mL) of **10** (1.93 g, 5.8 mmol) was added, and the reaction mixture was refluxed until the sodium spheres had disappeared. To the sodium salt was added a toluene solution (10 mL) of $(NPCl_2)_n$ (0.21 g, 1.8 mmol). After 15 h at reflux, the reaction mixture was cooled and quenched with trimethylsilyl chloride (0.33 g, 3.0 mmol) and was concentrated by evaporation of the solvents. The polymeric product was purified by precipitation from hot toluene into water/acetone (1:1) and ethanol/acetone (1:1). The product was further purified by Soxhlet extraction with methanol. Yield: 0.87 g, 72%.

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Zinc N-Substituted Porphyrins as Novel Initiators for the Living and Immortal Polymerizations of Episulfide

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ABSTRACT: Zinc N-substituted porphyrins such as zinc *N*-methyl and -phenyl-5,10,15,20-tetraphenylporphyrins carrying the thiolate group as the axial ligand ($R = CH_3$, $X = SCH_2CH_2CH_3$ (**1b**), $R = C_6H_5$, $X = SCH_2CH_2CH_3$ (**2b**)) brought about the living polymerization of 1,2-epithiopropane (propylene sulfide, PS), affording a polymer of very narrow molecular weight distribution. The number-average molecular weight of the polymer could be controlled by the mole ratio of the monomer reacted to the initiator. NMR studies demonstrated that the polymerization is initiated by the attack of the zinc–propylthio group of the initiator onto the monomer, generating a zinc thiolate as the growing species. The polymerization of 1,2-epithiopropane using **1b** as initiator proceeded with an immortal character in the presence of 1-propanethiol, affording a polymer of uniform molecular weight with the number of the polymer molecules exceeding that of the initiator molecules.

Introduction

Living polymerization to give polymers of uniform molecular weight is of fundamental as well as practical importance for the elaborate molecular design of polymer materials. We have so far shown that metalloporphyrins of aluminum are excellent initiators of wide applicability for ring-opening polymerizations of heterocyclic monomers[1] such as epoxides, lactones, and lactide and addition polymerizations of conjugate vinyl monomers such as methacrylic esters,[2] all of which proceed with living character at the aluminum–axial group bond, affording polymers of controlled molecular weight with narrow molecular weight distribution. On the basis of these

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successful examples, we have further attempted to apply aluminum porphyrin initiators ((porphinato)aluminum chloride and thiolate) to the polymerization of 1,2-epithiopropane (propylene sulfide), a three-membered cyclic thioether, but a polymer with a narrow molecular weight distribution was not obtained under similar conditions. In relation to these observations, we have recently found zinc *N*-methyltetraphenylporphyrin to be an excellent initiator for the living polymerization of epoxides such as epoxyethane and 1,2-epoxypropane, which proceeds at the zinc–axial group bond of the initiator under irradiation with visible light.[3]

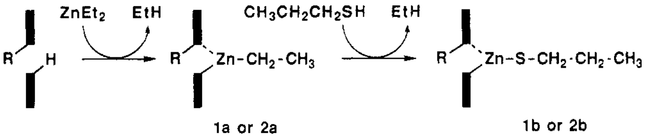
The present paper reports the polymerization of propylene sulfide using zinc complexes of N-substituted porphyrins as initiators, where the living[4] and immortal characters of the polymerization, stereoregularity of the produced polymer, and the structure of the growing species are described.

