

Synthesis of Phosphinodiselenoic Acid Ester Derivatives and their Application in the Controlled Radical Polymerization of Styrene

Eunjin Song, Youngshin Jo, Goun Bae, Il-Kwon Oh,^{*} Hyun Min Jung,[†] and Sunwoo Lee^{*}

Department of Chemistry, Chonnam National University, Gwangju 500-757, Korea. *E-mail: sunwoo@chonnam.ac.kr

[†]School of Mechanical Systems Engineering, Chonnam National University, Gwangju 500-757, Korea

[‡]Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon 305-600, Korea

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Controlled radical polymerizations have been used widely in industry because they are easy to perform and offer a vast range of advanced and well-defined materials.¹ Three main types of controlled radical polymerization have been developed: nitroxide-mediated polymerization (NMP),² atom transfer radical polymerization (ATRP)³ and reversible addition fragmentation transfer polymerization (RAFT).⁴ They all use the principle of dynamic equilibration between active species and dormant chains. This equilibrium affects the molecular weights and polydispersities of polymers as well as the polymerization rates. In the reaction of NMP, the stable nitroxide radical TEMPO has been most frequently used as a trap for reactive alkyl radicals. The reaction of ATRP is catalyzed by several transition metals, but Cu(I) complexes have received the most attention. However, both NMP and ATRP can only be applied to a limited number of monomers, and require high reaction temperature and expensive reagents. The RAFT reaction has been controlled by a radical polymerization technique that was most recently developed and used mainly for dithioesters **1** to trap propagating radicals reversibly (Figure 1). Instead of dithioester derivatives, dithiophosphinate esters **2** and phosphinodiselenoic acid esters **3**, developed by Gimes *et al.*⁵ and by our group,⁶ respectively, have been reported as RAFT agents. In our recent paper, we employed phosphinodiselenoic acid esters as RAFT agents in thermally initiated styrene polymerization. They showed some degree of control over the radical polymerization of styrene.

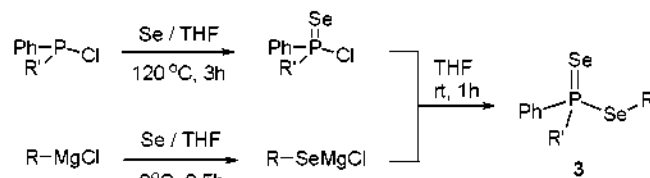
Based on our previous results and Murai's report,⁷ we synthesized several phosphinodiselenoic acid ester derivatives and investigated the relations between their structure features and their efficiencies as RAFT agents. We thought that the R group or R' group of the phosphinodiselenoic acid ester might affect the activities of control radical polymerization.

First, phosphinoselenoic chlorides were obtained from the reaction of phosphinic chlorides and selenium powder. The resulting products were stable to air and moisture and could therefore be used in the next step without further purification. The magnesium selenolates were easily obtained from the

reaction of selenium element and alkyl magnesium chloride in THF at 0 °C. Phosphinoselenoic chlorides and magnesium selenolates were reacted together to produce the corresponding phosphinodiselenoic acid alkyl esters in moderate to good yields. Diphenylphosphinodiselenoic acid butyl ester was obtained in 68% yield. And more sterically demanding alkylmagnesium chlorides, such as isopropylmagnesium chloride and cyclohexylmagnesium chloride, afforded the corresponding product with higher yield than *n*-butylmagnesium chloride. Benzylmagnesium chloride afforded the desired product in 80% yield. In addition, the chiral phosphinodiselenoic acid ester, such as *P*-isopropyl-*P*-phenylphosphinodiselenoic acid tolyl ester, was obtained in 51% yield from the reaction of 4-tolylselenomagnesium bromide and *P*-isopropyl-*P*-phenylphosphinoselenoic chloride in THF at room temperature. The product yield of the primary alkyl substituent in the R group was lower than that of the secondary or benzyl one. The synthetic method and final product yields are summarized in Table 1. All products were purified by column chromatography with silica gel and were stable toward air and moisture.

