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Communications to the Editor

Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process

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Block copolymers are a unique class of polymeric materials that can be used, for example, as dispersants, compatibilizers, and viscosity modifiers. However, free radical synthesis of block copolymers has been difficult due to the propensity of the propagating chains to undergo premature irreversible termination.[1−3] In 1993, we reported the use of stable free radical nitroxides (e.g., TEMPO) to control free radical polymerization, thus enabling the synthesis of resins with controlled molecular weights and narrow polydispersities.[4] Since these polymerizations behaved in a living manner, the syntheses of block copolymers seemed feasible and, in fact, have recently been reported.[5]

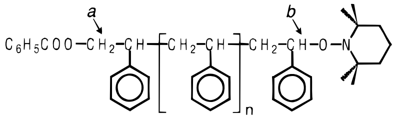
In this communication, we report the synthesis of diblock copolymers of styrene with 1,3-butadiene using the nitroxide-mediated free radical polymerization process with the express purpose of showing that the reaction proceeds by a reversible capping mechanism. The transfer of the chain-terminating nitroxide group from the end of the first block (styrene) to the end of the second block (butadiene) is unequivocally demonstrated by ^{1}H NMR spectroscopy. The extension of this work to well-defined di- and triblock copolymers of styrene with isoprene is also reported.

The block copolymers described in this paper were prepared in two steps. In the first step, a TEMPO-terminated styrene homopolymer was synthesized to a desired molecular weight as described by Georges et al.,[4] followed by precipitation into methanol.[6] Polystyrene-*b*-polybutadiene copolymers were then prepared in a second step by dissolving the TEMPO-terminated polystyrene and a small amount of benzoic acid[7] in a solution of ethyl acetate and dimethyl sulfoxide (DMSO) in a modified Parr bomb. 1,3-Butadiene was added to this solution under argon pressure and the reaction mixture heated at 125 °C for 10 h. Triblocks were prepared by reacting the resulting diblock copolymer with styrene under bulk reaction conditions at 135 °C.[4] Polystyrene-*b*-polyisoprene and polystyrene-*b*-polyisoprene-*b*-polystyrene polymers were prepared in a similar manner.

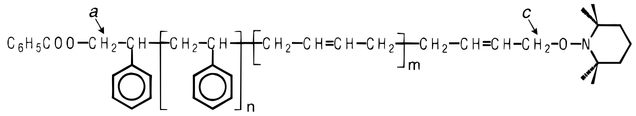
Molecular weights, relative to polystyrene standards, were determined by gel permeation chromatography (GPC) using Ultrastyragel columns of pore size 10^4, 10^3, 500, and 100 Å coupled to a Waters 410 differential refractometer. GPC samples were taken directly from the reaction mixture and analyzed without prior purification. NMR spectra of $CDCl_3$ solutions of the methanol-precipitated polymers were recorded on a Bruker AMX400 spectrometer at a probe temperature of 23 °C. Standard pulse programs were used for NOESY/EXSY, DEPT, and ^{1}H−^{13}C HETCOR experiments.[8]

To demonstrate the transfer of the chain-capping nitroxide group from the first to the second block, low molecular weight block copolymers were prepared so that the end groups of the polymer chain could be easily monitored by ^{1}H NMR spectroscopy. Attention was focused on the resonances of the methyl groups of the nitroxyl (piperidinyloxy) unit, the chemical shifts of which were expected to differ, depending on whether the nitroxyl group was attached to a styrene or butadiene monomer unit. The resonances of the benzylic methine and allylic methylene protons of the styrene and butadiene monomer units bonded to the piperidinyloxy group were also monitored (***b*** and ***c***, respectively, in structures **1** and **2**).

1: (PS-T)



2: (PS- *b*-PB-T)



The ^{1}H NMR spectrum of TEMPO-terminated polystyrene (PS-T: $M_n = 1550$, PD = 1.4; Figure 1) shows the four piperidinyloxy methyl resonances centered at 1.09, 0.91, 0.38, and 0.20 ppm (vertical arrows), characteristic of TEMPO bonded to polystyrene.[4b] The latter two peaks are at higher field than might be expected due, primarily, to the shielding aromatic ring-current effect of the phenyl ring of the terminal styrene monomer unit. Three broad resonances (***b***; inset of Figure 1), centered at 3.97, 4.40, and 4.53 ppm, were assigned, on the basis of ^{13}C DEPT and ^{1}H−^{13}C HETCOR experiments, to the benzylic proton of the styrene unit bonded to the piperidinyloxy group. Polystyrene tacticity effects cause this methine resonance to be split into three components. Between these peaks is a broad, complex resonance (4.06−4.35 ppm) similarly assigned to the methylene protons of the styrene unit attached to the benzoate group at the initiating chain end (***a***; structure **1**).

