Preparation and Kinetic Analysis of PS-*b*-PBA Block Copolymer by 4-oxo-TEMPO Capped Polystyrene Macroinitiators

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ABSTRACT: Polystyrene-block-poly(*n*-butyl acrylate) block copolymers were prepared from 4-oxo-2,2,6,6-tetramethylpiperidinooxy (4-oxo-TEMPO) capped polystyrene macroinitiators at a high temperature, 165°C. It was found that the number-average molecular weight of PBA chains in block copolymers could reach above 10,000 rapidly at early stage of polymerization with a narrow polydispersity index of 1.2–1.4, but after that, the polymerization seemed to be retarded. Furthermore, according to the kinetic analysis, the concentration of 4-oxo-TEMPO was increased mainly by the hydrogen transfer reaction of hydroxylamine (4-oxo-TEMPOH) to growing radicals during polymerization. This increase in 4-oxo-TEMPO concentration could retard the growth of polymer chains. The rate constant of the hydrogen transfer reaction of 4-oxo-TEMPOH to growing radicals, k_H, estimated by the kinetic model is about 9.33×10^4 M^{-1} s^{-1} at 165°C. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2833–2842, 2009

Key words: nitroxide-medicated polymerization; block copolymer; kinetic model

INTRODUCTION

In the past, living polymers were mainly prepared via ionic polymerization and group transfer polymerization. These methods need complicated experimental procedures and stringent purity requirements. Recently, synthesis of polymers with controlled molecular weight and narrow molecular weight distribution has attracted attention by controlled or living radical polymerization. In general, the controlled or living radical polymerization can be divided into three categories: nitroxide-mediated polymerization (NMP),[1–5] atom transfer radical polymerization,[1,6–8] and reversible addition-fragmentation chain transfer polymerization.[1,9–11] Compared with ionic living polymerization, controlled/living radical polymerization is easier to perform.

NMP has been widely investigated in many studies.[1–5] In 1993, Georges et al.[5] first used TEMPO as a stable free radical and BPO as an initiator to synthesize polystyrene. The reaction mixture was pre-heated to 95°C for 3.5 h to let BPO decompose completely and then the polymerization was carried out at 123°C for 69 h. The narrow molecular weight distribution of polystyrene could be obtained. However, using TEMPO as a stable free radical, attempt to obtain high molecular weight and narrow molecular weight distribution of polyacrylate homo or block copolymer was not facile in many studies.[3,4,12,13] It was believed that the capping rate of acrylate by TEMPO is faster in comparison with the styrene system. Therefore, a number of other nitroxides and alkoxyamines were developed to overcome this problem.[2,14,15] For example, it has shown that *n*-butyl acrylate could be polymerized in the presence of 4-oxo-2,2,6,6-tetramethylpiperidinooxy (4-oxo-TEMPO). The reaction temperature was higher, 145–155°C, but the molecular weight distribution was broader, of which the polydispersity index (PDI) was higher than about 1.5 normally.[16,17]

Gnanou and co-workers[18] reported the first successful nitroxide-mediated homo-polymerization of *n*-butyl acrylate (BA) by using *N*-tert-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide. In many studies, using this nitroxide mediator, polyacrylate homo or block copolymers could be successfully synthesized with narrow molecular weight distribution.[14,15,18] This is due to the fact that for the polymerization of acrylate mediated by *N*-tert-butyl-

N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide, the equilibrium constant K (k_{act}/k_{rec}) is much higher if compared withthe system mediated by TEMPO.[15]

In addition, the TEMPO-mediated polymerization of BA was successfully done by the addition of organic acid as an accelerating agent. Georges et al.[19] added ascorbic acid or its derivative continuously to the reaction mixture to control the concentration of excess free TEMPO. This process enabled successful homo-polymerization of BA at 135°C with M_n of almost 20,000 and PDI of 1.35. In our previous work, dodecylbenzenesulfonic acid was used as a rate enhancement additive to prepare poly (*n*-butyl acrylate). The preliminary kinetic model was proposed to explain the influence of dodecylbenzenesulfonic acid on the TEMPO-mediated polymerization of BA.[20]
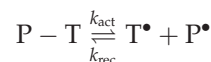
In this work, 4-oxo-TEMPO capped polystyrene macroinitiators were synthesized in the first step, and then the PS macroinitiators were used to prepare PS-*b*-PBA block copolymers at a higher temperature, 165°C. The structure and molecular weight of block copolymers were investigated. Furthermore, the kinetic models were proposed to explain the retardant mechanism of the polymerization of BA.

Reaction mechanism and kinetic analysis

Principal reactions

The principal reactions of NMP initiated by polymeric alkoxyamine (P − T) are listed in the following reactions (a)–(e). The polymerization is started by the dissociation of P − T and polymeric radicals (P•) and 4-oxo-TEMPO (T•) are produced [reaction (a)]. Then, monomer can react with P• [reaction (b)] to produce polymeric radicals with longer chains. When the concentrations of P• and T• reach a certain level, the recombination reaction between P• and T• becomes significant. This leads to an equilibrium between the activation rate of polymeric alkoxyamine (P − T) and the recombination rate between P• and T•, namely $k_{act}[P-T] = k_{rec}[P^\bullet][T^\bullet]$[21–24]; therefore, the living polymerization can be successfully controlled. Nevertheless, at the same time, some reactions that occurred during the polymerization can interfere with the reaction (a) and have important influences on the NMP. The formation of unsaturated polymer and hydroxylamine [reactions (c)],[25,26] hydrogen transfer reaction of hydroxylamine to propagating radicals [reactions (d)],[27,28] and the bimolecular termination of two polymeric radicals [reaction (e)][22] result in a decrease of P• and an increase of T• with time. These reactions probably lead to produce non-negligible dead polymers, broaden the molecular weight distribution, and even stop the progress of polymerization.

