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Synthesis of phosphinodiselenoic acid esters and their application as RAFT agents in styrene polymerization

Jeonju Moon [a], Hyungoog Nam [a], Sangseop Kim [b], Jeonga Ryu [b], Changhun Han [b], Chanhong Lee [b], Sunwoo Lee [a,*]

[a] *Department of Chemistry, Chonnam National University, 300 Yongbong-dong, Buk-gu, Gwangju 500-757, Republic of Korea*
[b] *Petrochemicals and Polymers R&D, LG Chem, Ltd/Research Park, 104-1, Moonji-dong, Yuseong-gu, Daejeon 305-380, Republic of Korea*

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ABSTRACT

Phosphinodiselenoic acid esters are synthesized from the reaction of chlorodiphenylphosphine and aryl- or alkyl-magnesium bromide in the presence of selenium powder. They are employed as RAFT agents in thermally initiated, styrene polymerization. The phosphinodiselenoic acid esters **6a** and **6b** showed some degree of control over the radical polymerization of styrene.

Conventional radical polymerization has been used widely in industry because of its simple procedure and water-friendliness, along with the functional group tolerance of monomers.[1] However, control of the polymerization is very difficult due to the very short average lifetime of a radical. In order to overcome such problems, three main types of controlled radical polymerization have been reported: nitroxide-mediated polymerization (NMP),[2] atom transfer radical polymerization (ATRP)[3] and reversible addition fragmentation transfer polymerization (RAFT).[4] The latter, which has recently been reported by Rizzardo et al., allows the synthesis of polymers with well-defined molecular weight, polydispersities and architectures, and can be applied to all monomers at low temperature.[5] The RAFT process has been found applicable in both homogeneous and heterogeneous media.

The general structure of RAFT agents is based on the dithiocarboxylate moieties **1** (Fig. 1). However, Gigmes et al. reported that dithiophosphinate esters **2** were used as RAFT agents instead of dithioesters.[6] Subsequently, Coote et al. suggested that phosphinodithiolate may have only limited use in controlling free-radical polymerization based on high-level, ab initio calculations.[7] Recently, Murai et al. reported the synthetic method of *P*-chiral phosphinodiselenoic esters **3** bearing a P=Se double bond and a P–Se single bond.[8] We expected the phosphinodiselenoic acid esters to show better activity than phosphinodithiolate, because the bond energy of carbon–selenium is lower than that of carbon–sulfur.[9] This expectation stimulated us to synthesize the phosphinodiselenoic acid esters and use them as RAFT agents. In the presence of phosphinodiselenoic acid esters, the polymerization of styrene proceeded in a similar way[6] in the presence of phosphinodithiolates (Scheme 1). The propagating radical is added to the selenium atom of the P=Se double bond and led to the phosphoranyl radical. This radical compound fragments the new propagating radical and generates the phosphinoselenium-capped polymer.

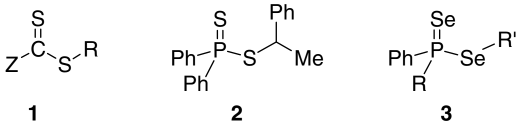

Figure 1. RAFT agents.

In this Letter, we report the synthesis of phosphinodiselenoic esters and demonstrate their efficiency as a RAFT agent in the polymerization of styrene. To synthesize the phosphinodiselenoic esters, we reacted the starting material chlorodiphenylphosphine ($ClPPh_2$) with selenium in toluene at 120 °C for 3 h (Scheme 2). The black brown suspension mixture was converted to clear solution, and thin layer chromatography (TLC) showed only one spot. The desired product, diphenylphosphinoselenoic chloride (**4**), was

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* Corresponding author. Tel.: +82 62 530 3385; fax: +82 62 530 3389.
E-mail address: sunwoo@chonnam.ac.kr (S. Lee).

