

Photodimerization and Polymerization of PEG Derivatives through Radical Coupling using Photochemistry of Dithiocarbamate

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This article reports the development of a novel polymerization based on the photochemistry of benzyl *N,N*-diethyldithiocarbamate (BDC), which dissociates to a pair of radicals, benzyl radicals and dithiocarbamyl radicals, by ultraviolet light (UV) irradiation. Upon UV irradiation to a *N,N*-dimethylformamide (DMF) solution with extremely thin thickness containing mono-BDC-derivatized poly(ethylene glycol) (PEG) dimerization of the PEG derivative occurred due to bibenzyl bond formation by radical coupling between benzyl radicals generated in the terminal of the PEG derivative. The reaction rate was about 90% by several tenth minutes of irradiation. On the other hand, UV irradiation of a DMF solution of bis-BDC-derivatized PEG produced high molecular weight PEG derivatives by inter-molecularly coupling between diradicals, which have benzyl radicals at both terminals of the PEG derivative. The products had alternative structure of PEG chain and bibenzyl bond. The chain length of the produced polymer grew with irradiation time. The reaction rate rapidly increased at higher light intensities, and further increased at shorter optical distance of the solution to reach about 90% by several tenth minutes of irradiation. Possibility and limitation of this polymerization method was discussed.

KEY WORDS: Iniferter / Radical Coupling / Photopolymerization / Benzyl *N,N*-Diethyldithiocarbamate / PEG /

Iniferter-based radical polymerization^{1,2} is one of the most popular living/controlled polymerizations,^{3–6} which have gained importance in polymer control in terms of molecular weight, molecular weight distribution, and architecture control. Recently, improvement of living/control properties in the iniferter-based radical polymerization was performed by combination with reversible addition-fragmentation chain transfer (RAFT)^{7–9} or selecting the irradiation wavelength.¹⁰

Ultraviolet light (UV) irradiation of benzyl *N,N*-diethyldithiocarbamate (BDC), which is one of an iniferter, induces reversible radical dissociation reaction to generate benzyl radicals and dithiocarbamyl radicals (Figure 1A, reaction I) but they are rapidly recombined to regenerate BDC (reaction II). In iniferter polymerization that induces living radical polymerization, the generated benzyl radicals act as the initiator of radical polymerization of vinyl monomer (reaction III), and living radical polymerization can occur by repeating reversible association/dissociation with dithiocarbamyl radicals at growth terminals (reactions IV and V). By using this polymerization, block copolymers having the ability to control the block chain lengths with minimal transfer or termination reactions or block copolymers with additional functionality were successfully synthesized in solution^{11,12} or on surface^{13–16} for biomedical applications.

If there are no monomers, chain transfer of the generated benzyl radicals and dithiocarbamyl radicals to solvent or polymer matrix, and coupling between the radicals occur simultaneously. As mentioned above, coupling between benzyl radicals and dithiocarbamyl radicals is reversible, and these radicals are regenerated by UV re-irradiation of BDC

(Figure 1A, reactions I and II). Coupling between dithiocarbamyl radicals generates *N,N,N',N'*-tetraethylthiuram disulfide, which is dissociated to dithiocarbamyl radicals by UV irradiation because the coupling is also reversible (reactions VII and VIII). On the other hand, coupling between benzyl radicals generates bibenzyl, which is not dissociated by UV irradiation (reaction VI). Therefore, benzyl radicals are selectively consumed by UV irradiation of BDC to generate bibenzyl. By using the photo-induced bibenzyl bond formation, hydrogels were prepared from BDC-derivatized hydrophilic copolymers to immobilize bioactive substances.¹⁷

Previously, we developed a surface modification method using the unique photoreactivity of BDC, in which functional groups could be derivatized into the surface of substrate materials, fixed with BDC groups, by cross-coupling reaction between heterogeneous radicals which had been generated on the surface and in a solution of dithiocarbamate with functional groups by UV irradiation. These results suggested the ability of the occurrence of radical coupling in solutions.¹⁸

