(6 H, $(CH_3)_2$), 2.6 (1 H, CH), 3.1 (2 H, CH_2CO), 4.0 (2 H, CH_2N); ^{13}C NMR ($CDCl_3$ with Me_4Si) δ 19.5 (CH_3), 34.5 (CH), 38 (CH_2CO), 41 (CH_2N), 174, 181 (C=O); IR (KBr) 1720–1680 cm^{-1}. **2d** (pale yellow powder materials): ^1H NMR ($CDCl_3$ with Me_4Si) δ 2.4–3.1 (2 H, CH_2CO), 3.2–3.9 (2 H, CH_2N), 7.0, 8.0, 8.4, 9.2 (four signals, total 1 H); IR (KBr) 1660, 1780 cm^{-1}. **2e** (pale yellow powdery materials): ^1H NMR ($CDCl_3$ with Me_4Si) broad signals δ 3.3 (2 H, CH_2), 6.1 (1 H, CHN), 7.5 (5 H, C_6H_5), 8.9 (1 H, CHO); IR (KBr) 1780, 1690–1660 cm^{-1}.

Thermal Polymerization. A nitrobenzene solution of monomer **1a** (0.35 mol/L × 7 mL = 2.45 mmol) was heated at 120 °C for 120 h in a sealed tube under nitrogen. The tube was opened and 0.1 mL of methanol and 0.4 mL of dimethylformamide were added to the solution. Then the mixture was poured into a mixed solvent of diethyl ether/*n*-hexane (110 mL/40 mL). The precipitated polymer materials were collected by filtration, washed three times with 10 mL of diethyl ether, and dried in vacuo to give 0.188 g of pale brown powder polymers (68% yield). Spectroscopic data were almost identical with those of polymer **2a** obtained by the cationic polymerization. The molecular weight was 1600.

Similarly, the thermal polymerization of monomer **1e** was carried out in acetonitrile at 110 °C for 45 h. After workup procedures, pale gray powdery polymers were obtained in low yield (31%). Spectral data were almost identical with those of polymer **2e** obtained by the cationic polymerization except for the lack of an IR band at 1780 cm^{-1}. This shows that the polymer obtained by the thermal polymerization has a regular structure given by **2e**.

Measurements. ^1H NMR and ^{13}C NMR spectra were taken respectively by a Hitachi 60-MHz R-20B NMR spectrometer and a Hitachi 22.6-MHz R-900 Fourier-transform NMR spectrometer. IR spectra were recorded on a Hitachi 260-50 infrared spectrophotometer. The molecular weights of polymers were determined by vapor pressure osmometry with a Corona 117 instrument in chloroform at 35 °C.

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Visible-Light-Mediated Living and Immortal Polymerizations of Epoxides Initiated with Zinc Complexes of N-Substituted Porphyrins

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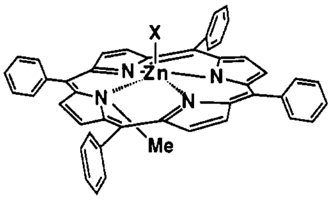
ABSTRACT: The novel, visible-light-mediated *living* polymerization of epoxides was developed by using as initiators zinc N-methylated tetraphenylporphyrin complexes ((NMTPP)ZnX; X = $SCH_2CH_2CH_3$ (**1b**), $OCH(CH_3)_2$ (**1c**)) in benzene at room temperature. The NMR studies demonstrated that the polymerization is initiated by the attack of the axial group of the initiator onto the monomer, affording a (*N*-methyltetraphenylporphinato)zinc alkoxide as the growing species. The polymerization of 1,2-epoxypropane with **1b** proceeded with immortal character in the presence of a protic compound such as 1-propanethiol or methanol to give the polymer of narrow molecular weight distribution with the number of the molecules corresponding to the sum of those of **1b** and the protic compound. The polymerization of an episulfide, followed by an epoxide under visible light irradiation, afforded a block copolymer consisting of polythioether and polyether blocks of uniform block lengths.

Introduction

Photoinduced polymerization is a matter of fundamental interest as well as practical importance. For the ring-opening polymerization of epoxides, some photoinitiating systems have been developed, most of which serve as cationic initiators upon photodecomposition to generate protons or carbonium species.[1] In a preliminary communication, we have reported a different type of photoinduced polymerization, developed in the addition polymerization of methacrylic esters with methylaluminum porphyrin, which is initiated upon irradiation with visible light by the nucleophilic attack of the Al–CH_3 bond of the initiator to the monomer and proceeds without any side reactions (*living* character) via a (porphinato)aluminum enolate as the growing species.[2] Detailed studies demonstrated that both the initiating and propagating steps are accelerated by irradiation with visible light owing to the enhanced reactivities of the central aluminum atom–axial ligand bonds of aluminum porphyrins by light.

In this paper, we wish to report the novel, visible-light-mediated living and immortal ring-opening polymerizations of epoxides using as initiators zinc *N*-methyltetraphenylporphyrins ((NMTPP)ZnX (1); X = $SCH_2CH_2CH_3$ (**1b**), $OCH(CH_3)_2$ (**1c**)).



