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Controlled Nitroxide-Mediated Radical Polymerization of Styrene, Styrene/Acrylonitrile Mixtures, and Dienes Using a Nitrone

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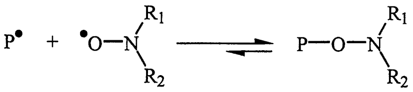
ABSTRACT: Radical polymerization of styrene and copolymerization of styrene and acrylonitrile (60/40) are controlled when conducted in the presence of *N*-*tert*-butyl-α-isopropylnitrone, which is easily synthesized from cheap reagents. However, for the control to be effective, the nitrone has to be prereacted with the radical initiator. Nitroxides are then formed "in situ", such that this nitrone system is an attractive alternative for the classical nitroxide-mediated polymerization (NMP), which may require a multistep synthesis of nitroxides or alkoxyamines. The choice of the radical initiator is important because it dictates the structure of the nitroxide and thus its capacity to control the radical polymerization. Well-defined poly(styrene)-*b*-poly(styrene-*co*-acrylonitrile), poly(styrene)-*b*-poly(*n*-butyl acrylate), and poly(styrene)-*b*-poly(isoprene) copolymers have been successfully synthesized by this process.

Introduction

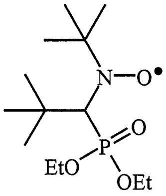
Controlled radical polymerization (CRP) of vinyl monomers mediated by nitroxides (NMP process) has expanded very rapidly during the past decade.[1] Success of NMP is based on the capture of propagating radicals by nitroxides with formation of thermally labile alkoxyamines (Scheme 1). The dormant species are fragmented at high temperature ($T > 100$ °C), and the released polymeric radicals add a limited number of monomers before recombining with nitroxides. Repetition of this homolysis−monomer addition−recombination cycle allows macromolecules to grow without interruption by irreversible termination.

Scheme 1



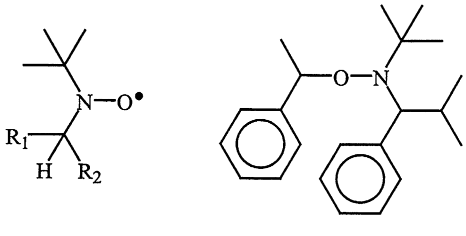
where P$^\bullet$ is the propagating chain

Scheme 2



DEPN

Scheme 3



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The pioneering work by Rizzardo,[2] who used 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) as a nitroxide, was refined by Georges[3] and continuously improved. One major contribution was by Grimaldi et al., who designed a novel nitroxide (DEPN, Scheme 2) bearing a bulky and electron-withdrawing phosphonate group in the β-position of the nitrogen atom.[4] DEPN is efficient to control polymerization of styrene and, more importantly, of acrylates. For the first time, well-defined poly(acrylate)s with polydispersity as low as 1.1 were synthesized by AIBN added with a 2:1 molar excess of DEPN, at a temperature ranging from 100 to 125 °C. Moreover, the synthesis of poly(styrene)-*b*-poly(*n*-butyl acrylate)-*b*-polystyrene triblock copolymers was also successful. Other phosphonylated nitroxides and the parent alkoxyamines were used, which emphasized the crucial role of the nitroxide structure in the success or failure of the controlled radical polymerization.[5] In an effort to extend the NMP process to a wider selection of monomers, Hawker et al. reported in 1999 the synthesis of a series of new acyclic α-hydrogen bearing nitroxides (Scheme 3) and parent alkoxyamines.[6,7] Compared to the traditional TEMPO-based systems, this type of alkoxyamine, particularly the alkoxyamine 1 (Scheme 3), significantly improved the polymerization control of a wide variety of monomers (styrene, acrylates, acrylamides, acrylonitrile, and isoprene) at 120 °C.

Nitrones[8] and nitroso compounds[9] are known for a long time as spin-trapping agents and formation of nitroxides by reaction with alkyl radicals. Quite recently, some authors paid attention to the controlled radical polymerization of vinyl monomers by nitrones and nitroso compounds.[10] Nesvadba et al. prepared alkoxyamines by reaction of radicals with nitrones or nitroso compounds (Scheme 4). These purified alkoxy-

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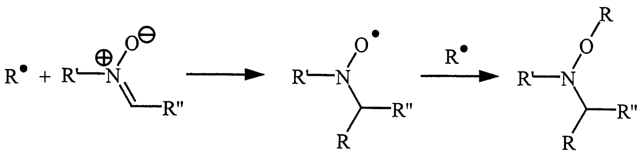
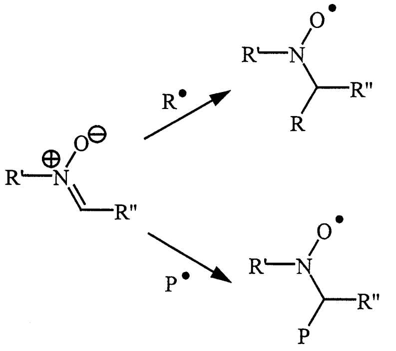
Scheme 4

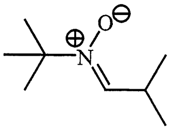


Scheme 5



Where P• is the propagating chain and
R• is the initiating radical

Scheme 6



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amines were used to initiate and control the free radical polymerization of acrylates and styrene according to a NMP process. In a second strategy, nitrones or nitroso compounds were added to the radical polymerization medium of vinyl monomers. Nitroxides "in situ" formed by reaction with radicals (Scheme 5) were able to control the radical polymerization of *n*-butyl acrylate (*n*-BuA). Polymerization of other monomers and synthesis of block copolymers were however not reported. Furthermore, only low molecular weight poly(*n*-BuA) (M_n < 10 000) was formed with a large polydispersity (M_w/M_n > 1.65). Later on, Grishin et al. reported on the radical polymerization of methyl methacrylate (MMA) regulated by *C*-phenyl-*N*-*tert*-butylnitrone (PBN)[11] and 2-methyl-2-nitrosopropane.[12] Molecular weight distribution was also broad (M_w/M_n > 1.7), and no experiment of block copolymerization was reported. Catala et al. used nitroso-*tert*-octane in CRP of styrene.[13] Finally, sodium nitrite was shown to be a precursor of nitroxides by Detrembleur et al.[14]

Although the "in situ" formation of nitroxides is attractive, a series of issues are still pending. Is it possible to control the radical polymerization of a large variety of monomers, including styrene, polar acrylates, and 1,3-dienes? Moreover, can block copolymers be prepared by the sequential radical polymerization of comonomers using a nitrone?

This paper discusses the conditions for the control of styrene and styrene–acrylonitrile (co)polymerizations using the nitrone **2** (*N*-*tert*-butyl-α-isopropylnitrone, Scheme 6). For the first time, synthesis of poly(styrene)-*b*-poly(styrene-*co*-acrylonitrile), poly(styrene)-*b*-poly(*n*-butyl acrylate), and poly(styrene)-*b*-poly(isoprene) diblock copolymers is reported by sequential nitrone-regulated copolymerization.

Experimental Section

Materials. Styrene (St, Aldrich, 99+%,), isoprene (IP, Janssen Chimica, 99%), acrylonitrile (AN, Aldrich, 99+%) and *n*-butyl acrylate (nBuA, Aldrich, 99+%) were dried over CaH_2 and distilled before use in order to remove the stabilizer. Toluene was degassed prior to use. AIBN (>98%, Aldrich) and BPO (75%, Fluka) were used as received. *N*-*tert*-Butyl-α-isopropylnitrone (nitrone **2**) was synthesized as described elsewhere.[6] Liquids were transferred under argon by syringes or stainless steel capillaries through rubber septa.

