capping of the growing polymer radical by a nitroxide to form the corresponding alkoxyamine (dormant species). Most experiments used 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO), which works reasonably well in styrene and its derivatives but is unsatisfactory for the controlled polymerization of other monomers such as acrylates. Several approaches have tried to extend the range of TEMPO polymerizable monomers, to speed up the polymerization rate, or to lower the polymerization temperature: (a) use of various additives such as strong acids,[3] pyridinium salts,[4] electron-deficient compounds,[5] acylating[6] or reducing[7] agents, or additional conventional free radical initiators[8] with the TEMPO system; (b) modification of the TEMPO structure by substitution in the 4-position;[9,10] (c) use of nitroxides other then TEMPO such as, for example, isoindoline-*N*-oxyls,[2] di-*tert*-butyl nitroxide,[2,11] pyrrolidine-*N*-oxyls,[12] nitronyl nitroxides,[13] oxazolidine-*N*-oxyls,[14] imidazolidinone-*N*-oxyls,[15] and morpholinone-, piperazinone-, or piperazindione-*N*-oxyls.[16] Significant improvement seems to have been achieved recently with some new acyclic nitroxides and the corresponding alkoxyamines.[17] Indeed, these new compounds polymerize a variety of monomers including styrene, acrylates, acrylamide, acrylonitrile, 1,3-dienes, or maleic anhydride in a controlled way.

In this paper we report polymerization results for a new alkoxyamines which can be easily synthesized through double addition of free radicals to a nitrone or nitroso compound.

Results and Discussion

Synthesis of the New Alkoxyamines. Nitrones[18] or nitroso compounds[19] react with free radicals forming nitroxides. In the presence of excess free radicals, these nitroxides couple with the latter to give the corresponding alkoxyamines. Using this principle, we have synthesized the new alkoxyamines **2** and **4** from the readily available starting materials **1** and **3** as depicted in Scheme 1. Even though the unoptimized yields of **2** and **4** are not very high (21−50%), multigram quantities can easily be prepared. Because the reaction product of AIBN with **3** is an oil, the easy to purify, crystalline ACCN adduct **4** was preferred in the case of **3**. No attempts have been made to isolate the intermediate nitroxides. Recently, the in situ formation of similar nitroxides and their activity as controlling species in the polymerization of methyl methacrylate conducted by combining an azoinitiator with 2,4,6-tri-*tert*-butylnitrosobenzene[9] 2-methyl-2-nitrosopropane,[9,20] or *N*-*tert*-butyl-α-phenylnitrone[21] have been demonstrated. However, the high polydispersity (1.7−1.9) of the obtained polymers indicates rather poor control of such polymerization processes.

Polymerization of Styrene with 2 and 4. The linear increase of the molecular weight M_n with monomer conversion is a key feature defining a living polymerization process. Figure 1 shows that this requirement is well fulfilled during the bulk polymerization of styrene with **2** and **4** at 110 °C. The conversions after 5 h (65% for **2** and 45% for **4**) indicate that the polymerization with **2** and **4** is faster then with TEMPO-based systems.[22] Furthermore, the experimentally determined M_n values agree well with the calculated ones, and the polydispersity indices are quite low (PD 1.15−1.35). Another typical feature of a living nitroxide mediated polymerization process is the nearly[23] linear development of $\ln M_0/M$ with time. Figure 2 shows that this requirement is also approximately fulfilled with **2** and to a lesser extent, especially at higher conversions, with **4**.

Polymerization of *n*-Butyl Acrylate with 2 and 4. *n*-Butyl acrylate could also be polymerized with the alkoxyamines **2** and **4** at 110 °C in bulk. However, as the data in Figure 3 show, the experimental molecular weights M_n were systematically much higher than the theoretical values. Moreover, the polydispersity of the resulting polymers was poor.

Conclusions

The reaction of nitrone **1** or nitroso compound **3** with free radicals generated by thermal decomposition of azoinitiators was used to prepare the new alkoxyamines **2** and **4**. These are active initiators for the rapid polymerization of styrene, affording a high yield of polystyrene with low polydispersity. In contrast, for *n*-butyl acrylate, only polymers with large polydispersity were obtained.

Experimental Section

^{1}H NMR (300 MHz) and ^{13}C NMR (75.37 MHz) spectra were recorded in $CDCl_3$ on a Bruker 300 spectrometer. IR spectra were taken on Nicolet Magna-IR 750 spectrometer in KBr pill.