Experimental Section

Materials. *N*-Methyl-5,10,15,20-tetraphenylporphine (NMTPPH) was synthesized by the reaction of 5,10,15,20-tetraphenylporphine ($TPPH_2$)[5] with methyl iodide in $CHCl_3$ containing 7.5% acetic acid in a sealed tube at 65–70 °C for 7 days.[6] The crude reaction mixture was chromatographed on silica gel followed by basic alumina using as eluents $CH_2Cl_2/CHCl_3$, and CH_2Cl_2/hexane, respectively. The bright green band collected was subjected to recrystallization from $CHCl_3/CH_3OH$, to give NMTPPH as purple crystals in 50% yield based on $TPPH_2$. (5,10,15,20-Tetraphenylporphinato)iron chloride ((TPP)FeCl) was prepared by refluxing a mixture of $TPPH_2$ and a small excess of $FeCl_2 \cdot (H_2O)_4$ in *N,N*-dimethylformamide and recrystallized from ethanol containing 1% HCl.[7] For the preparation of *N*-phenyl-5,10,15,20-tetraphenylporphine (NPhTPPH),[8] 0.9 equiv of phenyllithium (PhLi) was added to a dry tetrahydrofuran solution of (TPP)FeCl (1.45 mmol/50 mL) at room temperature under a nitrogen atmosphere to generate the iron phenyl species ((TPP)FePh). After 10 min of stirring at room temperature, 0.2 equiv of 2,6-di-*tert*-butyl-4-methylphenol with respect to (TPP)FeCl and CH_3OH (50 mL) containing 5% H_2SO_4 were successively added to the reaction mixture, and the mixture was stirred overnight under aerobic conditions. Then the reaction mixture was evaporated to dryness, and the nonvolatile residue was chromatographed on silica gel (eluent: $CH_2Cl_2/CHCl_3/CH_3OH$) followed by acidic alumina (eluent: $CHCl_3/CH_3OH$). The bright green band was collected, shaken with aqueous $NaHCO_3$, and subjected to recrystallization from benzene/hexane to give NPhTPPH as purple crystals in 10% yield based on (TPP)FeCl. Diethylzinc ($ZnEt_2$) was distilled under a nitrogen atmosphere under reduced pressure. CH_2Cl_2, washed successively with concentrated H_2SO_4, water, aqueous $NaHCO_3$, and water, was distilled after refluxing over CaH_2 under a nitrogen atmosphere. Benzene and benzene-d_6 (C_6D_6) were refluxed over sodium wire and distilled under a nitrogen atmosphere. Commercial $CDCl_3$ was used without further purification. 1-Propanethiol (PrSH) was distilled over calcium sulfate under nitrogen. Propylene sulfide (PS, 1,2-epithiopropane) was stirred with CaH_2 and distilled into a trap cooled with liquid nitrogen under a nitrogen atmosphere under reduced pressure.

Procedures. Preparation of (NMTPP)ZnSPr (1b) and (NPhTPP)ZnSPr (2b). A round-bottom flask (50 mL), wrapped in aluminum foil and equipped with a three-way stopcock, containing NMTPPH or NPhTPPH (0.2 mmol) and a Teflon-coated stirring bar was purged with dry nitrogen, and a benzene solution (4 mL) of $ZnEt_2$ (0.3 mmol) was added by means of a hypodermic syringe in a nitrogen stream. After the mixture was stirred magnetically for 1.5 h at room temperature in the dark, the volatile fractions were removed under reduced pressure at room temperature to leave (NMTPP)ZnEt (**1a**)[9,10] or (NPhTPP)ZnEt (**2a**) as a purple powder (Scheme I). To this flask, wrapped in aluminum foil, benzene (8 mL) and 3.3 equiv of 1-propanethiol were added in a nitrogen stream. After the mixture was stirred overnight at room temperature in the dark, volatile fractions were removed under reduced pressure at room temperature, and the residue was heated at 90 °C for 2 h under reduced pressure to leave (NMTPP)ZnSPr (**1b**)[10,11] or (NPhTPP)ZnSPr (**2b**)[10] as a dark green powder (Scheme I).

Scheme I



Preparation of (NMTPP)ZnCl (1c) and (NMTPP)-ZnO_2CCH_3 (1d). To a round-bottom flask containing a CH_2Cl_2 solution (50 mL) of NMTPPH (0.2 g, 0.318 mmol) and a stirring bar was added an CH_3CN solution (40 mL) of $ZnCl_2$ (0.2 g, 1.59 mmol) containing several drops of 2,6-di-*tert*-butylpyridine, and the mixture was stirred at room temperature for 2 h. The resulting bluish green solution was evaporated, and the residue was subjected to recrystallization from CH_2Cl_2/CH_3CN to give (NMTPP)ZnCl (**1c**) as greenish purple crystals in 34.2% yield.[12] (NMTPP)ZnCl (**1c**) was dissolved in CH_2Cl_2, and the solution was shaken repeatedly with aqueous CH_3CO_2Na and water. The organic layer was separated and evaporated to dryness, and the residue was subjected to recrystallization from CH_2Cl_2/hexane, affording (NMTPP)ZnO_2CCH_3 (**1d**) as purple crystals in 74% yield.[13]

Polymerization of Propylene Sulfide (PS) with (N-Substituted-TPP)ZnX as Initiator. A typical example of the polymerization initiated with **1b** is given below. To a 50-mL round-bottom flask, fitted with a three-way stopcock, containing a CH_2Cl_2 solution (2 mL) of (NMTPP)ZnSPr (**1b**) (0.1 mmol) and a stirring bar under dry nitrogen was added a prescribed amount of propylene sulfide through a three-way stopcock by means of a syringe in a nitrogen stream, and the mixture was stirred magnetically at 25 °C. An aliquot of the reaction mixture was periodically taken out by a syringe from the polymerization system in a nitrogen stream and evaporated to dryness under reduced pressure at room temperature. The residue was weighed to determine the conversion and then dissolved in tetrahydrofuran. The solution, filtered through a microporous Teflon membrane ($\Phi = 0.5\ \mu m$), was subjected to gel permeation chromatography (GPC) to estimate the average molecular weights and molecular weight distribution of the produced polymer. The polymerization in CH_2Cl_2 at 55 °C was carried out in a sealed polymerization ampule. For NMR studies, the polymerization was carried out in a sealed NMR tube using C_6D_6 as solvent at 25 °C under nitrogen.

