

## Development of an Arylthiobismuthine Cocatalyst in Organobismuthine-Mediated Living Radical Polymerization: Applications for Synthesis of Ultrahigh Molecular Weight Polystyrenes and Polyacrylates

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**Abstract:** Diphenyl(2,6-dimesitylphenylthio)bismuthine (**1a**) serves as an excellent cocatalyst in organobismuthine-mediated living radical polymerization (BIRP). Both low and high molecular weight polystyrenes and poly(butyl acrylate)s (PBAs) with controlled molecular weights and low polydispersity indexes (PDIs) were synthesized by the addition of a catalytic amount of **1a** to an organobismuthine chain-transfer agent, methyl 2-dimethylbismuthanyl-2-methylpropionate (**3**). The number-average molecular weight ( $M_n$ ) of the resulting polymers increases linearly with the monomer/3 ratio. Structurally well-defined polystyrenes with  $M_n$ 's in the range from  $1.0 \times 10^4$  to  $2.0 \times 10^5$  and PDIs of 1.07–1.15 as well as PBAs with  $M_n$ 's in the range from  $1.2 \times 10^4$  to  $2.8 \times 10^6$  and PDIs of 1.06–1.43 were successfully prepared under mild thermal conditions. Control experiments suggested that **1a** reversibly reacts with the polymer-end radical to generate an organobismuthine dormant species and 2,6-dimesitylphenylthiyl radical (**2a**). This reaction avoids the occurrence of chain termination reactions involving the polymer-end radicals and avoids undesired loss of the bismuthanyl polymer end group. The bulky 2,6-dimesitylphenyl group attached to the sulfur atom may prevent the addition of thiyl radicals to the vinyl monomers to generate new polymer chains.

### Introduction

Living radical polymerization (LRP) has become an indispensable method for the synthesis of well-defined, advanced polymeric materials because it allows the polymerization of a variety of functional vinyl monomers to give products with well-controlled molecular weights and molecular weight distributions.<sup>1–3</sup> LRP that have been widely used include nitroxide-mediated radical polymerization,<sup>4</sup> atom-transfer radical polymerization (ATRP),<sup>5–7</sup> and reversible addition–fragmentation chain-transfer radical polymerization (RAFT).<sup>8,9</sup> We have also developed organotellurium-,<sup>10–13</sup> organostibine-,<sup>14–16</sup> and or-

ganobismuthine-mediated<sup>17</sup> LRP (TERP, SBRP, and BIRP, respectively), which have proven to be powerful methods.<sup>18,19</sup> New variants of LRP have also emerged, such as cobalt-mediated polymerization,<sup>20–26</sup> single-electron-transfer (SET) LRP,<sup>27–30</sup> titanium-catalyzed polymerization,<sup>31</sup> and reversible chain-transfer catalyzed polymerization.<sup>32,33</sup>

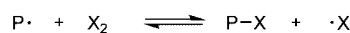
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Despite these developments, a significant drawback of LRP is the synthesis of high molecular weight polymers. Because the polymer-end radical is always subject to irreversible termination reactions,<sup>34</sup> dead polymers accumulate in the reaction mixture as the targeted molecular weight increases. Nevertheless, a few examples of the synthesis of high molecular weight polyacrylates and polymethacrylates have been reported, with number-average molecular weights ( $M_n$ 's) sometimes exceeding  $1 \times 10^6$ , which usually corresponds to a degree of polymerization of more than  $10^4$ . For example, ultrahigh molecular weight poly(methyl methacrylate), with  $M_n$ 's in the range  $(1.3\text{--}3.6) \times 10^6$  and low polydispersity indexes (PDIs) of less than 1.3 have been prepared by RAFT<sup>35</sup> and ATRP<sup>36,37</sup> under high-pressure conditions. However, this method requires special apparatus and is hence synthetically unattractive. The only examples under ambient conditions reported to date are the syntheses of poly[2-(dimethylamino)ethyl methacrylate] with  $M_n = 8.5 \times 10^5$  by ATRP,<sup>38</sup> poly(methyl acrylate) with  $M_n = 1.4 \times 10^6$  by SET LRP using a copper catalyst,<sup>28</sup> and poly(butyl methacrylate) with  $M_n = 1.0 \times 10^6$  by ATRP under miniemulsion conditions.<sup>39</sup> The synthesis of high molecular weight polystyrene is more difficult than that of polymethacrylates because of the existence of autoinitiation and the slow propagation rate. The synthesis of polystyrene by RAFT with an  $M_n$  of  $2 \times 10^5$  and a PDI of 1.12 has been reported, but it was performed under high-pressure conditions.<sup>40</sup> Ultrahigh molecular weight polymethacrylates and polystyrenes with  $M_n$ 's exceeding  $10^7$  were synthesized by plasma-initiated polymerization, but its synthetic efficiency and generality were quite limited.<sup>41</sup> Therefore, the development of a new method that allows the synthesis of high molecular weight polymers under ambient conditions is desirable but also a significant challenge.

