Accurate Structural Control and Block Formation in the Living Polymerization of 1,3-Dienes by Nitroxide-Mediated Procedures

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ABSTRACT: The living free radical polymerization of 1,3-dienes, such as isoprene and 1,3-butadiene, has been shown to be a facile process in the presence of alkoxyamine initiators based on a 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy, **2**, skeleton. These α-hydrido nitroxide derivatives were able to control the homopolymerization to high conversion and molecular weights from 1000 to 100 000 amu with polydispersities of 1.06−1.15 readily obtained. Block and random copolymers based on combinations of 1,3-dienes with a variety of functionalized vinyl monomers, such as styrene, acrylate, or methacrylate derivatives, could also be prepared with similar control. In comparison with 2,2,6,6-tetramethylpiperidinoxy (TEMPO), these new systems represent a dramatic improvement in the ability to control the polymerization of 1,3-dienes and further demonstrate the versatility of nitroxide-mediated living free radical procedures.

Introduction

The polymerization of 1,3-dienes, such as isoprene and butadiene, is a critically important process in both industrial and academic laboratories[1−4] with commercially important products such as styrene−butadiene−styrene block copolymers (Kratons) being produced.[5] These block copolymers are typically produced by anionic procedures that are synthetically difficult and not compatible with a wide range of functional groups or monomer units. A free radical procedure for the controlled homopolymerization of 1,3-dienes, as well as the synthesis of block copolymers, is therefore a highly desirable objective that would significantly expand this commercially important field.

Living free radical procedures[6−8] for the controlled polymerization of vinyl monomers has witnessed explosive growth in recent years with two major techniques, nitroxide-mediated[9−18] and atom transfer radical procedures (ATRP).[19−31] The underlying mechanism for both strategies is the reversible "capping" of growing radical chain ends to give dormant species, which significantly reduces the concentration of active species and therefore unwanted irreversible termination reactions. Recent developments[32−35] in both areas have permitted the polymerization of a wide variety of monomer families, such as styrenes, acrylates, acrylamides, and so on, with a level of structural control approaching traditional anionic procedures.

The controlled polymerization of 1,3-dienes, such as isoprene and butadiene, has remained an elusive target. Howell and Priddy[36,37] have reported the preparation of various isoprene block copolymers by the combination of normal free radical techniques with nitroxide-mediated processes. Because the initial isoprene blocks were prepared using normal free radical procedures, the blocks obtained were polydisperse and poorly defined. A more successful approach[38] has been developed by the Xerox group in which TEMPO-terminated polystyrene chains were chain-extended with 1,3-dienes to give block copolymers. Alternatively, the same group[39] reported that isoprene could be homopolymerized at 145 °C to moderate conversions in the presence of TEMPO and a reducing agent such as acetol to give polyisoprene with polydispersites ranging from 1.36 to 1.53. The challenges associated with both procedures are that the polydispersities are higher than those normally obtained with nitroxide-mediated procedures and that moderate conversions are obtained at high polymerization temperatures. In this manuscript, the application of a new nitroxide-based system is presented that overcomes many of these difficulties. The synthesis of a wide range of 1,3-diene-based homo-, random, and block copolymers can now be accomplished with structural control approaching anionic procedures while still retaining the functional group compatibility typically associated with traditional free radical techniques.

Experimental Section

General. All reactions were run under N_2 unless noted. Solvents were dried as follows: THF and toluene were distilled under N_2 from sodium benzophenone, and CH_2Cl_2 was distilled from calcium hydride. Analytical thin-layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel GF254 (0.25 mm thick). Silica gel for flash chromatography was either Merck Kieselgel 600 (230−400 mesh) or Universal Scientific, Inc., Silica Gel 63-200. Nuclear magnetic resonance (NMR) spectroscopy was performed on Bruker ACF 250, AM 500 MHz NMR spectrometers using deuterated chloroform ($CDCl_3$) as solvent and the internal solvent peak as reference. Gel permeation chromatography (GPC) was carried out on a Waters chromatograph (four Waters Styragel HR columns HR1, HR2, HR4, and HR5E in series) connected to a Waters 410 differential refractometer with THF as the carrier solvent. Molecular weight standards used for calibration of the GPC system were either narrow polydispersity polystyrene or poly(*tert*-butyl acrylate). IR spectra were recorded in $CDCl_3$ solution.

2,2,5-Trimethyl-4-phenyl-3-azahexane-3-nitroxide (2). *N*-*tert*-butyl-α-*iso*-propylnitrone (66.0 g, 461 mmol)[32] was dissolved in 500 mL of THF, and the solution was cooled to 0 °C. A 3.0 M solution of phenylmagnesium bromide (310 mL, 920