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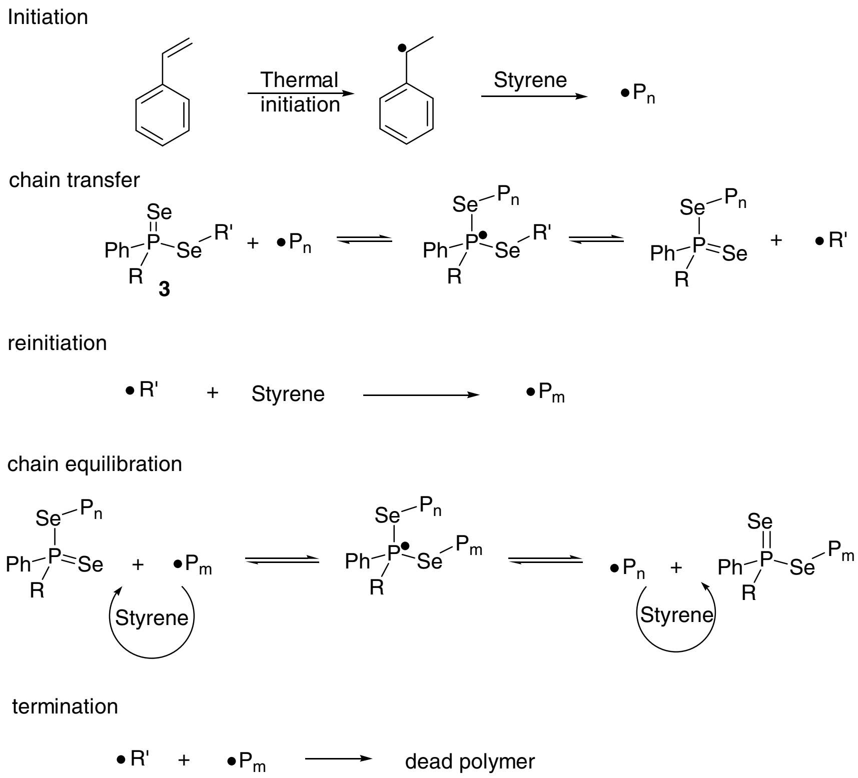
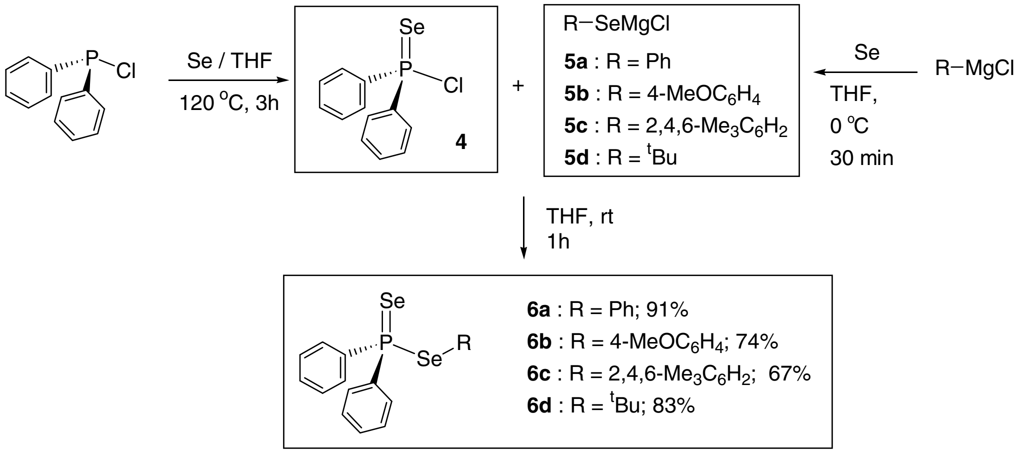


Scheme 1. Proposed mechanism of styrene polymerization in the presence of phosphinodiselenoic acid esters **3**.