Polymerization of Propylene Sulfide (PS) with (NMTPP)ZnSPr (1b) in the Presence of 1-Propanethiol (PrSH). To a 50-mL round-bottom flask equipped with a three-way stopcock containing a CH_2Cl_2 solution (2 mL) of (NMTPP)ZnSPr (**1b**, 0.05 mmol) and a stirring bar under dry nitrogen were successively added prescribed amounts of 1-propanethiol and propylene sulfide in a nitrogen stream, and the mixture was stirred at room temperature. After a definite time, the reaction mixture was evaporated to dryness under reduced pressure at room temperature to leave a nonvolatile, viscous residue, which was weighed to determine the conversion and subjected to NMR and GPC analyses.

Measurements. ^1H and ^{13}C NMR measurements were performed in C_6D_6 or $CDCl_3$ using a JEOL Type GSX-270 spectrometer, where the chemical shifts were determined with respect to C_6H_6 (δ 7.40) or $CHCl_3$ (δ 7.28) for ^1H NMR and C_6D_6 (δ 128.0) for ^{13}C NMR. For the determination of the tacticity of polymer, ^{13}C NMR measurements were performed with CCl_4/C_6D_6 (90/10 (v/v)) as solvent at 60 °C.[14] Gel permeation chromatography (GPC) was performed at 38 °C on a Toyo Soda HLC Model 802A gel permeation chromatograph equipped with a differential refractometer detector, using tetrahydrofuran as eluent at the flow rate of 1.1 mL·min^{-1}. The column set consisted of four Styragel columns (60 cm) of porosity ratings of 7000–3000 (two), 3000 (one), and 2000 Å (one). The molecular weight calibration curve was obtained by using standard polystyrenes: $M_n = 2.89 \times 10^6$ ($M_w/M_n = 1.09$), 4.22×10^5 (1.05), 1.07×10^5 (1.01), 4.39×10^4 (1.01), 1.67×10^4 (1.02), 6.2×10^3 (1.02), and

Table I
Polymerization of Propylene Sulfide (PS) Initiated with (N-Substituted-TPP)ZnX[a]

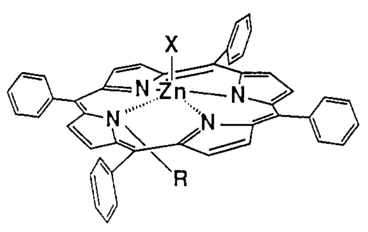
run	initiator	$[PS]_0/[\text{initiator}]_0$	time, h	conv, %	M_n[b]	M_w/M_n[b]	N_p/N_{Zn}[c]
1	(NMTPP)ZnSPr (**1b**)	400	0.5	69.0	26600	1.05	0.8
2	(NMTPP)ZnCl (**1c**)	100	3.5	7.0	nd	nd	nd
3	(NMTPP)ZnOAc (**1d**)	100	1.5	17.8	4160	1.18	0.3
4	(NPhTPP)ZnSPr (**2b**)	400	0.8	88.4	24400	1.05	1.1

[a] Polymerization was carried out in CH_2Cl_2 at 25 °C. [b] Estimated by gel permeation chromatography using polystyrene standards. [c] N_p/N_{Zn} (ratio of the numbers of the molecules of the produced polymer and **1b**) = $\{(\text{MW of PS}) \times [PS]_0/[Zn]_0 \times (\text{conv}/100)\}/M_n$.

2.8 × 10^3 (1.1) from Toyo Soda Manufacturing Co., Ltd., and 1.0 × 10^4 (1.06), 9.0 × 10^3 (1.06), 4.0 × 10^3 (1.10), and 2.1 × 10^3 (1.10) from Pressure Chemical Co.