We next tested the abilities of the phosphinodiselenoic acid esters as RAFT agents in the polymerization of styrene under a thermal initiation condition. The reaction was performed in neat at 126 °C. The molar ratio between the RAFT agent and styrene was maintained constant at 400. The results are summarized in Table 2. In addition, the evolutions of molar mass

Table 1. Synthesis of phosphinodiselenoic acid esters



Entry	Compound	R	R'	Yield (%) ^a
1	3a	CH ₂ CH ₂ CH ₂ CH ₃	C ₆ H ₅	68
2	3b	CH(CH ₃) ₂	C ₆ H ₅	73
3	3c	C ₆ H ₁₁	C ₆ H ₅	77
4	3d	CH ₂ C ₆ H ₅	C ₆ H ₅	80
5	3e	4-CH ₃ OC ₆ H ₄	CH(CH ₃) ₂	51

^aIsolated yields of the compounds are the average of at least two runs.

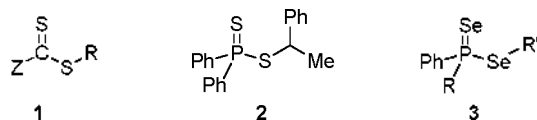


Figure 1. RAFT agents.

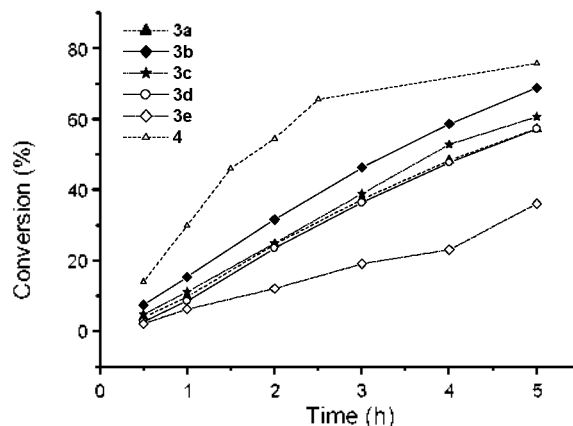
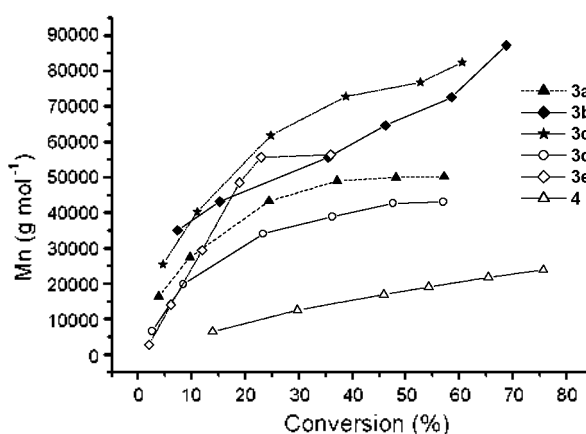
Table 2. Evolution of number-average molecular weight of polystyrene versus conversion rate of styrene using RAFT agents

RAFT agent	Time (h)	Conversion (%)	Mn (g mol ⁻¹)	PDI
3a	0.5	3.9	16400	2.0
	1	9.7	27400	2.2
	2	24.5	43200	2.2
	3	37.2	48900	2.2
	4	48.2	49900	2.2
3b	0.5	7.4	35000	1.8
	1	15.3	43100	1.9
	2	31.5	55500	1.8
	3	46.2	64500	1.8
	4	58.5	72400	1.8
3c	0.5	4.7	25500	2.2
	1	11.1	40200	2.3
	2	24.8	61700	2.2
	3	38.8	72600	2.2
	4	52.7	76600	2.3
3d	0.5	2.7	6670	2.2
	1	8.5	19800	2.2
	2	23.4	34000	2.2
	3	36.3	38800	2.2
	4	47.6	42600	2.2
3e	0.5	2.1	2842	1.9
	1	6.22	14103	1.9
	2	12.0	29423	1.8
	3	19.1	35422	1.9
	4	23.1	36411	1.9
	5	36.0	40253	1.9

were investigated as a function of time and conversion, as shown in Figure 2 and 3, respectively.

Some trends were evident in the styrene polymerization using phosphinodiselenic acid esters as RAFT agents. As shown in Figure 2, the styrene conversion rates using phosphinodiselenic acid esters were slower than those using dithioester. Compound **3e**, in which the alkyl group is bonded to a phosphorus atom, showed a slower conversion rate than the others, in which the phenyl group is bonded to a phosphorus atom. From Figure 3, most compounds showed higher molar mass and slower initial rates than those using the monocarboxyl-terminated trithiocarbonate such as 2-dodecylsulfanylthiocarbonylsulfanyl-2-methyl-propionic acid (**4**). However, butyl and benzyl seleno ester derivatives such as compounds **3a** and **3d** showed a slow increasing rate of Mn at conversion rates above 20%, which was a similar trend to that using trithiocarbonate **4**.