(NMTPP)ZnX (1)

Experimental Section

Materials. *N*-Methyl-5,10,15,20-tetraphenylporphine (NMTPPH) was synthesized by the reaction of 5,10,15,20-tetraphenylporphine ($TPPH_2$)[3] with methyl iodide in chloroform containing 7.5% acetic acid in a sealed tube at 65–70 °C for 7 days.[4] The crude reaction mixture was chromatographed on silica gel followed by basic alumina by using dichloromethane containing chloroform or *n*-hexane as eluent, and the bright green band collected was subjected to recrystallization from chloroform/methanol, to give NMTPPH as purple crystals. Diethylzinc ($ZnEt_2$) was distilled in a nitrogen atmosphere under reduced pressure. Benzene and benzene-d_6 (C_6D_6) were refluxed over sodium wire and distilled in a nitrogen atmosphere. Commercial chloroform-*d* ($CDCl_3$) was used without further purification. 1-Propanethiol was distilled over calcium sulfate under nitrogen. Methanol and 2-propanol were distilled over magnesium treated with iodine under nitrogen. 1,2-Epoxypropane (propylene oxide, PO) was distilled over a mixture of potassium hydroxide and calcium hydride in a nitrogen atmosphere. Epoxyethane (EO), stirred with a mixture of potassium hydroxide and calcium hydride, was collected in a trap cooled with liquid nitrogen. 1,2-Epithiopropane (propylene sulfide, PS) was stirred with calcium hydride and distilled into a trap cooled with liquid nitrogen.

Procedures. Preparation of (NMTPP)ZnSPr (1b). A round-bottom flask (50 mL), wrapped in aluminum foil and equipped with a three-way stopcock, containing NMTPPH (0.2 mmol) and a Teflon-coated magnetic 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 from the reaction mixture to leave (NMTPP)ZnEt (**1a**) as a purple powder.[5] To this flask, wrapped in aluminum foil, was added benzene (8 mL) to dissolve **1a**, followed by 3.3 equiv of 1-propanethiol 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**) as a green powder.[6,7]

Preparation of (NMTPP)ZnO^{i}Pr (1c). **1c** was prepared similar to the above by the reaction of **1a** with 2-propanol. To the flask, wrapped in aluminum foil, containing a benzene solution (8 mL) of **1a** (0.2 mmol) under nitrogen, was added 50 equiv of 2-propanol, and the reaction mixture was stirred magnetically at 50 °C for 4 days in the dark. Then, the volatile fractions were removed from the reaction mixture at room temperature under reduced pressure to leave (NMTPP)ZnO^{i}Pr (**1c**) as a purple powder.[7]

Polymerization of Epoxides. To a 50-mL flask, fitted with a three-way stopcock, containing a benzene solution (2 mL) of (NMTPP)ZnSPr (**1b**) or (NMTPP)ZnO^{i}Pr (**1c**) (0.1 mmol) under nitrogen, was added a prescribed amount of epoxide through a three-way stopcock by a syringe in a nitrogen stream. For the polymerization under irradiation, the mixture was illuminated with a 500-W Xenon arc lamp (Ushio UXL-500D) from a distance of 35 cm through a glass filter (Kenko type L42, Kenko Co., Ltd.) to cut out light of wavelength shorter than 420 nm. For the dark reaction, the flask was wrapped in aluminum foil. In both cases, the reaction mixture was stirred magnetically at room temperature (~25 °C) or 26 °C (thermostated). An aliquot of the reaction mixture was periodically taken out by a syringe from the polymerization system in a nitrogen stream and subjected to ^1H NMR analysis to determine the monomer conversion.[8] The conversion was also determined on the basis of the weight of the residue after evaporation of the reaction mixture to dryness. The nonvolatile material, thus obtained, was filtered through a microporous Teflon membrane (Φ = 0.5 μm) and subjected to gel permeation chromatography (GPC). For NMR studies, C_6D_6 was used as solvent for the reaction, and a portion of the reaction mixture was transferred in a nitrogen stream into an NMR tube, which was sealed off. The polymerization at 70 °C was carried out in a sealed ampule in the dark.

Block Copolymerization of 1,2-Epithiopropane and 1,2-Epoxypropane. To a round-bottom flask, wrapped in aluminum foil, fitted with a three-way stopcock containing a benzene solution (1 mL) of (NMTPP)ZnSPr (**1b**, 0.05 mmol) under dry nitrogen, was introduced 100 equiv of 1,2-epithiopropane by a syringe in a nitrogen stream, and the mixture was stirred magnetically at room temperature in the dark for 4.7 h to attain 40% monomer conversion.[9] The volatile fractions were then removed from the reaction mixture under reduced pressure, and benzene (0.7 mL) as solvent and 150 equiv of 1,2-epoxypropane were successively added. The mixture was stirred magnetically under irradiation for the first 3.5 h and in the dark for the next 19 h and subjected to evaporation under reduced pressure at room temperature. The residue was dissolved in dichloromethane, and the solution was added dropwise to a large volume of hexane with vigorous stirring and then centrifuged. The supernatant solution was evaporated to dryness to leave viscous liquid, which was subjected to ^1H NMR and gel permeation chromatography (GPC) analyses.