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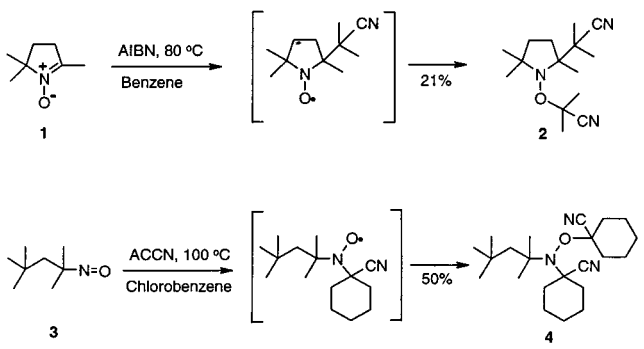
Scheme 1



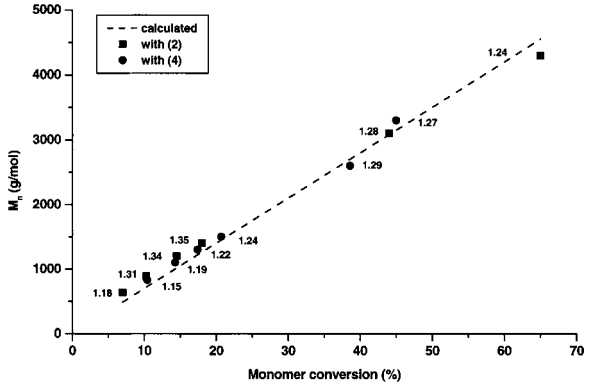


Figure 1. Evolution of experimental molecular weight, M_n, with conversion for the bulk polymerization of styrene at 110 °C with 1.5 mol % **2** or **4** with indicated PD values. Theoretical M_n = [styrene]$_0$ × conversion × 104.15/[initiator]$_0$.

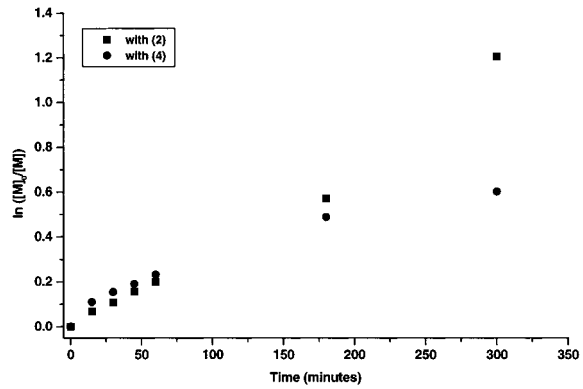


Figure 2. Evolution of ln M_0/M with time for the bulk polymerization of styrene at 110 °C with 1.5 mol % of **2** or **4**.

Styrene (>99.5%), *n*-butyl acrylate (>99%), ACCN (>97%), AIBN (>98%), and solvents (99.5%) were purchased from Fluka. Silica gel (0.063−0.2 mm) for column chromatography was from Merck. The monomers were distilled under vacuum and stored under nitrogen at 0 °C. Number-average molar mass (M_n) of the polymers was determined by size-exclusion chromatography (SEC) on a set of two PL-Gel 5 μm mixed C columns + one PL-Gel guard column using a Spark Holland Basic Marathon sampler and a Flux RHEOS 4000 pump, coupled with an ERC 7515A refractometer and an ERC7217 UV detector. The column temperature was 40 °C and the detector temperature 30 °C. Tetrahydrofuran was used as eluent (1 mL/min). Polystyrene standards were used for the calibration. Monomer conversion was determined by the measurement of the concentration of polymer in the reaction medium through SEC refractometer analysis of the reaction mixture.

2-[2-(Cyanodimethylmethyl)-2,5,5-trimethyl-pyrrolidin-1-yloxy]-2-methylpropionitrile (**2**). A solution of 32 g (0.25 mol) of 2,2,5-trimethyl-3,4-dihydro-2*H*-pyrrole-1-oxide[24] (**1**) and 61.6 g (0.375 mol) of AIBN in 300 mL of toluene was stirred at 90 °C under nitrogen for 6 h. Afterward, 200 mL of toluene was distilled off using a rotary evaporator, and the residue was diluted with 200 mL of hexane. The solution was left to crystallize overnight at 5 °C. The crystals (2,2,3,3-tetramethylsuccinonitrile) were filtered off and discarded. The filtrate was evaporated, and the residue was chromatographed on silica gel (600 g) column with hexanes−ethyl acetate (14:1). The combined pure fractions were recrystallized from 30 mL of hexane at −20 °C to afford 14.1 g (21%) of **2** as a white solid; mp 65−69 °C. For $C_{15}H_{25}N_3O$: calc % C 68.40, H 9.57, N 15.95; found C 68.53, H 9.44, N 16.07. ^{1}H NMR (δ ppm): 1.90−1.30 m (4H, CH_2CH_2), 1.81 s, 1.74 s, 1.44 s, 1.43 s, 1.38 s, 1.36 s, 1.32 s (7 × CH_3). ^{13}C{^{1}H} NMR (δ ppm): 125.79 (CN), 122.72 (CN), 74.83, 72.0, 66.41, 40.8, 36.86, 30.26, 29.95, 28.58, 25.41, 24.83, 23.02, 22.86, 20.31. IR (KBr): 2993 s, 2947 s, 2877 m, 2231 s (CN), 1470 s, 1384 s, 1323 m, 1261 m, 1213 s, 1160 s, 1101 s, 1074 m, 1024 m, 974 s, 927 m, 901 w, 861 m, 848 m, 728 s, 690 w.