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mmol) in diethyl ether was added by cannula at this temperature over 5 min. During the addition, some precipitate formed. The mixture was allowed to warm to room temperature. After 12 h, excess Grignard reagent was decomposed by the addition of 100 mL of concentrated ammonium chloride solution followed by 300 mL of water until all solids had dissolved. The organic layer was separated, and the aqueous layer was extracted with 500 mL of diethyl ether. The organic layers were combined, dried over magnesium sulfate, filtered, and concentrated, and the residue was treated with a mixture of 2000 mL of methanol, 150 mL of concentrated NH_4OH, and 4.59 mg (23 mmol) of $Cu(OAc)_2$ to give a pale yellow solution. A stream of air was bubbled through the yellow solution until it became dark blue (5−10 min). This was concentrated, and the residue was dissolved in a mixture of 2000 mL of chloroform, 500 mL of concentrated $NaHSO_4$ solution, and 2000 mL of water. The organic layer was separated, and the aqueous layer was extracted with 500 mL of chloroform. The organic layers were combined and washed with 600 mL of saturated sodium bicarbonate solution, dried over magnesium sulfate, and concentrated in vacuo to give 101.6 g of crude nitroxide. The nitroxide was then purified by flash column chromatography (20:1 hexane/ethyl acetate) to afford 72.6 g (71% yield) of pure **2** as an orange oil that crystallized at temperatures below 4 °C. TLC: 16:1 hexane/ethyl acetate Molybdenum stain, Rf = 0.49. ^{1}H NMR (250 MHz, CDCl3) in the presence of pentafluorophenyl hydrazine: δ 7.60−7.25 (m, 5H, Ph), 3.41 (d, 1H, J = 6.5 Hz), 2.28 (m, 1H), 1.44 and 0.97 (s, 9H), and 1.20 and 0.58 (d, 6H, J = 6.8 Hz). ^{13}C NMR (62.5 MHz, CDCl3) in the presence of pentafluorophenyl hydrazine: δ 154.26, 142.06, 141.20, 136.02, 129.50, 128.77, 128.43, 127.82, 127.25, 126.61, 73.37, 71.31, 63.30, 59.10, 31.51, 31.23, 30.19, 26.85, 21.54, 20.55, 18.48.

2,2,5-Trimethyl-3-(1′-phenylethoxy)-4-phenyl-3-azahexane (1). To a solution of styrene (4.16 g, 40.0 mmol) and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide, **2**, (4.40 g, 20.0 mmol) in 1:1 toluene/ethanol (150 mL) was added [*N*,*N*′-bis-(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato] manganese(III) chloride[40] (2.80 g, 4.0 mmol) followed by di-*tert*-butyl peroxide (4.30 g, 30.0 mmol) and sodium borohydride (2.28 g, 60.0 mmol). The reaction mixture was then stirred at room temperature for 12 h, evaporated to dryness, and partitioned between dichloromethane (150 mL) and water (200 mL), and the aqueous layer was further extracted with dichloromethane (3 × 100 mL). The combined organic layers were then dried (evaporated to dryness), and the crude product was purified by flash chromatography eluting with 1:9 dichloromethane/hexane gradually increasing to 1:3 dichloromethane/hexane. The desired alkoxyamine, **1**, was obtained as a colorless oil (5.26 g, 81%). IR ($CDCl_3$): 2950, 1490, 1450, 1390, 1210, 1065 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$, both diastereomers): δ 7.4−7.1 (m, 18H), 4.95 (q + q, 2H, J = 6.5 Hz, both diastereomers), 4.67 and 4.63 (each s, 4H, CH_2Cl), 3.49 (d, 1H, J = 10.8 Hz, major diastereomer), 3.36 (d, 1H, J = 10.8 Hz, minor diastereomer), 2.38 (two m, 2H, both diastereomers), 1.66 (d, 3H, J = 6.8 Hz, major diastereomer), 1.34 (d, 3H, J = 7.0 Hz, minor diastereomer), 1.08 (s, 9H, minor diastereomer), 0.95 (m, 3H, minor diastereomer), 0.79 (s, 9H, major diastereomer), 0.61 (d, 3H, J = 6.5 Hz, major diastereomer), and 0.30 (d, 3H, J = 6.5 Hz, minor diastereomer). ^{13}C NMR (APT) (63 MHz, $CDCl_3$, both diastereomers): δ 146.10 (s), 145.18 (s), 142.61 (s), 142.33 (s), 135.73 (d), 130.97 (d), 128.40 (d), 127.37 (d), 127.32 (d), 127.21 (d), 127.00 (d), 126.49 (d), 126.37 (d), 126.21 (d), 83.17 (d), 82.25 (d), 72.17 (d), 72.14 (d), 60.49 (s), 60.45 (s), 46.23 (t), 32.02 (d), 31.72 (d), 28.39 (q), 28.22 (q), 24.68 (q), 23.10 (q), 23.03 (q), 22.09 (q), 21.33 (q), 21.12 (q). Anal. Calcd for $C_{23}H_{32}ClNO$: C, 73.9; H, 8.62; N, 3.75. Found: C, 74.1; H, 8.84; N, 3.77.

General Procedure for Isoprene Polymerization from 1. A mixture of the α-hydrido alkoxyamine **1** (32.5 mg, 0.1 mmol) and isoprene (1.70 g, 25.0 mmol) was degassed by three freeze/thaw cycles, sealed under argon, and heated at 125 °C under nitrogen for 16 h. The viscous reaction mixture was then dissolved in dichloromethane (5 mL) and precipitated (twice) into methanol (200 mL). The gum was then collected and dried to give the desired polyisoprene, **3**, as a colorless gum (1.35 g, 78%), M_n = 20 000 amu, PD = 1.08. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.6−5.5, 5.1−5.0, and 4.9−4.6 (m, olefinic H), 2.1−1.9, and 1.7−1.3 (m, aliphatic H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 15.97, 23.38, 26.71, 28.25, 28.47, 30.84, 31.97, 38.49, 39.72, 40.0, 110.5, 124.23, 125.02, 134.88.