General Recipe for the Polymerization of Styrene Using the Nitrone 2. A mixture of BPO (0.36 g, 1.1×10^{-3} mol) and nitrone **2** (0.34 g, 2.36×10^{-3} mol) was degassed by three nitrogen–vacuum cycles. Degassed styrene (25 mL, 0.218 mol) was then added, and the flask was heated at 85 °C for 4 h. Finally, the flask was heated at 110 °C, and samples were withdrawn regularly from the polymerization medium. Monomer conversion was calculated by gravimetry after elimination of the residual monomer under vacuum at 80 °C and taking into account the amount of BPO and nitrone **2** initially introduced.

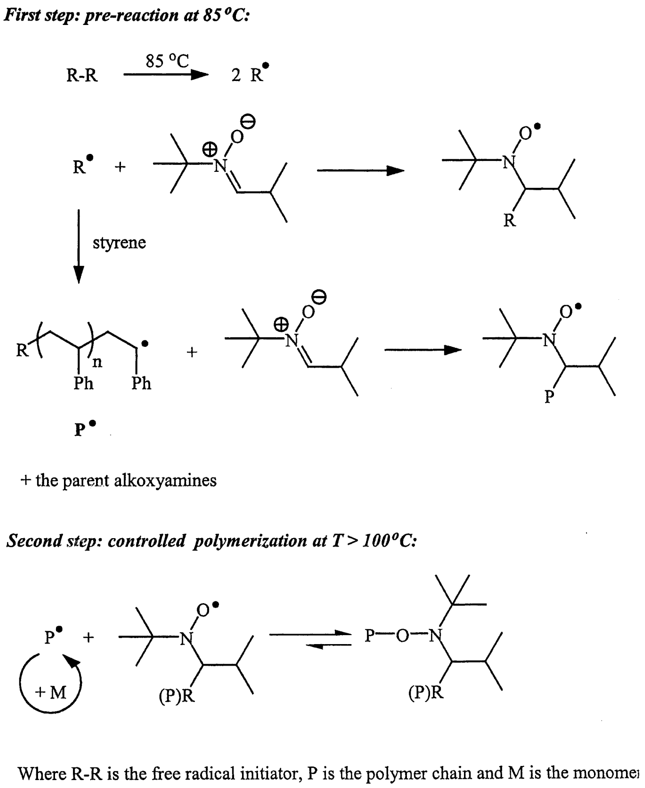
General Recipe for the Random Copolymerization of Styrene and Acrylonitrile Using the Nitrone 2. A mixture of BPO (0.232 g, 7.2×10^{-4} mol) and nitrone **2** (0.216 g, 1.5×10^{-3} mol) was degassed by repeated nitrogen–vacuum cycles. Degassed styrene (9.6 mL, 8.37×10^{-2} mol) was added, and the flask was heated at 85 °C for 4 h. Finally, acrylonitrile (3.8 mL, 5.77×10^{-2} mol) was added, and the flask was heated at 110 °C. Samples were regularly withdrawn from the polymerization medium, and the monomer conversion was calculated as before.

General Recipe for the PS-*b*-SAN Block Copolymer Synthesis. A mixture of BPO (0.42 g, 1.3×10^{-3} mol) and nitrone **2** (0.40 g, 2.8×10^{-3} mol) was degassed by three nitrogen–vacuum cycles, degassed styrene (8 mL, 6.98×10^{-2} mol) was added, and the flask was heated at 85 °C for 4 h and finally at 110 °C for 14 h. The residual monomer was eliminated under vacuum, and the monomer conversion was determined by weighing the collected polystyrene (yield = 62.5%, M_n = 25 500, M_w/M_n = 1.40). A sample of this polymer (0.5 g) was dissolved in a mixture of styrene (0.76 mL, 6.63×10^{-3} mol) and acrylonitrile (0.24 mL, 3.64×10^{-3} mol) and heated at 110 °C for 3 h. After elimination of the residual monomer under vacuum at 80 °C, the PS-*b*-(PS-*co*-SAN) diblock copolymer was collected (yield = 42%, M_n = 40 500, M_w/M_n = 1.45).

General Recipe for the PS-*b*-PnBuA Block Copolymer Synthesis. A mixture of BPO (0.079 g, 2.4×10^{-4} mol) and nitrone **2** (0.075 g, 5.2×10^{-4} mol) was degassed by three nitrogen–vacuum cycles, degassed styrene (3 mL, 2.61×10^{-2} mol) was added, and the flask was heated at 85 °C for 4 h and finally at 110 °C for 20 h. The residual monomer was eliminated under vacuum, and the monomer conversion was determined by weighing the collected polystyrene (yield = 86%, M_n = 37 500, M_w/M_n = 1.40). Part of this polymer (0.5 g) was dissolved in *n*-butyl acrylate (0.7 mL, 4.88×10^{-3} mol) and heated at 120 °C for 16 h. After elimination of the residual monomer under vacuum at 80 °C, the PS-*b*-PnBuA diblock copolymer was collected (yield = 35%, M_n = 45 000, M_w/M_n = 1.45).

General Recipe for the PS-*b*-PIP Block Copolymer Synthesis. A mixture of BPO (1.81 g, 5.6×10^{-3} mol) and nitrone **2** (1.69 g, 1.2×10^{-2} mol) was degassed by three nitrogen–vacuum cycles, degassed styrene (25 mL, 0.218 mol) was added, and the flask was heated at 85 °C for 4 h. Finally, the temperature was increased to 110 °C and a solution of AIBN (5.45 mL, solution 0.11 M in toluene) was added. After 20 h of reaction, the polymer was dissolved in toluene, purified by repeated precipitation in methanol (three times), and dried under vacuum at room temperature (M_n = 12 500 and M_w/M_n = 1.35). The polystyrene macroinitiator was dissolved in degassed isoprene; the reaction tube was sealed and heated at 120 °C for 24 h. The viscous reaction mixture was diluted by THF and precipitated into methanol. The copolymerization

Scheme 7



Where R-R is the free radical initiator, P is the polymer chain and M is the monomer

product was collected by filtration and dried under vacuum (yield = 28%, M_n = 26 500, M_w/M_n = 1.45).

Characterization. Size exclusion chromatography (SEC) was carried out in $CHCl_3$ at 40 °C using a Waters 600 liquid chromatograph equipped with a 410 refractive index detector (columns HP PL gel 5 μ (10^5, 10^4, 10^3, 100 Å)) and calibrated with polystyrene standards, and the flow rate was 1 mL/min. ^1H NMR spectra were recorded in $CDCl_3$ with Bruker AM 400 and 250 MHz spectrometers at 25 °C. The ESR spectra were recorded with a Bruker ESP-300 E ESR spectrometer (equipped with a temperature controller) at a frequency of 9.45 GHz, a microwave power of 20 mW, and a modulation amplitude of 1 G. The EPR tube (o.d. 4 mm) filled with 0.5 mL of solution was closed by a rubber septum. This solution was degassed three times by freeze−pump−thaw cycles, and the spectrum was recorded at the desired temperature.

Results and Discussion

Polymerization of Styrene. Whenever the nitrone **2**, an azoinitiator (AIBN), and styrene (nitrone **2**/AIBN/Sty: 1/0.5/250) are reacted at 120 °C for 14 h, the polymerization is out of control as assessed, for instance, by a broad molecular weight distribution (M_n = 58 000; M_w/M_n = 4.0; 85% monomer conversion). The very fast decomposition of AIBN at 120 °C ($t_{1/2}$ < 1 min) might be responsible for this lack of control.

