Synthesis and Characterization of a Novel Macroinitiator of Poly(ethylene oxide) with a 4-Hydroxy-2,2,6,6-tetramethylpiperidinyloxy End Group: Initiation of the Polymerization of Styrene by a "Living" Radical Mechanism

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ABSTRACT: A novel macroinitiator of poly(ethylene oxide) (PEO) with a 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (HTEMPO) end group (PEO_{HTM}) was prepared by the photochemical reaction of a tertiary amine end group of PEO with benzophenone (BP) in the presence of HTEMPO. Potassium 2-dimethylaminoethoxide was used to initiate the ring-opening polymerization of ethylene oxide first, then the dimethylamine end group of PEO constituted the charge-transfer complex with BP under UV irradiation, and finally ternary amine methylene and diphenyl methanol radicals were formed. The former reacted with HTEMPO to form the desired product. PEO_{HTM} can initiate the polymerization of styrene by a "living" radical mechanism. The molecular weight of the PS block increased with the polymerization time, and the molecular weight distribution (M_w/M_n) was less than 1.5, even though the molecular weight of the former was as high as 2×10^5. The DSC measurement of the copolymer confirmed that the T_g of the PS block was 106 °C, which was 6 to 7 °C higher than that of the PS prepared by the common radical method.

Introduction

Recently, much interest has been focused on the possibility of making polymer materials with controlled molecular weights, narrow polydispersities, well-defined chain lengths, and unusual architectures. The anionic, cationic, and group-transfer polymerizations traditionally have been used for these purposes. It is well-known, however, that these polymerization methods could be successfully practiced only in very strict conditions, and only a few monomers could be utilized for them. In comparison, the free-radical process is noted for its easy and economical performance and the fact that it can be carried out even in the presence of water, as in an emulsion or suspension polymerization.

In 1993, Georges et al.[1] first reported that a polystyrene with a narrow molecular weight distribution could be produced by a stable free-radical polymerization process. The mechanism involves reversible capping of the growing chain end by a stable free counterradical such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and its derivatives. In the beginning of this process, the relative weak bond formed by the coupling of the primary radical and TEMPO breaks at temperatures above 120 °C, and the monomer adds to the primary radical soon after; the propagating radical is reversibly terminated with the liberated nitroxide radical. These reactions can repeat until the monomer is consumed. During this process, a very small instantaneous concentration of propagating free radicals produced by reinitiation is moderated by TEMPO and leads to the stepwise growth of the chains mentioned above. Consequently, polymers with narrow polydispersities are obtained.

Since then, this method has been developed and applied to the preparation of block copolymers and random copolymers with narrow polydispersities, such as PS-*b*-PAN (PAN, polyacrylonitrile), PS-*b*-PMA (PMA, polymethyl acrylate), PS-*b*-PVCz [PVCz, poly(vinylcarbazole)],[2] block copolymer of PS-*b*-poly(styrene-*co*-butyl methacrylate),[3] and random copolymer of styrene (St) and acrylate.[4,5] All of these block copolymers, however, were prepared by a TEMPO-capped PS macroinitiator or in the presence of a monomer of St.

In our previous work, we found that the copolymerization of a PEO macromonomer with a methacryloyl end group with St is a controlled "living" radical process and that the molecular weight distribution of the copolymer is narrower than that of the copolymer formed by the copolymerization of St and MMA in the presence of TEMPO.[6]

The aim of this study was to prepare a new kind of macroinitiator of TEMPO-capped PEO that has a great effect on the living polymerization of St.

Experimental Section

Materials. Ethylene oxide (EO) and St were dried by calcium hydride and then distilled under N_2 before use. 2-Dimethylaminoethanol (Shanghai No. 3 Reagent Factory) was dried with anhydrous K_2CO_3 and then fractionally distilled, after which a fraction was collected at 41 °C and 7 mmHg. Benzophenone (BP) (Shanghai Chemical Reagent Factory) was purified by recrystallization from ethanol (mp 48−49 °C). 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyly (HTEMPO) was prepared by the oxidation of 4-hydroxy-2,2,6,6-tetramethylpiperidine (Beijing Chaoyang Huashan Auxiliary Factory) with hydrogen peroxide using sodium tungstate as a catalyst,[7] (mp 71−72 °C). All other solvents were purified by common methods.