General Procedure for the Polymerization of 1,3-Butadiene Using 1. A mixture of α-hydrido alkoxyamine **1**, (0.50 g, 1.54 mmol) was transferred to a Parr reactor. The reactor was evacuated and cooled with liquid nitrogen. 1,3-Butadiene (40 g, 740 mmol) was then condensed into the reactor. The reactor was then heated at 125 °C for 10 h. The mixture was dissolved in hexane and precipitated into methanol (300 mL). The resulting oil was then collected and dried to give the desired polybutadiene as a pale yellow oil (5.9 g), M_n = 5200 amu, PD = 1.14. ^{1}H NMR (400 MHz, CDCl3): δ 5.671, 5.405, 5.373, 4.954, 3.483, 2.174, 2.170, 2.168, 2.068, 2.029, 1.235, 1.217. ^{13}C NMR (100 MHz, CDCl3): δ 143.796, 142.685, 142.630, 131.239, 130.619, 130.547, 130.419, 130.182, 130.109, 130.000, 129.872, 129.818, 129.690, 129.599, 129.398, 129.234, 128.323, 128.250, 128.195, 127.867, 127.412, 126.993, 126.883, 126.318, 126.063, 125.790, 114.308, 114.198, 112.321, 72.097, 43.538, 43.465, 38.161, 34.097, 34.042, 33.933, 32.694, 32.639, 30.944, 30.179, 30.106, 27.664, 27.500, 27.372, 24.857.

General Procedure for Random Copolymerization: Preparation of Poly(methyl methacrylate)-*r*-*co*-poly(isoprene), 11, from 1. A mixture of the alkoxyamine **1**, (65 mg, 0.2 mmol), isoprene (1.70 g, 25.0 mmol), and methyl methacrylate (2.50 g, 25.0 mmol) was degassed by 3 freeze/thaw cycles, sealed under argon and heated at 125 °C under nitrogen for 36 h. The viscous reaction mixture was then dissolved in dichloromethane (5 mL) and precipitated (twice) into methanol (200 mL). The gummy precipitate was then collected and dried to give the desired random copolymer, **1**, as a colorless gum (3.53 g, 71%), M_n = 15 500 amu, PD = 1.15. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.9−2.4 (m, aliphatic H), 3.64 (s, OMe), and 5.0 (br s, olefinic H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 16.1−23.0 (complex m), 43.0−45.0 (m), 49.5−54.5 (m), 127−131 (m), and 176.8−178 (m).

General Procedure for Block Copolymer Formation: Preparation of Poly(*tert*-butyl acrylate)-*b*-polyisoprene, 6, from 1. A mixture of the alkoxyamine **1**, (32.5 mg, 0.1 mmol), the corresponding nitroxide, **2**, (1.1 mg, 0.005 mmol), and *tert*-butyl acrylate (3.20 g, 25 mmol) was degassed by 3 freeze/thaw cycles, sealed under argon, and heated at 125 °C under nitrogen for 16 h. The viscous reaction mixture was then dissolved in dichloromethane (50 mL) and precipitated (twice) into methanol (2 L). The gummy precipitate was then collected and dried to give the desired poly(*tert*-butyl acrylate), **5**, as a colorless gum (2.60 g, 80.4%), M_n = 22 000 amu, PD = 1.16. The poly(*tert*-butyl acrylate), **5**, starting block (2.00 g, 0.085 mmol) was then redissolved in isoprene (3.00 g, 44.1 mmol), and the polymerization reaction was heated at 125 °C for 36 h. The viscous reaction mixture was then dissolved in dichloromethane (10 mL) and precipitated (twice) into methanol (500 mL). The precipitate was then collected by vacuum filtration and dried to give the desired block copolymer, **6**, as a clear gum (3.80 g, 76%), M_n = 45 500 amu, PD = 1.17. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.20 (s, *t*-Bu), 1.25−2.4 (m, aliphatic H), 4.5−5.0 (br m, olefinic H), and 5.05 (br s, olefinic H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 16.0−27.0 (complex m), 42.0−45.0 (m), 49.0−55.0 (m), 127.0−131.0 (m), and 177.0−178.0 (m).

Results and Discussion

The observation by Bergbreiter and Walchuck[41] that allylic alkoxyamines, which resemble the growing chain end of poly(isoprene) or poly(butadiene), are efficient initiators for living free radical polymerizations suggests that the difficulties previously encountered in the polymerization of 1,3-dienes may not be due to incomplete fragmentation of the alkoxyamine chain ends during the polymerization. A more reasonable explanation for the

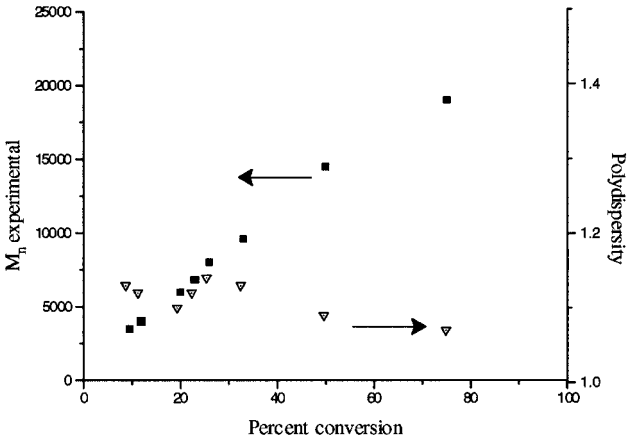
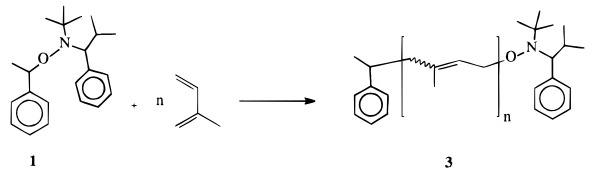


Figure 1. Evolution of experimental molecular weight, M_n, and polydispersity with theoretical MW for the polymerization of isoprene and **1** at 120 °C for 36 h.