To overcome this problem, the same experiment was repeated in the absence of free radical initiator (nitrone **2**/AIBN/Sty: 1/0/250). Self-initiation of styrene is then the unique source of radicals as was the case in the successful experiments of TEMPO-mediated radical polymerization of styrene.[15] After 14 h, the monomer conversion was low (ca. 28%), and an exceedingly high molecular weight polymer was formed (M_n = 310 000) with high polydispersity (M_w/M_n = 1.9). These preliminary experiments indicate that enough nitroxides were not formed at the early stage of reaction for the polymerization to be controlled. Therefore, nitroxides should be formed before the polymerization is initiated (Scheme 7). For this purpose, nitrone, azoinitiator, and styrene were prereacted at 85 °C for 4 h, such that the initiator would be completely decomposed. Under these conditions, radicals released by the thermal decomposition of the initiator either add to the nitrone with formation of nitroxides or initiate the styrene polymerization. The growing chains should be rapidly trapped by the nitrone and converted into nitroxides and/or by the previously formed nitroxides and converted into alkoxyamines (Scheme 7) which are stable at this temperature and block the polymerization. In this strategy, the prereaction is actually the “in situ” formation of nitroxides and alkoxyamines, which are required to control the polymerization conducted at a temperature high enough (>100 °C) for the C−ON bond of the alkoxyamine to be labile and the styrene polymerization to be self-initiated (Scheme 7).

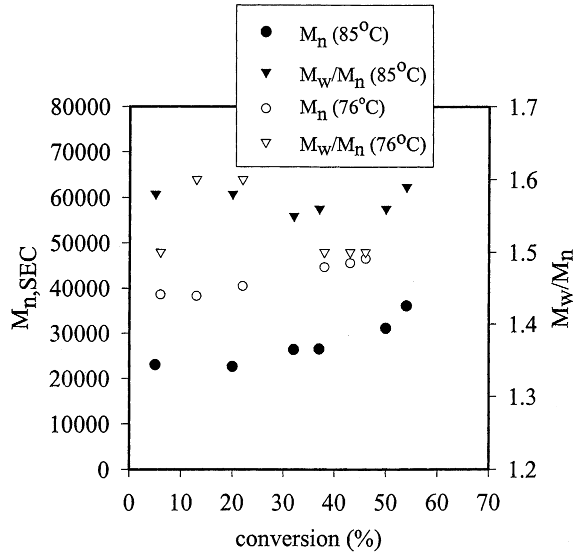


Figure 1. Dependence of $M_{n,SEC}$ and polydispersity on styrene conversion for the bulk polymerization of styrene initiated by AIBN in the presence of nitrone **2** at 85 °C and 76 °C [1 equiv of nitrone **2**, 0.5 equiv of AIBN, 185 equiv of styrene].

Unexpectedly, when styrene is reacted with AIBN in the presence of the nitrone **2** (nitrone **2**/AIBN/Sty: 1/0.5/185) at 85 °C and lower (76 °C), it polymerizes rapidly, such that the molecular weight does not increase significantly with monomer conversion and the polydispersity is high (Figure 1). Finally, BPO was substituted for AIBN in the prereaction step that was conducted at 85 °C because the half-life time of BPO at 85 °C is similar to that one of AIBN at 76 °C ($t_{1/2}$ BPO at 85 °C = 1.93 h; $t_{1/2}$ AIBN at 76 °C = 2 h). Although no reaction occurred at 85 °C in the presence of BPO, polymerization was slow and polydispersity decreased with increasing monomer conversion when the prereacted mixture was heated at 110 °C (Figure 2). The linear dependence of molecular weight on monomer conversion and the low polydispersity up to high molecular weight (ca. 60 000) were signatures of a controlled process. However, the high experimental molecular weight compared to the expected value indicates a low initiator efficiency (0.15−0.2) and thus a limited conversion of nitrone into nitroxide and/or a substantial decomposition of the nitroxide.

The linear time dependence of ln$[M]_0/[M]$) indicates that concentration of the active species remains constant during polymerization (Figure 3). The 10 h induction

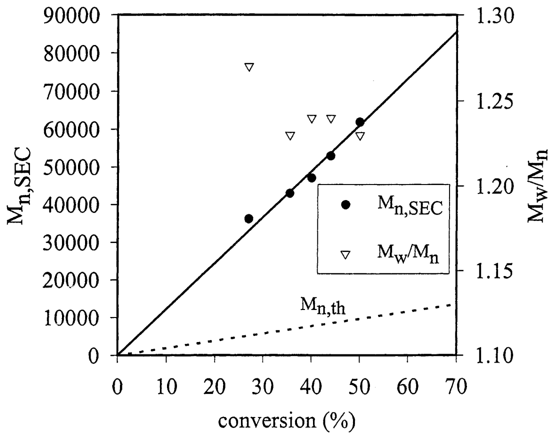


Figure 2. Dependence of $M_{n,SEC}$ and polydispersity on styrene conversion for the bulk polymerization of styrene at 110 °C, after styrene/nitrone/BPO were prereacted at 85 °C, and comparison with the theoretical molecular weight [prereaction: 1 equiv of nitrone **2**, 0.5 equiv of BPO, 185 equiv of styrene, 85 °C, 4 h; polymerization: 110 °C, no additional initiator].

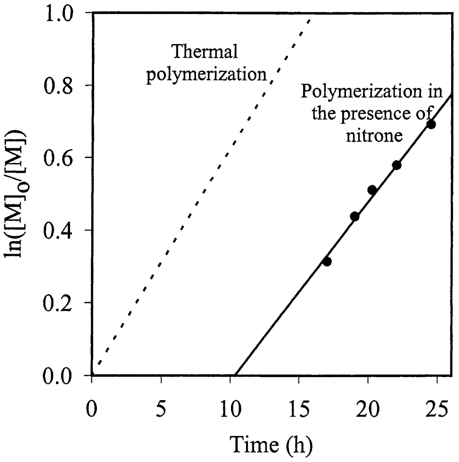


Figure 3. Comparison of time dependence of $\ln([M]_0/[M])$ for the bulk polymerization of styrene at 110 °C, after styrene/nitrone/BPO were prereacted at 85 °C, and for the thermal polymerization of styrene in bulk at 110 °C [prereaction: 1 equiv of nitrone **2**, 0.5 equiv of BPO, 185 equiv of styrene, 85 °C, 4 h; polymerization: 110 °C, no additional initiator].

time (Figure 3) is consistent with formation of a large excess of nitroxides during the prereaction compared to the initiating radicals that result from styrene self-initiation. Indeed, as soon as nitroxides are formed, the styrene radicals can react with them to form alkoxyamines. Only when most of the nitroxides are consumed can the polymerization start according to a NMP process, and the rate of polymerization can be governed by the thermal polymerization as shown in Figure 3.

Clearly, the choice of the initiator has a decisive effect on the course of the prereaction and ultimately on the polymerization control. Indeed, the structure of the nitroxide is the key parameter in the NMP process[3,16,17] because it dictates the relative rates of alkoxyamine (dormant species) formation and homolysis which, when appropriate, provide polymerization with control. In the strategy investigated in this work, the structure and reactivity of the nitroxide depend directly on the structure of both the free radical initiator and the nitrone, consistent with the huge difference in the polymerization control by BPO and AIBN, respectively. Moreover, in addition to reaction with the nitrones, the initiating radicals can also start the polymerization. Whenever this competition is not favorable to the nitroxide formation and/or when not enough nitroxides are formed, no control may be expected, which is more likely the case of AIBN.