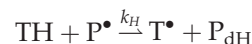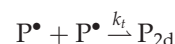(a) Activation and reversible recombination:

$$P - T \underset{k_{rec}}{\overset{k_{act}}{\rightleftharpoons}} T^\bullet + P^\bullet$$

(b) Propagation:

$$P^\bullet + M \overset{k_p}{\longrightarrow} P^\bullet$$

(c) Dormant chain decomposition:

$$P - T \overset{k_{dec}}{\longrightarrow} P_d = +TH$$

(d) Hydrogen transfer reaction of hydroxylamine to propagating radicals:

$$TH + P^\bullet \overset{k_H}{\longrightarrow} T^\bullet + P_{dH}$$

(e) Bimolecular termination:

$$P^\bullet + P^\bullet \overset{k_t}{\longrightarrow} P_{2d}$$

where P T is the polymeric alkoxyamine; T•, 4-oxo-TEMPO; P•, propagating radical; M, monomer; TH, hydroxylamine (4-oxo-TEMPOH); P_d, unsaturated dead polymer; P_{dH}, saturated dead polymer; and P_{2d}, dead polymer by bimolecular radical termination.

Before derivation of kinetic models, the system must meet the requirement of the following assumptions: (1) the quasi-equilibrium state between P•, T•, and P − T is reached throughout the polymerization; (2) the chains initiated by thermal initiation of monomer can be negligible compared with the chains initiated by P − T according to the observation of gel permeation chromatographic (GPC) curves; and (3) all the rate constants are independent of chain length.

Rate equations and kinetic analysis

Setting the above reactions into the rate equations of main species, we can write

$$\frac{d[P - T]}{dt} = k_{rec}[T]^\bullet[P^\bullet] - k_{act}[P - T] - k_{dec}[P - T] \quad (1)$$

$$\frac{d[P^\bullet]}{dt} = -k_{rec}[T]^\bullet[P^\bullet] + k_{act}[P - T] - 2k_t[P^\bullet]^2$$
$$- k_H[P^\bullet][TH] \quad (2)$$

$$\frac{d[T^\bullet]}{dt} = -k_{rec}[T]^\bullet[P^\bullet] + k_{act}[P - T] + k_H[TH][P^\bullet] \quad (3)$$

$$\frac{d[M]}{dt} = -k_p[M][P^\bullet] \tag{4}$$

$$\frac{d[TH]}{dt} = k_{\text{dec}}[P-T] - k_H[P^\bullet][TH] \tag{5}$$

The quasi-equilibrium state is assumed for reaction (a), $k_{\text{rec}}[T^\bullet][P^\bullet]$ is equal to $k_{\text{act}}[P-T]$, so $\frac{d[P-T]}{dt}$ in eq.(1) can be simplified as the following equation:

$$\frac{d[P-T]}{dt} = -k_{\text{dec}}[P-T]$$

and $[P-T] = [P-T]_0$ at $t = 0$, then $[P-T]$ can be solved analytically as:

$$[P-T] = [P-T]_0 e^{-k_{\text{dec}}t} \tag{6}$$

On basis of stoichiometry, the concentrations of compounds containing 4-oxo-TEMPO moiety are related by

$$[P-T] + [TH] + [T^\bullet] = [P-T]_0 \tag{7}$$

So the concentration of TH can be estimated by

$$[TH] = [P-T]_0 - [P-T] - [T^\bullet] \tag{8}$$

During polymerization, $[T^\bullet]$ is believed to be much smaller than $[P-T]$,[25,29,30] hence $[T^\bullet]$ can be negligible compared with $[P-T]$, and $[TH]$ can be solved analytically as:

$$[TH] = [P-T]_0(1 - e^{-k_{\text{dec}}t}) \tag{9}$$

Therefore, $[T^\bullet]$ and $[P^\bullet]$ can be approximately solved as the function of time by the difference of eqs. (3) and (2), and the following equation can be obtained:

$$\frac{d[T^\bullet]}{dt} - \frac{d[P^\bullet]}{dt} = 2k_H[TH][P^\bullet] + 2k_t[P^\bullet]^2 \tag{10}$$

Because $[T^\bullet]$ is found to be much larger than $[P^\bullet]$ in many studies,[22,24] so we conclude that $\frac{d[T^\bullet]}{dt}$ is much larger than $\frac{d[P^\bullet]}{dt}$, and the above equation can be reduced into:

$$\frac{d[T^\bullet]}{dt} = 2k_t[P^\bullet]^2 + 2k_H[TH][P^\bullet] \tag{11}$$

From eq. (11) we can see that $[T^\bullet]$ will steadily increase with time by two reactions: (I) bimolecular termination of two polymeric radicals [reaction (e)] and (II) hydrogen transfer reaction of hydroxylamine to propagating radicals [reaction (d)]. To understand which reaction mechanism may dominate the polymerization of BA, the integration of eq. (11) can be separated into two cases, and the effect of these two reactions will be discussed later.

Case I: Influence of bimolecular termination of two polymeric radicals on the polymerization

If the termination reaction [reaction (e)] is much more important than the hydrogen abstraction reaction of propagating radicals with hydroxylamine [reaction (d)], namely $2k_t[P^\bullet]^2 \gg 2k_H[TH][P^\bullet]$, eq. (11) can be simplified as follows:

$$\frac{d[T^\bullet]}{dt} = 2k_t[P^\bullet]^2 \tag{12}$$

With the relations of $[P^\bullet] = K\frac{[P-T]}{[T^\bullet]}$ and $[P-T] = [P-T]_0 e^{-k_{\text{dec}}t}$, $[T^\bullet]$ can be solved readily and found increasing with reaction time.

$$[T^\bullet] = \sqrt[3]{\left(\frac{3k_t K^2[P-T]_0^2}{k_{\text{dec}}}\right)(1 - e^{-2k_{\text{dec}}t}) + [T^\bullet]_0^3} \tag{13}$$

where $K = \frac{k_{\text{act}}}{k_{\text{rec}}}$, and $[T^\bullet] = [T^\bullet]_0$ at $t = 0$.

