New Selenium-Based Iniferter Agent for Living Free Radical Polymerization of Styrene Under UV Irradiation

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ABSTRACT: P,P'-Diphenyl phosphinodiselenoic acid benzyl ester was synthesized and used as a mediator for the polymerization of styrene under UV–vis irradiation. Moderately controlled evidence was found: linear polymerization kinetics, linear evolution of molecular weight with monomer conversion, and relatively narrow molecular weight distribution (1.5–2.0). The structure of the obtained polymers was characterized using NMR and oxidative elimination. Based on polymerization results, an iniferter mechanism was proposed for the current polymerization system.

INTRODUCTION In the past decades, the growing demand for functionalized, structurally well-defined, polymeric materials has been a driving force for the development of controlled/“living” radical polymerization (CRP) techniques. Several CRP methods have been well developed, such as atom transfer radical polymerization (ATRP),1,2 stable free radical polymerization,3,4 and reversible addition-fragmentation chain transfer (RAFT) polymerization, and so on.5,6 The key step for realizing CRP process is the establishment of a fast equilibrium between dormant species and active free radicals, which ensures the low concentration of propagating free radical to reduce the termination reaction while keeping considerable polymerization rate.7,8 Many compounds, such as dithiocarbonyl compounds,5 transition metals,9 and stable free radicals,5 have been developed as the mediator to establish such equilibrium. Among them, dithiocarbonyl compounds have proven as the most versatile mediator.10 For the RAFT polymerization, dithiocarbonyl compounds acted as a chain transfer agent, and through such reversible transfer and fragmentation, the polymerization process proceeded in a controlled way.5 Further investigation proved that dithiocarbonyl compounds also can be used as an ATRP mediator.11 Based on these earlier reports, selenium- and tellurium-containing organic compounds, which showed similar outer side electronic structure as sulfur, have been also investigated as the mediator for CRP.12–17

According to the mechanism of CRP, the moiety of mediator can be introduced into polymer chain end.8,18,19 Thus, selenium or tellurium elements can be attached to the polymer chain ends by using selenium- or tellurium-containing mediators. It was already known that organoselenium compounds play important roles in organic synthesis and biological system.20–22 Selenium-containing compounds have been widely used in the pharmacochemistry as antioxidants for the well-known glutathioneperoxidase activity.23–25 Over the last several years, various unusual and attractive compounds and polymers containing selenium moieties have been prepared. Han and coworkers developed a near-IR reversible fluorescent probe containing an organoselenium functional group.26 Zhang and coworkers synthesized selenide-containing block copolymers and investigated their dual redox responsive disassembly.27,28 Lee and cooperators synthesized phosphinodiselenoic esters and used it as the mediator for styrene polymerization. They suggested a RAFT mechanism for the phosphinodiselenoic ester-mediated polymerization.29,30

In this work, based on potential applications of polymers containing selenium moieties, we combined benzylseleno...
group and \(PP\)-diphenyl phosphinoseleno group together to compose \(RP\)-diphenyl phosphinodiselenoic acid benzyl ester (DPPSB). The polymerization behavior of styrene using DPPSB as the mediator under different conditions was investigated. The mechanism of the polymerization was proposed based on the polymerization behavior and polymer structures.

EXPERIMENTAL

Materials

Chlorodiphenylphosphine (ClPPh₂, 98%) was purchased from Subaosheng Chemical Reagents, China. Se powder (99.95%) was purchased from Shanghai Meixing Chemical Reagents, China. All other chemicals (analytical grade) used in this study were purchased from Shanghai Chemical Reagents. Styrene was washed with an aqueous solution of sodium hydroxide (5 wt %) three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, styrene was distilled under reduced pressure and kept in a refrigerator under 0°C to 14°C. 2,2'-Azobisobutyronitrile (AIBN, 98%) was recrystallized from ethanol and kept in a refrigerator under 4°C to 14°C. Diethyl ether (Et₂O) and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl prior to use. Other chemicals were used as received.

Synthesis of DPPSB

The DPPSB was synthesized according to the modified literature procedure (Scheme 2). To a suspension of elemental selenium (0.8 mg, 10.0 mmol) in Et₂O (30 mL), 5.0 mL of benzylmagnesium chloride (2.0 M in Et₂O, 10 mmol) was added at 0°C, and the mixture was stirred for 30 min. A 10 mL THF solution of diphenylphosphinoselenoic chloride (3.0 g, 10 mmol), obtained from the reaction of ClPPh₂ with selenium in toluene at 120°C for 3 h in almost quantitative yield, was then added dropwise to this mixture over a period of 10 min at 0°C with vigorous stirring. This reaction mixture was heated to room temperature and stirred for 1 h. After removal of the solvent, the mixture was purified by column chromatography on silica gel to afford crude product. The crude product was then purified by recrystallization from n-hexane, and a light yellow solid was obtained.