Scheme 1



observed difficulty in the homopolymerization of dienes may be a preponderance in these system for irreversible termination reactions leading to a buildup of excess 2,2,6,6-tetramethylpiperidinyloxy (TEMPO),[38,39] as the polymerization proceeds. According to the persistent radical mechanism proposed by Fischer[42] this excess nitroxide should dramatically slow the reaction and lead to incomplete conversion and nonliving behavior. Because α-hydrogen-based nitroxides, such as **2**, have a potential decomposition pathway via disproportionation, the buildup of excess nitroxide in these systems will thereby be prevented.

To examine this hypothesis, 100 equiv of isoprene was heated at 120 °C in the presence of 1 equiv of the alkoxyamine **1**, and 0.05 equiv of the free nitroxide, **2**. After being heated for 72 h, poly(isoprene), **3**, was isolated in 25% yield and found to have a molecular weight of 3500 and a polydispersity of 1.08. The low conversion found for this polymerization (ca. 30%) is in direct contrast to the high conversion (>90%) previously obtained for both styrenic and acrylate monomers using **1**. A possible explanation for this is that the rationale for adding excess free nitroxide to slow and control the polymerization of acrylates, i.e., very high k_p, does not apply in this case due to the significantly reduced k_p for isoprene when compared to that of acrylate monomers. On the basis of this hypothesis, repetition of the above experiment in the absence of free nitroxide lead to a 75% conversion after 36 h while still maintaining accurate control over polydispersity and molecular weight, $M_n = 9800$ and PD = 1.07 (Scheme 1). The living nature of the polymerization was further demonstrated by examining the evolution of molecular weight with conversion. As shown in Figure 1, the relationship between M_n and percent conversion is linear, with low polydispersities (1.07−1.14) being obtained for all the samples. In contrast, the use of TEMPO as the mediating nitroxide, either in a bimolecular system or as the unimolecular alkoxyamine, resulted in nonliving behavior under the same reaction conditions, with a distinct nonlinear relationship being observed between $\ln([M]_0/[M])$ and time. These results are in full agreement with those obtained by the Xerox group[38,39] and add further support to the notion that buildup of excess nitroxide is responsible for the nonliving behavior of TEMPO-based systems.

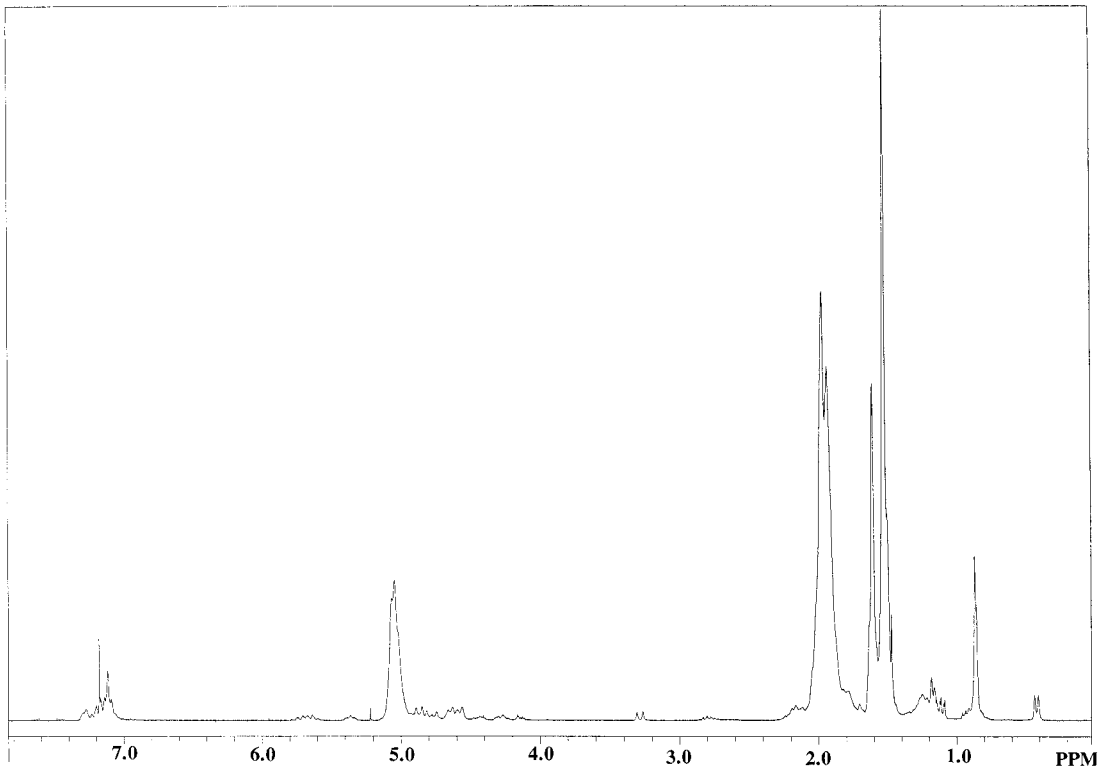


Figure 2. ^{1}H NMR spectrum of oligomeric poly(isoprene), **3**, prepared by the polymerization of isoprene (50 equiv) at 120 °C in the presence of 1.0 equiv of **1**.