Results and Discussion

Polymerization of Propylene Sulfide (PS) with (N-Substituted-TPP)ZnX (1b–d, 2b) as Initiator. Polymerization of propylene sulfide (PS) was attempted with (NMTPP)ZnX (X = SPr (**1b**), Cl (**1c**), O_2CCH_3 (**1d**)) or (NPhTPP)ZnX (X = SPr (**2b**)) as initiator, where the zinc complexes carrying the thiolate group at the axial position (**1b** and **2b**) were found to be quite effective as initiator (runs 1 and 4 in Table I). A typical example is given by the polymerization using **1b** as initiator with the initial monomer-to-initiator mole ratio ($[PS]_0/[\mathbf{1b}]_0$) of 400 in CH_2Cl_2 at 25 °C, which proceeded to 25, 61, and 69% conversion in 10, 30, and 60 min, respectively, and was completed in ca. 80 min. The gel permeation chromatography (GPC) profiles of the polymerization showed that the produced polymer exhibited a unimodal, sharp chromatogram, which shifted toward the higher molecular weight region as the polymerization proceeded. The number-average molecular weight (M_n) of the polymer, as estimated from the GPC chromatogram using polystyrene standards, increased linearly with the conversion, while the ratio of the weight- to number-average molecular weights (M_w/M_n) was almost constant at 1.06 (Figure 1). Furthermore, the estimated M_n values based on GPC are in good agreement with those (dashed line in Figure 1) obtained by assuming that every initiator molecule produces one polymer molecule.[15] Accordingly, the number-average molecular weight (M_n) of the produced polymer can be controlled over a wide range, retaining the M_w/M_n ratio close to unity by changing the mole ratio of the monomer reacted to **1b** ($[PS]_{\text{react}}/[\mathbf{1b}]_0$). For example, the polymerizations with the mole ratios $[PS]_0/[\mathbf{1b}]_0$ of 850 and 1250 gave at 100% conversion polymers with M_n as estimated by GPC, of 55 000 (M_w/M_n = 1.05) and 62 000 (1.06), respectively. Thus, the polymerization of propylene sulfide with (NMTPP)ZnSPr (**1b**) proceeds with living character without any chain-transfer and termination reactions. This development is of interest, since the polymerization of propylene sulfide initiated with zinc thiolates ($Zn(SR)_2$) is in some cases accompanied by side reactions such as desulfuration of the monomer.[4d]



1 : R = CH_3

(1a) X = CH_2CH_3 (NMTPP)ZnEt
(1b) X = $SCH_2CH_2CH_3$ (NMTPP)ZnSPr
(1c) X = Cl (NMTPP)ZnCl
(1d) X = O_2CCH_3 (NMTPP)ZnOAc

2 : R = C_6H_5

(2a) X = CH_2CH_3 (NPhTPP)ZnEt
(2b) X = $SCH_2CH_2CH_3$ (NPhTPP)ZnSPr

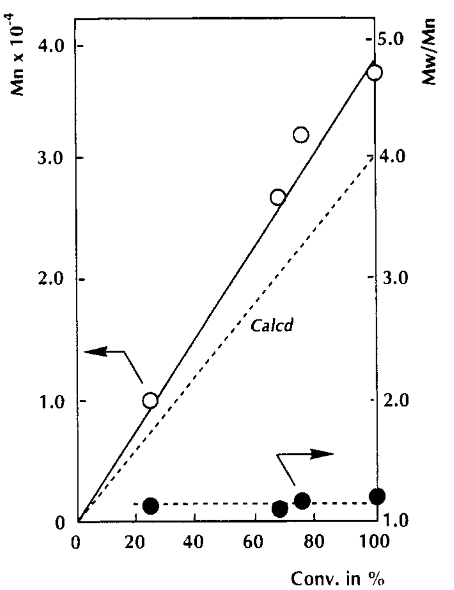


Figure 1. Polymerization of propylene sulfide (PS) initiated with (NMTPP)ZnSPr (**1b**) in CH_2Cl_2 at 25 °C with $[PS]_0/[\mathbf{1b}]_0$ of 400. M_n (M_w/M_n) vs conversion relationship. M_w and M_n were estimated by gel permeation chromatography using polystyrene standards.

(NPhTPP)ZnSPr (**2b**) as initiator also brings about the living polymerization of propylene sulfide, affording a polymer of controlled molecular weight with a narrow molecular weight distribution. For example, the polymerization with the initial mole ratio $[PS]_0/[\mathbf{2b}]_0$ of 400 in CH_2Cl_2 at 25 °C proceeded up to 88.4% conversion in 50 min, affording a polymer with M_n and M_w/M_n, respectively, of 24 400 and 1.05 (run 4 in Table I). The M_n value thus observed was very close to that estimated by assuming the formation of one polymer molecule per molecule of **2b** (M_n = 26 200).