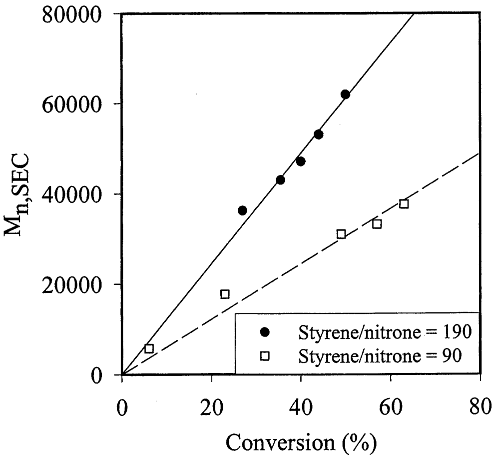


Figure 4. Dependence of $M_{n,SEC}$ on styrene conversion for the bulk polymerization of styrene at 110 °C, after styrene/nitrone/BPO were prereacted at 85 °C. The amount of nitrone and BPO were changed while keeping the nitrone/BPO molar ratio and the monomer concentration constant [prereaction: 1 equiv of nitrone **2**, 0.5 equiv of BPO, 185 and 90 equiv of styrene, 85 °C, 4 h; polymerization: 110 °C, no additional initiator].

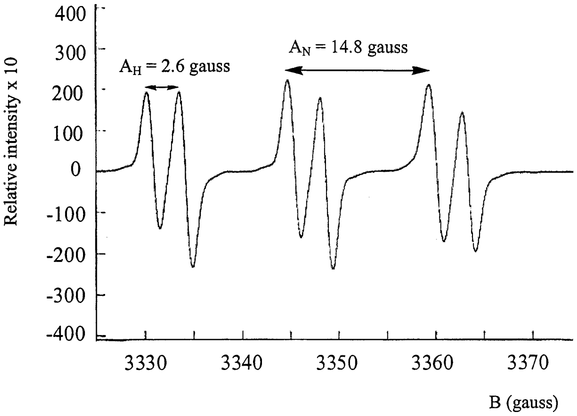
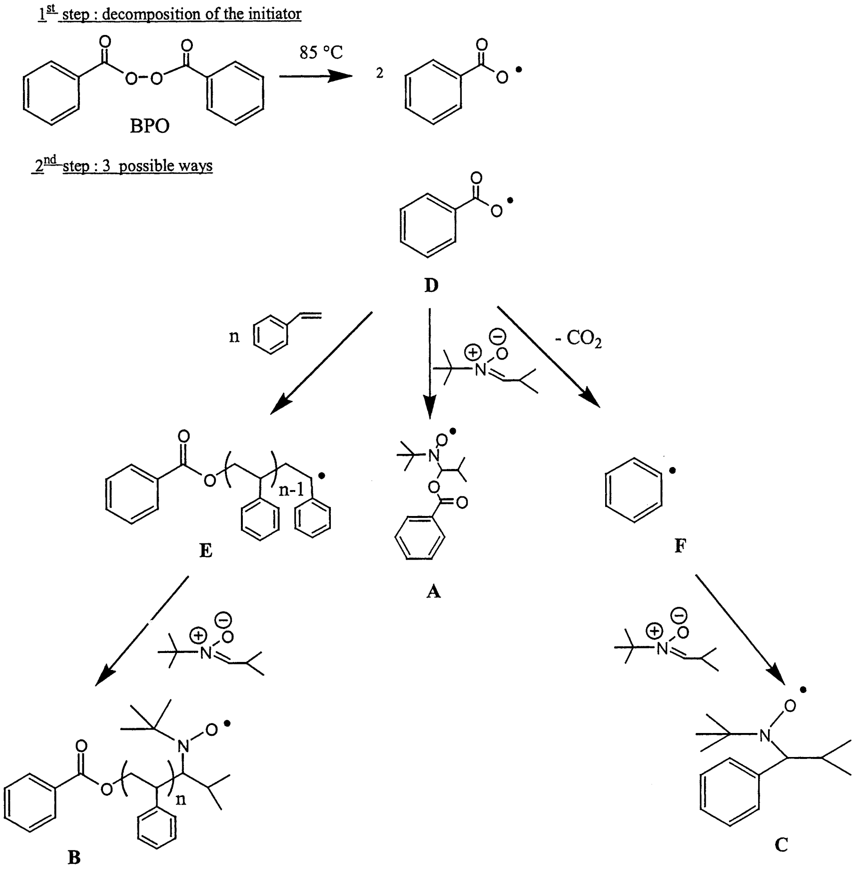


Figure 5. ESR spectrum for the nitroxide formed by reaction of styrene with BPO in the presence of the nitrone **2** (styrene/BPO/nitrone = 90/0.5/1; 85 °C, 4 h). *B* stands for the magnetic field (gauss).

Influence of the Amount of Nitrone. The amount of nitrone was changed at a constant nitrone/BPO molar ratio and constant amount of the other constituents (Figure 4). A decrease by two in the styrene/nitrone molar ratio (from 185/1 to 90/1) resulted in the same decrease in the polystyrene molecular weight whereas the polydispersity remained low (1.35−1.40). The chain molecular weight was thus directly controlled by the amount of nitrone (at least in the investigated range) and consequently by the amount of nitroxide formed in situ. This observation is consistent with the controlled radical polymerization of styrene self-initiated in the presence of TEMPO, for which the molecular weight is directly dictated by the amount of TEMPO.[15] Additionally, a low initiator efficiency (0.15−0.2) was found regardless of the amount of nitrone, more likely as consequence of limited conversion of nitrone into nitroxides and/or substantial decomposition of nitroxide.

ESR Study of the BPO/Nitrone Reaction Product in the Presence of Styrene or Not. Formation of nitroxide

Scheme 8



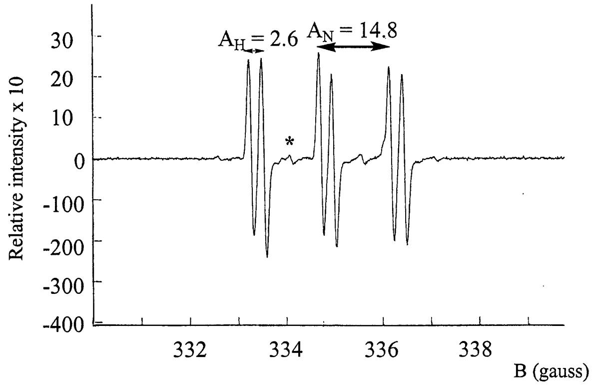


Figure 6. ESR spectrum for the nitroxide formed by reaction of BPO with the nitrone **2** in the absence of styrene (BPO/nitrone = 0.5/1; 85 °C, 4 h).

as result of the BPO/nitrone prereaction was investigated by ESR in order to investigate the structure of the reaction product and to support the reaction mechanism proposed in Scheme 7. Styrene, BPO, and the nitrone **2** were reacted at 85 °C for 4 h, and the electron spin resonance (ESR) spectra were recorded at different times. After a few seconds, a doublet of triplet with A_N = 14.8 G and g = 2.6 G was observed (Figure 5), which is characteristic of nitroxide bearing a hydrogen atom in the α-position of the nitrogen atom.[18] Indeed, in the absence of this hydrogen, only one triplet should be observed because of the hyperfine coupling of the nitrogen nucleus with the unpaired electron of the radical. The unpaired electron may also couple with the hydrogen atom and account for a doublet of triplet.

As shown in Scheme 8, three kinds of nitroxides can be formed in the prereaction as result of the addition of the nitrone[2] by a carbobenzoxy radical **(A)**, by a styrenyl radical (or a propagating polystyrene chain) **(B),** and by a phenyl radical (formed by decarboxylation of the carbobenzoxy radical) **(C)**. The ESR spectrum is consistent with the structure of these three nitroxides that contain a hydrogen atom α to the nitroxide.

When the prereaction is repeated in the absence of styrene, only the nitroxides **A** and **C** can be formed. Because the ESR signal remains unmodified (Figure 6), the nitroxides **B** are not formed in the BPO/nitrone/styrene prereaction. Further studies are in progress in order to discriminate the two nitroxides **A** and **C**.