Preparation of Potassium 2-Dimethylaminoethoxide. 2-Dimethylaminoethanol (0.2 mL, 2 mmol) was added to a 150 mL ampule containing 50 mL of dried THF, and then 0.1 g (2.56 mmol) of potassium with a fresh surface was introduced. After three cycles of freeze−pump−thaw, the sealed ampule was magnetically stirred for 24 h at 60 °C. The solution, a milk-white at the beginning of the reaction, turned to a light yellow

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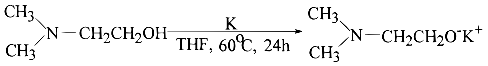
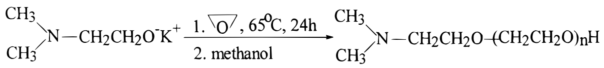
at the end. It was then cooled to room temperature and transferred to another ampule through a filter cloth in a vacuum system to remove unreacted potassium.



Anion Ring-Opening Polymerization of EO. To a 100 mL sealed ampule, which was degassed, 25 mL of potassium 2-dimethylaminoethoxide solution and 5 mL of EO were added by a syringe. The reaction was conducted at 65 °C for 24 h and then terminated by 1 mL of methanol. The product (PEO with a dimethylamine end group) (PEO_D) was precipitated with ether and purified twice by a dissolution/precipitation procedure with benzene/ether. IR (cm^{-1}): 1110 (C−O−C). UV (nm): 218 (amino group n → σ*). ^{1}H NMR (ppm): δ 3.64 ($-CH_2CH_2O-$).



(PEO_D)

Preparation of a Macroinitiator of PEO with a HTEMPO End Group (PEO_{HTM}). Into a 100 mL ampule containing 40 mL of benzene and 0.45 g (3.0×10^{-3} mol/L) of PEO_D were added 0.024 g (3.3×10^{-3} mol/L) of BP and 0.041 g (6.0×10^{-3} mol/L) of HTEMPO, and the ampule was linked to the vacuum system for degassing. After three cycles of freeze−pump−thaw at 77 K, the ampule was sealed off and irradiated by a 125 W high-pressure mercury lamp (Shanghai Ya Ming Lamp Factory, model DDZ-125) for 20 h at a constant 25 °C. Cupric sulfate aqueous solution was used as the photofilter to obtain 365 nm monochromatic light. The solution, orange-red at the beginning, turned to a light yellow at the end of the reaction. The solution was concentrated to about $^1/_3$ of its original volume and then precipitated by ether. The PEO_{HTM} was purified twice by a dissolution/precipitation procedure with benzene/ether.

Polymerization of St in the Presence of PEO_{HTM}. A typical polymerization process is described as followed. Styrene (1.5 mL, 13 mmol) and PEO_{HTM} (0.6 g, containing 0.14 mmol of the HTEMPO end group) were placed in an ampule. After two cycles of freeze−pump−thaw at 77 °C, the ampule was sealed off and placed into an oil bath at 125 °C. To control the reaction accurately, the system was frozen with liquid nitrogen after the end of the polymerization, then dissolved in benzene, and finally precipitated in petroleum ether. The copolymer was purified by successive extractions with cold water and cyclohexane to remove the unreacted PEO and possible PS homopolymer. However, no trace of PS was found. IR (cm^{-1}): 1111($-CH_2CH_2O-$) for the PEO block, 1601, 1451, 1493, 754, and 699 (benzene ring), and 3026 (benzene ring =C−H) for the PS block. ^{1}H NMR (ppm): δ 1.44 (CH_2-), 1.90 (−CH− connected with benzene ring), 6.40−7.20 (benzene ring) for PS and 3.64 ($-CH_2CH_2O-$) for PEO block.