Reaction of the TEMPO-terminated polystyrene with 1,3-butadiene resulted in the formation of a new resin, polystyrene-*b*-polybutadiene (PS-*b*-PB-T), whose GPC chromatogram showed a distinct shift to higher molec-

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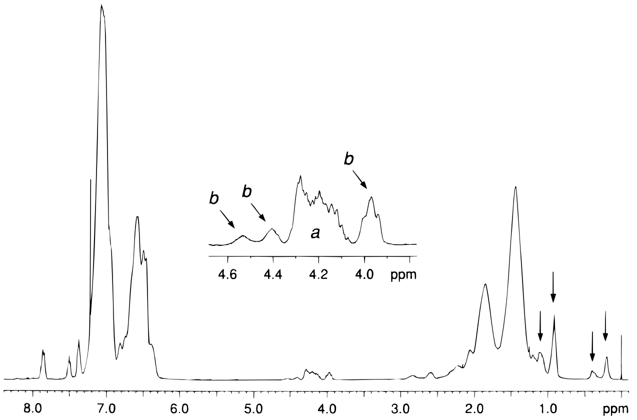

Figure 1. 400.13 MHz ^{1}H NMR spectrum of TEMPO-terminated polystyrene (PS-T; $M_n = 1550$, PD = 1.43). Inset peak assignments correspond to the proton labels in structure **1**.

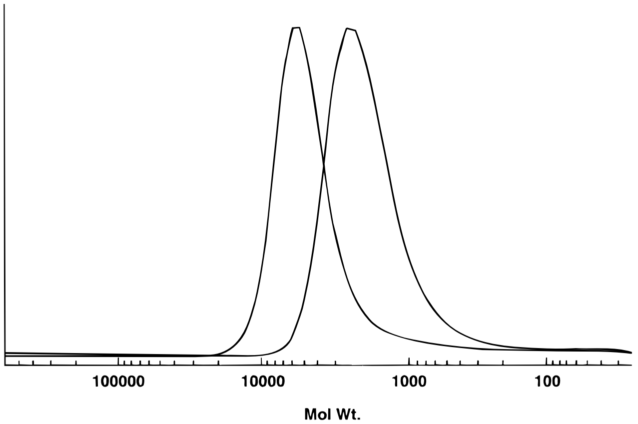

Figure 2. Overlay GPC chromatograms of a polystyrene-*b*-polybutadiene (PS-*b*-PB-T) block copolymer and the polystyrene (PS-T) starting material.

Table 1. Chain Extension of a Low Molecular Weight TEMPO-Terminated Polystyrene (PS-T) with 1,3-Butadiene to a TEMPO-Terminated Polystyrene-*b*-polybutadiene (PS-*b*-PB-T)

sample	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	PD
PS-T	1.55	2.22	1.43
PS-*b*-PB-T	4.07	5.44	1.34

ular weight (Figure 2). A decrease in polydispersity (Table 1) and no new or residual peaks in the GPC indicate that the product is free of both polybutadiene and polystyrene homopolymer. The methyl resonances of the piperidinyloxy group attached to polystyrene are absent from the ^{1}H NMR spectrum of the diblock copolymer (Figure 3), being replaced by two new methyl resonances at 1.10 and 1.16 ppm (vertical arrows; assignments of these resonances were confirmed by NOESY/EXSY, DEPT, and HETCOR experiments). The three resonances for the benzylic protons bonded to the oxygen of the piperidinyloxy fragment are similarily absent, being replaced by resonances centered at 4.22 and 4.33 ppm (***c***; inset of Figure 3); these peaks are attributed to terminal trans and cis isomer units, respectively, of the butadiene 1,4-addition product (***c***, structure 2).[9] Since chain extension to form the diblock occurs only at the TEMPO-terminated end of the polymer chain, the methylene resonances attributed to the benzoate attachment to styrene (***a***, structure 2; 4.06–4.35 ppm) remain unaffected. The chemical shifts and peak intensities of the olefin protons of the bulk polybutadiene block (4.8–5.8 ppm) indicate that its microstructure is similar to that obtained in a conventional free radical butadiene polymerization.[9] This is to be expected since the reversible capping mechanism implies that once dissociated from the nitroxide, the propagating chain is free to add monomer in a manner similar to that of the conventional free radical process until it is again capped by nitroxide.

