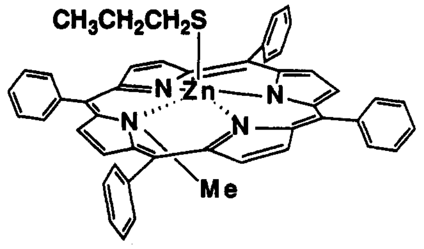
First Example of Photoinduced Copolymerizability Enhancement. Copolymerization of Epoxide and Episulfide Initiated with Zinc N-Substituted Porphyrin under Visible Light Irradiation

Copolymerization is a facile method to diversify the structure of polymer materials. However, if the polymerizabilities of comonomers are far from each other, copolymerization is essentially difficult, resulting in the formation of a mixture of the homopolymers and/or the copolymer with block sequences. This is the case for the anionic copolymerization of epoxide and episulfide, where the polymerizability of episulfide is much higher than that of epoxide, and the copolymer consisting mostly of –S–C–C–S– and –O–C–C–O– homosequences is formed.[1] In the present paper, we report the first example of *photoenhanced copolymerizability* of epoxide and episulfide in the reaction using as initiator the zinc complex of N-substituted porphyrin [(NMTPP)ZnSPr (1), (21-methyl-5,10,15,20-tetraphenylporphinato)zinc propanethiolate].



(NMTPP)ZnSPr (**1**)

Typically, into a 50-mL round-bottom flask fitted with a three-way stopcock containing 0.1 mmol of (NMTPP)ZnSPr (1)[2] under dry nitrogen was added a benzene-d_6 solution (2 mL) containing epoxyethane [ethylene oxide (EO), 5 mmol] and 1,2-epithiopropane [propylene sulfide (PS), 5 mmol]. Then, an aliquot of the reaction mixture was taken out and divided into three NMR tubes (5 mm ϕ), one of which was put in a water bath (~20 °C) and exposed to a 500-W xenon arc light ($\lambda > 420$ nm) from the distance of 35 cm, and the other two were kept in the dark wrapped in aluminum foil at room temperature (~20 °C) and 70 °C, respectively. The copolymerization was thus conducted under three different conditions and followed by NMR.[3]

In the copolymerization in the dark at room temperature, the consumptions of EO and PS took place rather slowly (25 and 80%, respectively, in 30 h), while both were accelerated by elevating the temperature to 70 °C (18 and 85% in 1 h) or irradiation with visible light (57 and 70% in 5.3 h). The consumptions of EO under three different conditions were plotted against those of PS in Figure 1, which demonstrates that the relative consumption of EO to PS in the dark at room temperature (A) is far from unity. This tendency is unchanged under accelerating conditions by elevating the temperature to 70 °C in the dark (B). However, of particular interest is that the rates of consumption of two comonomers come closer to each other under irradiation with visible light (C).

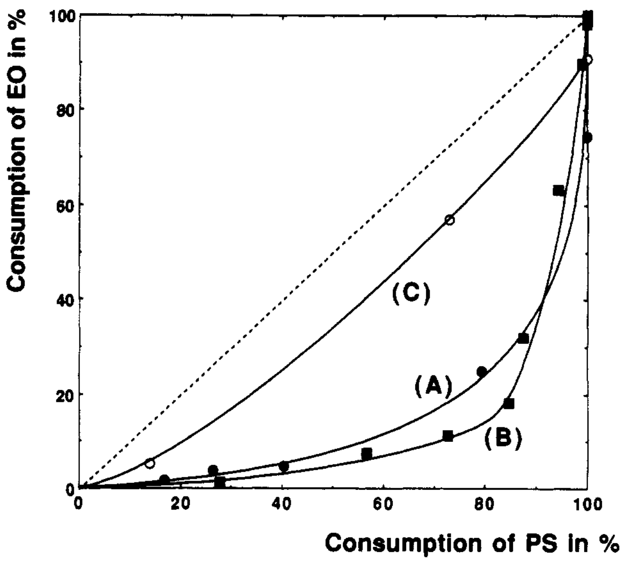


Figure 1. Copolymerizations of epoxyethane (EO) and 1,2-epithiopropane (PS) initiated with (NMTPP)ZnSPr (1) ($[EO]_0/[PS]_0/[1]_0 = 50/50/1$) in C_6D_6. Plots of EO consumptions vs PS consumptions in the dark at rooom temperature (A), in the dark at 70 °C (B), and under irradiation with xenon arc light (>420 nm) at room temperature (C).