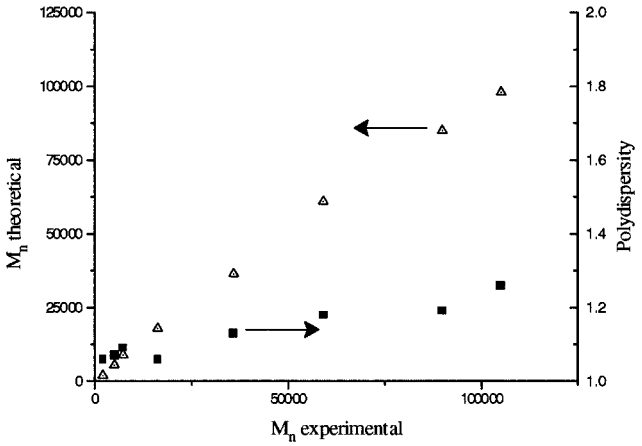
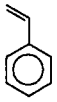
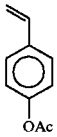
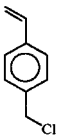


Figure 3. Relationship between theoretical molecular weight, polydispersity, and experimental molecular weight for the polymerization of isoprene in the presence of **1** at 120 °C for 36 h.

The ^{1}H spectra of low-molecular-weight poly(isoprene) (M_n = 4500, PD = 1.07) prepared by the above procedure showed the expected signals for both the aliphatic and olefinic protons of the isoprene backbone as well as resonances for the chain ends resulting from the initiating fragments at 0.4, 2.8, 3.3, and 7.1−7.3 ppm (Figure 2). This allowed the molecular weight, M_n = 4200, to be determined from end group analysis. This value compares favorably with those obtained from both GPC and MALDI mass spectrometry and is fully consistent with the proposed structure and living mechanism. NMR spectroscopy also provided valuable information on the microstructure of the poly(isoprene). The chemical shifts and peak intensities of the olefinic carbons in the ^{13}C NMR spectrum and vinyl hydrogens in the ^{1}H NMR spectrum (ca. 5.05 ppm) showed a microstructure of predominately 1,4-cis and trans repeat units that is essentially the same as that obtained in a conventional free radical isoprene polymerization.[43,44]

The living nature and high fidelity of the polymerization suggested that the molecular weight of the poly(isoprenes) could be simply controlled by varying the ratio of monomer to initiator. A series of polymerizations were then conducted at 130 °C for 48 h with initiator/isoprene ratios of 25:1 to 1500:1. For each example, the polymerization was stopped at 80% conversion, or less, due to the observation of a minor higher molecular weight shoulder at conversions greater than 85−90%. Presumably, this high molecular weight shoulder is due to chain−chain coupling, which is favored at high conversion and extended reaction times. The low glass-transition temperature of poly(isoprene), coupled with the extremely low viscosity of the bulk polymerization mixtures, even at 90% conversion, would also be expected to facilitate chain migration and hence coupling. As can be seen in Figure 3, molecular weight can be controlled up to 100 000 amu with polydispersities typically being less than 1.20. This level of structural control is comparable to the polymerization of styrenic and acrylate monomers by either nitroxide-mediated or ATRP processes and, at low molecular weights (<25 000), approaches anionic procedures for isoprene. Similar results were observed for 1,3-butadiene using high-pressure apparatus. In this case, reaction of **1** with 100 equiv of condensed 1,3-butadiene at 125 °C for 10 h gave a 50% conversion, and the resulting polybutadiene was shown to have a M_n of 5200 amu and a narrow polydispersity, PD = 1.14.

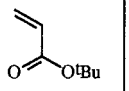
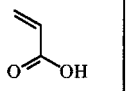
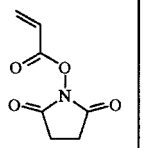
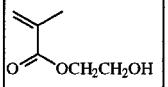
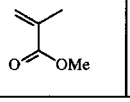
Table 1. Polydispersity and Polystyrene Equivalent Molecular Weights, M_n (g mol^{-1}), for the Bulk Random Copolymerization of Isoprene and a Variety of Styrenic Monomers (200 equiv) in the Presence of 1 at 120 °C

Comonomer	Ratio of Comonomer/Isoprene	Mn	Polydispersity
	90/10	17 000	1.18
	80/20	17 500	1.18
	70/30	16 000	1.21
	60/40	17 000	1.19
	50/50	15 500	1.15
	40/60	17 000	1.2
	30/70	17 500	1.11
	25/75	18 500	1.16
	20/80	17 000	1.18
	10/90	17 500	1.14
	75/25	17 000	1.28
	50/50	20 500	1.16
	25/75	19 000	1.14
	10/90	17 500	1.27
	20/80	16 500	1.19
	30/70	17 000	1.22