Then, $[P^\bullet]$ can be also obtained

$$[P^\bullet] = \frac{K[P-T]_0 e^{-k_{\text{dec}}t}}{\sqrt[3]{\left(\frac{3k_t K^2[P-T]_0^2}{k_{\text{dec}}}\right)(1 - e^{-2k_{\text{dec}}t}) + [T^\bullet]_0^3}} \tag{14}$$

Integration of eq. (4): $\frac{d[M]}{dt} = -k_p[P^\bullet][M]$, and $[M] = [M]_0$ at $t = 0$. eq. (15) can be derived.

$$\ln\left(\frac{[M]_0}{[M]}\right) = 2^{\frac{1}{3}}(1+\alpha)^{\frac{1}{6}}\xi[B\left(P[t];\frac{2}{3},\frac{2}{3}\right) - B\left(P[0];\frac{2}{3},\frac{2}{3}\right)] \tag{15}$$

$$\alpha = \frac{[T^\bullet]_0^3 k_{\text{dec}}}{3k_t K^2[P-T]_0^2} \tag{16}$$

$$\xi = k_p\left(\frac{[P-T]_0 K}{3k_{\text{dec}}^2 k_t}\right)^{\frac{1}{3}} \tag{17}$$

$$B\left(P[t];\frac{2}{3},\frac{2}{3}\right) = \int_0^{P[t]} x^{\frac{-1}{3}}(1-x)^{\frac{-1}{3}}dx \tag{18}$$

$$B\left(P[0];\frac{2}{3},\frac{2}{3}\right) = \int_0^{P[0]} x^{\frac{-1}{3}}(1-x)^{\frac{-1}{3}}dx \tag{19}$$

With $P[t] = \frac{1}{2}(1 - \frac{e^{-k_{\text{dec}}t}}{\sqrt{1+\alpha}})$, $B(P[t];\frac{2}{3},\frac{2}{3})$ and $B(P[0];\frac{2}{3},\frac{2}{3})$ are incomplete beta functions at time t and 0, respectively.

Two limiting conditions, high and low concentration of $[T^\bullet]_0$, Case I-a and Case I-b are further discussed here.

Case I-a: Large $[T^\bullet]_0$

If $[T^\bullet]_0$ is large and the polymerization time is short ($[T^\bullet]_0 \gg \sqrt[3]{3k_t k_{\text{dec}} K^2[P-T]_0^2 t^2}$), then eq. (15) can be changed into eq. (20) and the linear relationship

between $\ln\frac{([M]_0)}{[M]}$ and time can be obtained as shown in the following equation:

$$\ln\left(\frac{[M]_0}{[M]}\right) = \frac{Kk_p[P-T]_0}{[T^\bullet]_0}\, t$$

$$(\, k_{dec}\, t \to 0 \text{ and } [T^\bullet]_0 >> \sqrt[3]{3\, k_t k_{dec}\, K^2[P-T]_0^2\, t^2}\,) \quad (20)$$

Case I-b: $[T^\bullet]_0 = 0$

For the case of $[T^\bullet]_0 = 0$, it means that the NMP is carried out without adding excess nitroxide to the reaction mixture at $t = 0$. Therefore, $\alpha = 0$, and a simpler form can be obtained, which is the same model derived by Souaille and Fischer.[25]

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_p\left(\frac{2[P-T]_0\, K}{3\, k_{dec}^2\, k_t}\right)^{\frac{1}{3}}\left[B\left(\frac{1}{2}, 1-e^{-k_{dec}\, t}\right); \frac{2}{3}, \frac{2}{3}\right)\right]$$

$$([T^\bullet]_0 = 0) \quad (21)$$

At infinite time, the limiting conversion (x_∞) will achieve and can be obtained by eq. (22).

$$x_\infty = 1 - e^{-k_p\left(\frac{2[P-T]_0\, K}{3\, k_{dec}^2\, k_t\frac{1}{3}}\right)[B\left(\frac{1}{2};\frac{2}{3},\frac{2}{3}\right)]} \quad ([T^\bullet]_0 = 0 \text{ and } t \to \infty) \quad (22)$$

with

$$B\left(\frac{1}{2};\frac{2}{3},\frac{2}{3}\right) = \int_0^{\frac{1}{2}} x^{\frac{-1}{3}}(1-x)^{\frac{-1}{3}}dx \approx 1.0267 \quad (23)$$

Case II: Influence of hydrogen transfer reaction of hydroxylamine to propagating radicals on the polymerization

However, if the effect of hydrogen abstraction reaction of propagating radicals with hydroxylamine on the NMP is much more important than that of termination reaction between two polymeric radicals, namely $2k_t[P^\bullet]^2 << 2k_H[TH][P^\bullet]$, eq. (11) can be changed to the following equation:

$$\frac{d[T^\bullet]}{dt} = 2k_H[TH][P^\bullet] \quad (24)$$

$[P^\bullet]$ can be replaced by $K\frac{[P-T]}{[T^\bullet]}$ and $[TH] = [P-T]_0\,(1-e^{-k_{dec}t})$, hence $[T^\bullet]$ can be solved as a function of time:

$$[T^\bullet] = \sqrt{\frac{2k_H K[P-T]_0^2}{k_{dec}}(1-e^{-k_{dec}t})^2 + [T^\bullet]_0^2} \quad (25)$$

where $K = \frac{k_{act}}{k_{rec}}$, and $[T^\bullet] = [T^\bullet]_0$ at $t = 0$.

$[P^\bullet]$ can be also obtained as:

$$[P^\bullet] = K\frac{[P-T]}{[T^\bullet]} = \frac{K[P-T]_0 e^{-k_{dec}t}}{\sqrt{\frac{2k_H K[P-T]_0^2}{k_{dec}}(1-e^{-k_{dec}\, t})^2 + [T^\bullet]_0^2}} \quad (26)$$

Then the concentration of monomer and conversion can be solved by eq. (4) $\frac{d[M]}{dt} = -k_p[M][P^\bullet]$, with the initial condition of $[M] = [M]_0$ at $t = 0$, eq. (27) can be derived.

$$\ln\left(\frac{[M]_0}{[M]}\right) = C\,\ln[\sqrt{\Phi^2(1-e^{-k_{dec}t})^2 + 1} + \Phi(1-e^{-k_{dec}t})] \quad (27)$$

where

$$C = \sqrt{\frac{Kk_p^2}{2k_{dec}k_H}} \quad (28)$$

$$\Phi = \sqrt{\frac{2Kk_H[P-T]_0^2}{k_{dec}[T^\bullet]_0^2}} \quad (29)$$

Two limiting cases are also discussed here.