Typical Polymerization Procedure

A dry 1 mL ampule was filled with styrene (0.6 mL, 5.24 mmol) and DPPSB (11.4 mg, 0.026 mmol). The solution was deoxygenated with three standard freeze–pump–thaw cycles. The ampoule was then flame sealed and placed under UV–vis radiation of a 300 W high-pressure mercury vapor lamp with distance of 50 cm at 30°C ± 1°C. At timed intervals, the ampule was immersed in ice water and then opened. The contents were dissolved in 1 mL of THF and then precipitated into 200 mL of methanol. The polymer was obtained by filtration and dried at room temperature under vacuum to constant weight. Conversion of styrene was determined gravimetrically.

Typical Chain Extension Experiment

The procedure of chain extension experiment was similar to those described above except that the DPPSB was replaced by the obtained polystyrene.

Oxidative Elimination of Terminal Group

A solution of polystyrene (PS) (0.05 g, \(M_n\),GPC = 11,400 g/mol, polydispersity index (PDI) = 2.12) and 0.25 g hydrogen peroxide (30 wt %) in 2.0 mL of THF was stirred for a week at room temperature. The solution was poured into methanol to precipitate polymer. The polymer was collected by filtration and was dried in vacuum at room temperature.
TABLE 1 Polymerization of Styrene with DPPSB Under Heating

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymerization Condition</th>
<th>Con. (%)</th>
<th>M_n,GPC</th>
<th>M_n,SR</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>T = 80 °C, t = 3.5 h</td>
<td>35.2</td>
<td>36,400</td>
<td>12,200</td>
<td>2.23</td>
</tr>
<tr>
<td>2a</td>
<td>T = 80 °C, t = 7.0 h</td>
<td>45.8</td>
<td>42,200</td>
<td>15,900</td>
<td>2.72</td>
</tr>
<tr>
<td>3a</td>
<td>T = 60 °C, t = 22.0 h</td>
<td>27.5</td>
<td>46,300</td>
<td>9,500</td>
<td>2.51</td>
</tr>
<tr>
<td>4a</td>
<td>T = 60 °C, t = 5.3 h</td>
<td>39.8</td>
<td>9,300</td>
<td>1,400</td>
<td>1.77</td>
</tr>
<tr>
<td>5a</td>
<td>T = 120 °C, t = 8.0 h</td>
<td>5.4</td>
<td>6,100</td>
<td>1,100</td>
<td>1.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13,230</td>
<td></td>
<td>1.84</td>
</tr>
</tbody>
</table>

a Determined by GPC.
b PDIa = (Mn,MH×Mn,monomer)/Mn,monomer + Conversion + MDPSSB.

Characterization

The number-average molecular weight ($M_n$) and molecular weight distribution ($M_n/M_w$) of the resultant polymers were determined using a Waters 1515 gel permeation chromatography (GPC) equipped with a refractive-index detector. The sample was dissolved in 1:1 (v/v) acetoniqol and sample were introduced with PS standards purchased from Waters. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry measurement was performed using a Bruker Autoflex III (MALDI-TOF) mass spectrometer equipped with a 337 nm nitrogen laser. Both matrice 4-hydroxy-α-cyanocinnamic acid and sample were dissolved in 1:1 (v/v) acetonitrile: water with 1% trifluoroacetic acid. The mixture solution (0.5 mL) was placed on a metal sample plate. The sample was air-dried at ambient temperature. The $^1$H NMR, $^{31}$P NMR, and $^{13}$C NMR spectra were recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using CDCl₃ as the solvent.

RESULTS AND DISCUSSION

Polymerization with DPPSB Under Heating

Gigmers et al. reported that dithiophosphinate esters can be used as RAFT agent to conduct styrene polymerization in living free radical polymerization manner. Following such report, Lee and coworkers synthesized DPPSB and demonstrated the polymerization behavior of styrene in thermal initiating. They proposed a RAFT polymerization mechanism for such polymerization. The polymerization showed linear kinetics. However, the polymers with broad molecular weight distribution were obtained in their results. Actually, it seems to be dangerous to draw a conclusion of living behavior due to the lack of the key data, such as the relationship between measured molecular weight and theoretical value, and characterization of chain ends. In this work, we first investigated the DPPSB polymerizations of styrene both in cases of thermal initiation and AIBN initiation. It should be noted that the structure of DPPSB with benzyl group attached with selenium (Scheme 2), which differs with that reported by Lee and coworkers who used phenyl-type groups in their compounds. Normally, the benzyl group was superior to phenyl group as initiating free radical.