The nitroxide concentration calculated form the ESR spectra increases with time until reaching a plateau after 3 h of reaction (Figure 7). From the integration of the ESR signal after 3 h of prereaction, it appears that 10% of the nitrone is converted into nitroxide, which is a lower limit because part of the nitroxides has been consumed by alkyl radicals (phenyl radicals, styrenyl radicals) during the prereaction and possibly decomposed by disproportion at the polymerization temperature. Moreover, the percentage of nitroxide formed is of the same order of magnitude as the initiator efficiency (f = 15−20%) calculated from the polymerization kinetics. This provides additional evidence that the polymer molecular weight is controlled by the amount of nitroxide formed in situ.

Addition of a Free Radical Initiator (AIBN) after the Prereaction. A free radical initiator (AIBN) was added to the polymerization medium after the prereaction in order to generate more radicals than formed by styrene self-initiation and thus to modify polymerization rate and polystyrene molecular weight and polydispersity.

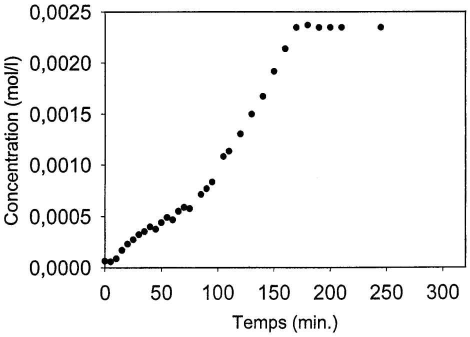


Figure 7. Time evolution of the nitroxide concentration during the styrene/BPO/nitrone **2** reaction at 85 °C (BPO/nitrone = 0.5/1; 85 °C, 4 h).

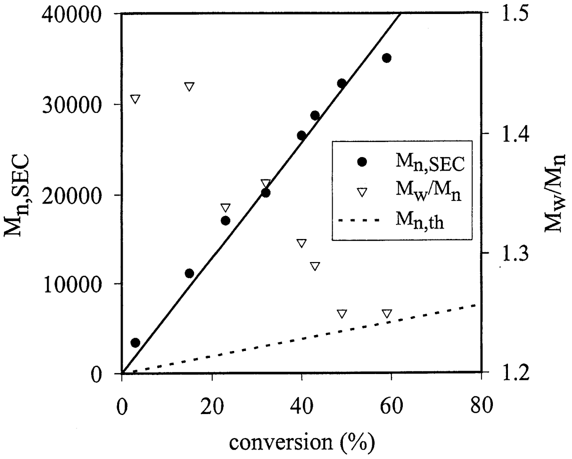


Figure 8. Dependence of $M_{n,SEC}$ and polydispersity on styrene conversion for the bulk polymerization of styrene at 110 °C, after styrene/nitrone/BPO were prereacted at 85 °C and subsequent addition of AIBN, and comparison with theoretical molecular weight ($M_{n,th}$) [prereaction: 1 equiv of nitrone **2**, 0.5 equiv of BPO, 90 equiv of styrene, 85 °C, 4 h; polymerization: 110 °C, 0.05 equiv of AIBN].

When a small amount of AIBN (0.05 equiv. AIBN compared to the nitrone) was added after the prereaction, the polymerization was well-controlled as supported by the linear dependence of molecular weight (Figure 8) and ln[M]$_0$/[M] (Figure 9) on monomer conversion and time, respectively. The addition of this small amount of AIBN decreases the molecular weight distribution as exemplified by $M_w/M_n = 1.25$ at 60% monomer conversion compared to 1.35−1.40 in absence of additional AIBN. Finally, the polymer molecular weight is not affected by the small additional amount of AIBN (Figure 10), which suggests that molecular weight is only controlled by the amount of the "in situ" formed nitroxide (at least in the investigated conditions). Similar results were observed when BPO was used instead of AIBN.

The styrene polymerization remained controlled when the amount of additional AIBN was increased by a factor of 5 (linear evolution of M_n vs conversion and ln([M]$_0$/[M]) vs time; Figures 11 and 12). The polymerization rate constant (slope of the ln([M]$_0$/[M]) vs time straight line) did not change significantly (Figure 12). The major modification was the disappearance of the induction period of time at the benefit of a burst effect confirmed by the extrapolation of ln([M]$_0$/[M]) vs time to a finite value at the initial time. This burst effect more likely results from the very fast decomposition of AIBN and thus the fast polymerization initiation.

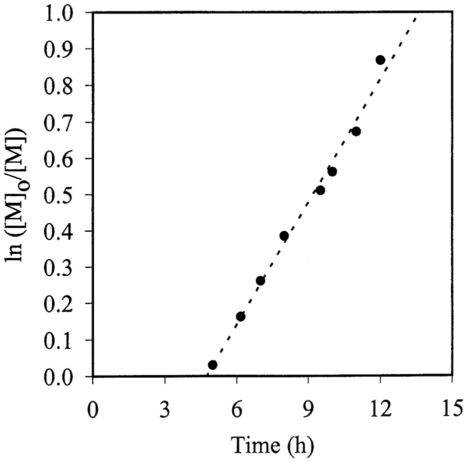


Figure 9. Time dependence of ln([M]$_0$/[M]) for the bulk polymerization of styrene at 110 °C, after styrene/nitrone/BPO were prereacted at 85 °C and subsequent addition of AIBN [prereaction: 1 equiv of nitrone **2**, 0.5 equiv of BPO, 90 equiv of styrene, 85 °C, 4 h; polymerization: 110 °C, 0.05 equiv of AIBN].

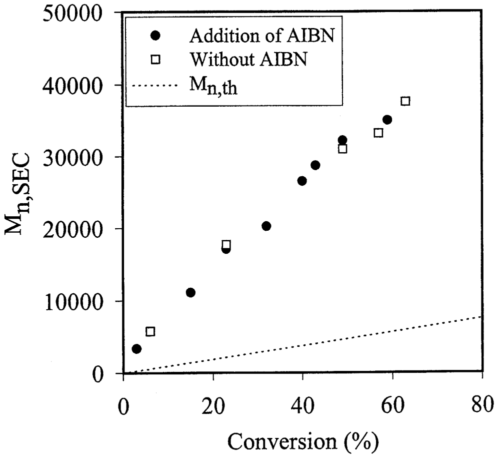


Figure 10. Comparison of the dependence of $M_{n,SEC}$ on styrene conversion for the bulk polymerization of styrene at 110 °C, after styrene/nitrone/BPO were prereacted at 85 °C and subsequent addition of AIBN or not, and comparison with theoretical molecular weight ($M_{n,th}$) [prereaction: 1 equiv of nitrone **2**, 0.5 equiv of BPO, 90 equiv of styrene, 85 °C, 4 h; polymerization: 110 °C, 0.05 equiv of AIBN if present].

Georges et al. reported the same observation when an excess of BPO compared to TEMPO was used to initiate the styrene polymerization.[19] They proposed that the amount of TEMPO was too low to control all of the chains that were initiated, thus leading to a population of low molecular weight dead polymer. In this study, although a burst effect is observed, no fraction of dead oligomers is detected. Moreover, the polydispersity index is large at the early stage of polymerization and increases with time. Furthermore, molecular weight is smaller compared to polystyrene formed in the absence of AIBN or when only a low amount of AIBN (0.05 equiv) is added after the prereaction (Figure 13). This apparently contradicts Georges et al.,[19,20] who reported that molecular weight was dictated by the amount of the nitroxide independent of the amount of initiator. This disagreement might be explained if part of the additional free radicals contributes to the "in situ" formation of nitroxides by reaction with unreacted nitrone. Further experiments are needed to confirm this hypothesis.