Contrary to the polymerizations initiated with zinc N-substituted porphyrins carrying the propylthio group (**1b** and **2b**), the polymerization with (NMTPP)ZnCl (**1c**) or (NMTPP)ZnO_2CCH_3 (**1d**) took place very slowly under similar conditions (runs 2 and 3 in Table I). Thus, the reactivities of the zinc atom–axial group bonds of **1c** and **1d** toward the monomer are considered to be much lower than those of **1b** and **2b**.

The ^{13}C NMR[14] spectrum in CCl_4/C_6D_6 (90/10 (v/v)) at 60 °C of poly(propylene sulfide) obtained in run 1 in Table I showed signals at δ 41.85, 41.65 (CH), 39.1 (CH_2), and 21.1 (CH_3), while the signal assignable to head-to-head (tail-to-tail) sequences (δ 39.5)[16] was absent, indicating that the polymer consists of regular head-to-tail sequences. The former two signals due to the CH group have been assigned to rr + mr triads and mm + rm triads, respectively.[14] The ratio of the peak areas of these two signals was almost unity (50.8:49.2), indicating the atac-

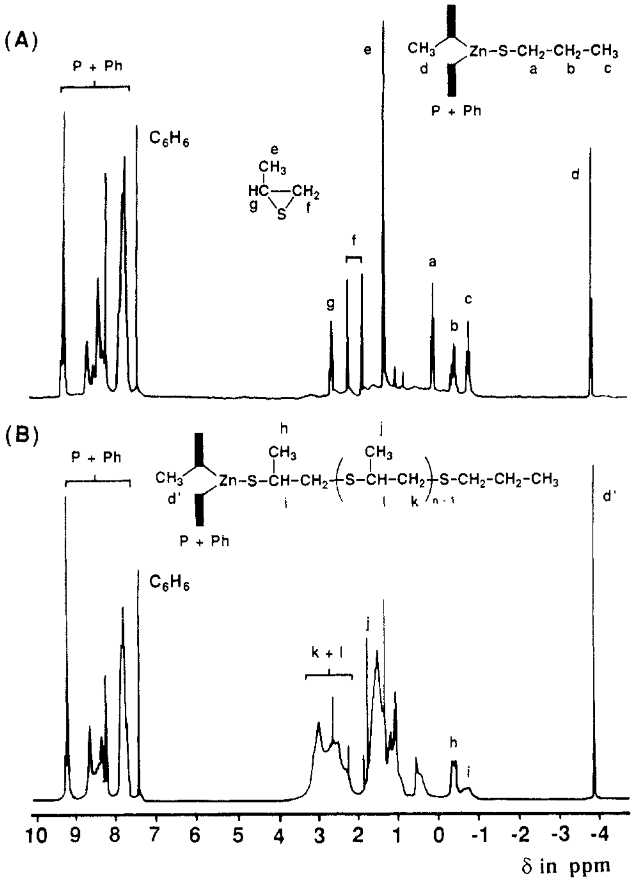


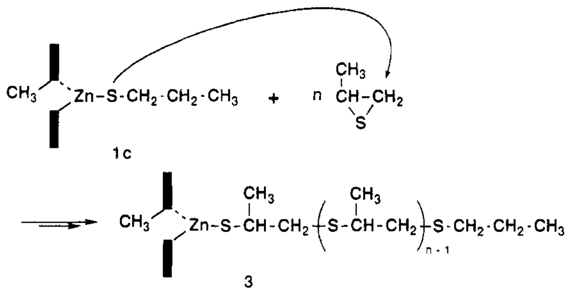
Figure 2. Polymerization of propylene sulfide (PS) initiated with (NMTPP)ZnSPr (**1b**) in C_6D_6 at 25 °C with $[PS]_0/[\mathbf{1b}]_0$ of 5.1. ^1H NMR spectra of the reaction mixture after stirring for 15 min (A) and 5 h (B).

tic structure of the polymer. The polymerization of propylene sulfide with **1b** in benzene at 25 °C also gave atactic poly(propylene sulfide).

As described in the Introduction, the polymerization of epoxides initiated with **1b** is dramatically accelerated by irradiation with visible light (xenon light, $\lambda > 420$ nm).[3] On the contrary, the polymerization of propylene sulfide with **1b** was not photoaccelerated under similar conditions.