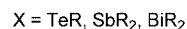
During the course of developing new LRP methods, we found that BIRP allows better control of PDI than TERP and SBRP for the synthesis of low molecular weight polymers ( $M_n < 1 \times 10^5$ ). However, when the target molecular weight of the polymers synthesized by BIRP was increased, we observed an apparent loss of PDI control. We also observed the precipitation of black particles, presumably bismuth metal, indicating the loss of the organobismuthine polymer end group. Therefore, if the loss of this polymer end group could be avoided, BIRP would

**Scheme 1.** Mechanisms of Activation/Deactivation of Polymer-End Radical  $P\cdot$  by (A) Ditelluride  $(TeR)_2$  or Distibine  $(SbR_2)_2$  and (b) Organotellurium  $(P-TeR)$ , Organostibine  $(P-SbR_2)$ , or Organobismuthine  $(P-BiR_2)$  Dormant Species

(a) Deactivation by ditelluride or distibine



(b) Deactivation by tellurium, stibine, or bismuthine dormant species



be suitable for the synthesis of high molecular weight polymers in a controlled manner.

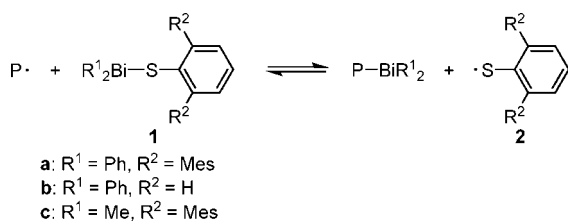
We have already reported that the addition of ditellurides<sup>11</sup> and distibines<sup>16</sup> effectively increases the PDI control that can be achieved in TERP and SBRP, respectively, for the polymerization of styrene and methyl methacrylate (MMA). Kinetic studies of the effect of ditelluride revealed that it acts as a capping reagent for the polymer-end radical ( $P\cdot$ ) through a homolytic substitution reaction, forming a dormant species  $P-TeR$  (Scheme 1a).<sup>42</sup> The liberated tellanyl radical ( $RTe\cdot$ ) is essentially inert toward the monomers but reacts with the organotellurium dormant species to regenerate the polymer-end radical and the ditelluride. In contrast, deactivation of the polymer-end radical to the dormant species in the absence of ditelluride proceeds by a homolytic substitution reaction with the organotellurium dormant species, that is, a degenerative transfer reaction (Scheme 1b).<sup>43,44</sup> In the case of the methyltellanyl group ( $X = TeMe$ ), the rate of deactivation by the ditelluride is  $\sim 100$  times faster than that by the organotellurium dormant species in the polymerization of styrene, and this is the origin of the increased PDI control achieved by the addition of ditellurides. We envisioned that faster deactivation would decrease the occurrence of undesired termination reactions of the polymer-end radicals and that this type of diheteroatom compound is thus potentially useful as a cocatalyst for the synthesis of high molecular weight polymers.

By analogy with the effects of ditellurides and distibines, dibismuthines would be a formidable cocatalyst for BIRP. However, these compounds are thermally labile. For example, tetramethyldibismuthine decomposes even at room temperature,<sup>45</sup> and thus, dibismuthines cannot be used as cocatalysts in this process. We focused on the arylthiobismuthines **1** as potential cocatalysts (Scheme 2). Barton et al.<sup>46</sup> have already reported that tris(phenylthio)bismuthine generates a benzenethiyl radical upon reaction with carbon-centered radicals. Therefore, we expected that **1** should react with polymer-end radicals to form an organobismuthine dormant species and an arylthiyl radical **2**. We have recently found that arylthiyl radicals are highly reactive toward organobismuthines, generating carbon-centered radicals through homolytic substitution reactions.<sup>47</sup> Therefore, radical **2** should react with the organobismuthine

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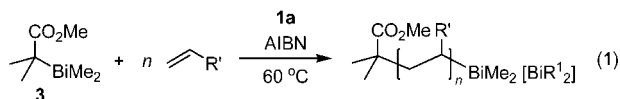
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**Scheme 2.** Hypothetical Reaction of Arylthiobismuthines with a Polymer-End Radical P•



dormant species to regenerate the polymer-end radical (P•) and **1**. Thiyl radicals are also reactive toward alkenes,<sup>48</sup> and the degree of control over the LRP would diminish if **2** were to react with the monomers. Therefore, we decided to use an arylthiyl radical bearing the sterically bulky mesityl group (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) at both the 2 and 6 positions. We chose this substituent because of its well-known steric shielding effect as well as the availability of 2,6-dimesitylbenzenethiol, the precursor of **1a** ( $R^1 = Ph, R^2 = Mes$ ).<sup>49,50</sup>

