

# New Dinitroxide for Stable Free Radical Polymerization of Styrene

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**ABSTRACT:** A new dinitroxide (1,4-di (1-oxy-2,2,6,6-tetramethyl-1-piperidin-4-yl)-xylene) (DTPX) was synthesized and successfully used in stable free radical polymerization of styrene. The results of the polymerizations showed that the DTPX was a suitable mediating agent for stable free radical polymerization of styrene. However, it was found that the dinitroxide mediating process resulted in a higher level of decomposition of the internal bisalkoxyamine linkage in the polymer chain, which resulted in polymers possessing a terminal alkoxyamine and an adjacent hydroxylamine, and the decomposition became more obvious at high conversion through monitoring the change of molecular weights with the conversion by gel permeation chromatog-

raphy and the polymer structure by  $^1\text{H-NMR}$ . The reaction temperature showed obvious effects on the polymerization, and the polymerization of styrene at  $110^\circ\text{C}$  led to a better controlled polymerization than that at  $125^\circ\text{C}$  with narrower molecular weight distributions and slight decomposition of the nitroxide up to monomer conversions of 76.7%, however, the rate of the polymerization was decreased and an induction period appeared at  $110^\circ\text{C}$ . © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1137–1145, 2006

**Key words:** dinitroxide; gel permeation chromatography; stable free radical polymerization; NMR; monomer

## INTRODUCTION

The main advantages of free-radical chemistry are the undemanding conditions required for polymerization and the large number of monomers that can be polymerized. The disadvantage of this method lies in the uncontrollable polymer structure. The application of living free radical polymerization<sup>1–4</sup> has opened the possibility of generating controllable macromolecular architectures with mild reaction conditions. Several living free radical polymerization techniques have been developed, including stable free radical polymerization (SFRP),<sup>5–9</sup> atom transfer radical polymerization (ATRP),<sup>10–13</sup> and reversible addition–fragmentation chain transfer (RAFT)<sup>14–18</sup> to yield well-defined polymeric structures and compositions.

Control of the polymerization in nitroxide-mediated “living” free radical polymerizations (NMP) is believed to be the reversible termination of the growing polymeric radical by the stable nitroxide free radical to give a dormant, or inactive, species in which the nitroxide moiety is covalently bound to the polymer

chain end (Scheme 1).<sup>2,19</sup> At lower temperatures, this trapping simply results in termination of the polymerization reaction. However, at high temperatures, the equilibrium between growing polymer chains and stable nitroxide free radical is established, which is shifted strongly toward the adducts. The concentration of growing polymer chains in the reaction medium is reduced. Consequently, the rate of bimolecular termination, which is second order with respect to radical concentration, is lower and does not lead to a broadening of the molecular weight distributions.

A variety of mononitroxides have been used to mediate the polymerizations of various monomers, including acrylates, dienes, and styrenic derivatives,<sup>20–23</sup> and a variety of polymer compositions and structures, including star and graft copolymers, have been investigated with SFRP methodologies.<sup>24–30</sup>

The use of a dinitroxide mediator for SFRP has only recently been reported by Long and Charleux.<sup>31–33</sup> Charleux and coworkers<sup>31</sup> used various dinitroxides, with both radical sites of similar reactivity, as mediators in the controlled radical polymerization of styrene and found that the typical features of a controlled radical polymerization were observed in the early stage of the polymerization, leading to the formation of two-arm macromolecules containing the dinitroxide at the core, however, at higher conversion, continuous decomposition reaction resulted in a break of the two-arm macromolecules into a dead chain having an unsaturation end group and a living chain capped by

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**Scheme 1** Stable free radical polymerization in the presence of TEMPO.

a modified dinitroxide. Long and coworkers<sup>33</sup> synthesized a novel dinitroxide mediator, 1,6-hexanedicarboxylic acid di(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl) ester, and found that the dinitroxide mediator proved to be a viable route for the facile two-step synthesis of triblock copolymers of styrene and *t*-butyl styrene, however, the dinitroxide mediation process resulted in a higher than expected level of nitroxide decomposition, which resulted in polymers possessing a terminal alkoxyamine and an adjacent hydroxylamine rather than a preferred internal bisalkoxyamine, and this decomposition resulted in the formation of diblock copolymer species during the triblock copolymer synthesis.

In this work, a new dinitroxide compound based on the 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy and 1,4-dichloromethyl-benzene was synthesized (Scheme 2) and successfully used in stable free radical polymerization of styrene. <sup>1</sup>H-NMR and gel permeation chromatography (GPC) were used to prove the existence of decomposition of the internal bisalkoxyamine linkage and the polymer structure. Polymerization temperature was lowered to 110°C to alleviate the chain end decomposition degree, trying to synthesize a two-arm polymer in one step.