Case II-a: Large $[T^\bullet]_0$

If $[T^\bullet]_0$ is large and the polymerization time is short $(([T^\bullet]_0 >> \sqrt{2Kk_H k_{dec}[P-T]_0^2 t^2}))$, eq. (27) can be reduced and linear relationship between $\ln(\frac{[M]_0}{[M]})$ and reaction time can be derived.

$$\ln\left(\frac{[M]_0}{[M]}\right) = \frac{Kk_p[P-T]_0}{[T^\bullet]_0}t$$

$$(k_{dec}t \to 0 \text{ and } [T^\bullet]_0 >> \sqrt{2Kk_H k_{dec}[P-T]_0^2 t^2}) \quad (30)$$

Case II-b: $[T^\bullet]_0 = 0$

If $[T^\bullet]_0$ is close to zero, so the value of $\Phi^2 >> 1$, then eq. (27) can be reduced to the following equation.

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_p\sqrt{\frac{K}{2k_{dec}k_H}}$$
$$\times\left[\ln\left(\sqrt{\frac{8Kk_H}{k_{dec}}}\frac{[P-T]_0}{[T^\bullet]_0}(1-e^{-k_{dec}t})\right)\right] ([T^\bullet]_0 \to 0) \quad (31)$$

However, $\frac{\ln([M]_0}{[M])}$ becomes infinite while $[T^\bullet]_0 = 0$. For convenience, a very small $[T^\bullet]_0$ assumed, which is estimated from the experimental data, is introduced into eq (31) and eq. (32) can be obtained.

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_p \sqrt{\frac{K}{2k_{dec}k_H}} \left[\ln\left(\sqrt{\frac{8Kk_H}{k_{dec}}} \frac{[P-T]_0}{[T^\bullet]_{0\ assumed}} \right.\right.$$

$$\left.\left. \left(1 - e^{-k_{dec}t}\right)\right)\right] \quad ([T^\bullet]_0 \to 0) \quad (32)$$

At infinite time, the limiting conversion (x_∞) can be obtained by eq. (33).

$$x_\infty = 1 - \left(\sqrt{\frac{8Kk_H}{k_{dec}}} \frac{[P-T]_0}{[T^\bullet]_{0\ assumed}}\right)^{-k_p \sqrt{\frac{K}{2k_{dec}k_H}}}$$

$$([T^\bullet]_0 \to 0 \text{ and } t \to \infty) \quad (33)$$

In this study, the polymerization was carried out in a reaction mixture of 4-oxo-TEMPO capped PS macroinitiator and BA with or without additional feed of 4-oxo-TEMPO at 165°C. By the comparison of the kinetic models of Case I and II with the experimental results, the effects of bimolecular termination of two propagating radicals as well as the hydrogen transfer reaction of hydroxylamine to propagating radical on the polymerization of BA will be discussed. Besides, the kinetic models were proposed to determine which reaction dominated the polymerization of BA, that allowed the determination of recombination rate constant (k_{rec}), and hydrogen transfer reaction of hydroxylamine rate constant (k_H). Furthermore, the kinetic analysis could be used to explain the retardant mechanism of polymerization of BA.

EXPERIMENTAL

Materials

Styrene (St, ACROS) and BA (ACROS) were purified by distillation before use. 2,2′-Azobisisobutyronitrile (AIBN, SHOWA) and 4-oxo-TEMPO (ACROS) were used as received. Methanol (MeOH, TEDIA), and tetrahydrofuran (THF, ACROS) were analytical grade and used without further purification.

Synthesis of polystyrene macroinitiators

4-oxo-TEMPO (1.68×10^{-3} mol) as a stable free radical and AIBN (1.20×10^{-3} mol) as an initiator were dissolved in styrene (60 mL) by magnetic stirring bar at room temperature under nitrogen condition. The reaction mixture was first preheated at 95°C for 1 h to let AIBN decompose completely, and then heated and kept at 130°C for a given time to synthesize the polystyrene macroinitiator. After polymerization, the reaction mixture was diluted in THF and then poured into a large amount of methanol. Polystyrene macroinitiator was precipitated in excess methanol, separated by centrifugation, and dried under reduced pressure at 50°C overnight.

Synthesis of PS-*b*-PBA block copolymer by using PS macroinitiators

A mixture of polystyrene macroinitiator and BA in a glass tube was deoxygenated by purge with nitrogen for 15 min and sealed, in which the concentration of PS macroinitiator with M_n of 13,400 and PDI of 1.21 was 0.009M. The polymerization was carried out at 165°C with a magnetic stirring bar for the prescribed time. In addition, another experiment was performed to estimate the recombination rate constant (k_{rec}) for the polymerization of BA. Various amount of 4-oxo-TEMPO were initially added to the reaction mixture to control the polymerization of BA at 165°C for 1 h. After polymerization, the purification method of PS-*b*-PBA was the same as polystyrene.

Analysis of polymers

The conversion of BA monomer was determined by gravimetry, which was defined as the following equation:

$$\text{Conversion of BA monomer} =$$

$$\frac{W_{PS\text{-}b\text{-}PBA} - W_{PS}}{W_{BA}} \times 100\% \quad (34)$$

where $W_{PS\text{-}b\text{-}PBA}$ was the weight of dried PS-*b*-PBA copolymer after the purification process. W_{PS} was the weight of dried PS macroinitiator after the purification process. W_{BA} was the weight of BA monomer before the polymerization.

Molecular weights and polydispersity of polymers were determined by GPC coupled with three columns (Waters1000 Å, Phenomenex 50,000 Å and 10^9 Å), and the RI detector (Shodex RI-71) under the effluent of THF of 1 mL/min. The columns were calibrated with polystyrene standards. The 500-MHz ^{1}H NMR spectra (Bruker Avance-500 MHz FT NMR) were measured at room temperature and CDCl$_3$ was used as a solvent.