Polymerization in the Presence of Protic Compounds. To a flask equipped with a three-way stopcock containing (NMTPP)ZnSPr (**1b**, 0.05 mmol) under dry nitrogen was added a mixture of 400 equiv of 1,2-epoxypropane and a protic compound such as 1-propanethiol or methanol (0.5 mmol) by means of a syringe, and the mixture was stirred under irradiation at room temperature. After a definite time, the reaction mixture was subjected to ^1H and ^{13}C NMR measurements. Then, the volatile fractions were removed from the reaction mixture, and the nonvolatile residue was subjected to gel permeation chromatography.

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) for ^1H NMR and C_6D_6 (δ 128.0) or $CDCl_3$ (δ 77.1) for ^{13}C NMR. For the quantitative end-group analyses of polymers, ^{13}C NMR spectra were measured without NOE by applying the pulse delay time of 15 s. 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 7000–3000 Å (two), 3000 Å (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 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.] together with poly(propylene glycols) [$M_n = 2.0 \times 10^3$ and 1.0×10^3 (M_w/M_n close to unity) from Lion Fat & Oil Co., Ltd.].

Results and Discussion

Polymerization of 1,2-Epoxypropane (2, R = CH_3) with (NMTPP)ZnSPr (1b) as Initiator. The poly-

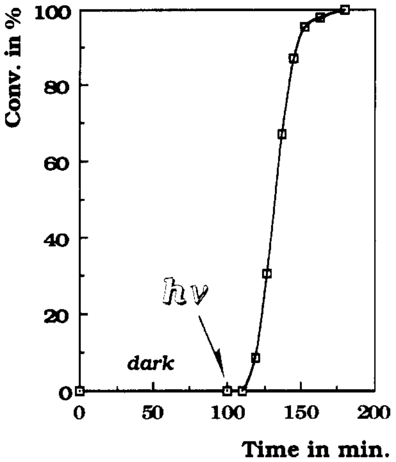


Figure 1. Polymerization of 1,2-epoxypropane (PO) initiated with (NMTPP)ZnSPr (**1b**) ($[\mathrm{PO}]_0/[\mathbf{1b}]_0$ = 40) at 26 °C in C_6D_6 in the dark for the initial 100 min, followed by irradiation (>420 nm) for 80 min: time–conversion curve.

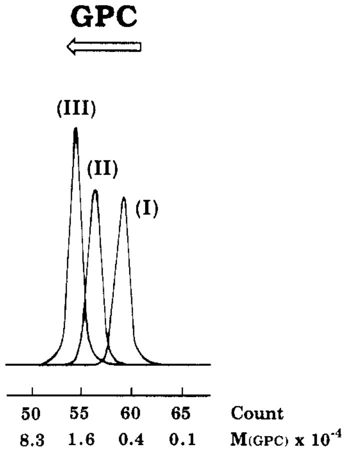


Figure 2. Polymerization of 1,2-epoxypropane (PO) initiated with (NMTPP)ZnSPr (**1b**) ($[\mathrm{PO}]_0/[\mathbf{1b}]_0$ = 430) at room temperature (~25 °C) in benzene under irradiation (>420 nm) for the initial 40 min, followed by stirring in the dark: GPC profiles at 24% (I), 59% (II), and 88% (III) conversion ($M_{(\mathrm{GPC})}$ based on standard polystyrenes).

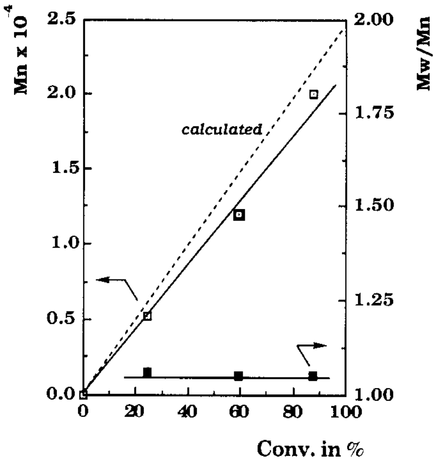


Figure 3. Polymerization of 1,2-epoxypropane (PO) initiated with (NMTPP)ZnSPr (**1b**) (reaction conditions, see Figure 2): relationship between M_n (□) or M_w/M_n (■) and conversion (M_n and M_w/M_n as estimated by GPC based on standard polystyrenes).