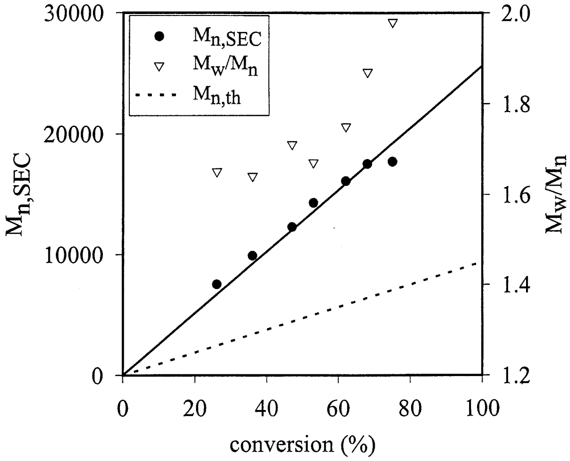


Figure 11. Dependence of $M_{n,SEC}$ and polydispersity on styrene conversion for the bulk polymerization of styrene at 110 °C, after styrene/nitrone/BPO were prereacted at 85 °C and subsequent addition of AIBN, and comparison with theoretical molecular weight ($M_{n,th}$) [prereaction: 1 equiv of nitrone **2**, 0.5 equiv of BPO, 90 equiv of styrene, 85 °C, 4 h; polymerization: 110 °C, 0.25 equiv of AIBN].

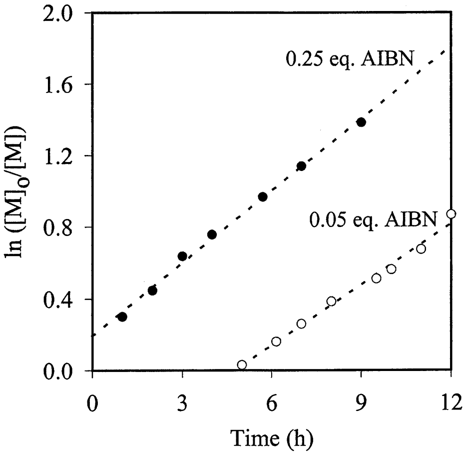


Figure 12. Time dependence of ln([M]$_0$/[M]) for the bulk polymerization of styrene at 110 °C, after styrene/nitrone/BPO were prereacted at 85 °C and subsequent addition of 0.05 and 0.25 equiv of AIBN [prereaction: 1 equiv of nitrone **2**, 0.5 equiv of BPO, 90 equiv of styrene, 85 °C, 4 h; polymerization: 110 °C, 0.05 and 0.25 equiv of AIBN].

Polymerization Resumption. Polymer resumption was conducted in order to collect information about the persistency of the growing species. Polystyrene chains (M_n = 12 300, M_w/M_n = 1.4) preformed by the nitrone system (see Experimental Section) were purified by repeated precipitation in methanol. After solubilization in styrene, they were heated at 110 °C under argon for 18 h. The polymer molecular weight increased to 25 000 with a monomer conversion of 83%. The polydispersity slightly increased (M_w/M_n = 1.53) because of a small tailing on the low molecular weight side of the SEC chromatogram. The experimental and theoretical molecular weights ($M_{n,th}$ = 23 500) agreed very well, which confirmed that the major part of PS initiated polymerization of the second monomer feed, consistent with a controlled process.

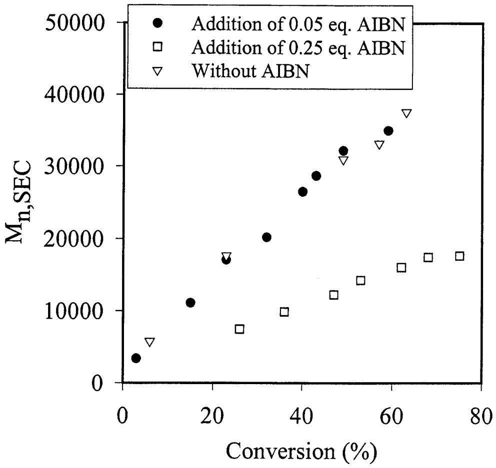
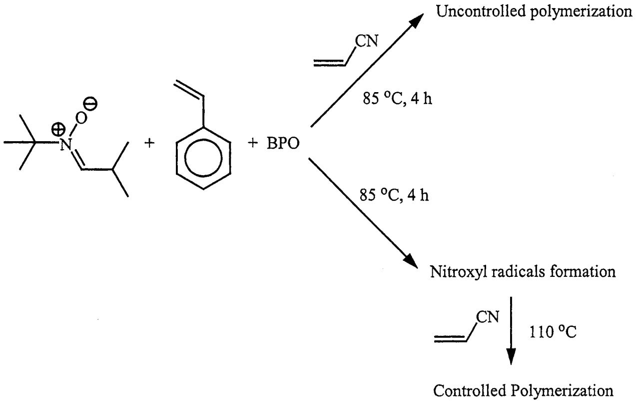


Figure 13. Comparison of the dependence of $M_{n,SEC}$ on styrene conversion for the bulk polymerization of styrene at 110 °C, after styrene/nitrone/BPO were prereacted at 85 °C and subsequent addition of AIBN or not [prereaction: 1 equiv of nitrone **2**, 0.5 equiv of BPO, 90 equiv of styrene, 85 °C, 4 h; polymerization: 110 °C, 0.05 and 0.25 equiv of AIBN if present].

Scheme 9



Random Copolymerization of Styrene and Acrylonitrile and Synthesis of Poly(styrene-*co*-acrylonitrile)-*b*-poly(styrene) (SAN-*b*-PS) Copolymers. The addition of acrylonitrile to styrene has a detrimental effect on the nitrone/BPO/monomer prereaction at 85 °C. Polymerization is fast (65% monomer conversion after 50 min) and out of control (no significant increase in molecular weight with monomer conversion and large polydispersity ($M_w/M_n \approx 2$)). This may be explained by a faster polymerization compared to the nitroxide formation. Uncontrolled polymer chains are thus formed before enough nitroxide is available to control the polymerization.

To restore control, the prereaction was conducted in the absence of acrylonitrile at 85 °C for 4 h; i.e., under conditions such that nitroxides are formed and no polymerization occurs. Acrylonitrile was added before increasing the temperature to 110 °C (Scheme 9). The apparent molecular weight of the copolymer can be controlled up to 50 000 (Figure 14), and the polydispersity, which is large at low monomer conversion ($1.5 \leq M_w/M_n \leq 1.8$ for monomer conversion lower than 30%), decreases with increasing monomer conversion ($M_w/M_n \approx 1.4$ at 45% monomer conversion). The time dependence of ln([M]$_0$/[M]) is linear (Figure 15), which indicates absence of irreversible termination.

Poly(styrene)-*co*-poly(acrylonitrile) chains should be end-capped by a thermolabile alkoxyamine (ω end group), which provides an opportunity to prepare diblock copolymers. For instance, a random copolymer (M_n = 35 500, M_w/M_n = 1.3, St/AN = 64/36) prepared by the nitrone system and purified by repeated precipitation

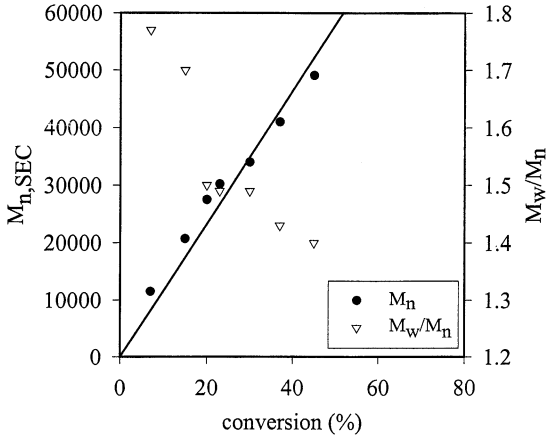


Figure 14. Dependence of $M_{n,SEC}$ and polydispersity on styrene and acrylonitrile conversion for the bulk polymerization of a styrene/acrylonitrile (60/40) mixture at 110 °C, after styrene/nitrone/BPO were prereacted at 85 °C and subsequent addition of acrylonitrile [prereaction: 1 equiv of nitrone **2**, 0.5 equiv of BPO, 56 equiv of styrene, 85 °C, 4 h; polymerization: 110 °C, 40 equiv of AN].