In the present study, we attempt to develop a new method for polymer synthesis through the coupling between benzyl radicals generated from BDC derivatives by UV irradiation. If radical dissociation of BDC groups will occur by UV irradiation of bifunctional compounds with BDC groups at both terminals, diradicals, which have benzyl radicals at both terminals will be generated (Figure 1B, reaction IX). Polymers will then be produced by successive coupling of these radicals intermolecularly (reactions X and XI). In the first part of this article, the preparation of poly(ethylene glycol) (PEG), which is one of the most popular biomedical polymers for biocom-

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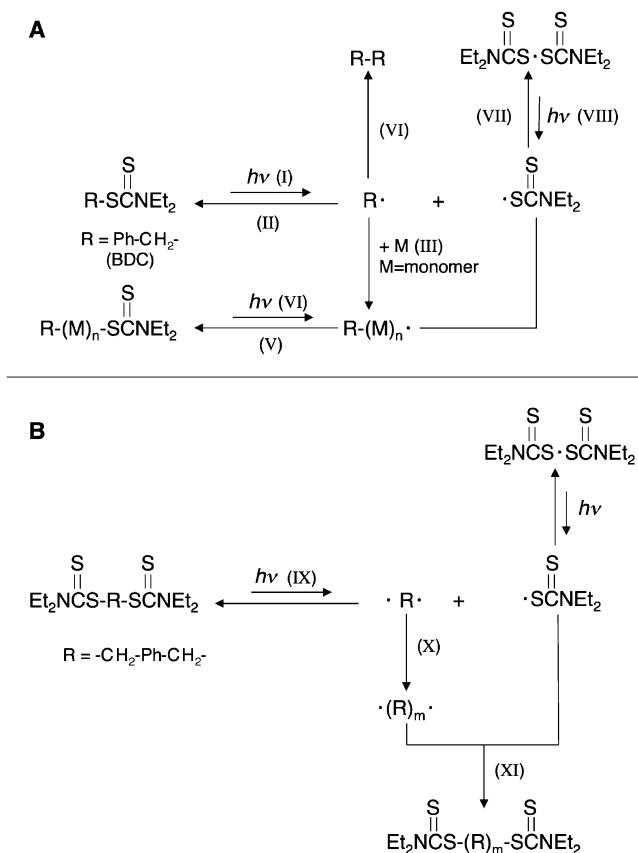


Figure 1. (A) Reaction mechanisms in the preparation of bibenzyl through the intermolecular coupling of benzyl radicals (Schemes I and VI) from benzyl *N,N*-diethyldithiocarbamate (BDC) and polymerization through Schemes I, III, and V. (B) Reaction mechanism in the polymerization through the intermolecular coupling between benzyl radicals generated from bifunctional BDC.

patible surface modifications^{19,20} or drug modification,^{21,22} derivative with a BDC group at one terminal and that with two BDC groups at both terminals as model compounds is described. Then, we examine whether UV irradiation of solutions of these compounds induces dimerization of the mono-BDC-derivatized PEG by the coupling of benzyl radicals and polymerization of the bis-BDC-derivatized PEG.

EXPERIMENTAL

General Procedure

¹H NMR spectra were recorded on a JEOL JNM-GX270 FT NMR spectrometer (270 MHz, Tokyo, Japan). The chemical shifts were given as δ values from Me₄Si as the internal standard. IR spectra were recorded on a Shimadzu DR-8020 FT-IR spectrophotometer (Kyoto, Japan). GPC analyses in DMF were carried out with a HPLC-8020 instrument (Tosoh, Tokyo, Japan) (column: Tosoh TSKgel α -3000 and α -5000). The columns were calibrated with narrow weight distribution PEG standards (Tosoh). UV-vis spectra in H₂O were recorded with a UV-vis spectrophotometer (UV-1700, Shimadzu Co., Kyoto, Japan).