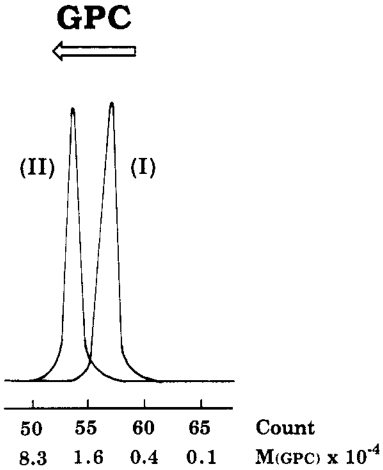


Figure 4. Two-stage polymerizations of 1,2-epoxypropane (PO) initiated with (NMTPP)ZnSPr (**1b**) at room temperature (~25 °C) in benzene. GPC profiles of the polymerization mixtures: the first stage, I, M_n = 10 300, M_w/M_n = 1.07, $[\mathrm{PO}]_0/[\mathbf{1b}]_0$ = 100, 1 h (irradiation) + 31 h (dark), 100% conversion; the second stage, II, M_n = 24 900, M_w/M_n = 1.07, $[\mathrm{PO}]_0/[\mathbf{1b}]_0$ = 200, 22.5 h (dark), 100% conversion (M_n and M_w/M_n as estimated by GPC based on standard polystyrenes).

merization of 1,2-epoxypropane (PO) with (NMTPP)ZnSPr (**1b**) was found to take place very rapidly under irradiation with Xenon lamp (visible region, λ > 420 nm). A typical example is shown by the polymerization with the initial monomer-to-initiator mole ratio ($[\mathrm{PO}]_0/[\mathbf{1b}]_0$) of 40 in C_6D_6 thermostated at 26 °C (Figure 1), where the polymerization did not occur in the dark for 100 min but was initiated rapidly upon irradiation and completed in 80 min. It should be also noted that the polymerization, once photoinitiated, did not subside upon turning off the light.

The GPC profiles of the polymerization with the mole ratio $[\mathrm{PO}]_0/[\mathbf{1b}]_0$ of 430, initiated by irradiation for 40 min, are shown in Figure 2, where the produced polymer exhibited 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, estimated from the GPC chromatogram, increased linearly with the monomer conversion, while the ratio of the weight- and number-average molecular weights (M_w/M_n) was almost constant at 1.05 (Figure 3). Furthermore, the M_n values based on GPC are close to those (broken line in Figure 3) calculated by assuming that every initiator molecule produces one polymer molecule.[10] When 200 equiv of 1,2-epoxypropane (PO) was again added to the polymerization system ($[\mathrm{PO}]_0/[\mathbf{1b}]_0$ = 100; irradiation for the initial 1 h and then in the dark) after the complete consumption of the monomer, the second-stage polymerization ensued in the dark and was completed in 22.5 h. The GPC chromatogram of the polymer (Figure 4) clearly shifted from curve I to curve II, retaining the narrow molecular weight distribution. Thus, the visible-light-mediated polymerization of 1,2-epoxypropane initiated with (NMTPP)ZnSPr (**1b**) has the character of *living* polymerization.

It was also noted that the polymerization of 1,2-epoxypropane using **1b** as initiator in benzene ($[\mathrm{PO}]_0/[\mathbf{1b}]_0$ = 100, $[\mathbf{1b}]_0$ = 37.0 mM) took place even in the dark when conducted at 70 °C, affording the polymer with M_n and M_w/M_n, respectively, of 6100 and 1.07 after the completion of polymerization (102 min).

Poly(1,2-epoxypropane) formed with **1b** as initiator under irradiation showed virtually the same ^{13}C NMR pattern as that for the polymer formed in the dark at 70 °C, where the resonance due to the methyl group was very simple, indicating that the polymer consists of regular head-to-tail linkages. The diad and triad tacticities of the polymer, as determined by ^{13}C NMR,[11] indicated the atactic structure: for the polymer formed under irra-

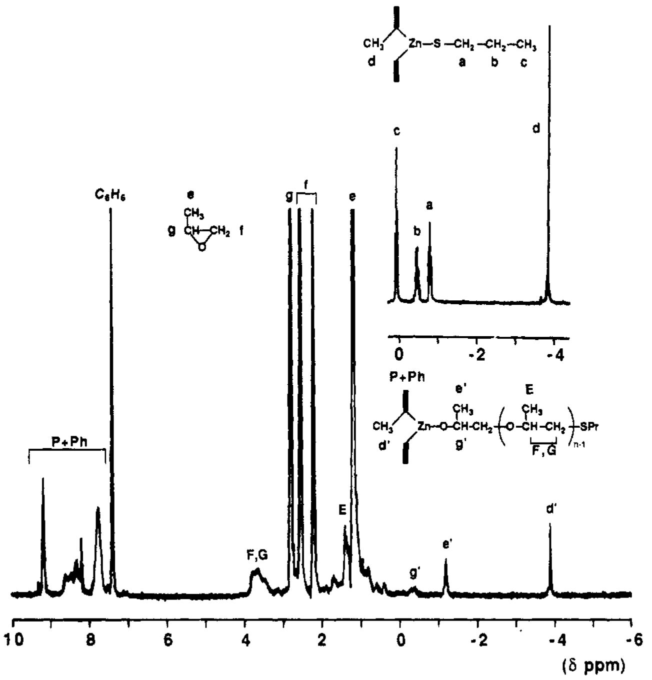


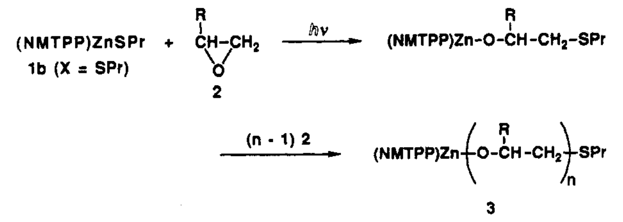
Figure 5. Polymerization of 1,2-epoxypropane (PO) initiated with (NMTPP)ZnSPr (**1b**) ($[\mathrm{PO}]_0/[\mathbf{1b}]_0 = 40$) at 26 °C in C_6D_6: ^{1}H NMR spectrum of the reaction mixture formed by stirring in the dark for the initial 100 min, followed by irradiation (>420 nm) for 17 min (8.3% conversion).