Compared with the arylseleno ester derivatives in the previous paper, compounds having the alkylseleno ester groups showed higher number average molecular weights in the styrene polymerization. The compound **3d**, which is capable of generating stable radical moieties such as benzyl, smoothly increased the Mn value as the conversion increased. We obtained a similar result in the *t*-butylseleno ester derivatives.⁶ Compounds **3b** and **3c**, which have secondary alkylseleno groups, showed

**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.

higher molar masses than the others. The larger PDI values comparing to typical RAFT reaction's value as shown in Table 2 obviously indicate that the rate of exchange in this systems are slow to give small rate ratio to propagation rate. However, the large molecular weight at high conversion in shorten reaction times without increasing PDI values might appeal the usefulness of new RAFT reagent as broadened spectrum of choice in RAFT reagent, although the substituents (R) of RAFT reagent in this report are not optimized as reported effective things such as C(alkyl)₂CN, C(alkyl)₂Ph, and C(alkyl)₂COOEt.

We synthesized several kinds of phosphinodiselenic acid ester in moderate to good yields. These ester derivatives showed potential activities as RAFT agents in the styrene polymerization.

Experimental Section

Synthesis of phosphinodiselenic acid esters (3a). To a suspension of elemental selenium (790 mg, 10.0 mmol) in THF (45 mL) was added 10.0 mL of *n*-butylmagnesium chloride (1.0 M in THF, 10 mmol) at 0 °C, and the mixture was stirred for 30 min. This mixture was then added dropwise to a 30-mL THF solution of diphenylphosphinoselenic chloride (2.85 g, 9.5 mmol) over a period of 10 mins at 0 °C with vigorous stirring. This reaction mixture was raised to room temperature and

stirred for 1 h. After removal of the solvent, the crude mixture was purified by column chromatography on silica gel to afford 2.58 g (6.45 mmol, 68%) of *P,P*-diphenylphosphinodiselenoic acid *n*-butyl ester (**3a**). $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.98-7.83 (m, 4H), 7.54-7.34 (m, 6H), 3.00 (t, $J = 7.5$ Hz, 2H), 1.62 (m, 2H), 1.38 (m, 2H), 0.84 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) δ 133.93 (d, $J = 67.9$ Hz), 131.83 (d, $J = 18.5$ Hz), 131.67 (d, $J = 3.39$ Hz), 128.47 (d, $J = 13.2$ Hz), 32.17 (d, $J = 3.8$ Hz), 31.57 (d, $J = 2.0$ Hz), 22.87, 13.47; $^{31}\text{P NMR}$ (CDCl_3 , 121.5 MHz) δ 41.11 (369.4, 765.7 Hz); MS(EI) m/z : 372(M^+ , 20), 345(87), 343(90), 310(36), 265(45), 263(30), 183(100), 125(45), 107(51), 77(31); Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{PSe}_2$: C, 48.02; H, 4.79. Found: C, 48.14; H, 5.04.

***P,P*-Diphenylphosphinodiselenoic acid isopropyl ester (3b)**, (73%). $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.94 (ddd, $J = 12.0$, 7.8, 1.8 Hz, 4H), 7.46-7.40 (m, 6H), 3.67 (m, 1H), 1.45 (d, $J = 5.7$ Hz, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) δ 133.98 (d, $J = 68.0$ Hz), 131.81 (d, $J = 11.5$ Hz), 131.56 (d, $J = 3.2$ Hz), 128.37 (d, $J = 13.3$ Hz), 41.25 (d, $J = 2.0$ Hz), 25.21 (d, $J = 4.6$ Hz); $^{31}\text{P NMR}$ (CDCl_3 , 121.5 MHz) δ 38.89 (376, 762.9 Hz); MS(EI) m/z : 388(M^+ , 21), 265(28), 201(28), 183(100), 125(37), 107(35); Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{PSe}_2$: C, 46.65; H, 4.44. Found: C, 46.51; H, 4.08.