We report here on the synthesis of arylthiobismuthine cocatalysts **1** and their effect on BIRP. We show that BIRP becomes more controllable in the presence of a catalytic amount of **1a**, allowing the synthesis of high molecular weight polystyrenes ( $M_n \approx 2 \times 10^5$ ) and ultrahigh molecular weight polyacrylates ( $M_n \approx 3 \times 10^6$ ) with well-controlled molecular weight distributions, starting from monofunctional organobismuthine chain-transfer agents such as methyl 2-dimethylbismuthanyl-2-methylpropionate (**3**)<sup>17</sup> (eq 1):

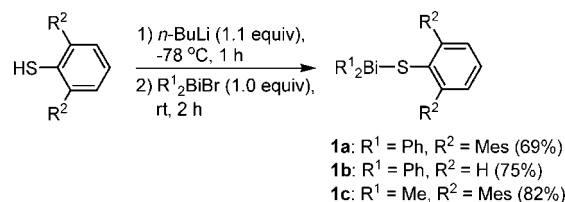


This is the first example in which the synthetic utility of thiobismuthines in controlling radical reactions and radical polymerization has been demonstrated. On the basis of several control experiments, we also propose the mechanism for the action of **1** shown in Scheme 2. This new mechanism for deactivation of polymer-end radicals in addition to the conventional degenerative transfer of organobismuthines (Scheme 1b, X = BiR<sub>2</sub>) should be responsible for the successful synthesis of ultrahigh molecular weight polymers.

## Results and Discussion

**Synthesis of Arylthiobismuthines 1.** 2,6-Dimesitylbenzenethiol<sup>50</sup> was treated with *n*-butyllithium (1.1 equiv) in THF at  $-78\text{ }^\circ\text{C}$  followed by diphenylbismuthanyl bromide<sup>51</sup> (Scheme 3). The desired thiobismuthine **1a** was isolated in 69% yield by silica gel chromatography followed by recrystallization as a yellow crystal that is stable toward air and moisture. Diphenyl(phenylthio)bismuthine (**1b**), which has no sterically bulky substituents on the arylthiyl group, was prepared in 75% yield starting from benzenethiol. Synthesis of dimethyl(2,6-dimesitylphenylthio)bismuthine (**1c**) was also carried out. Though **1c** was obtained as the major component in the form of an air-sensitive

**Scheme 3.** Synthesis of Arylthiobismuthine Derivatives



**Table 1.** Effect of Arylthiobismuthines **1** on Polymerization of Styrene<sup>a</sup>

| run | equiv of styrene | cocatalyst (equiv)                      | time (h) | conv. (%) <sup>b</sup> | $M_{n,theor}$ | $M_{n,exp}$ <sup>c</sup> | PDI <sup>c</sup> |
|-----|------------------|---|----------|------------------------|---------------|--------------------------|------------------|
| 1   | 1000             | <b>1a</b> (0.2)                         | 84       | 98                     | 102 000       | 103 000                  | 1.11             |
| 2   | 1000             | <b>1a</b> (0.5)                         | 84       | 83                     | 86 400        | 85 500                   | 1.13             |
| 3   | 1000             | <b>1a</b> (1.0)                         | 84       | 82                     | 85 400        | 80 500                   | 1.17             |
| 4   | 1000             | <b>1b</b> (0.2)                         | 84       | 88                     | 91 500        | 90 200                   | 1.27             |
| 5   | 1000             | none                                    | 84       | 96                     | 99 800        | 81 900                   | 1.21             |
| 6   | 1000             | (Ph <sub>2</sub> Bi) <sub>2</sub> (0.2) | 84       | 75                     | 78 100        | 69 200                   | 1.31             |
| 7   | 2000             | <b>1a</b> (0.2)                         | 96       | 94                     | 196 000       | 198 000                  | 1.15             |
| 8   | 2000             | <b>1a</b> (0.5)                         | 96       | 94                     | 167 000       | 147 000                  | 1.15             |
| 9   | 2000             | <b>1a</b> (1.0)                         | 96       | 81                     | 169 000       | 130 000                  | 1.22             |
| 10  | 2000             | none                                    | 96       | 55                     | 115 000       | 107 000                  | 1.34             |
| 11  | 100              | <b>1a</b> (0.2)                         | 24       | 96                     | 10 000        | 10 900                   | 1.07             |
| 12  | 200              | <b>1a</b> (0.2)                         | 32       | 99                     | 20 600        | 24 700                   | 1.09             |
| 13  | 500              | <b>1a</b> (0.2)                         | 60       | 99                     | 51 600        | 55 500                   | 1.10             |
| 14  | 700              | <b>1a</b> (0.2)                         | 65       | 100                    | 72 800        | 79 500                   | 1.11             |
| 15  | 1500             | <b>1a</b> (0.2)                         | 90       | 96                     | 150 000       | 139 000                  | 1.13             |
| 16  | 100              | <b>1b</b> (0.2)                         | 24       | 100                    | 10 400        | 13 600                   | 1.13             |
| 17  | 500              | <b>1b</b> (0.2)                         | 60       | 100                    | 52 000        | 54 700                   | 1.18             |
| 18  | 1000             | <b>1a</b> (0.2)                         | 84       | 86                     | 89 600        | 84 600                   | 1.13             |

<sup>a</sup> A mixture of **3**, **1** (0–1.0 equiv), AIBN (0.2 equiv), and styrene (100–2000 equiv) was heated under a nitrogen atmosphere. <sup>b</sup> Monomer conversion was determined by <sup>1</sup>H NMR. <sup>c</sup> Number-average molecular weight ( $M_n$ ) and polydispersity index (PDI =  $M_w/M_n$ ) were obtained by size exclusion chromatography, which was calibrated with polystyrene standards, using CHCl<sub>3</sub> as the eluent.

amorphous solid, some impurities could not be completely removed. Therefore, we used **1c** only for mechanistic studies, because the degree of control achievable in LRP is sometimes strongly influenced by small amounts of an impurity.