diation at room temperature (~25 °C), i:s = 0.48:0.52, I:H:S = 0.23:0.49:0.28; for the polymer formed in the dark at 70 °C, i:s = 0.49:0.51, I:H:S = 0.24:0.50:0.26.

Polymerization of Epoxyethane (2, R = H) with (NMTPP)ZnSPr (1b) as Initiator. The polymerization of epoxyethane with **1b** also proceeded by irradiation with visible light. An example is shown by the polymerization with the mole ratio $[\mathrm{EO}]_0/[\mathbf{1b}]_0$ of 190 in benzene at room temperature (~25 °C), where the monomer conversion after 205 min was very low (<2%, determined by ^{1}H NMR) in the dark, while under irradiation the polymerization proceeded to 97% conversion in only 80 min. The number-average molecular weight (M_n) of the polymer, as estimated from the GPC chromatogram, was 8700, which is in excellent agreement with the expected value of 8100 provided that the numbers of the molecules of the produced polymer and **1b** are equal.[10] The ratio M_w/M_n of the polymer (1.05) was close to unity, indicating the livingness of the visible-light-mediated polymerization of epoxyethane initiated with (NMTPP)ZnSPr (**1b**).

Structure of the Growing Species of the Polymerization of Epoxides Initiated with (NMTPP)ZnSPr (1b). In the ^{1}H NMR spectrum of the mixture of (NMTPP)ZnSPr (**1b**) and 1,2-epoxypropane ($[\mathrm{PO}]_0/[\mathbf{1b}]_0 = 40$) standing in the dark at 26 °C in C_6D_6 (Figure 5), the signals a (δ -0.8 ppm), b (-0.45), and c (0.1) due to the axial propylthio group and d (-3.83) due to the N-CH_3 group of the initiator (**1b**) were observed at the upfield region in addition to the signals e–g due to 1,2-epoxypropane, while the signals assignable to poly(1,2-epoxypropane) were not detected. However, when the mixture was illuminated by visible light for 17 min, the signals a–c disappeared completely, the signal due to the N-CH_3 group slightly shifted to δ -3.9 ppm (d′) retaining the original intensity, and the signals due to the polymeric units (E, δ 1.4 (CH_3); F, G, 3.7 (CH_2, CH)) appeared. In addition to these spectral changes, new signals e′ and g′ appeared at the upfield region (δ -1.17 and -0.35 ppm), which are assignable to a (*N*-methylporphinato)zinc alkoxide group at the terminal of the growing polymer (**3** (R = CH_3) in Scheme I), taking into account the 3:1 intensity ratio of the signals e′ and g′ together with the similarity of their chemical shift values to those of the corresponding signals of (NMTPP)ZnO^{i}Pr (**1c**) separately prepared (CCH_3, δ -1.33; OCH, 0.13; N-CH_3, -3.89 ppm, in C_6D_6). The reaction mixture of 1,2-epoxypropane with (NMTPP)ZnSPr (**1b**) in C_6D_6 at 70 °C without irradiation provided essentially the same ^{1}H NMR profiles as those in Figure 5.

Scheme I



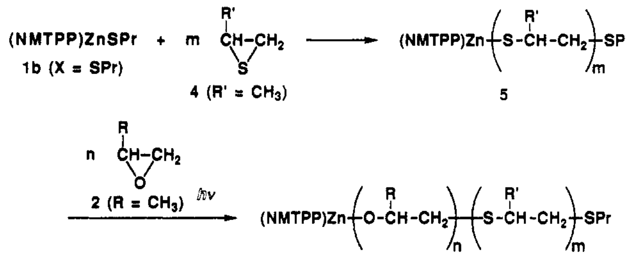
The ^{1}H NMR spectrum in C_6D_6 of the reaction mixture of epoxyethane (EO) with **1b** with the mole ratio $[\mathrm{EO}]_0/[\mathbf{1b}]_0$ of 15 at 100% conversion (30 min under irradiation plus 17 h in the dark) showed three characteristic signals at the upfield region, two of which at δ 0.07 and 0.91 ppm are assignable to the terminal alkoxide structure of the living polymer (NMTPP)ZnOC*H*$_2$C*H*$_2$– and the other at δ -3.9 ppm assignable to N-CH_3 of the porphyrin ligand. Besides these signals, the signals due to poly(oxyethylene) chain centered at δ 3.7 ppm and those due to the porphyrin moiety (P + Ph) were also observed. In this case, the signals assignable to the initiating terminal of the polymer chain, $-OCH_2CH_2SCH_2CH_2CH_3$, were clearly observed at δ 2.79 ($OCCH_2$, t), 2.55 (SCH_2-Et, t), 1.67 (CH_2Me, m), and 1.07 (CH_3, t).[12]

All the above NMR profiles demonstrate that the polymerization of epoxides with (NMTPP)ZnSPr (**1b**) is initiated by the attack of the axial propylthio group of **1b** onto the monomer, affording a (NMTPP)Zn alkoxide (**3**) as the growing species (Scheme I).