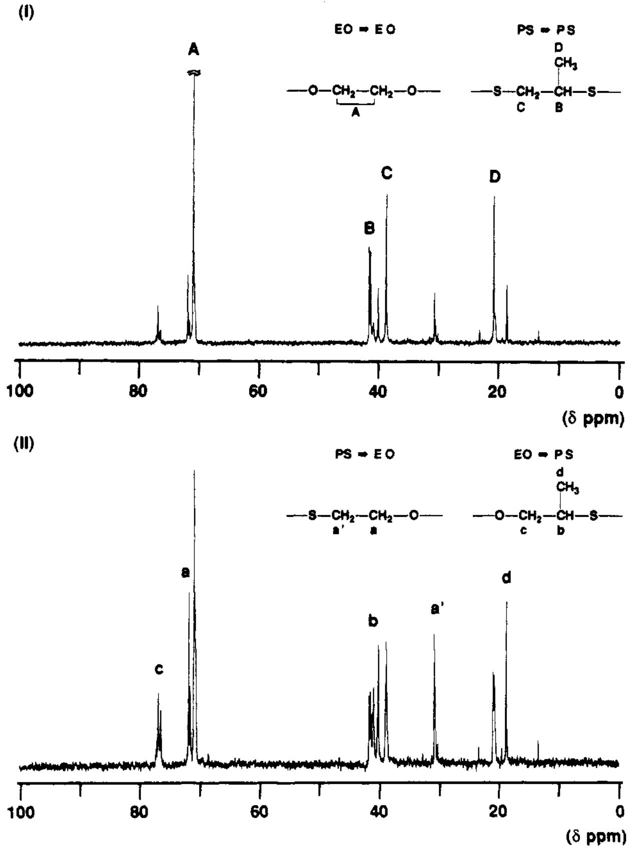


Figure 2. Copolymerizations of epoxyethane (EO) and 1,2-epithiopropane (PS) initiated with (NMTPP)ZnSPr (1) at room temperature. ^{13}C NMR (270-MHz) spectra in C_6D_6 [C_6D_6 (δ 128.0) as internal standard] of the products formed in the dark [(I); run 1 (Table I)] and under irradiation with xenon arc light [(II); run 3].

The homopolymerizations of epoxide and episulfide initiated with (NMTPP)ZnSPr (1) have been demonstrated to proceed with living character via an (NMTPP)Zn alcoholate and thiolate, respectively, as the growing species by the repeated insertions of monomers into the Zn–S bond of the initiator.[4,5] Therefore, the copolymerization of epoxyethane (EO) and 1,2-epithiopropane (PS) with 1 as initiator is considered to proceed via the following four elementary reactions: the reactions of an (NMTPP)Zn alcoholate (EO growing end) with EO producing an EO → EO homosequence ($-OCH_2CH_2O-$) and with PS producing an EO → PS cross sequence ($-OCH_2CH(CH_3)S-$) and the reactions of an (NMTPP)Zn thio-

Table I
Copolymerizations of Epoxyethane (EO) and 1,2-Epithiopropane (PS) Initiated with (NMTPP)ZnSPr (1): Contents of Homosequences and Cross Sequences in the Products[a]

run	$[EO]_0/[PS]_0/[1]_0$	temp	light	content,[b] %					
				EO → EO	EO → PS	PS → PS	PS → EO	EO → EO/EO → PS	PS → PS/PS → EO
1[c]	50/50/1	rt[e]	dark	41.3	10.5	37.0	11.2	3.9	3.3
2[c]	50/50/1	70 °C	dark	42.8	8.9	38.4	9.9	4.8	3.9
3[c]	50/50/1	rt[e]	irradn[f]	31.5	20.3	27.0	21.2	1.6	1.3
4[d]	200/200/1	rt	dark	46.7	3.9	45.1	4.3	12.0	10.5
5[d]	200/200/1	rt	irradn[f]	41.3	13.1	31.1	14.5	3.2	2.1

[a] At 100% consumptions of comonomers. [b] ^{13}C NMR. [c] In C_6D_6 (5-mm-ϕ NMR tube). [d] In C_6H_6 (10-mL flask). [e] Room temperature (~20 °C). [f] Xenon arc light ($\lambda > 420$ nm).