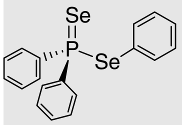
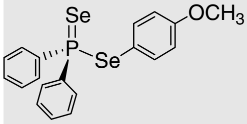
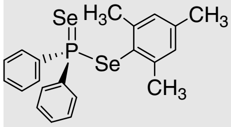
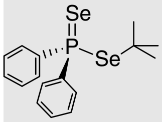
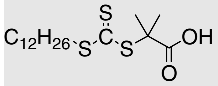


Scheme 2. Synthesis of diphenylphosphinodiselenoic (Ed-confirm spelling) acid esters.

obtained in almost quantitative yield and used in the next step without further purification. The addition of the reaction mixture of aryl- or alkyl-magnesium chloride (e.g., PhMgCl, 4-$MeOC_6H_4MgCl$, 2,4,6-$Me_3C_6H_2MgCl$, ^{t}BuMgCl) and elemental selenium, which formed the magnesium selenolate **5**, to phosphinoselenoic chloride afforded the corresponding diphenylphosphinodiselenoic acid esters **6** in moderate to good yields. Diphenylphosphinodiselenoic acid phenyl ester (**6a**) was obtained in 91% yield. More sterically hindered aryl-magnesium chlorides such as 2,4,6-$Me_3C_6H_2MgCl$ afforded the desired product **6c** with lower yield than the others. All products were purified by column chromatography and were stable under air and moisture condition. They were all characterized by nuclear magnetic resonance (NMR: ^{1}H, ^{13}C, ^{31}P), and mass and elemental analyses.[10]

Next, styrene was polymerized with diphenylphosphinodiselenoic acid esters as RAFT agents using thermal initiation. The purity of all RAFT agents was established by NMR analysis prior to use. RAFT styrene polymerization was performed at 126 °C without any solvent.[11] The molar ratio between the RAFT agent and styrene was kept constant at 400 in all the polymerization processes. The molar mass characteristics of the polymers were determined by gel permission chromatography. The molar mass evolutions were studied as a function of the conversion rate and time. In addition, in order to check their effectiveness as RAFT agents, we also obtained the polymerization data using the monocarboxyl-terminated trithiocarbonate **7**. The results are summarized in Table 1. Figures 2 and 3 illustrate the trends of M_n as a function of time and conversion rate of the polystyrenes.

Table 1
Evolution of number-average molecular weight of polystyrene versus conversion rate of styrene using RAFT agents

RAFT agent	Time (h)	Conversion (%)	M_n (g mol^{-1})	PDI
 **6a**	0.5	3.5	3970	1.6
	1	7.7	7130	2.5
	2	22.0	15,300	2.6
	3	35.9	16,900	2.6
	4	48.7	19,700	2.6
	5	58.7	21,800	2.6
 **6b**	0.5	3.0	2630	1.8
	1	6.9	5840	2.2
	2	22.0	15,600	2.4
	3	35.9	20,000	2.5
	4	47.3	21,600	2.5
	5	46.3	25,500	2.5
 **6c**	0.5	5.3	3740	1.8
	1	10.76	4880	2.0
	2	22.1	7910	2.8
	3	35.5	11,800	3.8
	4	47.9	14,800	4.8
	5	60.4	18,100	4.8
 **6d**	0.5	4.3	16,700	1.8
	1	7.7	18,100	2.0
	2	17.3	25,100	2.2
	3	27.2	30,800	2.3
	4	37.9	37,200	2.3
	5	46.7	39,500	2.2
 **7**	0.5	14.0	6527	1.1
	1	29.8	12,561	1.1
	1.5	45.9	16,966	1.1
	2	54.3	19,065	1.1
	2.5	65.4	21,796	1.1
	3	75.6	23,890	1.1
No RAFT agent	0.5	11.2	121,500	4.7
	1	18.5	160,800	5.3
	2	42.0	174,520	5.8

As shown in Table 1 and Figures 2 and 3, the number-average molecular weight increased linearly with time and degree of monomer conversion. The increasing trends with phosphinodiselenoic acid esters **6** were similar to those of RAFT agent **7**. Amongst them, **6a** and **6b** showed very similar trends in styrene polymerization. However, the polymerization performed in the presence of the phosphinodiselenoic acid esters **6** was somewhat slower than that performed with **7**. In 3 h, the phosphinodiselenoic acid esters **6** afforded a conversion yield below 36%, compared to over 75% for the trithiocarbonate **7**. The **6d** showed a low polymerization rate.