Structure of the Growing Species of the Polymerization of Propylene Sulfide Initiated with (NMTPP)ZnSPr (1b). Figure 2A shows the ^1H NMR spectrum in C_6D_6 at 25 °C of the mixture of (NMTPP)-ZnSPr (**1b**) and propylene sulfide ($[PS]_0/[\mathbf{1b}]_0 = 5.1$) 15 min after mixing, where signals a (δ −0.8, t), b (−0.45, m), and c (0.1, t) are due to SCH_2, CH_2, and CH_3 resonances of the axial propylthio group, signal d (−3.83, s) is due to the N–CH_3 group of the initiator (**1b**), and signals e–g are assigned to CH_3, CH_2, and CH resonances of the monomer. The signals observed in the aromatic region (P + Ph, δ 7.6–9.3) are due to the proton resonances of the porphyrin skeleton (P) and the peripheral phenyl groups (Ph). In the ^1H NMR spectrum after 5 h (Figure 2B), the signals due to the monomer together with those due to the propylthio group of the initiator (**1b**) disappeared completely, while signals h (0.35, d) and i (−0.75, br) assignable to the CH_3 and CH groups at the reactive terminal of the growing polymer newly appeared. In addition, a slight upfield shift was observed for the signal due due to the N–CH_3 group of the (NMTPP)Zn moiety from d to d′ (δ −3.86, s), where the relative intensity of signals h, i, and d′ was 3:1:3. Thus, the polymerization of propylene sulfide with (NMTPP)-ZnSPr (**1b**) is initiated by the attack of the zinc–propylthio group of the initiator onto the monomer, to generate the corresponding zinc thiolate group (**3**) as the propagating species (Scheme II).

Scheme II



Polymerization of Propylene Sulfide (PS) Initiated with (NMTPP)ZnSPr (1b) in the Presence of Protic Compounds. The concept of "immortal" polymerization has been established on the basis of the polymerization of epoxides and lactones initiated with aluminum porphyrins in the presence of protic compounds, where the rapid, reversible chain-transfer reaction occurs between the molecules of the growing polymer and protic compounds. Immortal polymerization is of practical importance as well as fundamental interest, since the faster chain-transfer reaction than the chain growth allows the formation of polymer of uniform molecular weight with the number of molecules equal to the sum of those of aluminum porphyrin initiator and protic chain-transfer agent.[17] Recently, we have found that the polymerization of an epoxide such as 1,2-epoxypropane initiated with zinc complexes of *N*-methyltetraphenylporphyrin ((NMTPP)-ZnX (**1**)) takes place with an immortal character in the presence of 1-propanethiol or methanol as protic compound.[3]

Table II summarizes the results of the polymerization of propylene sulfide (PS) initiated with (NMTPP)-ZnSPr (**1b**) in the presence of 1-propanethiol (PrSH) in CH_2Cl_2 at room temperature (25 °C). For example, the polymerization with the initial mole ratio $[PS]_0/[\mathbf{1b}]_0/[PrSH]_0$ of 400/1/4.4 proceeded with a comparable rate to that in the absence of PrSH and was completed in 100 min (run 7). In this case, the produced polymer exhibited a very sharp GPC chromatogram, which was observed to shift toward the higher molecular weight region as the polymerization proceeded. The number-average molecular weight (M_n) of the polymer, as estimated by GPC, increased linearly with conversion (solid line in Figure 3), retaining the ratio M_w/M_n almost constant at 1.05. This straight line was very close to that estimated by assuming that every molecule of the initiator (**1b**) and the protic compound produces one polymer molecule (broken line). When the initial mole ratio $[PrSH]_0/[\mathbf{1b}]_0$ was increased to 18.7, the estimated M_n value of the produced polymer at 100% conversion decreased without broadening the molecular weight distribution ($M_w/M_n = 1.08$) (run 8 in Table II). Similar results were obtained in the polymerizations with the initial monomer-to-initiator mole ratios of 100 (runs 1 and 2) and 200 (runs 3 and 4). In all these cases, the number of produced polymer molecules (N_p) was in good agreement with the sum of those of the molecules of (NMTPP)ZnSPr (**1b**) and PrSH ($N_{Zn} + N_{PrSH}$). It should also be noted that the polymerization was accelerated to a great extent by elevating the polymerization temperature, for example, to 55 °C, without broadening the molecular weight distribution of the polymer (run 6).