**Effect of 1 on Polymerization of Styrene by BIRP.** We first examined the effects of **1a** on the polymerization of styrene using organobismuthine **3** as a chain-transfer agent (Table 1). When a mixture of **3**, 2,2'-azobis(isobutyronitrile) (AIBN) (0.2 equiv), **1a** (0.2 equiv), and styrene (1000 equiv) was heated at 60 °C under a nitrogen atmosphere in a glovebox, polystyrene formed with quantitative monomer conversion, as judged by <sup>1</sup>H NMR spectroscopy (Table 1, run 1). The slightly yellowish crude product (Figure 1a) was dissolved in chloroform, and precipitation from methanol gave polystyrene as a white powder. Analysis by gel permeation chromatography (GPC) indicated the formation of highly controlled polystyrene with an  $M_n$  of 103 000, which is close to the value calculated from the monomer/**3** ratio ( $M_{n,theor} = 102\ 000$ ), and a low PDI of 1.11. When the amount of **1a** was increased to 0.5 and 1.0 equiv, we also obtained highly controlled polystyrenes with low PDIs (1.13–1.14) as colorless products (Table 1, runs 2 and 3). However, the degree of control achieved, as indicated by the  $M_n$  and PDI values, was slightly lower than that attained in the presence of 0.2 equiv of **1a**.

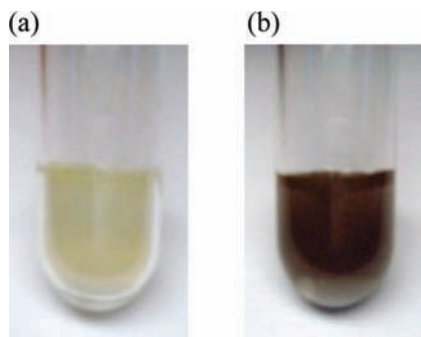
The addition of 0.2 equiv of **1b** also resulted in the formation of a colorless product, but the polymerization was less controlled than that in the presence of **1a** in terms of both  $M_n$  and PDI (Table 1, run 4). This result clearly indicates the importance of using a sterically bulky mesityl group as a substituent. Polym-

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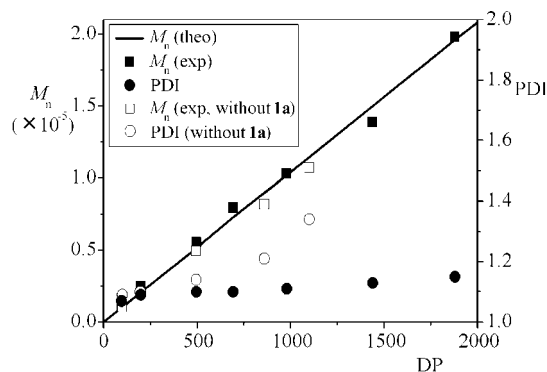
**Figure 1.** Effect of **1a** on the color of polystyrene crude product prepared (a) in the presence of **1a** (Table 1, run 1) and (b) in its absence (Table 1, run 5).

erization under the same reaction conditions without the addition of **1a** resulted in a high monomer conversion (96%), but a black precipitate appeared in the reaction mixture (Figure 1b). Furthermore, the  $M_n$  of the resulting polymer was  $\sim 20\%$  lower than the theoretical value, and the PDI was larger than that of the product formed in the presence of **1a** (Table 1, run 5). The effects of tetraphenyldibismuthine, which is thermally more stable than the tetramethyl derivative,<sup>41</sup> were also investigated. However, the reaction mixture became black, and no improvement of the PDI control was observed (run 6). These results clearly indicate that the addition of **1a** considerably suppresses the loss of the organobismuthanyl polymer end group and increases the control over the  $M_n$  and PDI of the product.