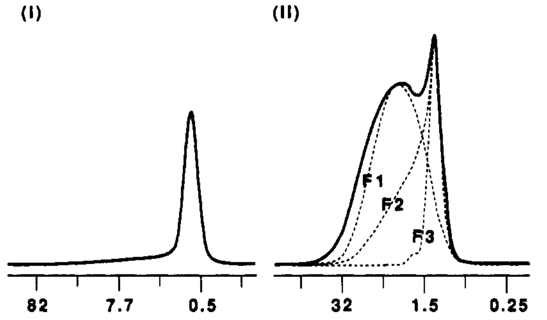


Figure 3. Copolymerizations of epoxyethane (EO) and 1,2-epithiopropane (PS) initiated with (NMTPP)ZnSPr (1) at room temperature. GPC profiles of the products formed under irradiation with xenon arc light [(I); run 3 (Table 1)] and in the dark [(II); run 4]. F1–F3 correspond to the fractions separated by column chromatography on silica gel with THF/$CHCl_3$/MeOH as eluent.

late (PS growing end) with PS producing a PS → PS homosequence ($-SCH_2CH(CH_3)S-$) and with EO producing a PS → EO cross sequence ($-SCH_2CH_2O-$). The contents of these four sequences in the products could be separately evaluated by ^{13}C NMR (Figure 2),[6] and the results were summarized in Table I. In the copolymerizations in the dark [runs 1 [see also Figure 2 (I)] and 2], the contents of the cross sequences in the products are only about 10%, while those of the homosequences are about 40% irrespective of the copolymerization temperature. The ratios of the contents of the homosequences and cross sequences [(EO → EO)/(EO → PS), (PS → PS)/(PS → EO)] in the products are thus calculated to be in the range of 3.3–4.8. On the other hand, in the product formed under irradiation with visible light (Figure 2 (II)), the sum of the contents of the cross sequences is more than 40%, with the ratios (EO → EO)/(EO → PS) and (PS → PS)/(PS → EO) being 1.6 and 1.3, respectively (run 3). A similar tendency was observed in the copolymerizations starting from the molar ratio $[EO]_0/[PS]_0/[1]_0$ of 200/200/1 (runs 4 and 5). Thus, by using (NMTPP)ZnSPr (1) as initiator for the copolymerization of epoxide and episulfide, the copolymerizability could be enhanced by irradiation with visible light.

The GPC chromatograms of the products formed under irradiation with visible light were much simpler than those obtained in the dark. The product in run 3 (Table I) showed a unimodal GPC chromatogram with the M_w/M_n ratio of 1.27 (M_n = 6800) (Figure 3 (I)). On the other hand, the GPC chromatogram of the product in run 4 exhibited a bimodal molecular weight distribution consisting of a broad peak with a sharp shoulder on the low molecular weight side (Figure 3 (II)). This product could be separated into three major fractions (total recovery: 89%), F1 (isolated yield: 33%), F2 (52%), F3 (4%), by column chromatography on silica gel with THF/$CHCl_3$/MeOH as eluent, and identified with the aid of ^{1}H and ^{13}C NMR to the block copolymer of EO (33%) and PS (67%) (EO → PS and PS → EO cross sequences not detected by ^{13}C NMR), the copolymer of EO (62%) and PS (38%) with low contents of cross sequences (EO → EO/EO → PS/PS → PS/PS → EO = 61/4/29/6), and the homopolymer of EO, respectively. Thus, the product formed in the dark does not contain such a fraction rich in the cross sequences as formed under irradiation.