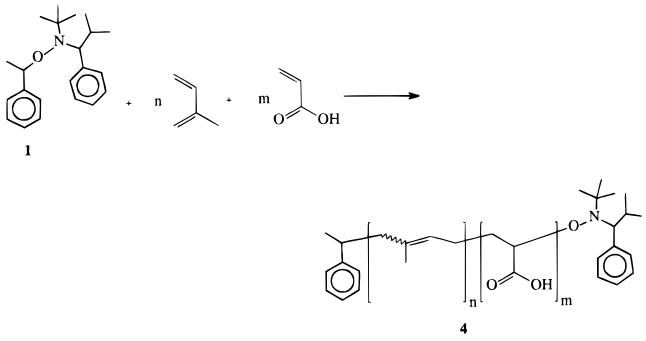
Although the use of **1** as an initiator for isoprene polymerization may approximate living anionic procedures in terms of polydispersity and molecular weight control, one of the major advantages of living free radical techniques is their compatibility with functional groups and their ability to readily prepare random copolymers.[45−49] Both of these issues were addressed by the synthesis of a wide variety of well-defined random copolymers of isoprene with styrenic and acrylate monomers under standard conditions. For styrene, well-defined random copolymers could be prepared over the whole comonomer range from 90 to 10% isoprene with no change in molecular weight control or polydispersity (PD = 1.1−1.2). Of particular note is the ability to readily include functionalized monomers such as *p*-acetoxystyrene or *p*-chloromethylstyrene at high levels of incorporation with little, if any, change in the degree of control (Table 1).

The ability to prepare homopolymers of isoprene, as well as random copolymer with styrenics, suggested that random copolymers could also be formed with both acrylates and methacrylates. As can be seen in Table 2, this indeed proved to be the case with controlled polymerization being observed for both *tert*-butyl acrylate and methyl methacrylate. Functional monomers such as acrylic acid and 2-hydroxyethyl methacrylate (HEMA) could also be readily copolymerized with isoprene to give low polydispersity materials, **4**, (PD = 1.14−1.19) with controlled molecular weights (Scheme 2). From these results, it can be concluded that the living free radical polymerization of isoprene, mediated by the α-hydrido nitroxide, **2**, is a controlled process and random copolymers can be prepared with a wide range of functionalized monomer units, for example, styrenics, acrylates, and methacrylates. Interestingly, the addition of free nitroxide was unnecessary in the preparation of acrylate or methacrylate random copolymers with isoprene, which is analogous to styrene-based systems.

Table 2. Polydispersity and Polystyrene Equivalent Molecular Weights for the Bulk Random Copolymerization of Isoprene and a Variety of Acrylate/Methacrylate Monomers (200 equiv) in the Presence of 1 at 120 °C

Comonomer	Ratio of Comonomer/Isoprene	M_n	Polydispersity
	90/10	19 500	1.17
	70/30	17 500	1.27
	50/50	15 500	1.15
	30/70	15 500	1.25
	10/90	18 000	1.19
	10/90	15 000	1.14
	20/80	18 500	1.16
	10/90	15 000	1.19
	20/80	17 500	1.22
	10/90	14 000	1.18
	20/80	17 000	1.19
	80/20	18 000	1.17
	50/50	15 500	1.12
	20/80	17 000	1.26

Scheme 2



The presence of dormant initiating centers at the chain end/s of the poly(isoprene) homopolymers prepared by nitroxide-mediated procedures in the presence of **1** provides an opportunity for the preparation of 1,3-diene block copolymers.[50−56] Initially, a poly(*tert*-butyl acrylate) macroinitiator, **5** (M_n = 3900 amu, PD = 1.11), was prepared from **1** and 45 equiv of *tert*-butyl acrylate in the presence of 0.05 equiv of **2** and was purified by precipitation into methanol. A poly(isoprene) block was then grown by dissolution of **5** in isoprene (100 equiv) followed by heating at 123 °C under argon for 36 h. This resulted in a 72% conversion for the isoprene, and after purification, the desired block copolymer, **6** (M_n = 9700 amu, PD = 1.09), was obtained (Scheme 3). As evidenced by the GPC traces for the block copolymer, **6**, versus the starting material, **5**, controlled growth is achieved with no evidence of homopolymer contamination (Figure 4). Similar experiments with higher molecular weight starting poly(*tert*-butyl acrylate) blocks and varying amounts of isoprene gave a family of novel poly(*tert*-butyl acrylate)-*b*-poly(isoprene) block copolymers in which the relative amount of isoprene ranged from 20 to 90% (Table 3).