The block copolymer sample of PEO-*b*-PS in which the PS block was made by a common radical mechanism was prepared by the combination of anionic and charge-transfer polymerization (M_n of the PEO block = 24 800 and of the PS block = 49 700; M_w/M_n = 1.65).[8]

Measurements. IR spectra were obtained on a Magna-550 FTIR spectrometer. NMR spectra were recorded on a Bruker MSL-300 spectrometer with TMS as an internal standard and $CDCl_3$ as the solvent. DSC studies were conducted with a Perkin−Elmer TAC7/DX in a nitrogen atmosphere at a heating rate of 10 °C/min. UV spectra were taken on a 756 MC UV−Vis spectrophotometer (Shanghai Third Analytical Instrument Factory). The number-average molecular weight of the copolymers was determined with a Shimadzu LC-3A gel permeation chromatograph (GPC) with a computer: detector = UV, column length = 1.2 m, filler = cross-linking polystyrene gel (1250 mesh), injection volume = 1 mL (concentration = 0.1 g/mL), solvent and eluent = chloroform, flow rate = 1.0 mL/min, pump pressure = 40 kg/cm^2 (3.99×10^6 Pa). Monodisperse PSs were used as standards for calibration.

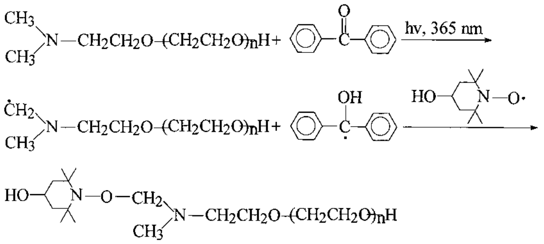
Table 1. Data of PEO_D[a]

prepolymer	M_n ($\times 10^{-3}$)	M_w/M_n	conversion of EO (%)
PEO_{D-1}	3.7	1.24	90
PEO_{D-2}	12.0	1.28	95

[a] Polymerization conditions for (i) PEO_{D-1} = 5 mL EO, 25 mL THF initiator solution, 65 °C, and 24 h and (ii) PEO_{D-2} = 15 mL EO, 25 mL THF initiator solution, 65 °C, and 24 h.

Results and Discussion

Characterization of PEO_{HTM}. PEO_{HTM} was prepared by photochemical reaction of PEO_D with BP in the presence of HTEMPO as described by the following equations:



(PEO_{HTM})

Two kinds of PEO_D with different molecular weight were used as shown in Table 1.

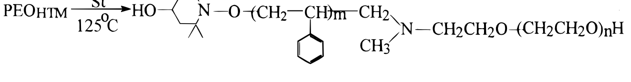
As is well-known, it is not easy to characterize an end group for a polymer, especially when the polymer has a high molecular weight. In the IR spectrum of HTEMPO-capped PEO, we cannot clearly find the peaks corresponding to the HTEMPO end group. However, the repeating scanning NMR technique increased the intensity of the weak signals and successfully detected the HTEMPO-capping reaction with PEO_D. Figure 1 gives the ^{1}H NMR spectra of PEO_{D1} (M_n = 3700) (A) before and (B) after capping with HTEMPO. The new proton signals appearing in part B, such as those at 1.2 ($-CH_3$), 1.5 and 1.8 ($-CH_2$-), and 4.9(−CH-), proved the existence of the HTEMPO end group of PEO.

The capping efficiency (*f*) of HTEMPO could also be calculated from NMR data by the following equation using the peak area ratio of the methyl proton of HTEMPO at 1.2 ppm versus the methylene proton of the PEO chain at 3.6 ppm:

$$f = \frac{\text{area of methyl protons of HTEMPO at 1.2 ppm}/12}{\text{area of methylene protons of oxylene at 3.6 ppm}/N}$$

where N (number of methylene protons of each PEO chain) = M_n of PEO × 4/44; the values are 89% for PEO_{D1} and 85% for PEO_{D2}.