Materials

PEG monomethyl ether (M_n ; 340, polydispersity (M_w/M_n); 1.0, determined by GPC) was obtained from Aldrich Chemical Company Inc. (Milwaukee, WI, USA). Solvents and the other reagents, all of which are special reagent grade, were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used after conventional purification.

Preparation of Mono-BDC-derivatized PEG (1)

To a 1,2-dichloroethane solution (100 mL) of PEG monomethyl ether (10.0 g, 29.4 mmol) 1,2-dichloroethane solution (100 mL) of *p*-(chloromethyl)benzoyl chloride (11.0 g, 58 mmol) was added dropwisely at 0 °C. To the mixed solution 5 mL of pyridine was added. After stirring for 24 h at room temperature, the filtrate of the reaction mixture concentrated under vacuum. The obtained residue was dissolved in ethanol (50 mL) and added to an ethanol solution (100 mL) of sodium *N,N*-diethyldithiocarbamate trihydrate (15.7 g, 70 mmol) at 0 °C. After stirring for 22 h at room temperature, the filtrate of the reaction mixture was concentrated under vacuum. The obtained residue was purified by column chromatography (silica gel 60, elution chloroform). Yield of (**1**) was 9.3 g (64%). The molecular weight (M_n) of (**1**), determined by GPC, was 605 with polydispersity of 1.1. ¹H NMR (DMSO-*d*₆): δ 7.91 (d, 2H, $J = 14.0$ Hz, C₄H₆), 7.54 (d, 2H, $J = 14.0$ Hz, C₆H₄), 4.62 (s, 2H, CH₂S), 4.38 (t, 2H, $J = 5.0$ Hz, C(O)OCH₂), 4.00 (q, 2H, $J = 7.0$ Hz, NCH₂), 3.75 (q, 2H, $J = 7.0$ Hz, NCH₂), 3.60–3.40 (m, 29H, (CH₂CH₂O)_{7.3}), 3.23 (s, 3H, CH₃O), 1.20 (t, 6H, $J = 7.3$ Hz, CH₂CH₃), FT-IR (KBr) 2782 cm⁻¹ (CH₂), 1717 cm⁻¹ (C(O)C₆H₄), 1611 cm⁻¹ (C₆H₄), 1489, 1207 cm⁻¹ (C(S)N), 1111 cm⁻¹ (CH₂OCH₂).

Preparation of Bis-BDC-derivatized PEG (2)

To a 1,2-dichloroethane solution (40 mL) containing PEG (M_n ; 414, polydispersity; 1.0, 8 g, 19.3 mmol) and pyridine (10 mL, 160 mmol) 1,2-dichloroethane solution (30 mL) of *p*-(chloromethyl)benzoyl chloride (15.1 g, 80 mmol) was added dropwisely at 0 °C. After stirring for 18 h at room temperature, the filtrate of the reaction mixture concentrated under vacuum. The obtained residue was dissolved in methanol (200 mL) and added with sodium *N,N*-diethyldithiocarbamate trihydrate (22.0 g, 100 mmol). After stirring for over night at room temperature, the filtrate of the reaction mixture was concentrated under vacuum. The obtained residue was purified by column chromatography (silica gel 60, elution mixture of chloroform and methanol). Yield of (**1**) was 8.6 g (45.5%). The molecular weight (M_n) of (**2**), determined by GPC, was 974 with polydispersity of 1.1. ¹H NMR (CHCl₃-*d*): δ 8.00 (d, 4H, $J = 14.1$ Hz, C₄H₆), 7.46 (d, 4H, $J = 14.1$ Hz, C₆H₄), 4.61 (s, 4H, CH₂S), 4.46 (t, 2H, $J = 5.4$ Hz, C(O)OCH₂), 4.09 (q, 4H, $J = 7.1$ Hz, NCH₂), 3.84 (q, 4H, $J = 7.1$ Hz, NCH₂), 3.68–3.39 (m, 35H, (CH₂CH₂O)_{8.8}), 1.28 (t, 12H, $J = 6.8$ Hz, CH₂CH₃), FT-IR (KBr) 1720 cm⁻¹ (C(O)C₆H₄), 1480, 1210 cm⁻¹ (C(S)N), 1105 cm⁻¹ (CH₂OCH₂).