Scheme 3

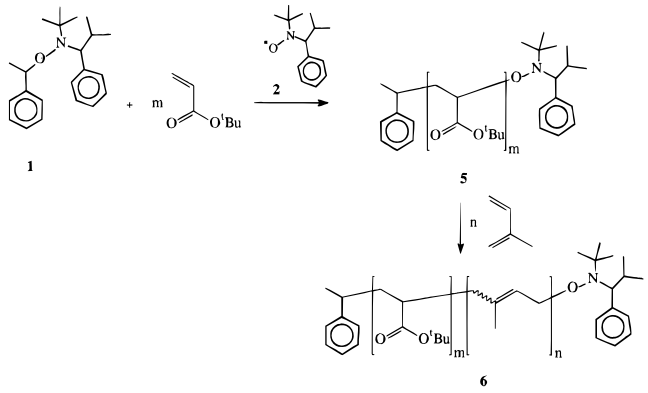
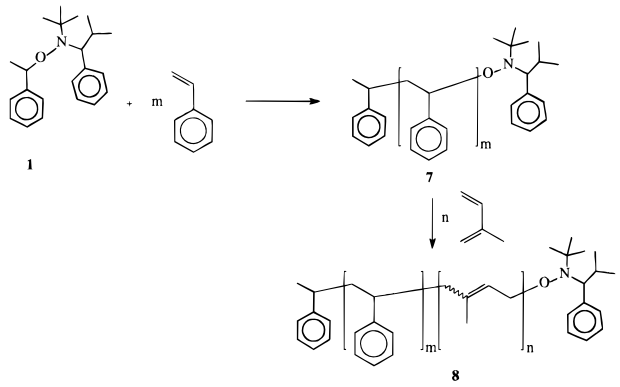


Table 3. Molecular Weight and Polydispersity for Poly(*tert*-butyl acrylate)-*b*-poly(isoprene) Block Copolymers, 6, Prepared Using 1 under Bulk Conditions at 120 °C

poly(*tert*-butyl acrylate) starting block		composition[a]	P(t-BA)-*b*-PI block copolymer[b]	
M_n	polydispersity	IP/t−BA	M_n	polydispersity
3 900	1.11	60/40	9 700	1.09
3 900	1.11	75/25	17 000	1.12
3 900	1.11	90/10	30 300	1.14
9 000	1.15	70/30	37 000	1.16
9 000	1.15	80/20	78 500	1.22
9 000	1.15	85/15	86 500	1.17
22 000	1.16	20/80	27 000	1.19
22 000	1.16	35/65	33 500	1.15
22 000	1.16	50/50	45 500	1.17

[a] Determined by ^{1}H NMR spectroscopy. [b] Polystyrene equivalent molecular weights.

Scheme 4



A similar strategy was examined for the preparation of styrene/isoprene block copolymers. In this case, an alkoxyamine functionalized polystyrene block, **7** (M_n = 11 400, PD = 1.08), was initially grown and then used to polymerize 1000 equiv of isoprene at 120 °C under argon for 36 h. This resulted in 78% conversion and gave the block copolymer, **8**, analysis of which revealed the expected increase in molecular weight (M_n = 105 000, PD = 1.17) (Scheme 4). More importantly, the polydispersity remained very low, and there was no unreacted starting polystyrene block detectable by a combination of GPC and hplc techniques. This block copolymer formation proved to be a general procedure and permitted a wide compositional range of polystyrene-*b*-poly(isoprene) block copolymers to be prepared with accurate control of molecular weight up to 105 000 amu and polydispersities typically in the range of 1.13−1.20 (Table 4). The advantage of greater availability and a

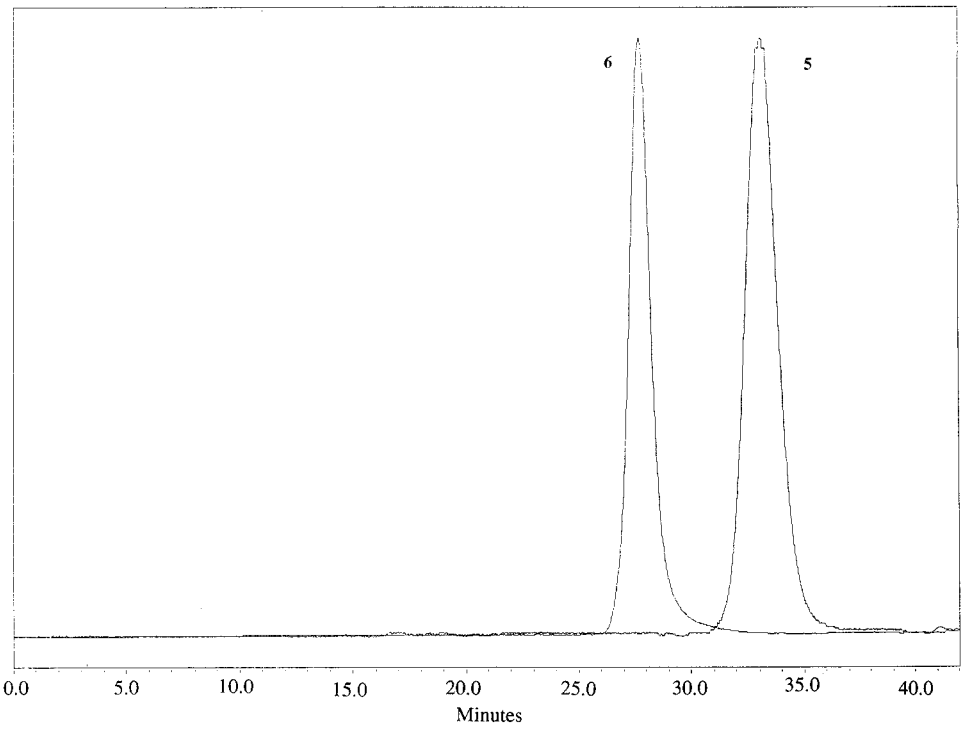


Figure 4. Comparison of GPC traces for (a) the starting poly(*tert*-butyl acrylate) polymer, **5**, and (b) the poly(*tert*-butyl acrylate)-*b*-polyisoprene block copolymer, **6**, obtained after chain extension with isoprene.