St Polymerization in the Presence of PEO_{HTM} and Characterization of Product. The results of the polymerization of St using PEO_{HTM} macroinitiators with different molecular weights are presented in Table 2. The purified copolymers were characterized in detail by IR and ^{1}H NMR as described in the Experimental Section.



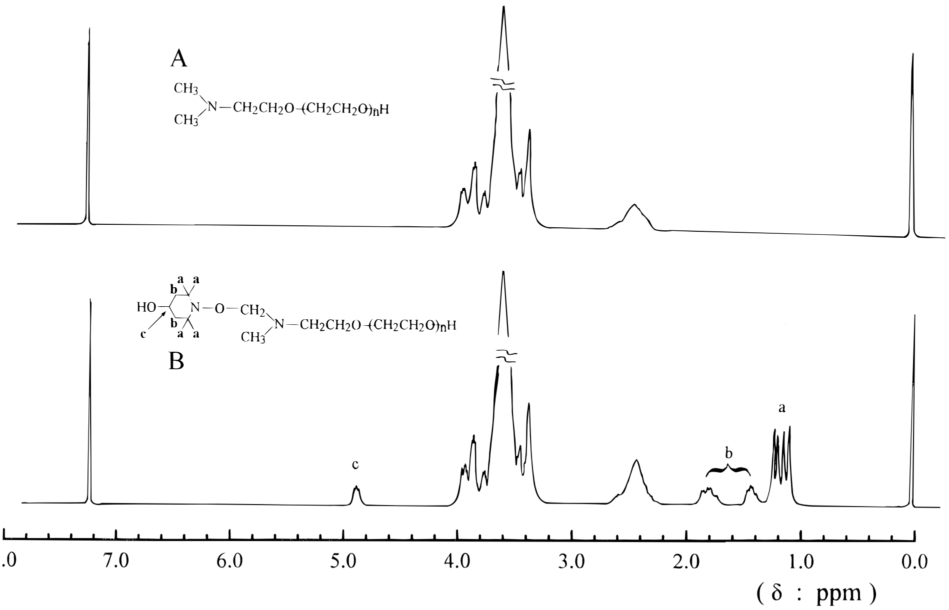


Figure 1. ^{1}H NMR spectra of PEO_D before (A) and after capping with HTEMPO (B)

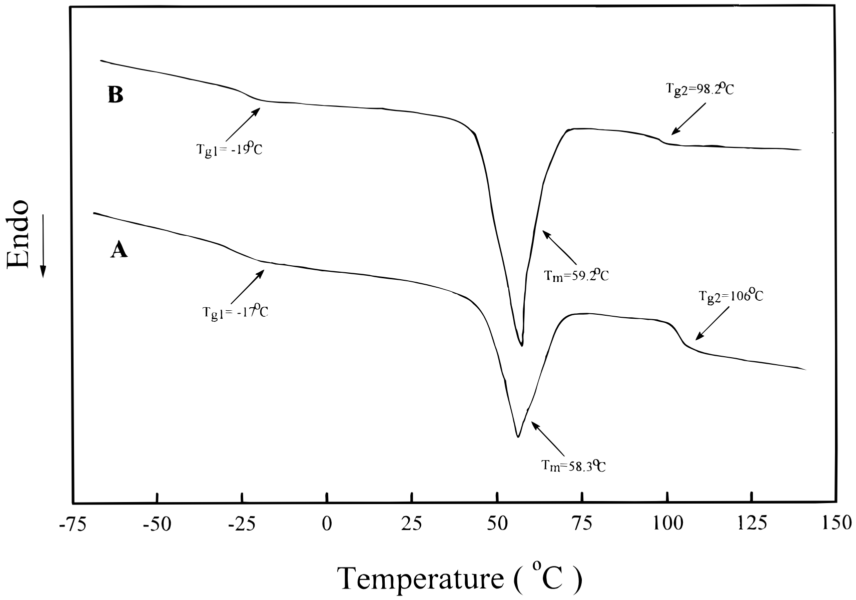


Figure 2. DSC measurement of block copolymers of PEO-*b*-PS [(A): PS block formed by HTEMPO technique; (B): PS block formed by common radical mechanism].