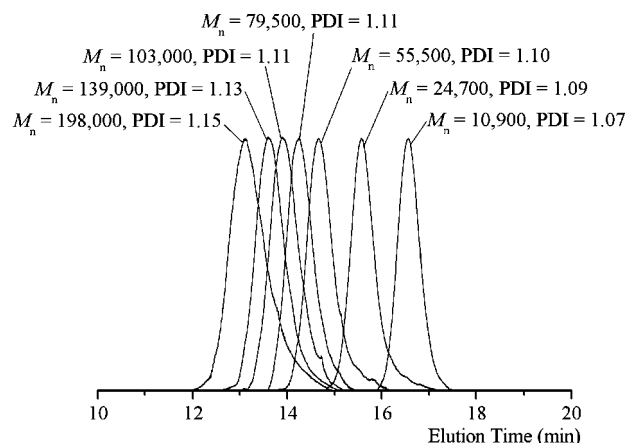
The effects of **1a** were further investigated by carrying out the polymerization of 2000 equiv of styrene (Table 1, runs 7–10). Polymerization in the presence of **1a** (0.2–1.0 equiv) resulted in high monomer conversions and gave colorless polymers in all cases (Table 1, runs 7–9). Highly controlled polystyrenes with low PDIs and  $M_n$ 's close to the theoretical values were obtained in all cases. The use of 0.2 equiv of **1a** was most effective in attaining a high monomer conversion, a high degree of control of the  $M_n$ , and a low PDI. Polystyrene with an  $M_n$  of  $2.0 \times 10^5$  and a PDI of 1.15 was obtained under optimized conditions (run 7). In contrast, polymerization carried out in the absence of **1a** (Table 1, run 10) did not reach a high monomer conversion after 96 h, and it afforded polystyrene with a rather high PDI of 1.34. The formation of a black precipitate was also observed in the reaction mixture.

The  $M_n$  of the polystyrene could be controlled by the styrene/**3** ratio but not the styrene/**1a** ratio, and thus, low ( $M_n \approx 10\,000$ ) and high molecular weight polystyrenes could be selectively synthesized by varying the styrene/**3** ratio in the presence of 0.2 equiv of **1a** (Table 1, runs 11–15, and Figure 2). These results clearly indicate that **1a** does not initiate the polymerization. The effects of **1a** on the  $M_n$  and PDI of the product were marginal for the synthesis of low molecular weight polystyrenes ( $M_n < 50\,000$ ), but it became more significant as the targeted molecular weight increased ( $M_n > 50\,000$ ). The  $M_n$ 's for polystyrene prepared in the presence of **1a** linearly increased with the amount of styrene used, as shown by the filled squares in Figure 2, and were all close to the corresponding theoretical values. This linear correlation is consistent with the living character of the polymerization. GPC traces of the polystyrenes were unimodal in all cases, and the peak maxima shifted toward higher molecular weight as the styrene/**3** ratio increased (Figure 3).

The living character of the polymerization was further confirmed by control experiments. At first, kinetic studies were



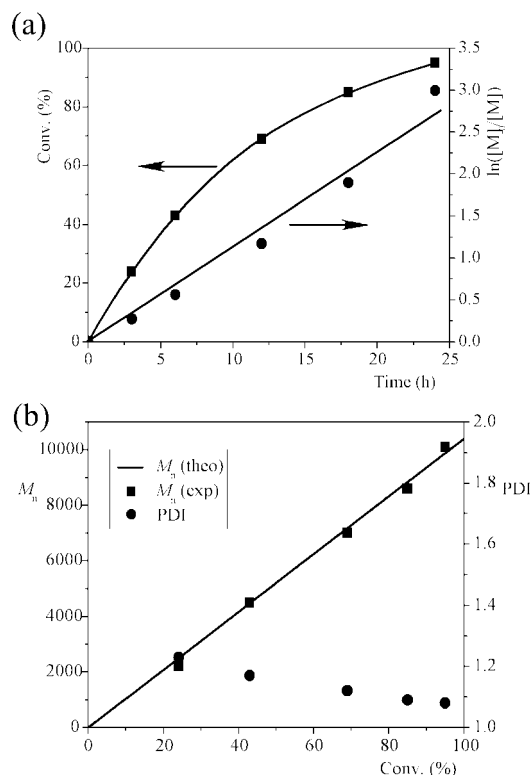
**Figure 2.** Correlation between the degree of polymerization (DP) of styrene and the number-average molecular weight ( $M_n$ ) and polydispersity index ( $PDI = M_w/M_n$ ) of the resulting polystyrenes, for the bulk polymerization of styrene with **3** at  $60^\circ\text{C}$  in the presence or absence of **1a**.



**Figure 3.** GPC traces of polystyrenes synthesized by varying the styrene/**3** ratio.

carried out by using 100 equiv of styrene. The plot of monomer conversion versus time shown in Figure 4a indicates that pseudo-first-order kinetics with respect to the monomer were followed, implying that the concentration of the radical species remained constant during the polymerization. The apparent rate constant ( $k_p^{\text{app}}$ ) was determined to be  $0.11\text{ h}^{-1}$ . A linear correlation between the  $M_n$  of the polystyrene and the monomer conversion was observed (Figure 4b). The PDI was rather high at low monomer conversion ( $PDI = 1.23$  at 24% conversion) but decreased as the polymerization progressed ( $PDI = 1.08$  at 95% conversion). Second, a chain-extension experiment was examined. Thus, polystyrene ( $M_n = 8200$ ,  $PDI = 1.09$ ) was prepared from **3** and 100 equiv of styrene in the presence of 0.2 equiv of **1a** and AIBN at  $60^\circ\text{C}$  in 85% monomer conversion, and styrene (100 equiv) was added to the crude reaction mixture. After the mixture was heated at  $60^\circ\text{C}$  for 18 h, we obtained the chain-extended polystyrene with  $M_n = 19\,600$  and  $PDI = 1.12$ . GPC traces clearly revealed that the initially formed polystyrene was completely converted (see the Supporting Information). All of these results are consistent with the living character of the polymerization under the current conditions.