Polymerization of 1,2-Epoxypropane (2, R = CH_3) with (NMTPP)ZnO^{i}Pr (1c) as Initiator. The polymerization of 1,2-epoxypropane (PO) with (NMTPP)ZnO^{i}Pr (**1c**), which is a model compound of the growing species (**3**, Scheme I), takes place in the dark even at room temperature. For example, the polymerization with the initial mole ratio $[\mathrm{PO}]_0/[\mathbf{1c}]_0$ of 200 in benzene at 20 °C in the dark proceeded to 80% conversion in 9 h. This result is in conformity with the observation that the polymerization of epoxides with (NMTPP)ZnSPr (**1b**), once photoinitiated to generate **3**, proceeds under the dark conditions. However, the acceleration effect by visible light is also remarkable in the polymerization initiated with **1c**. For example, the polymerization with $[\mathrm{PO}]_0/[\mathbf{1c}]_0$ of 29 proceeded to 50% monomer conversion in 1 h under irradiation at room temperature. A similar result was obtained for the polymerization of 150 equiv of 1,2-epoxypropane (PO) at room temperature initiated with the living poly(1,2-epoxypropane) (**3** (R = CH_3), M_n = 590, M_w/M_n = 1.08; prepared at 70 °C in the dark), which was completed in 1.7 h under irradiation but required 4 days in the dark to attain 74% conversion.

Block Copolymerization of 1,2-Epithiopropane (4, R′ = CH_3) and 1,2-Epoxypropane (2, R = CH_3) Initiated with (NMTPP)ZnSPr (1b). (NMTPP)ZnSPr (**1b**) is also an excellent initiator for the polymerization of 1,2-epithiopropane (PS), producing the living polymer carrying a (NMTPP)Zn thiolate growing terminal (**5**, R′ = CH_3) (Scheme II).[9] Thus, the polymerization of 1,2-ep-

Scheme II



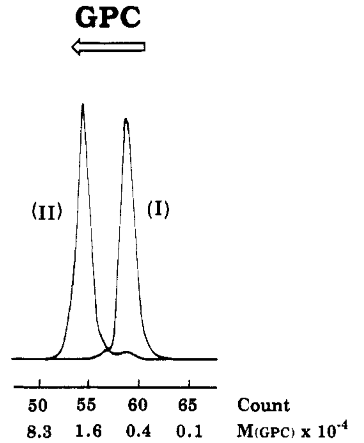


Figure 6. GPC profile of the block copolymerization of 1,2-epoxypropane (PO) initiated by the living prepolymer of 1,2-epithiopropane (PS) obtained with (NMTPP)ZnSPr (**1b**) ($[PS]_0/[\mathbf{1b}]_0 = 100$, in the dark for 4.7 h in benzene, 40% conversion), $[PO]_0/[\text{living prepolymer}]_0$ of 150: (I) prepolymer, $M_n = 3400$, $M_w/M_n = 1.06$ (poly(propylene glycols) as standard); (II) block copolymer formed at 99.5% conversion (3.5 h (irradiation) + 19 h (dark)), $M_n = 20\,300$, $M_w/M_n = 1.06$ (polystyrenes as standard).

oxypropane (PO) from the living polymer of 1,2-epithiopropane (**5**, R' = CH_3) was attempted by adding 150 equiv of 1,2-epoxypropane to a benzene solution of **5** (R' = CH_3; $M_n = 3400$, $M_w/M_n = 1.06$; preparation, see Experimental Section). The polymerization of 1,2-epoxypropane was observed to start upon irradiation with visible light and proceeded at room temperature up to 99.5% monomer conversion after 22.5 h (3.5 h under irradiation plus 19 h in the dark). The GPC chromatogram of the polymerization mixture (Figure 6) showed a unimodal, sharp elution pattern (curve II; $M_n = 20\,300$, $M_w/M_n = 1.06$), which clearly shifted from that of the prepolymer (curve I). Thus, the product is a block copolymer consisting of polythioether and polyether blocks with uniform block lengths. The polyether content in the block copolymer, as determined by ^{1}H NMR,[13] was 80.8%, which is in good agreement with the calculated value (78.2%) based on the amounts of the two monomers reacted. The successful block copolymerization of 1,2-epoxypropane from the living polymer **5** confirms the fact that the polymerization of epoxides with (NMTPP)ZnSPr (**1b**) is initiated by the insertion of monomer into the Zn–S bond of **1b**.