## EXPERIMENTAL

### Materials

Styrene (from Shanghai Chemical Reagent Co, China.) was washed with an aqueous solution of sodium hydroxide (5 wt %) three times and then with deionized water until neutralization. After being dried with an-

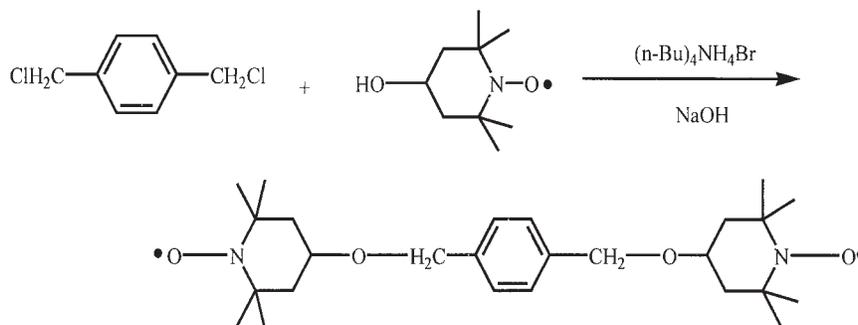
hydrous magnesium sulfate, it was distilled under reduced pressure and kept under 4°C in a refrigerator. 4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (HO-TEMPO) (98%, from Wuxi Fuan Chemical Plant, China) was recrystallized from *n*-hexane. 1,4-dichloromethyl-benzene (WuHan Organic Chemical Plant, China) was recrystallized from ethanol twice. All other reagents were used as received unless otherwise noted.

### Instrument

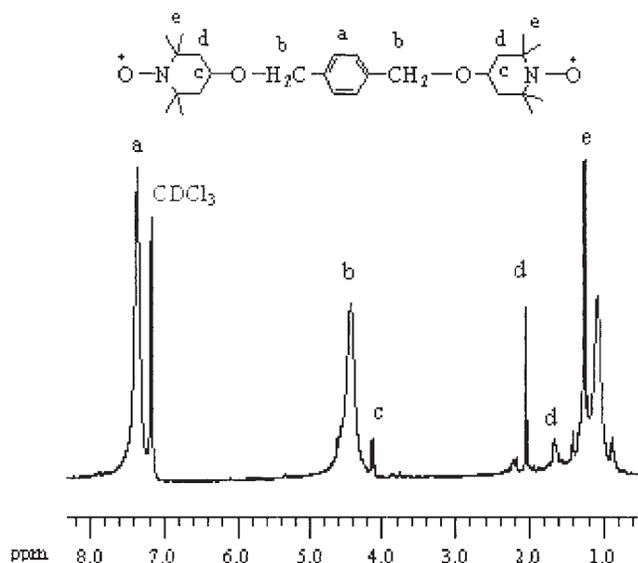
The molecular weights and molecular weight distribution of polymers were determined with a Waters 1515 GPC equipped with refractive index detector, using HR 1, HR 3, and HR 4 column with molecular weight range 100–500,000, calibrated with polystyrene standard samples, and tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL min<sup>-1</sup> operated at 30°C. <sup>1</sup>H-NMR spectra were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument using CDCl<sub>3</sub> as a solvent and tetramethylsilane (TMS) as the internal standard. Element analysis was determined by EA1110 (CARLO ERBA Co., Italy). Mass Spectrometry was measured by Micromass Time-Of-Flight, 70 eV, EI source.

### Synthesis and characterization of 1,4-di (1-oxy-2,2,6,6-tetramethyl-1-piperidin-4-yl)-xylene (DTPX)

The DTPX was prepared via a classical Williamson reaction using tetrabutyl ammonium bromide as the phase transfer catalyst. Aqueous NaOH (50%, 30 mL) and tetrabutyl ammonium bromide (0.8 g) were added to a 50 mL round-bottom flask equipped with a magnetic stirring bar. The reaction mixture was then stirred to dissolve the tetrabutyl ammonium bromide. Benzene solution (33 mL) of 1,4-dichloromethyl benzene (3.15 g, 0.018 mol) was then added. Subsequently, a solution of HO-TEMPO (8.6 g, 0.05 mol) dissolved in benzene (30 mL) was added drop wise to the flask in 2 h. After the reaction mixture was stirred



**Scheme 2** Synthesis route of 1,4-di(1-oxy-2,2,6,6-tetramethyl-1-piperidin-4-yl)-xylene (DTPX).



**Figure 1**  $^1\text{H-NMR}$  spectrum of the dinitroxide mediating agent in  $\text{CDCl}_3$ .

at room temperature for 24 h, the resulting suspension was filtered and the filtrate was washed with water until neutral, then the benzene solution was dried by the magnesium sulfate overnight, the product was recrystallized twice from ethyl acetate, the orange-red powder DTPX (5.14 g, 0.012 mol) was obtained in a 64% yield.