Table 2. Bulk Polymerization of St Initiated by PEO_{HTM} Macroinitiators[a]

no. of copolymer[b]	time (h)	M_n ($\times 10^{-4}$)	M_w/M_n	conversion of St (%)
1	12	0.8	1.33	9.0
2	24	2.1	1.40	35.4
3	36	4.0	1.45	65.7
4	6	2.0	1.35	7.6
5	12	5.7	1.41	35.6
6	24	10.6	1.45	73.3

[a] Polymerization conditions 0.6 g of macroinitiator, 1.5 mL of St, and 125 °C. [b] Samples 1−3 were prepared using PEO_{HTM} with a molecular weight of 3700 and 4−6 were prepared by PEO_{HTM} with a molecular weight of 12 000.

Table 2 illustrates that the molecular weight of the PS block and the conversion of the St monomers increased simultaneously with the polymerization time, no matter whether the molecular weight of PEO_{HTM} is high or low. It showed that PEO_{HTM} initiated the polymerization of St as a living radical process. We also found that under the same conditions PEO_{HTM} with a high molecular weight can exert a much greater influence on the bulk polymerization of St than can PEO_{HTM} with a low molecular weight because of the lower HTEMPO concentration for the former. The molecular weight of the block copolymer obtained with PEO_{HTM} ($M_n = 12\,000$) and the conversion of St are 5−7 and 2−4 times as much, respectively, as those obtained with PEO_{HTM} ($M_n = 3700$). However, the molecular weight distribution of the latter, as Table 2 indicated, is narrower than that of the former. It is well-known that the concentration of TEMPO and its derivatives plays a very important role in living St polymerization.[9,10] When the amount of macroinitiator is kept constant, the concentration of the HTEMPO end group of PEO_{HTM} with a higher molecular weight is lower than that of PEO_{HTM} with a lower molecular weight. Thus, St polymerization was restricted much more strictly in the

Table 3. Effect of Concentration of PEO_{HTM} Macroinitiators on the Bulk Polymerization of St at 125 °C[a]

concentration of PEO_{HTM} ($\times 10^{-2}$ mol/L)	time (h)	M_n ($\times 10^{-4}$)	M_w/M_n	conversion of St (%)
2.8	6	2.0	1.35	7.6
2.8	12	5.7	1.41	35.6
2.8	24	10.6	1.45	73.3
1.4	6	5.8	1.40	20.5
1.4	12	11.2	1.42	44.8
1.4	16	14.9	1.42	54.2
1.4	20	20.3	1.46	73.6
1.4	24	23.8	1.49	81.6

[a] Molecular weight of PEO_{HTM} = 12 000 and $M_w/M_n = 1.28$.

latter case. We will explain this phenomenon in detail later in the text.

In our experimental conditions, no PS homopolymer was found. This may attributed to the higher concentration of the PEO_{HTM} that inhibited the homopolymerization of St.[3] However, if the St concentration is raised, PS homopolymers were found, and the higher the concentration of St, the more the PS homopolymer there is.

Figure 2 shows the result of DSC measurement of block copolymers of PEO-*b*-PS prepared by (A) the TEMPO technique and (B) the common radical mechanism. Both of the PEO-*b*-PS samples were melted at 170 °C and then immediately quenched in liquid nitrogen to inhibit rapid crystallization of the PEO. The T_g's of the PEO block appeared at about −17 and −19 °C for samples A and B, respectively, which makes them about 25 °C and 23 °C higher than that of the PEO homopolymer (−42 °C) with the same molecular weight. At the same time, the crystal melting temperature of the PEO block in PEO-*b*-PS is shifted from 65 °C for the pure PEO homopolymer to (A) 58.3 and (B) 59.2 °C for the block copolymer. This difference may be caused by the decrease in the packing density of PEO chains due to the insertion of PS chain block, but the preparation mode of PS block did not exert an evident effect on the PEO thermal properties. It was found, however, that the T_g of the PS chain block of (A) prepared by PEO_{HTM} macroinitiator is about 106 °C, which is about 6 °C higher than that of ordinary PS (about 100 °C), and the T_g of the PS chain segment of B prepared by the common radical method is 98.2 °C, which is close to that of the ordinary PS. The higher T_g might be attributed to the restrictions of HTEMPO end group on the addition mode of the St monomer that leads to the decrease in free volume.[11]