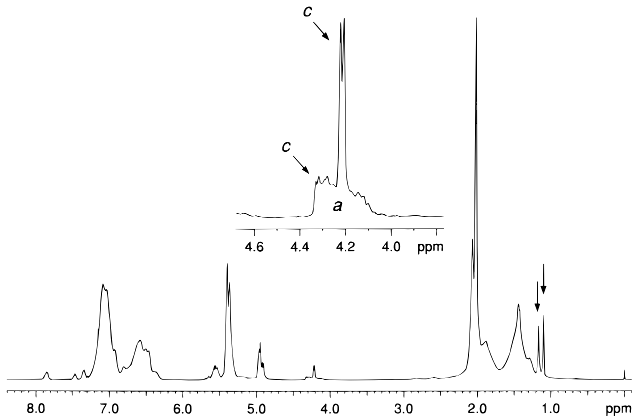

Figure 3. 400.13 MHz ^{1}H NMR spectrum of TEMPO-terminated polystyrene-*b*-polybutadiene (PS-*b*-PB-T; M_n = 4070, PD = 1.33). Inset peak assignments correspond to the proton labels in structure **2**.

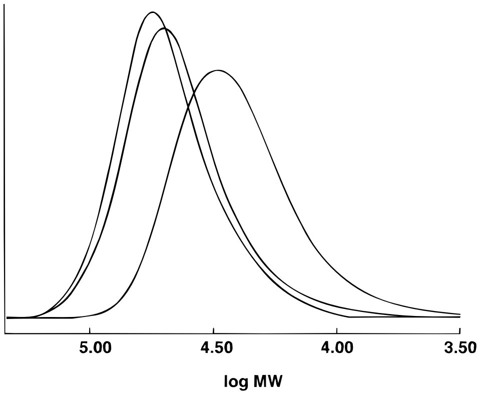

Figure 4. Overlay GPC chromatograms of a polystyrene-*b*-polyisoprene-*b*-styrene copolymer (PS-*b*-PI-*b*-PS-T), a polystyrene-*b*-polyisoprene copolymer (PS-*b*-PI-T), and the polystyrene (PS-T) starting material.

Table 2. Chain Extension of a High Molecular Weight TEMPO-Terminated Polystyrene (PS-T) First to a TEMPO-Terminated Polystyrene-*b*-polyisoprene (PS-*b*-PI-T) and Then to a TEMPO-Terminated Polystyrene-*b*-polyisoprene-*b*-polystyrene (PS-*b*-PI-*b*-PS-T)

sample	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	PD
PS-T	21.7	29.4	1.36
PS-*b*-PI-T	38.1	49.7	1.30
PS-*b*-PI-*b*-PS-T	43.6	54.0	1.24

In the aforementioned PS-*b*-PB-T copolymer, the molecular weights of the individual blocks were intentionally kept low so that the end groups could be studied. However, higher molecular weight block copolymers are also feasible, as illustrated by the polystyrene-*b*-polyisoprene-*b*-polystyrene triblock synthesis summarized in Table 2. An overlay of the GPC chromatograms of the starting homopolymer (PS-T), the styrene–isoprene block copolymer (PS-*b*-PI-T), and the triblock (PS-*b*-PI-*b*-PS-T) is shown in Figure 4. As would be expected for a living system,[10] there is a decrease in polydispersity as each new block is added.

In summary, it has been shown that well-defined block copolymers of styrene and dienes can be prepared by the nitroxide-mediated free radical polymerization process. The transfer of the nitroxide unit from the end of one block to another can readily be monitored by ^{1}H NMR spectroscopy, confirming that the nitroxide-mediated polymerization process occurs by a reversible chain-capping mechanism. The controlled syntheses of block copolymers of both low and high molecular weights are possible and the ability to prepare triblocks further demonstrates the continued living nature of these systems. The synthesis of diblock and triblock copolymers incorporating acrylates has also recently been accomplished.[11]

References and Notes

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