$^1\text{H-NMR}$  analysis confirmed the dinitroxide structure, showing the characteristic resonances protons of the benzene 7.2 ppm (Fig. 1). Also, the benzylic proton of the benzyl chloride bonded to the piperidinyloxy group was observed at 4.4 ppm. EA Calcd: C, 69.95; H, 9.42; N, 6.28. Found: C, 69.62; H, 9.21; N, 6.03. Furthermore, the  $m/z$  value 446.31 amu, determined experimentally with mass spectrometry was consistent with the theoretical  $m/z$  value of 446.2 amu.

### Dinitroxide-mediated polymerization of styrene

A typical polymerization procedure was as follows: A solution of styrene, BPO, and DTPX (prescribed molar ratio) was added to a dry ampule, the content was purged with argon for approximately 10 min to eliminate the oxygen, then the ampule was flame-sealed, and placed in an oil bath held by a thermostat at the desired temperature to polymerize. After the desired polymerization time, the ampule was cooled with ice water to stop the polymerization. Afterwards, it was opened and the contents were dissolved in THF and precipitated into a large amount of methanol. The polymer obtained by filtrate was dried under vacuum until constant weight at room temperature. The monomer conversion was determined gravimetrically.

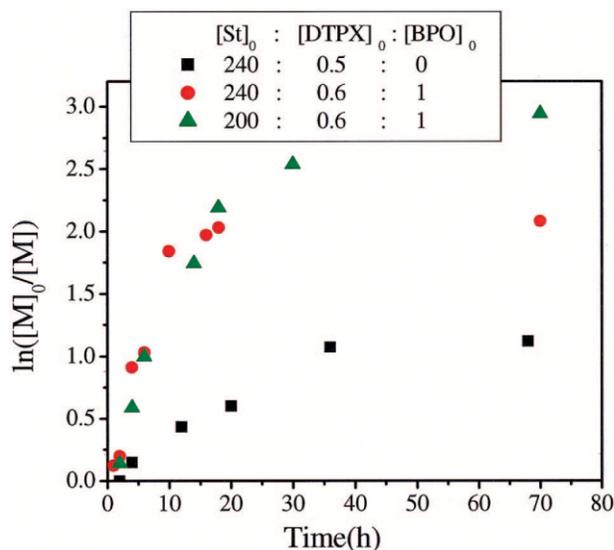
### Degradation of polymer in the presence of ascorbic acid

A 5 mL ampule was charged with polymer (0.1 g), ascorbic acid (0.05 g) and chlorobenzene (2 mL), then it was cycled between vacuum and argon three times to remove the oxygen, sealed and placed in an oil bath held by a thermostat at  $120^\circ\text{C}$  for 6 h. Subsequently, the ampule was quenched with ice water, broken and the contents were precipitated into a large amount of methanol (about 250 mL). The obtained product was dried under vacuum until constant weight at room temperature.

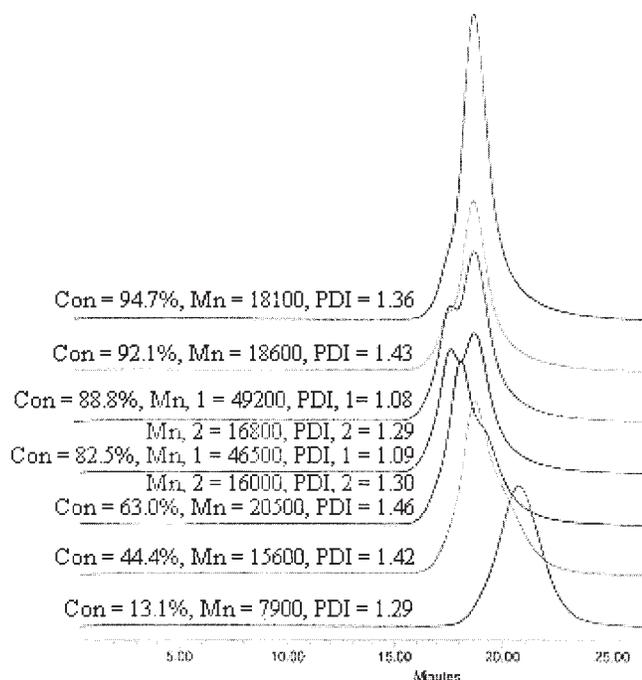
## RESULTS AND DISCUSSION

### Bulk polymerization of styrene mediated by DTPX at $125^\circ\text{C}$

The bulk polymerizations of styrene at  $125^\circ\text{C}$  in the presence of the dinitroxide mediator were conducted under conditions similar to those of conventional TEMPO-mediated SFRP. The effect of molar ratios of  $[\text{St}]_0 : [\text{DTPX}]_0 : [\text{BPO}]_0$  on polymerization were examined. From Figure 2, it can be found that the kinetics presented the approximately first-order plots in the earlier stage of the polymerization, and the polymerization rate increased with the increasing of the concentration of BPO, the case without BPO showed an apparent induction period for about 2 h. However, at higher conversion (about larger than 60%) the polymerization rate decreased sharply, which may be attributed to the accumulation of nitroxide because of the inevitable termination of the growing chains and