Effect of the PEO_{HTM} Concentration on the Polymerization of St. Table 3 gives the data which describes the influence of the HTEMPO-capped PEO_{HTM} concentration on polymerization. In the common radical polymerization, the conversion of monomer decreases with the decreasing initiator concentration, whereas the molecular weight of product increases. However, in our experiment, the conversion of monomer and the molecular weight of product increased simultaneously with the decrease of the HTEMPO-capped PEO_{HTM} concentration.

As we mentioned before, the concentration of HTEMPO plays an important role in controlling the polymerization, and the following equilibrium could be used to describe it:[12]

$$P\cdot + HTEMPO\cdot \rightleftharpoons P{-}HTEMPO$$

where P· is the propagation macromolecule active species, HTEMPO· is the free radical, and P−HTEMPO represents the dormant compound. In the case of low concentration of PEO_{HTM}, the concentration of HTEMPO· is also low, so that the polymerization of St is not restricted much by HTEMPO·. Therefore, the molecular weight distribution of the PS block was broader, and for a constant St concentration, the polymerization rate, molecular weight, and conversion were higher. When a high PEO_{HTM} concentration was used, the concentration of HTEMPO· radicals was also higher, and the polymerization of St was efficiently controlled by HTEMPO·, which leads to decreases in the polymerization rate, molecular weight, and conversion of St and narrowing of the molecular weight distribution of the PS block (see Table 3).

It is worthwhile to point out that in stable free-radical-mediated polymerization, it is not easy to obtain a polymer with a high molecular weight because of the existence of side reactions such as chain transfer, chain termination and thermal decomposition of chain segments,[13] and the molecular weight of the polymer is commonly no more than 1×10^5. Furthermore, the higher the molecular weight, the broader the molecular weight distribution. However, in our system, either in the case of high or low concentrations of PEO_{HTM}, the molecular weight of which is high or low, the molecular weight distribution of the PS block is rather narrow and less than 1.5 even if the molecular weight of PS is up to 2×10^5 and the conversion of St is as high as 81.6%. The influence of the PEO chain on the St polymerization in the living fashion is remarkable. Further investigation is ongoing.

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References and Notes

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(2) Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T. *Macromolecules* **1996**, *29*, 3050.
(3) Butz, S.; Baethge, H.; Schmidt-Naake, G. *Macromol. Rapid Commun.* **1997**, *18*, 1049.
(4) Hawker, C. J.; Elce, E.; Dao, J.; Volksen, W.; Russell, T. P.; Barclay, G. G. *Macromolecules* **1996**, *29*, 2686.
(5) Schmidt-Naake, G.; Butz, S. *Macromol. Rapid Commun.* **1996**, *17*, 661.
(6) Wang, Y.; Huang, J. *Macromolecules* **1998**, *31*, 4057.
(7) Kurosaki, T.; Lee, K. W.; Okawara, M. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 3295
(8) Huang, J.; Huang, X.; Zhang, S. *Macromolecules* **1995**, *28*, 4421.
(9) MacLeod, P. J.; Veregin, R. P. N.; Odell, P. G.; Georges, M. K. *Macromolecules* **1997**, *30*, 2207.
(10) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 2746.
(11) Barclay, G. G.; Hawker, C. J.; Orelana, A.; Malenfant, P. R. L.; Sinta, R. F. *Macromolecules* **1998**, *31*, 1024.
(12) Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. *Macromolecules* **1996**, *29*, 6393.
(13) Tsujii, Y.; Fukuda, T.; Miyamoto, T. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1997**, *38* (1), 657.

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