RESULTS AND DISCUSSION

Preparation of PS-*b*-PBA initiated by PS macroinitiator

The TEMPO-mediated polymerization has been successfully developed to synthesize polystyrene and its derivatives, because the equilibrium constant ($K = k_{act}/k_{rec} \sim 3.4 \times 10^{-12}$ mol L^{-1} at 120°C[15,31,32]) is larger than TEMPO/acrylate system at 120°C and reactions (c), (d), and (e) are not important for the polymerization,[15,21] so the growing radicals in the reaction mixture cannot be terminated easily to produce dead chains, and the high molecular weight, narrow molecular weight distribution of polystyrene can be successfully synthesized.

However, the polymerization of BA at low temperature (125–130°C) was unsuccessful in many studies.[3,4,12,33] Because the acrylate/TEMPO bonds were too strong to break at a reasonable rate at temperatures 125–130°C to allow the propagation of monomer to continue, namely, the activation rate constant of acrylate/TEMPO bonds was smaller than that of styrene/TEMPO bonds. Besides, the recombination rate constant of acrylate/TEMPO system was larger than that of styrene/TEMPO system. These two reasons resulted in smaller equilibrium constant for acrylate/TEMPO system (e.g., in the system of TEMPO-EEst, $K \sim 1.0 \times 10^{-14}$ mol L^{-1} at 120°C[15,21]), which was about two order of magnitude smaller than the system of TEMPO–styrene. The low concentration of propagating radicals in acrylate/TEMPO system caused the slow rate of polymerization.

Therefore, we tried to perform the polymerization of BA at a higher temperature to increase the rate of the polymerization. In this study, the polystyrene macroinitiator was prepared first with addition of 4-oxo-TEMPO as a stable free radical; then the 4-oxo-TEMPO capped-PS macroinitiator was further extended with BA at a higher temperature, 165°C, to prepare PS-b-PBA block copolymers. As indicated in Table I and Figure 1, in the system of PS-b-PBA (system A), the number-average molecular weight of PBA block (ΔM_n in Table I) increased quickly to 10,000 with PDI of 1.37 in the first 30 min of polymerization, but after that the growth became slow. Figure 2 illustrates the relationship between M_n of PBA block and conversion. We believed that some unwanted reactions occurred which seemed to slow down the polymerization when the PBA block reached a certain length.[25–28,33]

From the reactions (c)–(e), three different dead polymers, $P_{d=}$, P_{dH}, and P_{2d}, were produced. Because the concentration of dead polymer increased with time, molecular weight distribution of PS-b-
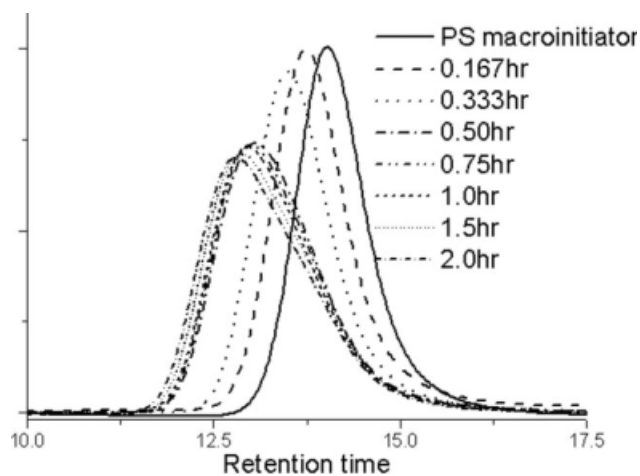

Figure 1 GPC curve of PS-b-PBA obtained in system A.

PBA became broader and broader. Besides, because T$^\bullet$ reproduced in the reaction (d), concentration of T$^\bullet$ increased and P$^\bullet$ decreased with time. Therefore, rate of polymerization became slow and conversion of BA monomer was low.

Figure 3 shows the ^{1}H NMR spectrum of PS-b-PBA (system A at 1.5 h), and all the characteristic peaks of PS and PBA are listed in Table II. It is clear to see that the signals between 6.3 and 7.2 ppm are assigned to the five protons of aromatic ring of styrene segment. The signals at 4.1 (—OCH$_2$—), 1.6 (—CH$_2$CH$_2$CH$_2$—), 1.4 (—CH$_2$CH$_2$CH$_3$), and 0.9 ppm (—CH$_2$CH$_2$CH$_3$) are the characteristic peaks of BA segment. From the integration areas of peak c of PS block and peak f of PBA block, the molar ratio of styrene to BA in PS-b-PBA was calculated as 51%/49%. Based on the M_n of PS block determined by GPC being 13,400, the M_n of PBA block in PS-b-PBA was then calculated as 15,500 from the molar ratio determination in NMR spectrum, which was close to the M_n of PBA block ($M_n \sim 12100$) by GPC determination.

TABLE I
Molecular Weight of PS-b-PBA Initiated by 4-oxo-TEMPO Capped PS Macroinitiator

System	Reaction time (h)	M_n	PDI	ΔM_n[a]	Conversion (%)
A	0.167	17100	1.18	3700	2.6%
	0.333	19500	1.24	6100	6.0%
	0.5	24100	1.37	10700	12.2%
	0.75	24600	1.39	11200	14.0%
	1.0	24900	1.41	11500	14.4%
	1.5	25500	1.45	12100	15.2%
	2.0	27100	1.45	13700	16.8%