**Polymerization of *n*-Butyl Acrylate by BIRP in the Presence of a Cocatalyst.** We next studied the polymerization of 100 equiv of *n*-butyl acrylate (BA) by BIRP using chain-transfer agent **3** and AIBN (0.2 equiv) in the presence of **1a** (0.2 equiv) at  $60^\circ\text{C}$ . The polymerization was complete within 0.5 h, and the desired poly(butyl acrylate) (PBA) was obtained in 82% yield. The  $M_n$  of 11 600 was close to the theoretical value



**Figure 4.** (a) First-order plot of monomer conversion vs time and (b) correlation of  $M_n$  and PDI with monomer conversion for the bulk polymerization of styrene (100 equiv) at 60 °C in the presence of **3** and **1a**.

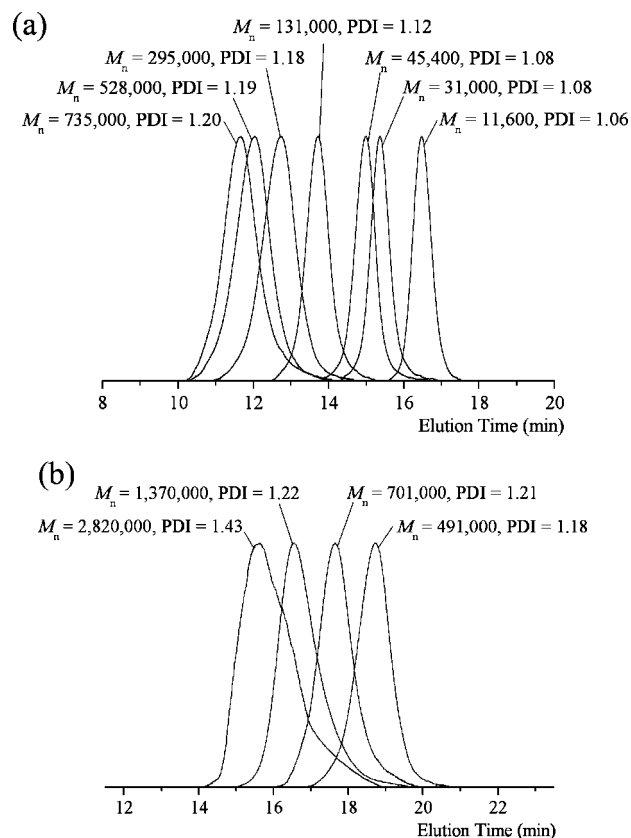
**Table 2.** Organobismuthine-Mediated Living Radical Polymerization of BA in the Presence of Cocatalyst **1a**<sup>a</sup>

| run | equiv of BA | time (h) | conv. (%) <sup>b</sup> | $M_{n,theor}$ | $M_{n,exp}$ <sup>c</sup> | PDI <sup>c</sup> |
|-----|-------------|----------|------------------------|---------------|--------------------------|------------------|
| 1   | 100         | 0.5      | 82                     | 10 500        | 11 600                   | 1.06             |
| 2   | 500         | 1.5      | 85                     | 54 400        | 45 400                   | 1.08             |
| 3   | 1000        | 2        | 82                     | 105 000       | 131 000                  | 1.12             |
| 4   | 4000        | 4        | 72                     | 369 000       | 295 000                  | 1.18             |
| 5   | 8000        | 5        | 63                     | 646 000       | 528 000                  | 1.19             |
|     |             |          |                        |               | (491 000)                | (1.18)           |
| 6   | 10000       | 6        | 58                     | 743 000       | 735 000                  | 1.20             |
|     |             |          |                        |               | (701 000)                | (1.21)           |
| 7   | 20000       | 7        | 47                     | 1 200 000     | 1 370 000                | 1.22             |
| 8   | 50000       | 9        | 41                     | 2 630 000     | 2 820 000                | 1.43             |

<sup>a</sup> A mixture of **3**, **1a** (0.2 equiv), AIBN (0.2 equiv), and BA (100–50000 equiv) was heated under a nitrogen atmosphere. <sup>b</sup> Monomer conversion was determined by <sup>1</sup>H NMR. <sup>c</sup> Number-average molecular weight ( $M_n$ ) and polydispersity index (PDI =  $M_w/M_n$ ) were obtained by size exclusion chromatography, which was calibrated using polyMMA standards. Two linearly connected columns with exclusion limits of  $2 \times 10^6$  using CHCl<sub>3</sub> as the eluent were used for runs 1–6, and a similar setup with exclusion limits of  $2 \times 10^7$  using THF as the eluent was used for runs 5–8. The data obtained for runs 5 and 6 using the THF system are shown in parentheses.

calculated from the BA/2 ratio, and the PDI was 1.06 (Table 2, run 1). The rate of polymerization followed first-order kinetics with respect to the monomer, and  $M_n$  increased linearly with monomer conversion (see the Supporting Information). These results are again consistent with the living character of the polymerization.