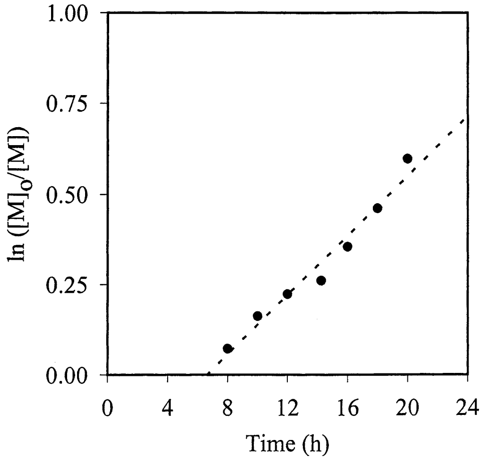


Figure 15. Time dependence of ln[M]$_0$/[M] for the bulk polymerization of a styrene/acrylonitrile (60/40) mixture at 110 °C, after styrene/nitrone/BPO were prereacted at 85 °C and subsequent addition of acrylonitrile [prereaction: 1 equiv of nitrone **2**, 0.5 equiv of BPO, 56 equiv of styrene, 85 °C, 4 h; polymerization: 110 °C, 40 equiv of AN].

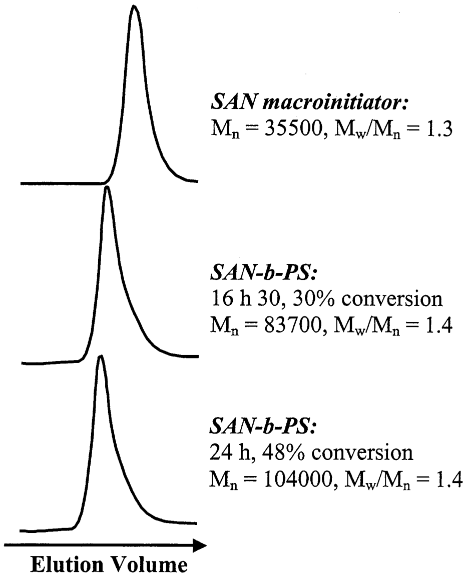


Figure 16. Comparison of SEC traces for (a) the poly(styrene)-*co*-poly(acrylonitrile) macroinitiator, (b) the (poly(styrene)-*co*-poly(acrylonitrile))-*b*-poly(styrene) diblock copolymer after 16.5 h, and (c) the (poly(styrene)-*co*-poly(acrylonitrile))-*b*-poly(styrene) diblock copolymer after 24 h.

Table 1. Molecular Characteristics of Poly(styrene)-*b*-poly(styrene-*co*-acrylonitrile) Diblock Copolymers Prepared by the Nitrone System, in Bulk at 110 °C

	PS first block[b]		PS-*b*-SAN diblock[c]		
expt	$M_{n,SEC}$	M_w/M_n	$M_{n,SEC}$[a]	M_w/M_n	conv (time)
1	39 000	1.40	47 500	1.40	44% (5 h)
2	25 500	1.40	40 500	1.45	42% (3 h)

[a] Polystyrene standards. [b] First block: prereaction of nitrone (2.8 × 10^{-3} mol) and BPO (1.3 × 10^{-3} mol) in the presence of styrene (1.40 × 10^{-1} mol, expt 1; 6.98 × 10^{-2} mol, expt 2) at 85 °C for 4 h, followed by polymerization at 110 °C for 24 h. [c] Diblock copolymer: 0.5 g of purified polystyrene macroinitiator was dissolved in styrene (0.38 mL, expt 1; 0.76 mL, expt 2) and acrylonitrile (0.12 mL, expt 1; 0.24 mL, expt 2) and heated at 110 °C for 3 h.

in methanol was dissolved in toluene, added with styrene, and heated under argon at 110 °C (see Experimental Section). Figure 16 shows that the SEC chromatogram of the macroinitiator is completely shifted toward lower elution volumes, which indicates that the macroinitiator initiated the styrene polymerization. The molecular weight of the diblock copolymer increased with monomer conversion, and high molecular weight (M_n > 100 000) copolymer was formed with a low polydispersity index (M_w/M_n = 1.4).

Similarly, polystyrene of different molecular weights was synthesized by the nitrone system and used as a macroinitiator for the synthesis of poly(styrene)-*b*-(poly(styrene)-*co*-poly(acrylonitrile)) diblocks. The polystyrene macroinitiator was dissolved in a styrene/acrylonitrile mixture (60/40 molar ratio) and heated at 110 °C in sealed tubes. Table 1 shows that molecular weight of the polystyrene macroinitiator increased substantially and that the molecular weight distribution remained narrow ($M_w/M_n \approx 1.4$).

Synthesis of Poly(styrene)-*b*-poly(*n*-butyl acrylate) Copolymers. A polystyrene macroinitiator **A** (Scheme 10) was prepared according to the two-step method discussed above (M_n = 62 000, M_w/M_n = 1.25), dissolved in *n*-butyl acrylate (nBuA), and heated at 120 °C under argon for 16 h. Figure 17 shows that the copolymerization product is bimodal. The high molecular weight SEC peak might result from a coupling reaction of two growing PS-*b*-PnBuA chains (thus two growing acrylate radicals). Moreover, the relative height of the two elution peaks increases with the reaction time in favor of the larger molecular weight peak (possibly a triblock), and the polymerization medium becomes milky.

When a lower molecular weight PS macroinitiator (M_n = 39 000, M_w/M_n = 1.37) was used, the SEC chromatogram of the diblock copolymer remained monomodal (M_n = 43 000, M_w/M_n = 1.6, 48% monomer conversion) and shifted toward lower elution volume, in agreement with formation of the expected diblock. In parallel, the molecular weight distribution increased slightly.

To improve the synthesis of PS-*b*-PnBuA diblock copolymers, the PS macroinitiator was not purified by precipitation before use; only the residual monomer was eliminated under vacuum. Therefore, the excess of nitroxide that controlled the styrene polymerization was preserved and participated in the *n*-butyl acrylate polymerization. Under these conditions, well-defined

Scheme 10

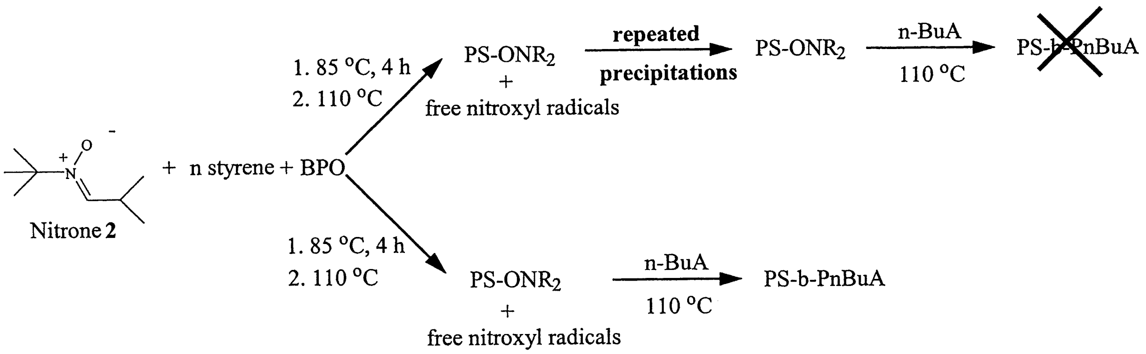


Table 2. Molecular Characteristics of Poly(styrene)-*b*-poly(*n*-butyl acrylate) Diblock Copolymers Prepared by the Nitrone System, in Bulk at 120 °C for 16 h