***P,P*-Diphenylphosphinodiselenoic acid cyclohexyl ester (3c)**, (77%). $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.92 (ddd, $J = 14.7$, 7.8, 2.1 Hz, 4H), 7.46-7.40 (m, 6H), 3.64 (m, 1H), 1.97 (m, 2H), 1.72-1.61 (m, 4H), 1.51-1.26 (m, 4H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) δ 134.27 (d, $J = 68.2$ Hz), 131.82 (d, $J = 11.2$ Hz), 131.55 (d, $J = 3.2$ Hz), 128.39 (d, $J = 13.0$ Hz), 50.20, 34.88 (d, $J = 3.8$ Hz), 26.56, 25.42; $^{31}\text{P NMR}$ (CDCl_3 , 121.5 MHz) δ 39.05 (402.7, 750.5 Hz); MS(EI) m/z : 428(M^+ , 12), 344(22), 265(39), 183(100), 152(24), 107(30); Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{PSe}_2$: C, 50.72; H, 4.97. Found: C, 51.02; H, 5.06.

***P,P*-Diphenylphosphinodiselenoic acid benzyl ester (3d)**, (80%). $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.90-7.82 (m, 4H), 7.47-7.37 (m, 6H), 7.24 (m, 2H), 7.14 (m, 3H), 4.23 (d, $J = 11.4$ Hz, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) δ 133.24 (d, $J = 133.2$ Hz), 131.82 (d, $J = 11.5$ Hz), 131.67 (d, $J = 3.2$ Hz), 129.29, 128.48 (d, $J = 5.7$ Hz), 128.34, 128.05, 127.15, 34.97 (d, $J = 2.9$ Hz); $^{31}\text{P NMR}$ (CDCl_3 , 121.5 MHz) δ 42.53 (294.5, 698.5 Hz); MS(EI) m/z : 436(M^+ , 3), 300(15), 265(13), 201(34), 183(47), 149(62), 91(100), 77(19); Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{PSe}_2$: C, 52.55; H, 3.95. Found: C, 52.17; H, 3.77.

***P*-(4-Methoxyphenyl)-*P*-phenylphosphinodiselenoic acid isopropyl ester (3e)**, (51%). $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.78 (m, 2H), 7.50-7.31 (m, 3H), 7.21 (dd, $J = 8.1$, 1.5 Hz, 2H), 7.02 (d, $J = 8.1$ Hz, 2H), 2.78 (m, 1H), 2.31 (s, 3H), 1.43 (dd, $J = 28.8$, 6.9 Hz, 3H), 1.00 (dd, $J = 21.3$, 6.9 Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) δ 136.9 (d, $J = 2.8$ Hz), 136.1 (d, $J = 3.2$ Hz), 132.1 (d, $J = 9.8$ Hz), 131.6 (d, $J = 3.2$ Hz), 130.2 (d,

$J = 56.1$ Hz), 130.0 (d, $J = 1.9$ Hz), 128.1 (d, $J = 12.1$ Hz), 122.2 (d, $J = 6.6$ Hz), 32.8 (d, $J = 38.9$ Hz), 21.3, 17.3, 16.8; $^{31}\text{P NMR}$ (CDCl_3 , 121.5 MHz) δ 65.5 (389.2, 741.7 Hz); MS(EI) m/z : 402(M^+ , 3), 231(100), 189(50), 125(30), 111(42), 91(70); Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{PSe}_2$: C, 48.02; H, 4.79. Found: C, 47.76; H, 4.84.

Polymerization. Phosphinodiselenoic acid ester **3** (0.48 mmol) and styrene (20.0 g, 192.0 mmol) were mixed in a Schlenk flask. The reaction mixture was degassed by freeze and thaw cycles and sealed under argon. Bulk thermally initiated polymerization was carried out at 126 °C. In the middle of reaction, a sample was taken under argon atmosphere and quenched in cold water, and then diluted with dichloromethane. The polymer was purified by precipitation from dichloromethane solution to methanol. Gel permeation chromatography (GPC) for determination of M_n , M_w and PDI was performed by a set of a SpectraSystem P1000 HPLC pump, a Wyatt Technology WREX-06 differential refractometer, and three Thermo Hypergel columns (OP60, OP45, OP25) using THF as eluent at a flow rate 0.5 mL/min at 35 °C. Polystyrene standards were used for the calibration.

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