1-[1-Cyanocyclohexyloxy-(1,1,3,3-tetramethyl-butyl)amino]cyclohexanecarbonitrile (**4**). A solution of 12.65 g (0.088 mol) of 2,2,4-trimethyl-4-nitrosopentane[25] (**3**) and 43.2 g (0.176 mol) of 1,1′-azobis(cyclohexanecarbonitrile) (ACCN) in 150 mL of chlorobenzene was stirred at 100 °C under nitrogen for 5 h. Afterward, 100 mL of chlorobenzene were distilled off using a rotary evaporator, and the residue was diluted with 100 mL of hexane. The solution was left to crystallize overnight at 5 °C. The crystals (bicyclohexyl-1,1′-dicarbonitrile) were filtered off and discarded. The filtrate was evaporated, and the residue was chromatographed on silica gel column (600 g) with toluene−hexane (2:1). The combined pure fractions were recrystallized from 50 mL of hexane to afford 16 g (50%) of **4** as a white solid; mp 108−112 °C. For $C_{22}H_{37}N_3O$: calc % C 73.49, H 10.37, N 11.69; found C 73.44, H 10.39, N 11.62. ^{1}H NMR (δ ppm): 2.31−2.22 m (4H), 1.97−1.54 m (16H), 1.47 s (6H, $C(CH_3)_2$), 1.25−1.12 m (2H), 1.04 s (9H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (δ ppm): 120.94 (CN), 119.88 (CN), 82.2, 67.72, 64.64, 49.36, 37.77, 36.6, 36.14, 36.07, 32.06, 31.69, 30.49, 29.32, 24.58, 24.39, 23.51, 23.22. IR (KBr): 2934 s, 2869 s, 2226 m (CN), 1477 s, 1454 s, 1386 s, 1366 s, 1340 m, 1256 m, 1158 m, 1019 s, 974 m, 932 s, 912 s, 850 m, 816 m, 778 m.

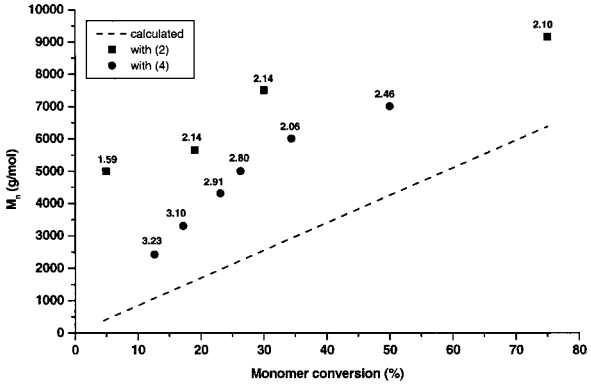


Figure 3. Evolution of experimental molecular weight, M_n, with conversion for the bulk polymerization of *n*-butyl acrylate at 110 °C with 1.5 mol % **2** or **4** with indicated PD values. Theoretical M_n = [*n*-butyl acrylate]$_0$ × conversion × 128.17/[initiator]$_0$.

Examples of Polymerization. a. Polymerization of Styrene with 2. A 50 mL round-bottom, three-necked flask equipped with thermometer, condenser, and magnetic stirrer was charged with 0.379 g (1.44 mmol) of **2** and 10 g (96 mmol) of styrene. The resulting solution was degassed by three vacuum/argon cycles and then heated at 110 °C under argon. The samples for analysis were withdrawn through the rubber septum with a syringe at due intervals. After 5 h, the mixture was cooled to 60 °C, and the remaining monomer was evaporated on a rotary evaporator at 60 °C/5 mbar until constant weight to afford 6.5 g (65%) of a colorless solid polystyrene. GPC: M_n = 4300, PD = 1.24.

b. Polymerization of *n*-Butyl Acrylate with 2. A 50 mL round-bottom, three-necked flask equipped with thermometer, condenser, and magnetic stirrer was charged with 0.308 g (1.17 mmol) of **2** and 10 g (78 mmol) of *n*-butyl acrylate. The resulting solution was degassed by three vacuum/argon cycles and then heated at 110 °C under argon. The samples for analysis were withdrawn through the rubber septum with a syringe at due intervals. After 5 h, the mixture was cooled to 60 °C, and the remaining monomer was evaporated on a rotary evaporator at 60 °C/5 mbar until constant weight to afford 7.5 g (75%) of viscous, pale yellow poly-*n*-butyl acrylate. GPC: M_n = 9150, PD = 2.10.

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