All the above observations lead to the following conclusions: Irradiation with visible light and elevation of the reaction temperature both result in the accelerated consumptions of comonomers. At 70 °C in the dark, four elementary reactions are almost equally accelerated, taking into account the unchanged sequence distribution and GPC chromatogram of the product compared with the case at room temperature in the dark. On the other hand, irradiation with visible light is considered to accelerate the cross propagation steps much more than the homopropagation steps, resulting in the contents of the four sequences coming closer to one another and the change in the GPC chromatogram of the product.

Photoinduced polymerization has been the subject of much interest from fundamental as well as practical viewpoints, and numerous examples of photoinitiating systems have been reported to date.[7] However, in most cases, the effect of irradiation appears only in the initiation step to generate the initiating species, while the subsequent chain propagation steps are not affected by irradiation. The only exceptional cases are the polymerizations of methacrylic esters initiated with alkylaluminum porphyrins[8] and of epoxides with (NMTPP)ZnSPr (1),[4] where the light-absorbable metalloporphyrin moieties are subsequently transferred to the newly formed growing terminals, and not only the initiation step but also the propagation steps are photoaccelerated. Thus, the present paper provides the unprecedented example of photoenhanced copolymerizability of comonomers with very different polymerizabilities. Further studies are in progress to generalize this phenomenon using other monomers and metalloporphyrin initiators.

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(2) (NMTPP)ZnSPr (1) was prepared by the reaction of the free-base N-substituted porphyrin 21-methyl-5,10,15,20-tetraphenylporphine with diethylzinc in benzene at room temperature under nitrogen, followed by the reaction of the produced (NMTPP)ZnEt with 1-propanethiol (see refs 4 and 5).

(3) Consumptions of comonomers were determined, respectively, from the intensities of the signals due to $-CH_2OCH_2-$ and $-CHSCH_2-$ units in the product relative to those of the comonomers. ^1H NMR in C_6D_6 (C_6H_6 (δ 7.4) as internal standard): epoxyethane (EO), δ 2.4 (s, CH_2); 1,2-epithiopropane (PS), δ 2.75 (m, CH), 2.32, 1.95 (d, d, CH_2), 1.4 (d, CH_3); polymeric units, 3.4–3.8 ($-\mathrm{C}H_2\mathrm{OC}H_2-$), 2.6–3.3 ($-\mathrm{C}H\mathrm{SC}H_2-$), and 1.5 ($CH_3$). The assignment of the signals of the polymeric units was made based on the spectra of the following compounds: poly-EO, δ 3.5–4.0 ($-(CH_2OCH_2)-$); poly-PS, 2.7–3.3 ($\mathrm{C}H\mathrm{C}H_2$) and 1.5 (CH_3); $EtOCH_2CH(CH_3)SEt$, 3.5–3.7 (CH_2), 3.12 (m, CH), and 1.53 (d, CH_3); $EtSCH_2CH_2OEt$, 2.81 (t, SCH_2) and 3.66 (t, CH_2O).

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(6) ^{13}C NMR in C_6D_6 (C_6D_6 (δ 128.0) as internal standard): EO → EO ($-OCH_2CH_2O-$), δ 70.9 (CH_2); EO → PS ($-OCH_2CH(CH_3)$-$S-$), δ 76.8 (CH_2), 40.1 (CH), and 18.8 (CH_3); PS → PS ($-SCH_2CH(CH_3)S-$), δ 41.6 (CH), 38.8 (CH_2), and 20.9 (CH_3); PS → EO ($-SCH_2CH_2O-$), δ 30.7 (SCH_2) and 71.8 (CH_2O). The assignment of the signals was made based on the spectra of the following compounds: poly-EO, δ 71.0 (CH_2); poly-PS, δ 41.5 (CH), 38.8 (CH_2), and 20.9 (CH_3); $EtOCH_2CH(CH_3)SEt$, δ 76.2 (CH_2), 39.5 (CH), and 18.7 (CH_3); $EtSCH_2CH_2OEt$, δ 31.5 (SCH_2) and 71.1 (CH_2O).

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