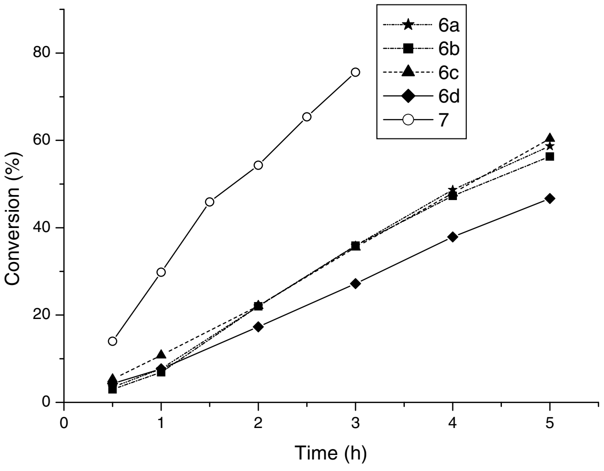


Figure 2. Trend of the conversion of thermally initiated RAFT polystyrenes as a function of time.

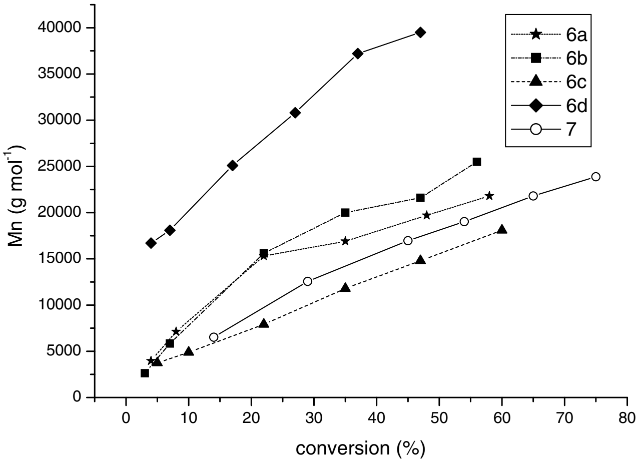


Figure 3. Trend of the number-average molar mass of thermally initiated RAFT polystyrenes as a function of conversion rate.

The number-average molecular weight of polystyrene using alkyl ester derivative **6d** was higher, and the polymerization rate was lower than those with the aryl ester derivatives (**6a**, **6b** and **6c**) and RAFT agent **7**. The polydispersity indices of polystyrene using **6a** and **6b** were 1.6–2.5, whilst that of polystyrene using **6c** was 4.8. These results suggested that phosphinodiselenoic acid esters **6a** and **6b** can act as RAFT agents, and exhibited living character in the polymerization of styrene.

We synthesized diphenylphosphinodiselenoic acid esters at high yields from chlorodiphenylphosphine. They were very stable towards air and moisture. To the best of our knowledge, this is the first report of their use as RAFT agents in styrene polymerization. Amongst them, the phosphinodiselenoic acid esters **6a** and **6b** showed living character in the polymerization of styrene.