The polymerization results are summarized in Table 1. The polymers with uncontrolled molecular weights and broad molecular weight distributions were obtained in all of these attempts. These results were similar to the literature, however, differed far away from typical RAFT polymerization. In the case of thermal-initiated polymerization, the GPC of obtained polymer even showed double peaks with one peak at 6100 g/mol and another peak at 13,230 g/mol. These results indicated that under heating conditions, DPPSB was not an effective mediator for the controlled polymerization of styrene.

Polymerization of Styrene With DPPSB Under UV-vis

UV-vis was another initiating source for free radical polymerization. One of the first living/controlled free radical polymerization examples was conducted under the irradiation of UV-vis, reported by Otsu et al. in 1980s. Since then, many dithiocarbamate compounds have been used to mediate CRPs under UV-vis irradiation. In this work, we investigated the polymerization behavior of styrene with the presence of DPPSB under UV-vis irradiation.

The polymerization was performed using 300 W high-pressure mercury lamp as the light source with distance of 50 cm. The light power at 365 nm was 282 μW/cm².

Figure 1 shows the polymerization kinetics in different conditions. As shown in Figure 1, styrene could be polymerized under the 365 nm UV irradiation with the apparent rate constant $k_{app} = 1.68 \times 10^{-3}$ h⁻¹ of the polymerization. After introducing DPPSB, the polymerization rate was enhanced significantly. The $k_{app}$ increased to $6.83 \times 10^{-3}$ h⁻¹ in the
case of \([\text{styrene}]_0:[\text{DPPSB}]_0 = 800:1\), which implied that DPPSB was involved in the initiating process of the polymerization. This hypothesis was confirmed by the increasing of polymerization rate to \(7.49 \times 10^{-3}\) \(\text{h}^{-1}\) when the ratio of \([\text{styrene}]_0:[\text{DPPSB}]_0\) was changed to 400:1. Similar polymerization rate was observed by further increasing the concentration of DPPSB to \([\text{styrene}]_0:[\text{DPPSB}]_0 = 200:1\). The kinetic results differed with the characters of RAFT polymerization. In RAFT polymerization, the increase of RAFT agent concentration could not result in an elevated polymerization rate.

The relationships of molecular weight and PDI of the polymer with conversion are shown in Figure 2. The molecular weight of the polymer increased linearly with the conversion in all cases and the value determined by GPC agreed well with the theoretical one, especially in cases of \([\text{styrene}]_0:[\text{DPPSB}]_0 = 800:1, 400:1\), and 200:1, respectively.

The polymerization was further investigated in various solvents. Different solvents, such as THF, \(\text{CH}_2\text{Cl}_2\), \(\text{CH}_3\text{Cl}\), toluene, DMF, and pyridine, were used in the polymerization. Similar polymerization behavior was found, for example, moderately controlled molecular weight with broad molecular weight distribution as shown in Table 2. These results indicated that the current polymerization system can be applied to control the molecular weight of polystyrene in various conditions, both in bulk and in solutions. The polymerization rate in solution was lower than that in bulk, and the polymerization rate was significantly reduced in THF, which may due to the high chain transfer effect occurred in THF. In other solvents, the polymerization showed comparable polymerization rate.

**Investigation of the End Groups to Clarify the Polymerization Mechanism**

The polymers obtained by DPPSB produced moderately controlled molecular weights (high PDI values), and the polymerization rate increased with the increase of DPPSB.
concentration. This result differed far from those from RAFT polymerization, as in RAFT polymerization, the polymerization rate usually decreased with the increase of RAFT agent. It would be valuable to investigate the chain end groups of the polymer for clarifying the polymerization mechanism.

First of all, PS-DPPSB was characterized with the $^1$H NMR spectrum, which was shown in Figure 3. There are two signals at $\delta = 3.90$–4.15 ppm (integral ratio = 1/2), which are ascribed to the protons of methyne (d) and methylene (f) neighboring at the Se atom. The signal at about $\delta = 3.25$–3.53 ppm is ascribed to the protons of the methylene (c) neighboring at the P atom. No signal at $\delta = 4.24$ ppm (as DPPSB) or lower field can be found in the spectrum.

Meanwhile, we determined the $^{31}$P NMR of the polymer and DPPSB. The spectra are shown in Figure 4.