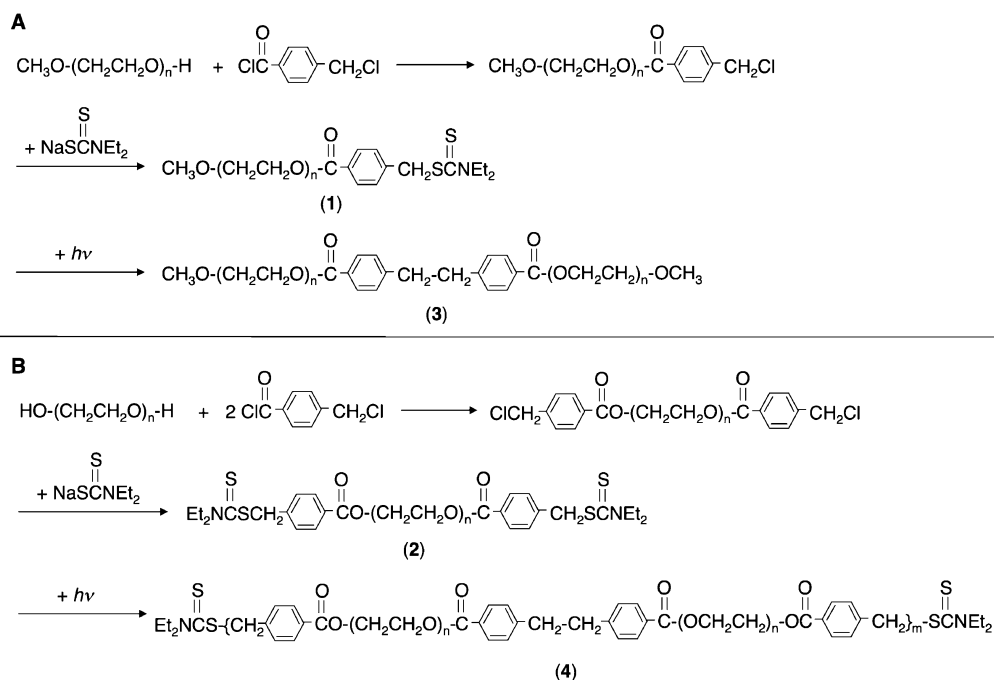


Figure 2. (A) Preparation schemes of mono-BDC-derivatized PEG (1) and its dimerization. (B) Preparation schemes of bis-BDC-derivatized PEG (2) and its polymerization.

Photo-coupling

An *N,N*-dimethylformamide (DMF) solution containing the BDC-derivatized PEGs (1 or 2) were placed between two quartz glass slides (30 × 40 mm). The solution was UV irradiated through the slide. The irradiation was carried out on a Hamamatsu Photonics L5662-02 (250 W mercury-xenon (Hg-Xe) lamp, Shizuoka, Japan). The intensity of UV light source was measured at 250 nm on a TOPCON UVR-25 (Tokyo, Japan).