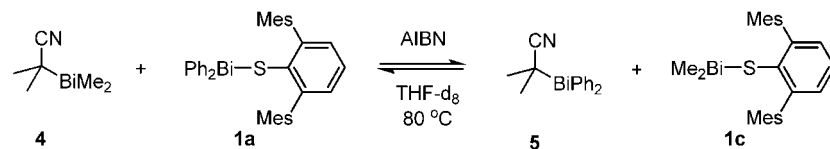
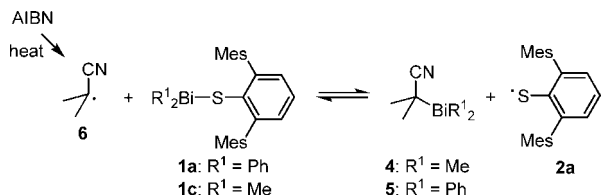
We also examined the synthesis of high and ultrahigh molecular weight PBAs by increasing the BA/3 ratio from 500 to 50 000 in the presence of 0.2 equiv of **1a** (Table 2, runs 2–8). The range of  $M_n$ 's obtained for the resulting PBAs was so wide that two sets of GPC columns were necessary for the analysis:



**Figure 5.** GPC traces of PBA samples prepared by varying the BA/3 ratio, as measured by GPC columns with exclusion limits of (a)  $2 \times 10^6$  and (b)  $2 \times 10^7$ .

the exclusion limit of the first system was  $M_n = 2 \times 10^6$  and that of the second was  $2 \times 10^7$ . We found that the  $M_n$  increased linearly with the BA/3 ratio, although the monomer conversion decreased as a result of the increase in viscosity of the reaction mixture. Highly controlled PBAs with low PDIs and  $M_n$ 's close to their theoretical values were obtained in all cases. The GPC traces for all of the PBAs were unimodal, and the peak maxima shifted to higher molecular weight as the targeted molecular weight increased (Figure 5). It is worth noting that a PBA with an  $M_n$  of  $1.4 \times 10^6$  and a PDI of 1.22 was obtained at 47% monomer conversion when 20 000 equiv of BA was employed (Table 2, run 7). Moreover, a PBA with an  $M_n$  of  $2.8 \times 10^6$  was obtained at 41% monomer conversion when 50 000 equiv of BA was employed (Table 2, run 8). Although the PDI of the latter product was slightly larger (1.43) than those of the smaller molecular weight polymers, it is still acceptable. This product represents the highest molecular weight polyacrylate synthesized to date in a controlled manner by LRP from a monofunctional chain-transfer agent under ambient conditions.

**Mechanism of Action of the Cocatalyst.** The role of cocatalyst **1** was examined. First, a 1:1 mixture of organobismuthine chain-transfer agent **4** and thiobismuthine **1a** was heated in the presence of AIBN (0.1 equiv) in THF-*d*<sub>8</sub> at 80 °C in an NMR tube (Scheme 4), and the reaction mixture was monitored by <sup>1</sup>H NMR. Equal amounts of **4** and **1a** were slowly consumed, and a new set of signals corresponding to organobismuthine **5** and thiobismuthine **1c** appeared. The reaction reached a 4/5 (or **1a/1c**) ratio of 8:2 after 3 h, and the ratio did not change further on prolonged heating. Next, the reverse reaction, starting from a mixture of **5** and **1c**, was examined at 80 °C in the presence of 0.1 equiv of AIBN. Although the reaction was slow and

**Scheme 4.** Bismuthanyl-Group Exchange Reaction between Organobismuthine and Thiobismuthine**Scheme 5.** Radical-Mediated Exchange Reaction of Bismuthanyl Groups

further addition of AIBN was required (0.1 equiv at 3, 6, and 9 h), an 8:2 mixture of **4** (or **1a**) and **5** (or **1c**) was eventually reached after 11 h. These results indicate that equilibrium was reached in both cases.

A plausible mechanism to account for this exchange reaction is shown in Scheme 5. The carbon-centered radical **6** generated from AIBN reacts with **1a** or **1c** to give **5** or **4**, respectively, and 2,6-dimesitylphenylthiyl radical (**2a**). This thiyl radical then reacts with **5** or **4** to regenerate **6** and **1a** or **1c**, respectively. Both the reaction of **6** with **1** and that of **2a** with **4** or **5** take place unselectively, regardless of the substituent on the bismuth atom ( $R^1 = \text{Ph}$  or  $\text{Me}$ ). Therefore, the reaction eventually reaches equilibrium to give a statistical mixture of compounds.