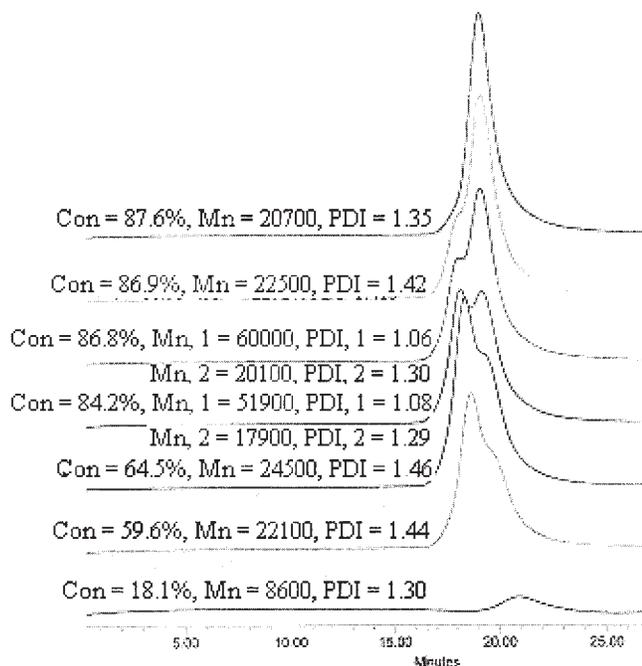
**Figure 2** Kinetic plots of  $\ln([M]_0/[M])$  versus time for bulk polymerization of styrene at various ratios of  $[\text{St}]_0$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



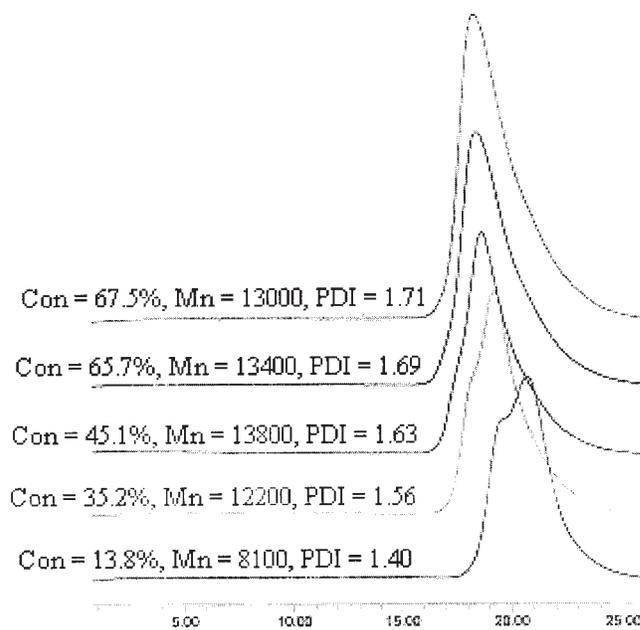
**Figure 3** GPC traces at different conversion for bulk polymerization of styrene. ( $[St]_0 : [DTPX]_0 : [BPO]_0 = 200 : 0.6 : 1$ ,  $125^\circ\text{C}$ ).

higher level of nitroxide decomposition with the increasing of the conversion.<sup>34</sup>

From Figure 3, 4, and 5, it can be found that while the overall peak shifted with conversion toward the lower elution time (larger molar masses) a bimodal distribution was observed. However, the proportions of the both



**Figure 4** GPC traces at different conversion for bulk polymerization of styrene. ( $[St]_0 : [DTPX]_0 : [BPO]_0 = 240 : 0.6 : 1$ ,  $125^\circ\text{C}$ ).



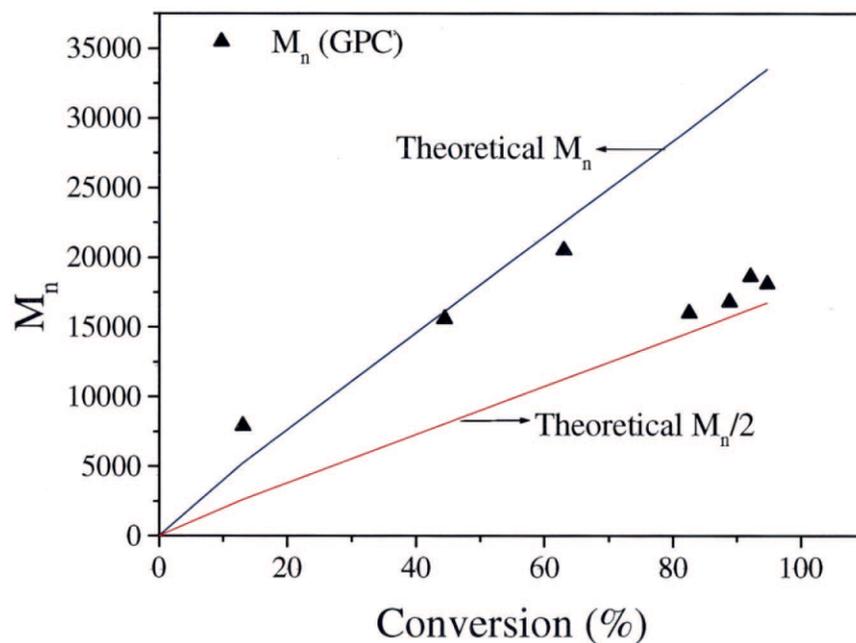
**Figure 5** GPC traces at different conversion for bulk polymerization of styrene. ( $[St]_0 : [DTPX]_0 = 240 : 0.5$ ,  $125^\circ\text{C}$ ).