Table 4. Molecular Weight and Polydispersity for Poly(styrene)-*b*-poly(isoprene) Block Copolymers, 8, Prepared Using 1 under Bulk Conditions at 120 °C

poly(styrene) starting block		composition[a]	PSt-*b*-PIP block copolymer[b]	
M_n	polydispersity	IP/St	M_n	polydispersity
11 400	1.15	70/30	41 500	1.16
11 400	1.15	80/20	56 000	1.17
11 400	1.15	85/15	64 500	1.24
11 400	1.08	90/10	105 000	1.17
14 000	1.14	60/40	32 500	1.16
14 000	1.14	40/60	21 000	1.13
24 000	1.13	20/80	29 500	1.19
24 000	1.13	40/60	40 500	1.20

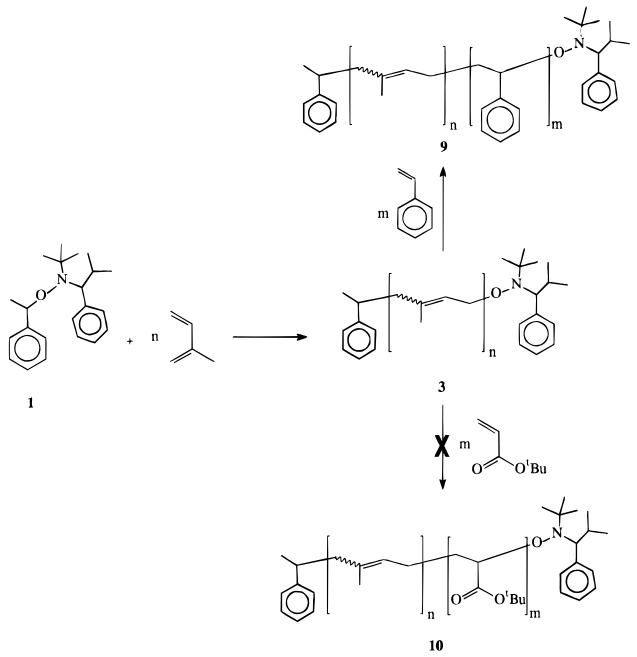
[a] Determined by ^{1}H NMR spectroscopy. [b] Polystyrene equivalent molecular weights.

significantly greater tolerance of functional groups suggest a number of potential technological applications for these novel materials.[57−62]

One of the interesting features concerning the preparation of block copolymers using **1** as the initiator is that the success of block copolymer formation is dependent on the sequence of monomer addition, an occurrence that has also been observed in other living polymerizations, such as anionic. For example, the preparation of styrene−acrylate block copolymers is facile if the acrylate block is grown first, followed by the styrene block.[32] However the reverse strategy fails, the initial growth of a styrene block followed by the acrylate block does not lead to efficient block copolymer formation with significant amounts of unreacted polystyrene block remaining. To determine whether isoprene-based blocks were also sensitive to the sequence of monomer addition to the alkoxyamine initiator **1**, the preparation of the above block copolymers was performed with the order of monomers reversed.

In the case of poly(isoprene)-*b*-poly(styrene), **9**, the initiation of the second styrene block from the starting

Scheme 5



poly(isoprene) blocks proceeded smoothly to give well-defined block copolymers with no detectable amounts of unreacted homopoly(isoprene) (Scheme 5). Although the polydispersities are slightly greater than those found for the reverse case, PD = 1.15−1.30, the control is comparable to block copolymers prepared by other living free radical techniques (Table 5). In contrast, the initiation of acrylate polymerization from a homo(polyisoprene) macroinitiator did not give clean block copolymer **10** formation. As was observed in the case of growing a poly(acrylate) block from polystyrene, incomplete initiation was observed leading to a polydisperse sample with a significant amount of unreacted ho-

Table 5. Molecular Weight and Polydispersity for Poly(isoprene)-*b*-polystyrene Block Copolymers, 9, Prepared Using 1 under Bulk Conditions at 120 °C

poly(isoprene) starting block		composition[a]	PIP-*b*-PSt block copolymer[b]	
M_n	polydispersity	IP/St	M_n	polydispersity
1 500	1.09	60/40	2 500	1.17
1 500	1.09	40/60	3 300	1.25
1 500	1.09	25/75	5 700	1.19
4 000	1.08	60/40	6 600	1.19
4 000	1.08	30/70	10 000	1.26
4 000	1.08	25/75	14 500	1.15
25 000	1.14	30/70	79 500	1.24
25 000	1.14	20/80	142 000	1.30

[a] Determined by ^{1}H NMR spectroscopy. [b] Polystyrene equivalent molecular weights.

mopolystyrene contamination.

Conclusion

The efficiency of α-hydrido alkoxyamines, such as **1**, for the living free radical polymerization of vinyl monomers has been further demonstrated by the polymerization of 1,3-dienes to give a variety of controlled molecular weight and low polydispersity macromolecules. In comparison with traditional TEMPO-based systems, the performance of **1** is significantly improved, with living characteristics and high conversions being obtained. The versatility of this approach to diene polymerization can be gauged by the ability to prepare functionalized random copolymers and block copolymers, many of which are not available using traditional techniques. Future work will entail the evaluation of these functionalized diene random and block copolymers in a variety of applications.

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