These results also imply that the homolytic substitution reaction of the polymer-end radical with **1a** occurs as shown in Scheme 2. This effective deactivation of the polymer-end radical must be responsible for both the increased control of the PDI and the successful synthesis of high molecular weight polymers that was possible in the presence of **1a**. The results may also be explained by the formation of a stable (but not persistent) hypervalent bismuthanyl radical via the reaction of the polymer-end radical with **1a**. However, this scenario is less likely, because if such a radical formed, retardation of the polymerization rate would be observed as a result of the occurrence of chain-breaking termination reactions, as observed in RAFT polymerization.<sup>52–56</sup>

## Conclusion

We have shown that highly controlled BIRP is possible by carrying out the polymerization in the presence of a newly designed arylthiobismuthine cocatalyst **1a**. High molecular weight polystyrenes and ultrahigh molecular weight poly(butyl acrylate)s have been synthesized in a controlled manner in the presence of this cocatalyst. In addition to its synthetic utility, this work also provides insight into the fundamental reactivities of diheteroatom compounds in radical reactions. The reactivity

of the Bi–S bond toward carbon-centered radicals and the presence of a sterically bulky aryl group on the sulfur atom of the cocatalyst are responsible for our success in the synthesis of high molecular weight polymers. We believe that this work opens the possibility of designing new heteroatom compounds for the precise control of radical reactions and living radical polymerization.

## Experimental Section

**Preparation of Diphenyl(2,6-dimesitylphenylthio)bismuthine (1a).** *n*-Butyllithium (11.0 mL, 1.55 M solution in hexane, 17 mmol) was slowly added to a solution of 2,6-dimesitylbenzenethiol<sup>50</sup> (5.89 g, 17 mmol) in ether (30 mL) at  $-78$  °C. The resulting mixture was stirred for 1 h at this temperature and then slowly warmed to room temperature over 1 h. Diphenylbismuthanyl bromide<sup>51</sup> (6.65 g, 15 mmol) was added to the reaction mixture at 0 °C, after which the mixture was stirred for 2 h at room temperature. Water was added, and the organic phase was separated. The organic phase was successively washed with saturated aqueous  $\text{NH}_4\text{Cl}$  solution and saturated aqueous  $\text{NaCl}$  solution, dried over  $\text{MgSO}_4$ , and then passed through a pad of Celite. Removal of the solvent under reduced pressure and recrystallization of the residue from chloroform/hexane gave 7.32 g of **1a** as pale-yellow crystals (69% yield). Mp: 140.0–142.4 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.03 (s, 12H, *o*- $\text{CH}_3$  of mesityl), 2.30 (s, 6H, *p*- $\text{CH}_3$  of mesityl), 6.87 (s, 4H, *m*-H of mesityl), 7.13 (d,  $J = 7.6$  Hz, 2H, *m*-H of SAR), 7.20 (tt,  $J = 7.6, 1.2$  Hz, 2H, *p*-H of  $\text{BiPh}_2$ ), 7.26–7.32 (m, 1H, *p*-H of SAR, 4H, *m*-H of  $\text{BiPh}_2$ ), 7.44 (dt,  $J = 6.8, 1.2$  Hz, 4H, *o*-H of  $\text{BiPh}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.00, 21.12, 127.19, 127.55, 128.28, 128.82, 130.65, 133.84, 135.79, 136.46, 136.92, 139.37, 146.63, 165.51. HRMS (EI)  $m/z$ : calcd for  $\text{C}_{36}\text{H}_{35}\text{SBi}$  ( $M$ )<sup>+</sup>, 708.2262; found, 708.2263. IR (neat): 815, 1135, 1185, 1270, 1460, 1695, 2940  $\text{cm}^{-1}$ .

**Typical Procedure for Polymerization of Styrene.** A solution of styrene (1.15 mL, 10.0 mmol), **1a** (14.2 mg, 0.020 mmol), AIBN (3.28 mg, 0.020 mmol), and **3**<sup>17</sup> (18.28  $\mu\text{L}$ , 0.10 mmol) was heated at 60 °C for 24 h with stirring under a nitrogen atmosphere in a glovebox. A small portion of the reaction mixture was extracted and dissolved in  $\text{CDCl}_3$ . The conversion of the monomer (96%) was determined by  $^1\text{H}$  NMR. The rest of the reaction mixture was dissolved in a 10 mM TEMPO/ $\text{CHCl}_3$  solution (4 mL) and poured into vigorously stirred methanol (200 mL). The product was collected by filtration and dried under reduced pressure at 40 °C to give 0.99 g of polystyrene. The  $M_n$  (10 900) and PDI (1.07) were determined by GPC calibrated using polystyrene standards.

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**Supporting Information Available:** Synthesis of **1b**, **1c**, and **4**; typical procedure and kinetic plots for polymerization of butyl acrylates; and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for all of the new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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