peaks changed dramatically with the progress of monomer conversion: the relative area of the low molar mass peak increased whereas that of the high molar mass peak decreased. All the above phenomenon was not the same as the case of the mononitroxide-mediated polymerization, which could be attributed to the higher level of decomposition of the internal bisalkoxyamine linkage in polymer chain, and resulted in polymers possessing a terminal alkoxyamine and an adjacent hydroxylamine.<sup>31,33</sup> The decomposition became more obvious at higher conversion through monitoring the change of molecular weights with the conversion by GPC.

#### Confirmation of the polymer structure mediated by DTPX at $125^\circ\text{C}$

Comparing the theoretical  $M_n$  with  $M_n$  measured by GPC

As discussed above, the  $M_n(\text{GPC})$  changed with the monomer conversion: from singlet to bimodal distribution, and the relative area of the two peaks changed with conversion, the  $M_n(\text{GPC})$  versus conversion displayed in the Figure 6 was not linear. Initially, the  $M_n(\text{GPC})$  followed the theoretical line corresponding to polymers with two growing chains attached to a central bisalkoxyamine, then the  $M_n(\text{GPC})$  values deviated from linearity to reach another theoretical line referred to as  $M_n/2$  and corresponding to branches that have disconnected from the core, and the polymerization at other  $[St]_0 : [DTPX]_0 : [BPO]_0$  ratios had the similar results as showed in Figure 6. At lower conversion, the chain end decomposition was slight, the

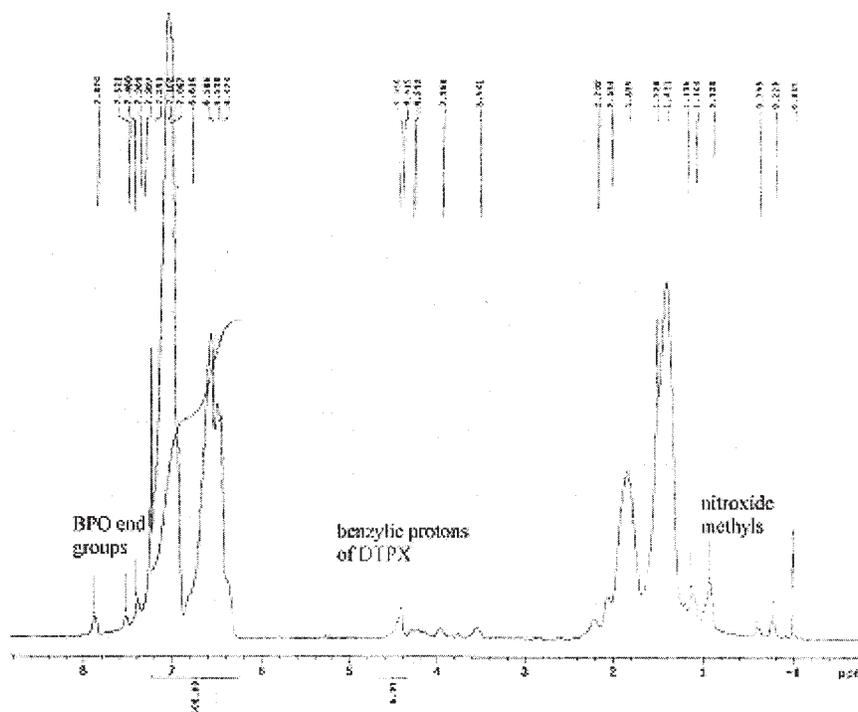


**Figure 6**  $M_n$  versus monomer conversion for bulk polymerization of styrene. ( $[St]_0 : [DTPX]_0 : [BPO]_0 = 200 : 0.6 : 1$ ,  $125^\circ\text{C}$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

obtained polymer possessed bisalkoxyamine linkage. At higher conversion, the polymer possessed a single terminal nitroxide as the result of obvious chain end decomposition, exhibiting only one-half molecular weight of the theoretical  $M_n$ , these results agreed well with the earlier efforts by Vairon et al.<sup>31</sup>