When the polymerization with the initial mole ratio $[PS]_0/[\mathbf{1b}]_0/[PrSH]_0$ of 100/1/4.4 was followed at 100%

Table II
Polymerization of Propylene Sulfide (PS) Initiated with (NMTPP)ZnSPr (1b) in the Presence of 1-Propanethiol (PrSH)[a]

run	$[PS]_0/[\mathbf{1b}]_0$	$[PrSH]_0/[\mathbf{1b}]_0$	time, min	conv, %	M_n[b]	M_w/M_n[b]	N_p/N_{Zn}[c]
1	100	1.1	220	100	4300	1.07	1.7
2	100	4.4	220	100	1400	1.10	5.3
3	200	3.8	220	100	3700	1.06	4.0
4	200	8.8	220	100	1800	1.08	8.2
5	400	4.4	10	28	1400	1.10	5.9
6	400	4.4	10[d]	58	4200	1.09	4.1
7	400	4.4	100	100	7500	1.04	3.9
8	400	18.7	335	100	1700	1.08	17.4

[a] Polymerization was carried out with 0.05 mmol of **1b** in CH_2Cl_2 (2 mL) at room temperature (25 °C). [b] Estimated by gel permeation chromatography using polystyrene standards. [c] N_p/N_{Zn} (ratio of the numbers of the molecules of the produced polymer and **1b**) = $\{(\text{MW of PS}) \times [PS]_0/[\mathbf{1b}]_0 \times (\text{conv}/100)\}/M_n$. [d] Polymerization was carried out in CH_2Cl_2 at 55 °C in a sealed polymerization tube.

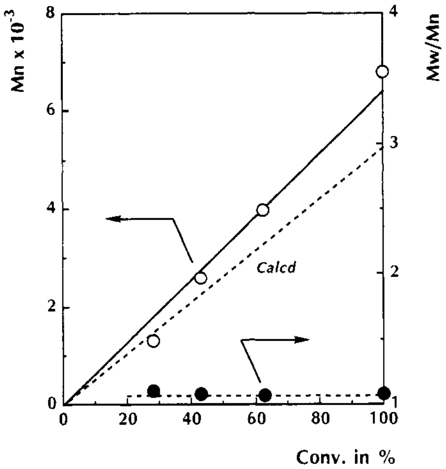


Figure 3. Polymerization of propylene sulfide (PS) initiated with (NMTPP)ZnSPr (**1b**) in the presence of 1-propanethiol (PrSH) in CH_2Cl_2 at 25 °C with $[PS]_0/[PrSH]_0/[\mathbf{1b}]_0$ of 400/4.4/1. M_n (M_w/M_n) vs conversion relationship. M_w and M_n were estimated by gel permeation chromatography using polystyrene standards.

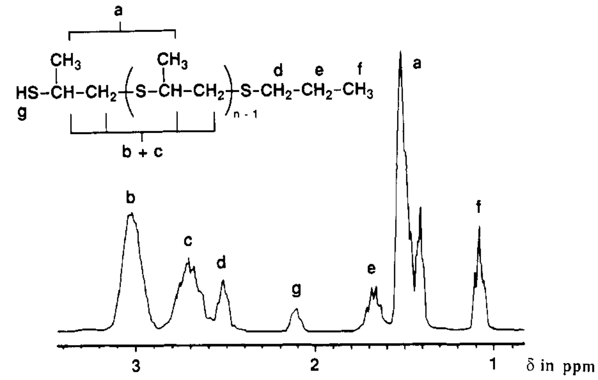
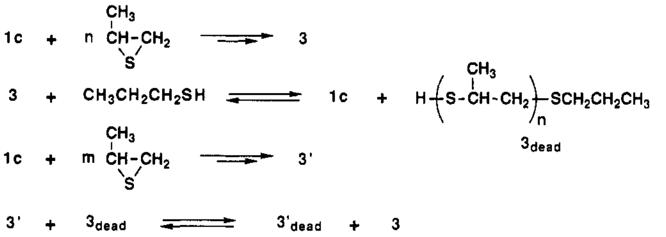


Figure 4. ^1H NMR spectrum in C_6D_6 of the polymerization mixture obtained by the polymerization of propylene sulfide (PS) with (NMTPP)ZnSPr (**1b**) in the presence of 1-propanethiol (PrSH) with the initial mole ratio $[PS]_0/[PrSH]_0/[\mathbf{1b}]_0$ of 400/18.7/1 at 100% conversion.