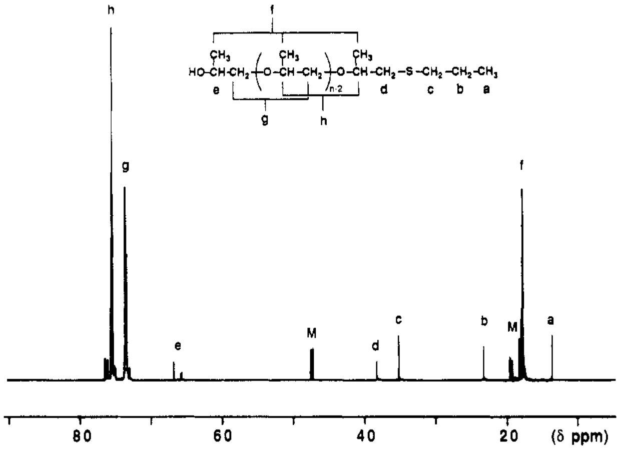
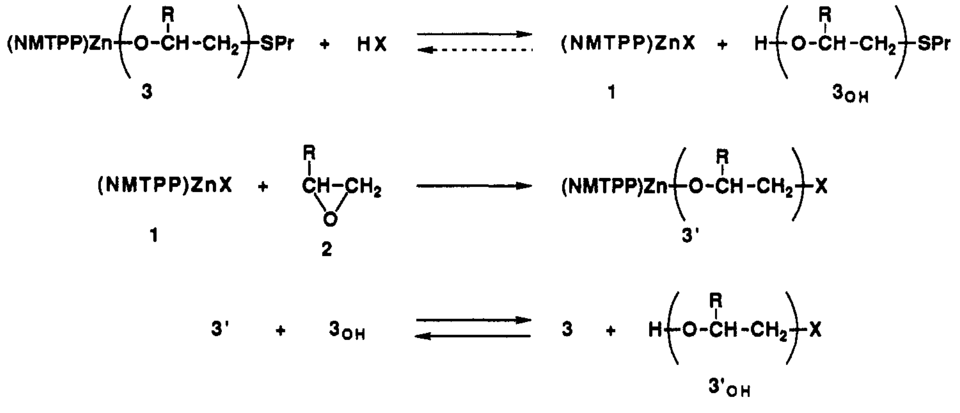


Figure 7. Polymerization of 1,2-epoxypropane (PO) with (NMTPP)ZnSPr (**1b**) in the presence of 1-propanethiol (PrSH) with $[PO]_0/[PrSH]_0/[\mathbf{1b}]_0$ of 400/10/1 without solvent at room temperature. ^{13}C NMR spectrum in C_6D_6 of the reaction mixture obtained at 93% conversion under irradiation for 45.5 h. M denotes the signals for the monomer remaining unreacted.

Polymerization of 1,2-Epoxypropane Initiated with (NMTPP)ZnSPr (1b) in the Presence of Protic Compounds. We have recently established the concept of "*immortal*" polymerization in the polymerizations of epoxides and lactones initiated with aluminum porphyrin in the presence of a protic compound, where the polymers of uniform molecular weight are formed with the number of the molecules equal to the sum of those of aluminum porphyrin and the protic compound.[14] This is due to the rapid, reversible chain-transfer reaction between the molecules of growing polymer and the protic compound, which takes place much faster than the propagation reaction. Thus, the polymerization of 1,2-epoxypropane (PO) with (NMTPP)ZnSPr (**1b**) was attempted in the presence of a protic compound (HX) such as 1-propanethiol (PrSH) or methanol (MeOH) under the irradiation by visible light with the initial mole ratio $[PO]_0/[HX]_0/[\mathbf{1b}]_0$ of 400/10/1.

In the presence of PrSH as a protic compound, the polymerization proceeded to 93% conversion in 45.5 h at room temperature under irradiation, producing the polymer with M_n and M_w/M_n of 1660 and 1.11, respectively. The number of the polymer molecules relative to that of **1b** (N_p/N_{Zn}), as estimated from M_n and the yield of the

Scheme III



polymer,[15] is 13.0, being close to the initial mole fraction ($[PrSH]_0$ + $[\mathbf{1b}]_0$)/$[\mathbf{1b}]_0$ of 11. The ^{13}C NMR spectrum in C_6D_6 of the polymerization mixture is shown in Figure 7, where the signals assignable to the propylthio (PrS–) group (a, δ 13.5 ppm (CH_3); b, 23.2 ($MeCH_2$); c, 35.2 (SCH_2)) attached to the polymer terminal,[16] the methylene group of the terminal unit (d, δ 38.3) attached to the PrS– group, and the methine group (e, δ 66–67) on the other terminal of the polymer chain attached to the hydroxyl group[14c] were observed in addition to the signals due to the polymer chain (f (CH_3), g (CH_2), h (CH)). The degree of polymerization of the polymer, as estimated from the intensity ratio of the signals g and a, was 33.4, which nicely agrees to the mole fraction $[PO]_{reacted}$/($[PrSH]_0$ + $[\mathbf{1b}]_0$) of 33.8. Thus, every polymer molecule carries one propylthio group. The polymerization of 1,2-epoxypropane initiated with **1b** in the presence of methanol proceeded also with *immortal* character under similar conditions, giving at 100% conversion (under irradiation, 18 h) the polymer with M_n and M_w/M_n, respectively, of 1680 and 1.08, and the number of the polymer molecules relative to **1b** being 13.8. The ^{13}C NMR spectrum of the polymer showed a signal at δ 58.9 ppm due to the terminal methoxy group,[14c] in addition to one set of relatively weak signals due to the terminal propylthio group originating from **1b**. The degree of polymerization of the polymer (34.7), as estimated from the intensities of these characteristic signals, was in good agreement with the initial mole fraction $[PO]_0$/($[MeOH]_0$ + $[\mathbf{1b}]_0$) of 36.4.