#### $^1\text{H-NMR}$ of the polymers with low molecular weights

$^1\text{H-NMR}$  of the polymer with relatively low molecular weights (singlet distribution in GPC trace,  $M_n(\text{GPC}) = 7900$ ,  $\text{PDI} = 1.29$ ) was measured to further investi-



**Figure 7**  $^1\text{H-NMR}$  of the low-molecular weight polystyrene with a bisalkoxyamine linkage.

TABLE I  
Polystyrene Molecular Weights Based on GPC and  $^1\text{H}$ -NMR Spectroscopy

$M_n$ (GPC) (g/mol)	$M_w/M_n$	$M_n$ (NMR) (g/mol)
7900	1.29	6600
8600	1.30	7500

gate polymer structure obtained at the low conversion. The  $^1\text{H}$ -NMR spectrum (Fig. 7) showed the four piperidinyloxy methyl resonances centered at 1.10, 0.92, 0.39, and 0.22 ppm (vertical arrows), characteristic of TEMPO bonded to polystyrene. 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.<sup>20</sup> Benzylic protons (4.41 ppm) of the DTPX at the polymer core and BPO end group can also be identified.

The molecular weights of the polystyrene samples based on integration of the benzylic protons of the DTPX peaks were shown in Table I and agreed well with the molecular weights determined with GPC, indicating that the polymer at low conversion was a two-arm structure.

#### GPC traces for the bimodal distribution polymer degradation by ascorbic

As regards the polymer with obvious bimodal GPC trace, the molar mass values at the maximum of the two peaks were about in a ratio of 1.72, which indicated that the polymer obtained was a mixture of the polymer possessing bisalkoxylamine linkage and the polymer possessing a single terminal nitroxide, and the ratio of molecular weight of the former and latter approximately equal to 2. To further investigate the structure, the polymer was degraded in the presence of ascorbic acid at 120°C for 6 h. The GPC trace of the degraded polymer considerably changed to display a singlet peak (see Fig. 8), which closed to the peak of lower molar mass one in the distribution before degradation. Indeed, when the polymer was heated to 120°C, the alkoxyamine C—O bonds in the polymer chains were broken resulting in a break of the two-arm macromolecules in the middle and the nitroxides were reduced into hydroxylamine by ascorbic.

All the above results demonstrated that the bisalkoxyamine bonds were not perfectly stable during the course of the polymerization and the level of this side reaction, resulted in an irreversible arm separation, was much larger than in the mononitroxide-mediated polymerization of styrene. At low conversion, the obtained polymer possessed bisalkoxylamine linkage (a two-arm structure), and the bimodal distribution could be assigned to a mixture of two-arm and

one-arm macromolecules, which was showed in Scheme 3.

#### Bulk polymerization of styrene mediated by DTPX at 110°C

Because of the structure of the dinitroxide mediator and the nature of the mediation process, chain end decomposition occurred more extensively than in mononitroxide polymerization system.<sup>33</sup> The function of temperature was important for effective polymerization control. From Figure 9, it can be found that the polymerization rate was slower at 110°C than at 125°C, an inducing period about 4 h appeared before polymerization. However, a better control of the polymerization was observed at 110°C, the yielded poly-