The DPPSB shows $^{31}$P resonance signal at $\delta = 42.45$ ppm. This $^{31}$P resonance signal shifts to $32.45$–34.10 ppm in the polymer, which implies that (1) the phosphorus structure remained intact in the polymer; (2) the chemical environment around phosphorus atom was different in DPPSB and the polymer. There are two possibilities for phosphorus structure being attached to the polymer; for example, the polymer connected with phosphorus atom (showed in Fig. 4) or the polymer connected with selenium atom. The final structure would be decided by the bonding energy difference between C–Se and P–Se. The bonding energy of C–Se is 362 kJ/mol, whereas the bonding energy of P–Se is 324 kJ/mol, which is more close to the energy of 365 nm light (328 kJ/mol). Thus, under the irradiation of 365 nm of UV light, DPPSB prefers to decompose by the cleavage of P–Se bond, which evidently resulted in the phosphorus atom attached directly with polymer chain (structure shown in Fig. 3). The UV-vis absorptions of (1) DPPSB, (2) PS-DPPSB, (3) BzSe-PS-SeBz, and (4) p-styryl phenyl selenide were compared in Figure 5. The maximum adsorption peak of DPPSB was appeared at wavelength lower than 230 nm. However, in the case of PS-DPPSB, it showed maximum adsorption peak at 262 nm, which was very similar to the adsorption peak of BzSe-PS-SeBz and p-styryl phenyl selenide. The results implied that the Ph$_2$P(Se)=Se moiety of DPPSB may decompose during the polymerization resulting in the formation of –C–Se–C– moiety in the polymer. Such result agreed with the structure deduced from NMR analysis.

![Figure 4](Image)

**FIGURE 4** $^{31}$P NMR spectrum of polystyrene obtained from DPPSB-mediated polymerization. ($M_{n,GPC} = 17,000$ g/mol, PDI = 2.62) obtained in toluene under UV–vis irradiation at 30 °C with the molar ratio of [DPPSB]:[St]$_0$ = 1:400 with CDCl$_3$ as the solvent.

![Figure 5](Image)

**FIGURE 5** UV–vis spectra in CH$_2$Cl$_2$ solution with $10^{-4}$ M concentration at room temperature. (1) DPPSB. (2) PS obtained from DPPSB-mediated polymerization under UV–vis irradiation ($M_{n,GPC} = 19,000$, PDI = 2.62). (3) PS obtained from dibenzyl diselenide-mediated polymerization with the molar ratio [St]$_0$:[Dibenzyl diselenide]$_0$:[AIBN]$_0$ = 400:1:0.5 under heating at 60 °C ($M_{n,GPC} = 19,100$, PDI = 2.44 Con. = 48.5%). (4) p-styryl phenyl selenide.

![Scheme 3](Image)

**SCHEME 3** Oxidative elimination of DPPSB moiety from polystyrene by H$_2$O$_2$. 

![Mathml View](Image)

**Mathml View**
The C-Se structure could be cleaved under oxidation condition, which was used to confirm the hypothetical structure (Scheme 3). The polymer reacted with H₂O₂ in room temperature for 1 week to eliminate C-Se structure. The ³¹P resonance signal in oxidized polymer shifted to 30.67–31.72 ppm (Fig. 6) from the original 32.45–34.10 ppm, which was the result of oxidation of the remained selenium (structure shown in Fig. 6). The ¹H NMR spectrum of oxidized polymer (Fig. 7) further confirmed the cleavage of C-Se bond to form carbon–carbon double bond in the chain end. In Figure 5, the signals at about δ = 7.32–7.70 ppm (a) were ascribed to the protons of the phenyl from oxydic P,P-diphenyl phosphinoseleno group. The signals at δ = 3.06 ppm (b) corresponded to the protons of methylene neighboring at P,P-diphenyl phosphinoseleno group. The signals at δ = 3.74 ppm (c) were ascribed to the proton of methylene neighboring at the C–C double bond. The signals at δ = 6.00–6.20 ppm (d, f) corresponded to the vinylene protons.

The molecular weight and molecular weight distribution of the polymers with their GPC traces before and after oxidation are shown in Figure 8. The molecular weight of oxidative polymer was 11,000 g/mol, which was very close to the molecular weight of the polymer before oxidative, for example, 11,400 g/mol. This result indicated that the C-Se bond was connected on the terminal rather than in the middle of the polymer chain. The unimodal GPC trace of the polymer before and after oxidation further confirmed that the C-Se bond was attached on the chain end of the polymer.