[a] ΔM_n was the number-average molecular weight of PBA chain in the block copolymer, which was defined as the following equation: $\Delta M_n = M_{nPS\text{-}b\text{-}PBA} - M_{nPS}$ where $M_{nPS\text{-}b\text{-}PBA}$ was the number-average molecular weight of PS-b-PBA determined by GPC, M_{nPS} was the number-average molecular weight of PS macroinitiator determined by GPC.
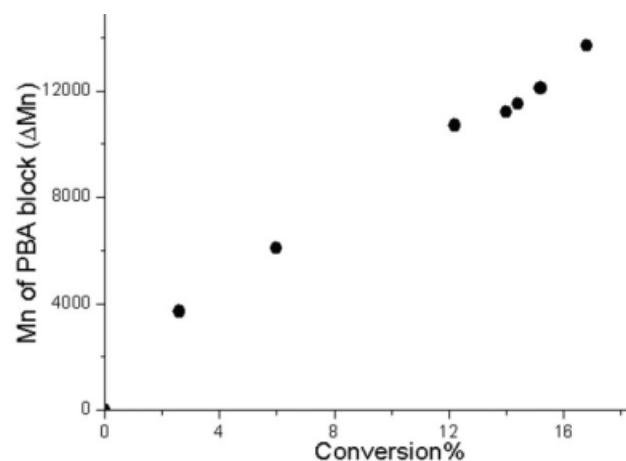

Figure 2 M_n of PBA block in PS-b-PBA of system A versus conversion.
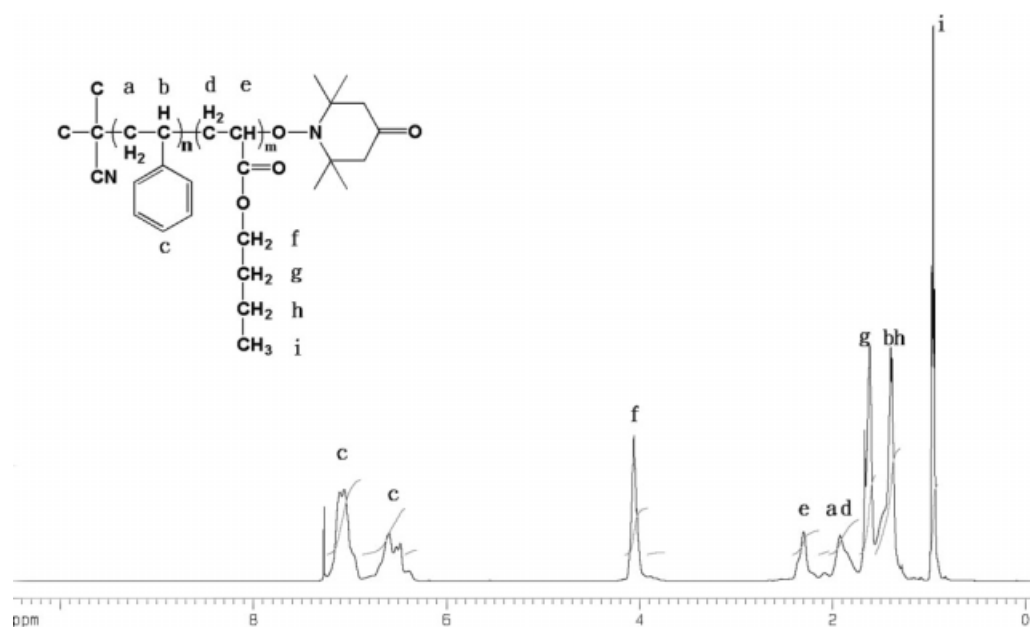
Figure 3 NMR spectrum of PS-*b*-PBA (system A at 1.5 h).

Kinetic analysis on the polymerization of BA

The influences of reactions (a)–(e) on the polymerization of BA will be discussed. To estimate the recombination rate constant k_{rec}, the polymerization of BA was carried out at 165°C for 1 h with 4-oxo-TEMPO capped PS macroinitiator of $0.009M$. Various amounts of additional 4-oxo-TEMPO were added to the reaction mixture to control the polymerization. Table III shows that the number-average molecular weight and PDI of PBA block in PS-*b*-PBA copolymers change with the concentration of added 4-oxo-TEMPO. It is found that the conversion of BA and the molecular weight of PBA block decrease with increasing the concentration of 4-oxo-TEMPO. Fig-

ure 4 exhibits the relationship between $\frac{\ln([M]_0}{[M]}$ and $\frac{[P-T]_0}{[T^\bullet]_0}$ in the experiments of system B as shown in Table III. According to the kinetic model, with high concentration of 4-oxo-TEMPO, Cases I-a and II-a, $\ln\left(\frac{[M]_0}{[M]}\right)$ is linearly proportional to $\frac{[P-T]_0}{[T^\bullet]_0}$ at early stage of polymerization as indicated in eqs. (20) and (30). The value of K, or k_{rec}, can be calculated from the initial slope in Figure 4, and it is listed in Table IV.

In the case of polymerization of BA without the addition of 4-oxo-TEMPO (System A), if the hydrogen transfer reaction of hydroxylamine to propagating radicals is neglected, that is Case I-b, the profile of $\frac{\ln([M]_0}{[M])}$ can be calculated by eq. (21), and plotted in Figure 5. However, the predicted growth rate of polymerization is faster than the experimental results shown in Table I and Figure 5. Therefore, we suppose that the hydrogen transfer reaction is necessarily further taken into consideration.

TABLE II
Chemical Shift, Number of Hydrogen and Molar Ratio of Styrene to BA in PS-*b*-PBA (System A at 1.5 h)

Peak label[a]	C	f
Chemical shift	6.4–7.2	4.1
Number of hydrogen	5	2
Peak area	1.6144	0.6245
The molar ratio of styrene to BA in PS-*b*-PBA[b]	Styrene/BA = 51%/49%	
The M_n of styrene and BA blocks in PS-*b*-PBA[c]	Styrene/BA = 13,400/15,500	
The M_n of styrene and BA blocks in PS-*b*-PBA[d]	Styrene/BA = 13,400/12,100	

[a] See Figure 3.
[b] The molar ratio between styrene and BA in PS-*b*-PBA was estimated by ^{1}H NMR analysis
[c] Using the M_n of PS in PS-*b*-PBA determined by GPC, the M_n of PBA block was estimated by ^{1}H NMR analysis.
[d] The M_n of PS and PBA blocks in PS-*b*-PBA were determined by GPC.