Thus, in the polymerization of 1,2-epoxypropane initiated with (NMTPP)ZnSPr (**1b**) in the presence of a protic compound (HX) such as 1-propanethiol or methanol (Scheme III), exchange of the growing polymer (**3**) with HX to give (NMTPP)ZnX (**1**) and the polymer with a hydroxyl terminal ($\mathbf{3}_{OH}$), reinitiation of the polymerization by **1** to form the living polymer (**3′**), and reversible exchange between $\mathbf{3}_{OH}$ and **3′** take place. Consequently, all the molecules of **1b** and HX participate in chain growth. Narrow molecular weight distribution of the produced polymer indicates that the exchange reaction takes place much faster than the propagation reaction.

Conclusion

Zinc *N*-methyltetraphenylporphyrins are novel initiators for visible-light-mediated ring-opening polymerization of epoxides. The polymerization proceeds with *living* and *immortal* characters to afford the polymer of controlled molecular weight with narrow molecular weight distribution. The chain growth takes place at the axial position of the initiator, where the reactivity of the initiating and propagating species bound to the central zinc atom may be remarkably enhanced upon photoexcitation of the light-absorbable porphyrin ligand.

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(7) UV–vis (benzene, under N_2)[λ_{max}, nm (log ϵ)]: **1b**, 450 (5.25), 568 (4.75), 617 (4.79), 630 (4.28), 656 (4.79); **1c** (in the presence of 30 equiv of 2-PrOH), 442 (5.37), 564 (4.25), 614 (4.37), 659 (4.26). The following absorption maxima were observed for both **1b** and **1c** unless the measurements were made quickly or when the solutions were exposed to air: 440, 450, 563, 612, 629, 655 nm.

(8) Monomer conversion was determined from the intensities of the signals due to –OC*H*RC*H*$_2$– in the polymer chain relative to those of the monomer.

(9) Aida, T.; Kawaguchi, K.; Inoue, S. *Macromolecules*, in press.

(10) M_n(calc) = {$[\text{monomer}]_0/[\mathbf{1b}]_0$} × MW (monomer) × (convn/100).

(11) The distributions of isotactic (i) and syndiotactic (s) diad together with isotactic (I), heterotactic (H), and syndiotactic (S) triad sequences were determined from the resonances due to methylene and methine carbons: Oguni, N.; Lee, K.; Tani, H. *Macromolecules* **1972**, *5*, 819.

(12) The assignments were made on the basis of the ^1H NMR spectra for $(CH_3CH_2CH_2)_2S$, δ 2.51 (SCH_2), 1.70 (CH_2Me), and 1.11 (CH_3), and for $CH_3CH_2CH_2SH$, δ 2.33 (SCH_2), 1.54 (CH_2Me), and 0.96 (CH_3), in C_6D_6.

(13) For $-SCH(CH_3)CH_2-$ in the polymer chain: δ 1.6 (CH_3), 3.1 (CH_2), 2.8 (CH) in C_6D_6.

(14) (a) Asano, S.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1148. (b) Aida, T.; Maekawa, Y.; Asano, S.; Inoue, S. *Macromolecules* **1988**, *21*, 1195. (c) Inoue, S.; Aida, T. *Makromol. Chem., Macromol. Symp.* **1986**, *6*, 217.

(15) N_p/N_{Zn} = ($[\text{monomer}]_0/[\mathbf{1b}]_0$) × (convn/100) × MW(monomer)/M_n.

(16) The assignments were made based on the ^{13}C NMR spectra for $(CH_3CH_2CH_2)_2S$, δ 34.3 (SCH_2), 23.3 (CH_2Me), and 13.6 (CH_3), and for $CH_3CH_2CH_2SH$, δ 27.4 (SCH_2), 26.6 (CH_2Me), and 12.9 (CH_3), in C_6D_6.

Registry No. **1a**, 71381-00-5; **1b**, 126421-40-7; **1c**, 126378-26-5; NMTPPH, 51552-53-5; $ZnEt_2$, 557-20-0; $H_3CCH(OH)CH_3$, 67-63-0; 1-propanethiol, 107-03-9; methanol, 67-56-1; 1,2-epoxypropane, 75-56-9; epoxyethane, 75-21-8; 1,2-epithiopropane, 1072-43-1.