Based on aforementioned investigations, the mechanism of the polymerization is assumed as shown in Scheme 4. DPPSB decomposed under UV–vis irradiation into two parts by the cleavage of P-Se bond to form P,P-diphenyl phosphinoseleno radical (1) and benzylseleno radical (2). Species 3 reacted with monomer forming the propagating radical 4. The polymerization was controlled by reversible termination of active propagating radicals 4 with benzylseleno radical (2) to form dormant species 5. Control experiment showed that benzylseleno radical (2) cannot initiate styrene to polymerize (Table 3). It shows that dibenzyl diselenide cannot initiate the polymerization within 120 h under the irradiation of 365 nm light. Therefore, the current polymerization was supposed to be via an iniferter process. The results from the polymerization profiles with the variation of DPPSB also supported the iniferter process (Fig. 1), for example, linear relationship between molecular weight and conversion,
polymers showed higher molecular weight than theoretical value and broad molecular weight distribution.\(^{10}\)

**Chain Extension and Polymerization of Methyl (Meth)acrylate Under UV–vis Irradiation**

Based on the iniferter mechanism, the polymers can be used as microiniferter agent to conduct chain extension reaction. The chain extension experiments of the polystyrene obtained by using DPPSB as mediator under irradiation of 365 nm light were carried out to confirm the mechanism. Figure 9 shows the respective GPC curves of DPPSB-PS before (a) and after (b) the chain extensions with styrene. There was an obvious peak shift from the macroiniferter agent to the chain-extended product. The molecular weight increased from 5200 g/mol (PDI = 1.68) to 27,100 g/mol (PDI = 3.36, time = 102 h, and conversion = 33.8%). PDI value of the chain extension product was larger than that of the original polymer, which might be caused by a fraction of the dead polymer chains in the original polymer and the side reactions during the chain extension. It can be concluded from the above results that most chains of DPPSB-PS were still living, and the polymerizations complied with the classical iniferter polymerization mechanism.

Similar polymerization procedure can be applicable to other monomers to investigate the universality of polymerization mediated by DPPSB. The monomers of methyl methacrylate (MMA) and methyl acrylate (MA) were polymerized under same conditions. The polymerization results summarized in Table 4 indicated poor controllability of DPPSB for these monomers with largely deviated molecular weights.

**TABLE 3** Polymerization of Styrene With Dibenzyl Diselenide Under UV–Vis Irradiation at 30 °C

<table>
<thead>
<tr>
<th>Entry</th>
<th>t (h)</th>
<th>Con. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{a})</td>
<td>120</td>
<td>0</td>
</tr>
<tr>
<td>2(^{b})</td>
<td>85</td>
<td>24.2</td>
</tr>
</tbody>
</table>

\(^{a}\) [St]_0:[Dibenzyl diselenide]_0 = 200:1, St = 0.5 mL, toluene = 0.5 mL.  
\(^{b}\) [St]_0:[Diphenyl diselenide]_0 = 200:1, St = 0.5 mL, toluene = 0.25 mL.

**TABLE 4** Polymerization of MMA and MA Under UV–Vis Irradiation at 30 °C

<table>
<thead>
<tr>
<th>Item</th>
<th>Monomer</th>
<th>t (h)</th>
<th>Con. (%)</th>
<th>(M_{n,GPC})</th>
<th>(M_{n,THF})</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{a})</td>
<td>MMA</td>
<td>38</td>
<td>38.9</td>
<td>26,700</td>
<td>19,400</td>
<td>1.70</td>
</tr>
<tr>
<td>2</td>
<td>MA</td>
<td>38</td>
<td>22.1</td>
<td>23,300</td>
<td>9,500</td>
<td>2.31</td>
</tr>
<tr>
<td>3(^{b})</td>
<td>MMA</td>
<td>58</td>
<td>50.9</td>
<td>28,200</td>
<td>10,200</td>
<td>1.73</td>
</tr>
<tr>
<td>4</td>
<td>MA</td>
<td>86</td>
<td>45.4</td>
<td>22,300</td>
<td>7,800</td>
<td>1.29</td>
</tr>
</tbody>
</table>

\(^{a}\) 1–2: [Monomer]_0:[DPPSB]_0 = 500:1, monomer = 0.5 mL, THF = 0.25 mL.  
\(^{b}\) 3–4: [Monomer]_0:[DPPSB]_0 = 200:1, monomer = 0.5 mL, toluene = 0.25 mL.

**CONCLUSIONS**

In this work, DPPSB was synthesized and used as a mediator for the polymerization of styrene. Through variation of polymerization condition, ultimately, the polymerization of styrene with DPPSB as the iniferter under UV-vis irradiation proceeded via a living radical mechanism. The
polymerization mediated by DPPSB was mildly controlled. Based on polymerization results, an iniferter mechanism was suggested. Despite of the not so perfect control over the polymerization, the polymerization from selenium-containing mediator provided an alternative method to synthesis selenium-containing polymers, which may have potential application in biological and biomedical area.

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