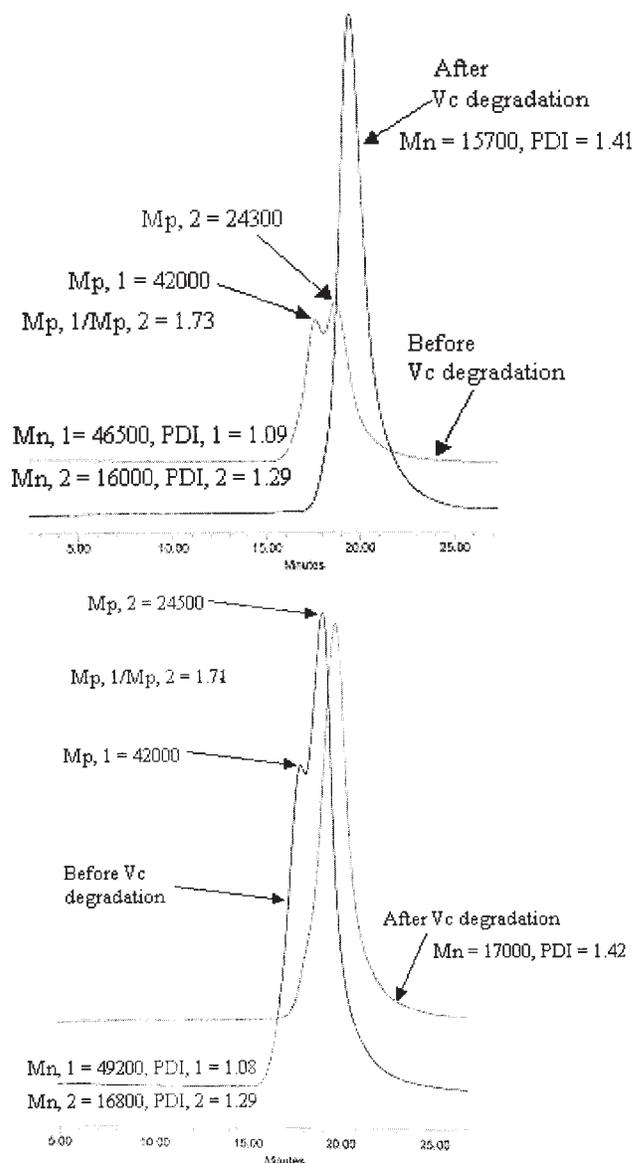
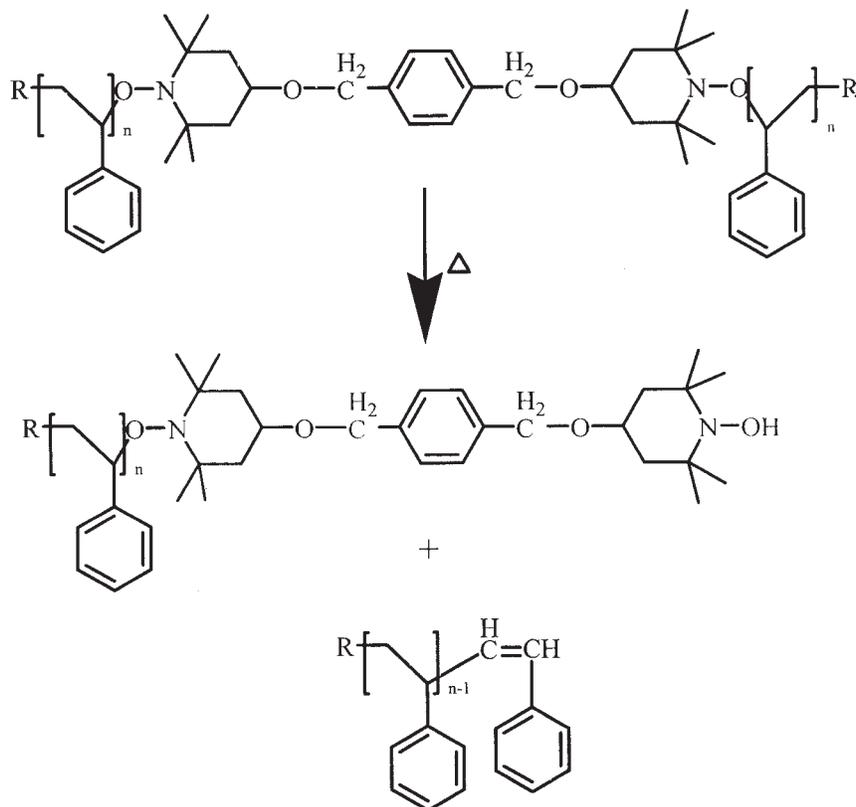


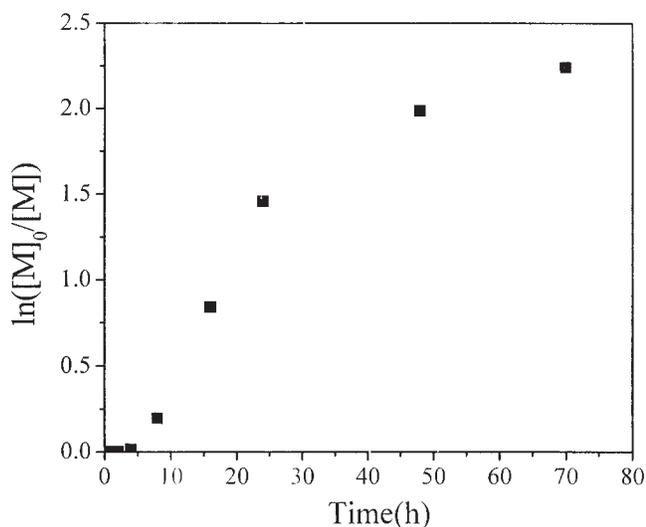
Figure 8 GPC traces for the polymer before and after the degradation by ascorbic.