PS macroinitiator		poly(n-BuA) block[d]		PS-*b*-PnBuA[e]		
$M_{n,SEC}$	M_w/M_n	$M_{n,th}$	$M_{n,exp}$[a]	$M_{n,SEC}$[b]	M_w/M_n	conv (%)
37 500	1.4	16 500	15 000	45 000	1.45	35
37 500	1.4	18 900	not determined	49 000	1.45	40[c]

[a] ^{1}H NMR analysis. [b] Polystyrene standards. [c] 8 equiv of acetic anhydride (compared to PS) added to the PS macroinitiator. [d] First block: prereaction of nitrone (5.2×10^{-4} mol) and BPO (2.4×10^{-4} mol) in the presence of styrene (2.61×10^{-2} mol) at 85 °C for 4 h, followed by polymerization at 110 °C for 20 h. Residual monomer was eliminated under vacuum at 80 °C. [e] Diblock copolymer: 0.5 g of crude polystyrene macroinitiator was dissolved in *n*-butyl acrylate (4.88×10^{-3} mol) and heated at 120 °C for 16 h.

Table 3. Molecular Characteristics of Poly(styrene)-*b*-poly(isoprene) Diblock Copolymers Prepared by the Nitrone System, in Bulk at 125 °C

PS macroinitiator		poly(isoprene) block[c]		PS-*b*-PIP[d]		
$M_{n,exp}$	M_w/M_n	$M_{n,th}$	$M_{n,exp}$[a]	$M_{n,SEC}$[b]	M_w/M_n	microstructure of poly(isoprene)[a]
12 500	1.35	16 400	17 500	43 000	1.70	89.8% (1,4); 5.9% (3,4); 4.3% (1,2)
12 500	1.35	7 200	7 900	26 500	1.45	91.1% (1,4); 5.3% (3,4); 3.6% (1,2)
39 000	1.35	17 500	18 000	61 000	1.45	88.2% (1,4); 6.5% (3,4); 5.3% (1,2)
39 000	1.35	12 100	10 500	56 000	1.30	84.1% (1,4); 9.3% (3,4); 6.6% (1,2)
44 000	1.30	29 700	20 500	78 000	1.45	89.5% (1,4); 6% (3,4); 4.5% (1,2)

[a] ^{1}H NMR analysis. [b] Polystyrene standards. [c] First block: prereaction of nitrone (1.2×10^{-2} mol) and BPO (5.6×10^{-3} mol) in the presence of styrene (0.22 mol, $M_n = 12\,500$; 0.69 mol, $M_n = 39\,000$; 0.77 mol, $M_n = 44\,000$,) at 85 °C for 4 h, followed by polymerization at 110 °C for 20 h. [d] Diblock copolymer: 0.5 g of purified polystyrene macroinitiator was dissolved in isoprene and heated at 120 °C for 24 h in sealed tubes.

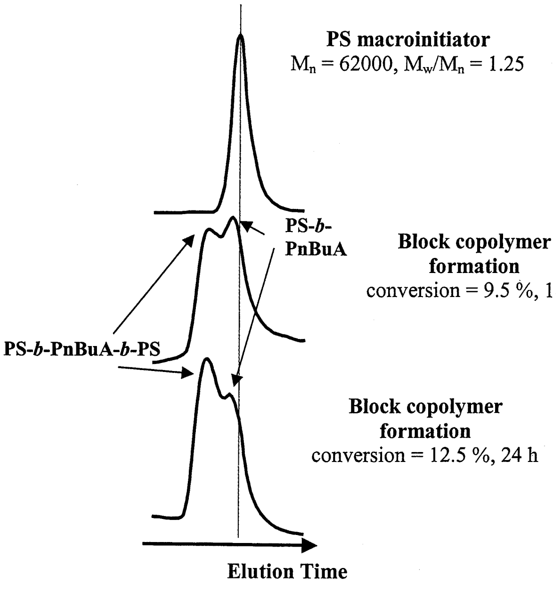


Figure 17. Comparison of SEC traces for the poly(styrene) macroinitiator and the copolymer formed after dissolution in *n*-butyl acrylate and heating at 110 °C.

PS-*b*-PnBuA diblock copolymers were formed at 120 °C (Table 2). According to Hawker,[6] excess nitroxide decreases the acrylate polymerization rate and thus improves the polymerization control. The SEC chromatogram of the macroinitiator remains monomodal, and the polydispersity remains quasi-unchanged (Table 2). The experimental and theoretical molecular weights for the second block agree well. Nevertheless, the monomer conversion is limited to ca. 40% after 16 h. A too large excess of nitroxide in the PS macroinitiator could be responsible for this observation, i.e., for a shift of the active chains/dormant chains equilibrium toward the dormant polyacrylate chains.[6]

Synthesis of Poly(styrene)-*b*-poly(isoprene) Copolymers. In 1998, Georges et al. reported the controlled polymerization of isoprene[21] and the synthesis of poly(styrene)-*b*-poly(isoprene) and poly(styrene)-*b*-poly(butadiene) diblock copolymers[22] by using TEMPO as a mediator. Two years later, Hawker et al. reported on the efficiency of the α-hydrido alkoxyamine **1** (Scheme 3) in promoting the controlled polymerization of isoprene to high molecular weight and on the synthesis of well-defined poly(styrene)-*b*-poly(isoprene) and poly(*tert*-butyl acrylate)-*b*-poly(isoprene) copolymers.[7]

To illustrate the versatility of the nitrone system reported in this work, the synthesis of poly(styrene)-*b*-poly(isoprene) diblocks was examined. Polystyrene was first prepared, purified by repeated precipitation in methanol, and heated at 125 °C in sealed tubes containing isoprene for 17−24 h. Table 3 shows that well-defined block copolymers were formed. Indeed, the polydispersity ($1.3 \leq M_w/M_n \leq 1.45$, except for the first sample) is low, and the experimental molecular weight ($M_{n,exp}$) agrees well with the theoretical value ($M_{n,th}$). The microstructure of the isoprene block (determined by ^{1}H NMR of the vinylic protons of the polyisoprene[23]) is close to 90% of 1,4-units, in agreement with the microstructure for polyisoprene synthesized by classical radical polymerization.

Conclusions

The *N-tert*-butyl-α-isopropylnitrone imparts control to the radical polymerization of styrene. A nitrone/styrene/BPO prereaction at 85 °C is however required before the polymerization is started at 110 °C. Nitroxides are preformed during this prereaction, which control the polymerization self-initiated at 110 °C. Approximately 15−20% of the nitrone would be converted into nitroxides under the conditions used in this study. The reaction control is lost when AIBN is substituted for BPO in the prereaction, which might emphasize the key role of the structure of the nitroxide formed.

Random copolymerization of styrene and acrylonitrile is also controlled provided that acrylonitrile is not part of the prereaction. Moreover, poly(styrene)-*b*-(poly(styrene)-*co*-poly(acrylonitrile)) diblock copolymers were successfully prepared regardless of the block used as macroinitiator. This nitrone system was extended to the synthesis of well-defined poly(styrene)-*b*-poly(*n*-butyl acrylate) and poly(styrene)-*b*-poly(isoprene) copolymers.

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