TABLE III
Molecular Weight of PS-*b*-PBA Initiated by 4-oxo-TEMPO Capped PS Macroinitiator with the Addition of 4-oxo-TEMPO

System	Concentration of 4-oxo-TEMPO	M_n	PDI	ΔM_n	Conversion (%)
B	$5 \times 10^{-5}M$	22,900	1.35	9500	11.5
	$1 \times 10^{-4}M$	22,300	1.33	8900	9.7
	$2 \times 10^{-4}M$	20,000	1.27	6600	7.0
	$4 \times 10^{-4}M$	17,800	1.20	4400	4.4
	$8 \times 10^{-4}M$	16,700	1.18	3300	2.4
	$1.6 \times 10^{-3}M$	15,700	1.19	2300	1.3
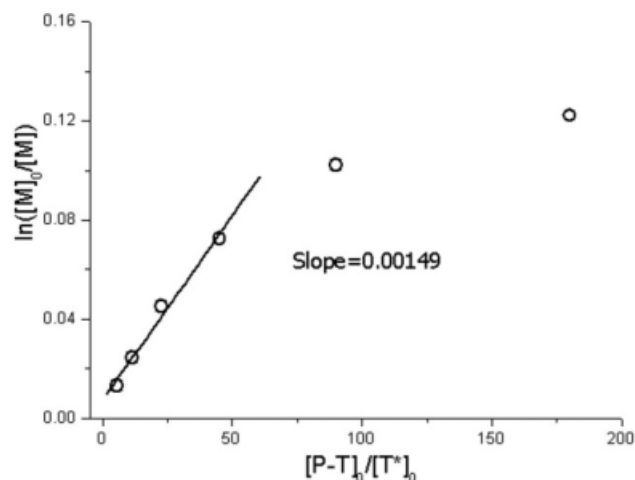
Figure 4 The relationship between $\ln([M]_0/[M])$ and $[P-T]_0/[T^\bullet]_0$ for System B (in Table III). $[P-T]_0 = 0.009M$, $[T^\bullet]_0 = 5 \times 10^{-5}$–$1.6 \times 10^{-3}M$, and time = 3600 s.

According to eq. (32), in Case II-b, the linear relationship between $\ln\left(\frac{[M]_0}{[M]}\right)$ and $\ln(1 - e^{-k_{\mathrm{dec}}t})$ could be obtained in Figure 6. The rate constant k_H was determined from the slope as $9.33 \times 10^4 M^{-1}$ s^{-1}, about $0.622k_p$, at 165°C. Also, $[T^\bullet]_{0\mathrm{assumed}}$ was estimated from the intercept of $\ln\left(\frac{[M]_0}{[M]}\right)$ versus $\ln(1 - e^{-k_{\mathrm{dec}}t})$ as $6.6 \times 10^{-5}M$ in Figure 6. Figure 5 also shows the calculated results by eq. (32). It is found that the model, Case II-b, agrees very well with the experimental data and numerical results, and $\ln\left(\frac{[M]_0}{[M]}\right)$ does not linearly increase with time and quickly levels off. Moreover, the limiting conversion calculated by eq. (33) was about 22.2%, close to the experimental result, 16.8% after 2 h.

Furthermore, the competition between the hydrogen transfer reaction of hydroxylamine to propagating radicals and the bimolecular termination could be estimated by the following equation:

$$\frac{\text{rate of hydrogen transfer reaction of hydroxylamine to propagating radicals}}{\text{rate of bimolecular termination of two polymeric radicals}} = \frac{R_H}{R_t} = \frac{(k_H[\mathrm{TH}][P^\bullet])}{(k_t[P^\bullet]^2)} \quad (35)$$

The ratio of R_H to R_t at 165°C was calculated by a numerical analysis from eq. (1)–(5) at initial conditions of $[P-T]_0 = 0.009M$, $[M]_0 = 6.975M$, and $[P^\bullet]_0 = [T^\bullet]_0 = [\mathrm{TH}]_0 = 0$, in which the kinetic parameters were listed in Table IV. As shown in Figure 7, the rate ratio is less than one at first 3 min, and increases to 50 at about 30 min. then to 800 after 2 h. This implies that the kinetic model of Case II is better to explain our polymerization system after the beginning of polymerization.

Figure 8 indicates the concentration of 4-oxo-TEMPO, $[T^\bullet]$, versus reaction time calculated from eq. (13) of Case I and eq. (25) of Case II, respectively. In Case I, the hydrogen transfer reaction is neglected, $[T^\bullet]$ increases more quickly than that in Case II in the beginning of polymerization, but is retarded after about 30 min. On the other hand, in Case II, the hydrogen transfer reaction is much more important, $[T^\bullet]$ keeps increasing to a higher concentration, and reaches $3 \times 10^{-4}M$ after 2 h, which is about six times larger than that in Case I. This

implies that the hydrogen transfer reaction of hydroxylamine to propagating radicals plays an important role during polymerization of BA and large amount of T$^\bullet$ is reproduced by the reaction mechanism (d), causing the excess free 4-oxo-TEMPO to accumulate in the reaction mixture. The excess free TEMPO shifts the equilibrium to the left side in reaction (a), resulting in the propagating chains to stay in their dormant state. Therefore, the concentration of propagating radicals gradually decreases with time, which results in the polymerization to slow down and eventually stop. If the excess free T$^\bullet$

TABLE IV
Rate Constants of Polymerization of BA at 165°C

Rate Constant		Reference
k_{act}	2.64×10^{-3} s^{-1}	34
k_{rec}	9.57×10^8 M^{-1} s^{-1}	This work
k_p	1.5×10^5 M^{-1} s^{-1}	35–39[a]
k_{dec}	$0.03 \times k_{\mathrm{act}}$	21,25
k_H	9.33×10^4 M^{-1} s^{-1}	This work
k_t	$0.416 \times k_p^2$	36