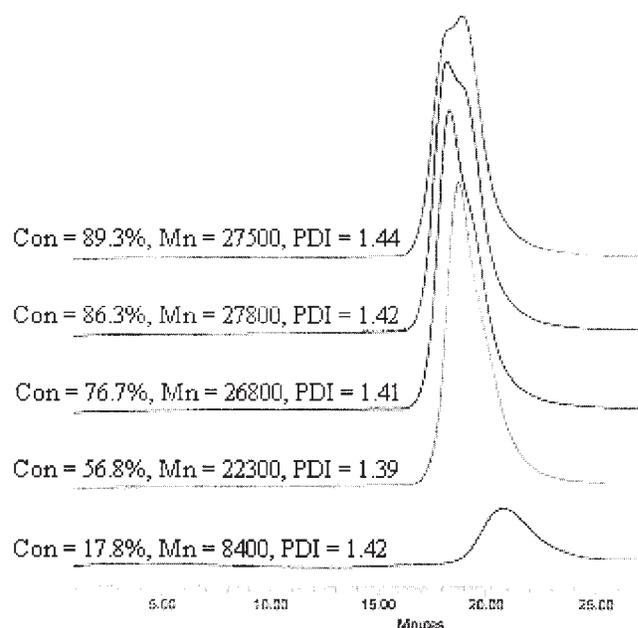
**Scheme 3** Chain end decomposition of the internal bisalkoxyamine linkage in the chain of polymer.

mers had the narrow molecular weight distributions up to 76.7% conversion (see Fig. 10 and 11). When conversion was above 76.7%, the results of the bimodal distribution in GPC, larger PDI values, and the obvious deviation of  $M_n(\text{GPC})$  from theoretical  $M_n$  indicated that the chain end decomposition became

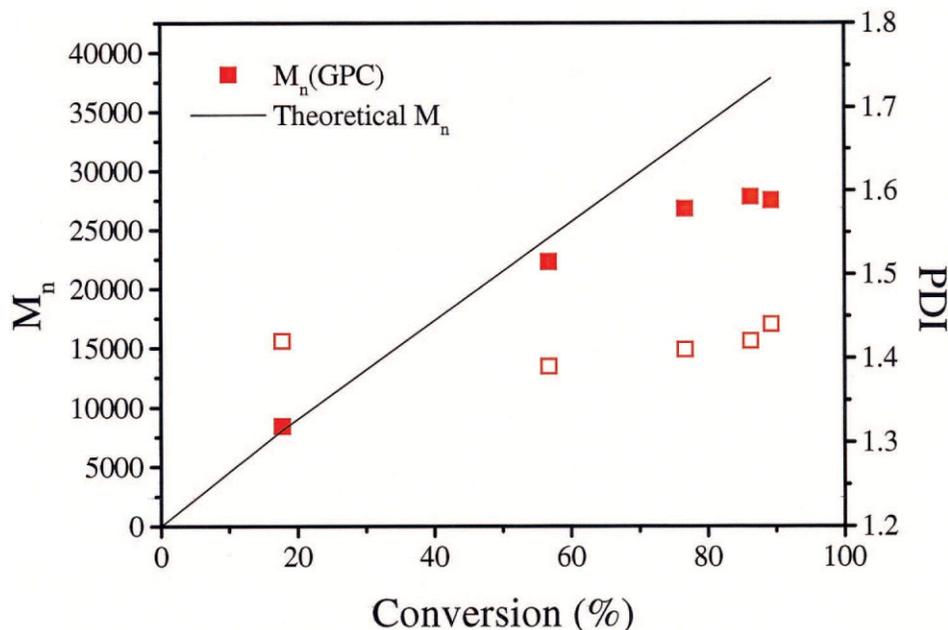
extensive. In conclusion, at lower temperature, the bisalkoxyamine linkage was more stable because of a lower rate constant value of the chain end decompo-



**Figure 9** Kinetic plots of  $\ln([M]_0/[M])$  versus time for bulk polymerization of styrene.  $[\text{St}]_0 : [\text{DTPX}]_0 : [\text{BPO}]_0 = 240 : 0.6 : 1$ ,  $110^\circ\text{C}$ .



**Figure 10** GPC traces with the conversion for bulk polymerization of styrene.  $[\text{St}]_0 : [\text{DTPX}]_0 : [\text{BPO}]_0 = 240 : 0.6 : 1$ ,  $110^\circ\text{C}$ .



**Figure 11** Evolution of  $M_n$  and polydispersity with conversion for bulk polymerization of styrene.  $[St]_0 : [DTPX]_0 : [BPO]_0 = 240 : 0.6 : 1$ ,  $110^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

sition<sup>31</sup> and a two-arm structure polymer can be gained, especially at low conversion.

## CONCLUSIONS

A new dinitroxide mediating agent for SFRP methodologies was synthesized and successfully used in the polymerization of styrene, the typical features of a controlled polymerization were observed in the early stage of the polymerization, leading to the formation of two arm macromolecules containing the dinitroxide at the core. However, a deviation occurred owing to continuous irreversible termination leading to unsaturated polymer and hydroxylamine at higher conversion. This behavior was particularly observed in the GPC traces, with a bimodal distribution assigned to a mixture of two-arm and one-arm polymers. At lower temperature, the dinitroxide decomposition was slight up to monomer conversions of 76.7%, as expected, the polymerization of styrene at  $110^\circ\text{C}$  can yield well-defined polymer with the narrower molecular weight distributions and two-arm structure.

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