Acknowledgement

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10. *Synthesis of phosphinodiselenoic acid esters*: To a suspension of elemental selenium (870 mg, 11.0 mmol) in THF (50 mL) was added 11.0 mL of phenylmagnesium chloride (1.0 M in THF, 11 mmol) at 0 °C, and the mixture was stirred at that temperature for 30 min. This mixture was added to 3.14 g of diphenylphosphinoselenoic chloride (10.5 mmol) in THF (30 mL) dropwise over a period of 10 min at 0 °C with vigorous stirring. The reaction mixture was raised to room temperature and stirred for 1 h. The desired product spot appeared in TLC (eluent hexane/EtOAc = 2:1, $R_f = 0.45$). After removal of the solvent, the crude mixture was purified by column chromatography on silica gel to afford 4.01 g (9.54 mmol, 91%) of **6a**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.88 (ddd, *J* = 14.7, 7.8, 1.8 Hz, 4H), 7.48–7.30 (m, 9H), 7.18 (dd, *J* = 7.8, 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 136.85 (d, *J* = 2.9 Hz), 13.277 (d, *J* = 66.8 Hz), 132.07 (d, *J* = 11.2 Hz), 131.78 (d, *J* = 3.2 Hz), 129.51 (d, *J* = 2.3 Hz), 129.37 (d, *J* = 13.3 Hz), 126.24 (d, *J* = 6.3 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 43.50 (366.4, 774.4 Hz); MS(EI) *m*/*z*: 422 (M^+); Anal. Calcd for $C_{18}H_{15}PSe_2$: C, 51.45; H, 3.60. Found: C, 51.74; H, 4.00. Compound **6b** (74%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.88 (ddd, *J* = 12.0, 7.8, 1.8 Hz, 4 H), 7.49–7.36 (m, 6H), 7.27 (dd, *J* = 8.7, 2.1 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 3.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.86 (d, *J* = 2.9 Hz), 138.40 (d, *J* = 2.8 Hz), 132.79 (d, *J* = 65.9 Hz), 132.07 (d, *J* = 11.2 Hz), 131.72 (d, *J* = 3.5 Hz), 128.35 (d, *J* = 13.3 Hz), 116.45 (d, *J* = 5.7 Hz), 114.79 (d, *J* = 2.6 Hz), 55.17; ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 43.29 (373.2, 771.5 Hz); MS(EI) *m*/*z*: 452 (M^+); Anal. Calcd for $C_{19}H_{17}OPSe_2$: C, 50.69; H, 3.81. Found: C, 51.02; H, 4.07. Compound **6c** (67%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.90 (ddd, *J* = 14.7, 8.4, 1.8 Hz, 4H), 7.45–7.36 (m, 6H), 6.88 (s, 2H), 2.24 (d, *J* = 2.4 Hz, 3H), 2.19 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.81 (d,*J* = 3.8 Hz), 139.78 (d, *J* = 3.8 Hz), 134.31 (d, *J* = 66.0 Hz), 131.87 (d, *J* = 10.9 Hz), 131.53 (d, *J* = 3.2 Hz), 128.97 (d, *J* = 2.9 Hz), 128.25 (d, *J* = 13.0 Hz), 125.98 (d, *J* = 6.3 Hz), 24.78, 21.06; ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 39.51 (380.9, 774.3 Hz); MS(EI) *m*/*z*: 464 (M^+); Anal. Calcd for $C_{21}H_{21}PSe_2$: C, 54.56; H, 4.58. Found: C, 54.83; H, 4.92. Compound **6d** (83%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.01 (ddd, *J* = 14.7, 7.8, 2.1 Hz, 4H), 7.47–7.42 (m, 6H), 1.57 (td, *J* = 6.0, 1.2 Hz, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 133.97 (d, *J* = 66.9 Hz), 132.14 (d, *J* = 11.2 Hz), 131.50 (d, *J* = 3.2 Hz), 128.33 (d, *J* = 12.9 Hz), 54.29 (d, *J* = 4.0 Hz), 32.97 (d, *J* = 3.8 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 30.92 (403.0, 760.9 Hz); MS(EI) *m*/*z*: 402 (M^+); Anal. Calcd for $C_{16}H_{19}PSe_2$: C, 48.02; H, 4.79. Found: C, 47.94; H, 4.88.
11. *Polymerization*: RAFT agent **6** (0.48 mmol) and styrene (20.0 g, 192.0 mmol) were added in a Schlenk flask. The reaction mixture was degassed by freeze and thaw cycles and sealed under nitrogen. Bulk thermally initiated polymerization was conducted at 126 °C. During the reaction, a sample was taken under nitrogen atmosphere and quenched in cold water, and then diluted with methylene chloride. The polymer was purified by precipitation from methylene chloride solution into methanol.