[a] k_p was estimated by Arrhenius equation.
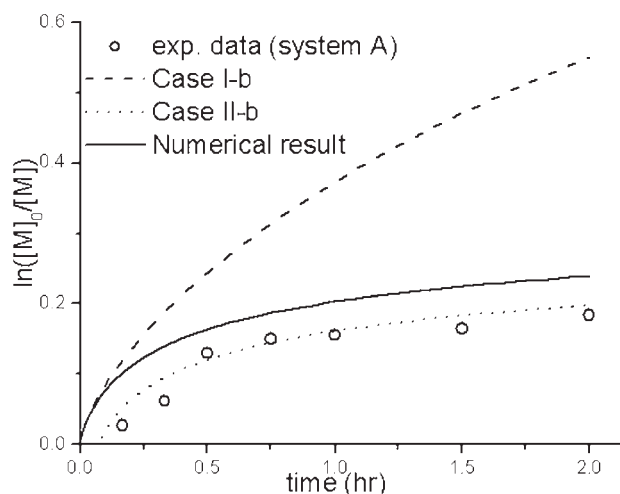
Figure 5 $\ln([M]_0/[M])$ versus time from kinetic models of Case I-b, II-b, numerical results, and experimental results (System A) at 165°C with $[P-T]_0 = 0.009M$ and $[T^\bullet]_0 = 0$.
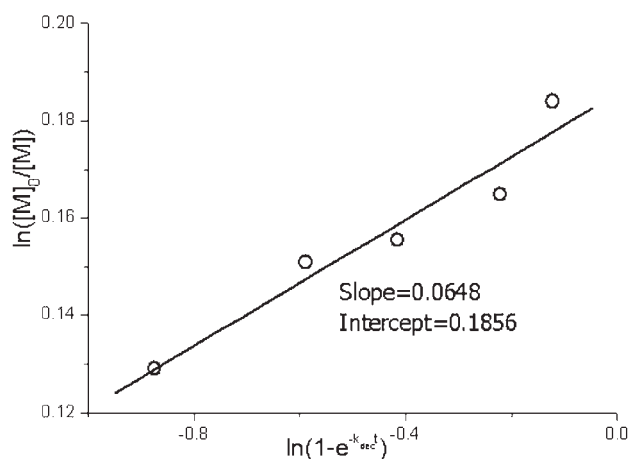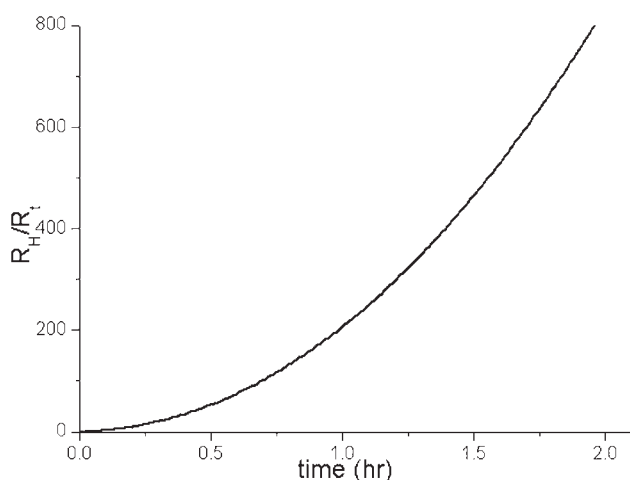
Figure 6 The relationship between $\ln([M]_0/[M])$ and $\ln(1 - e^{-k_{dec}t})$ at 165°C for System A (in Table I) at $t = 30$–120 min.

Figure 8 [T$^\bullet$] as a function of reaction time. Dash line: eq. (13) of Case I. solid line: eq. (25) of Case I.
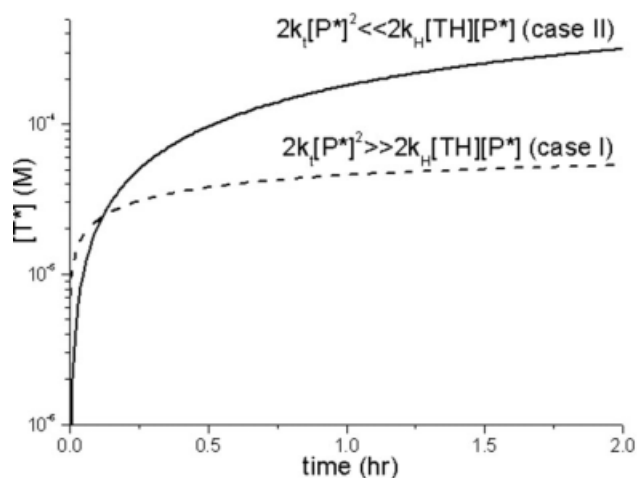
produced from reaction (d) can be reduced or eliminated, the polymerization of BA initiated by PS macroinitiator should be facile and high conversion can be obtained. Some studies reported that the TEMPO-mediated polymerizations of BA was successfully done by the addition of organic acid, such as ascorbic acid or dodecylbenzenesulfonic acid, which could react with the excess free TEMPO produced by termination reaction or hydrogen transfer reaction and allow the polymerization to proceed.[19,20]

CONCLUSION

4-oxo-TEMPO capped PS living polymer was used to prepare PS-*b*-PBA block copolymers at 165°C. The M_n of PBA block could reach above 10,000 rapidly at early stage of polymerization, but after that the polymerization was almost retarded. Kinetic model and analysis were proposed to calculate the recombination rate

Figure 7 The ratio of R_H to R_t estimated by numerical analysis.

constant k_{rec} ($9.57 \times 10^8 M^{-1}$ s^{-1} at 165°C). Furthermore, according to the kinetic analysis, the polymerization of BA was strongly influenced by the hydrogen transfer reaction of hydroxylamine (4-oxo-TEMPOH) to the growing radicals. This reaction caused the production of free 4-oxo-TEMPO. The accumulation of free 4-oxo-TEMPO with reaction time slowed down the polymerization and resulted in a low conversion of BA. During polymerization, $\ln\left(\frac{[M]_0}{[M]}\right)$ was found to be proportional to $\ln(1 - e^{-k_{dec}t})$ after the beginning of polymerization. The rate constant of the hydrogen transfer reaction of hydroxylamine (4-oxo-TEMPOH) to the growing radicals of BA could be estimated as $k_H = 9.33 \times 10^4 M^{-1}$ s^{-1} at 165°C.

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