Scheme III



conversion by adding another 100 molar equiv of the monomer, the second stage of polymerization ensued, and the GPC chromatogram of the polymer shifted toward the higher molecular weight region (M_n(GPC); from 1600 to 3650), retaining the original sharp shape of the chromatogram (M_w/M_n; from 1.09 to 1.08), while the ratio of the number of polymer molecules (N_p) to that of the initiator molecules (N_{Zn}) (N_p/N_{Zn}) was almost unchanged (from 4.6 to 4.0). Thus, the polymerization of propylene sulfide (PS) with (NMTPP)ZnSPr (**1b**) in the presence of 1-propanethiol is of an *immortal* character, where the exchange reaction between the molecules of (*N*-methyltetraphenylporphinato)zinc thiolate and thiol is considered to take place reversibly and rapidly (Scheme III). The introduction of the propylthio group into the polymer terminal was demonstrated by end-group analysis of the produced polymer by NMR. Figure 4 shows the ^1H NMR spectrum of the polymerization mixture obtained with the mole ratio $[PS]_0/[\mathbf{1b}]_0/[PrSH]_0$ of 100/1/19.7 at 100% conversion in C_6D_6, where signals a, b, and c are assigned to the resonances of the CH_3, CH_2, and CH groups of the repeating monomeric units. Signals due to PrSH (e.g., δ 0.94 (CH_3)) were absent. The relatively weak signals d (δ 1.09, 3 H), e (1.68, 2 H), and g (2.52, 2 H) are assignable to CH_3, $MeCH_2$, and CH_2S of the propylthio group attached to the polymer terminal, and signal h (2.12, 1 H) is assignable to the SH group on the other terminal of the polymer chain. The degree of polymerization of the polymer, as estimated from the relative intensity of signals b and e, is 4.5, which is very close to the estimated values from $[PS]_0/([\mathbf{1b}]_0 + [PrSH]_0)$ of 4.8.

Contrary to the above cases using thiol as protic compound, methanol (CH_3OH) does not work as a chain-transfer agent for the polymerization of propylene sulfide with (NMTPP)ZnSPr (**1b**). An example is shown by the polymerization of propylene sulfide (PS) with (NMTPP)ZnSPr (**1b**) in the presence of 5 molar equiv of CH_3OH with the initial mole ratio $[PS]_0/[\mathbf{1b}]_0/[CH_3OH]_0$ of 100/1/5 in CH_2Cl_2 at 25 °C, which afforded at 100% conversion (6 h) a polymer with an average molecular weight (M_n(GPC) = 7600 [M_w/M_n = 1.15]) very close to that in the absence of added CH_3OH (M_n(GPC) = 8100). A similar result was obtained for the polymerization with the initial mole ratio $[PS]_0/[\mathbf{1b}]_0$ of 100/1 in the presence of 4.4 equiv of PrSH using CH_3OH as solvent (500 equiv with respect to **1b**) at 25 °C, which proceeded rather slowly (34.1% conversion in 4 h) compared with that in CH_2Cl_2 solvent, where the number of polymer molecules relative to that of **1b** (N_p/N_{Zn}) of 4.1, calculated from the number-average molecular weight (M_n = 1800 [M_w/M_n = 1.12], by GPC) and conversion, was in good agreement with that observed for the polymer obtained in the absence of CH_3OH under similar conditions (see run 2 in Table II). In relation to this observation, the ^1H NMR spectrum of (NMTPP)ZnSPr (**1b**) in the presence of 25 equiv of 2-propanol at room temperature showed only signals due to **1b** (for SPr; δ 0.01 (CH_3), −0.54 (CH_2), and −0.92 (SCH_2)), while (NMTPP)$ZnOCH(CH_3)_2$ (for $OCH(CH_3)_2$ in C_6D_6; δ −1.33 (CH_3), 0.13 (CH))[3,18] and 1-propanethiol (δ 0.96

(CH_3), 1.54 (CH_2), and 2.33 (SCH_2) in C_6D_6), which are the possible products of the exchange reaction between **1b** and 2-propanol, were not detected at all even after 12 h. This is in contrast to the successful immortal polymerization of epoxide with **1b** in the presence of 1-propanethiol,[3] which possibly involves the exchange reaction of(NMTPP)Zn-alkoxide as the growing species with 1-propanethiol.

Conclusion

The present study has developed the potential utility of zinc N-substituted porphyrins as initiators for the polymerization of propylene sulfide, which enables the synthesis of polythioether with uniform, controlled molecular weight. The polymerization proceeds without any side reactions via an (N-substituted porphinato)zinc thiolate as the growing species, which can subsequently initiate the polymerization of epoxide under irradiation with visible light, affording polythioether–polyether block copolymer with uniform block lengths.[3] Attempted *immortal* polymerizations of propylene sulfide initiated with an (*N*-methylporphinato)zinc thiolate in the presence of thiol and alcohol has indiciated the reversible exchange of the zinc thiolate species with thiol but no exchange with alcohol. The reactivities of zinc N-substituted porphyrins thus developed are also interesting in the sense that the back side of the active site is protected from the coordinative interaction with monomer by the presence of the N substituent. This is in sharp contrast to the case for aluminum porphyrins, which possibly coordinate with monomer on the back side, and thereby the reactivities of monomer and/or the growing species may be changed.[19]

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