RESULTS

Synthesis of BDC-derivatized PEGs

Two kind of BDC-derivatized PEGs, PEG with a BDC group at one terminal (1) and those at both terminals (2), were synthesized using monomethoxy PEG (M_n ; 340 by GPC) or PEG (M_n ; 414 by GPC) as a starting material, respectively (Figure 2). At first, the PEGs were derivatized with benzyl chloride groups by esterification with chloromethylbenzoyl chloride of hydroxyl groups at the terminals of PEGs. Subsequently, the chloride groups were substituted by *N,N*-diethylthiocarbamyl groups by desalting reaction with sodium *N,N*-diethylthiocarbamate. The molecular weight (M_n), determined by GPC, of the synthesized mono-BDC-derivatized PEG (1) was 605 with polydispersity of 1.1 and that of bis-BDC-derivatized PEG (2) was 974 with polydispersity of 1.1. On the other hand, the molecular weights, obtained by UV-vis absorption spectroscopy, of (1) and (2) were 644 and 928, respectively. Therefore, the number of BDC groups per molecule was 0.94 in (1) and 2.1 in (2), indicating that PEG derivatives with BDC groups introduced into one terminal for (1) or both terminals for (2) were synthesized.

Photodimerization of Mono-BDC-derivatized PEG (1)

A DMF solution containing mono-BDC-derivatized PEG (1) (0.88 mol/dm³) was placed between two quartz glass slides held a short distance apart (optical distance, 33 μm), and photoirradiated (10 mW/cm²) through the slide. GPC spectra indicated the appearance of 2 new peaks on the sides of a high molecular weight (elution time, about 38 min) and a low molecular weight (about 41 min) in addition to the peak at an elution time of about 39 min corresponding to the original material (1) (Figure 3). The molecular weight (M_n) of the product showing the peak on the high molecular weight side was about 1,000. This product showed the disappearance of absorption at around 280 nm derived from dithiocarbamyl group by UV absorption spectra (Figure 4A), and the disappearance of the signals of *N*-methylene proton (3.8, 4.0 ppm) and *S*-methylene proton (4.6 ppm) derived from dithiocarbamyl groups and the appearance of the signal of methylene proton (2.99 ppm) derived from bibenzyl by ¹H NMR spectra (Figure 4B). These results indicated that dimerization occurred at the benzyl position to generate bibenzyl derivative (3), of which chemical structure was shown in Figure 2A, by the UV irradiation of BDC-derivatized PEG (1). The product showing the peak on the low molecular weight side on the GPC spectra was identified as *N,N,N',N'*-tetraethylthiuram disulfide formed by coupling of dithiocarbamyl radicals. With the prolongation of irradiation time, the peak of the starting material (1) decreased gradually, while the peak of the bibenzyl derivative (3) was elevated on the GPC spectra (Figure 3). The reaction rate of (3) determined using the decrease in the peak area of (1) in the GPC was about 90% by 30-min irradiation.

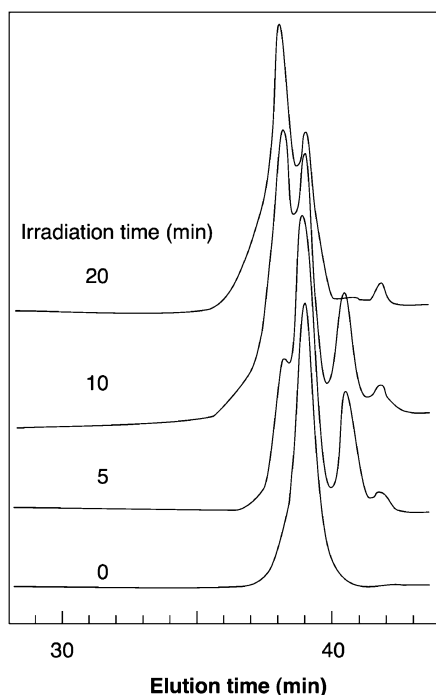


Figure 3. GPC spectral change of mono-BDC-derivatized PEG (1) by UV irradiation. Conditions: initial concentration of (1); 0.88 mol/dm^3 , UV intensity; 10 mW/cm^2 , optical distance; $33 \mu\text{m}$.

In 20-min irradiation at a fixed light intensity (10 mW/cm^2) and optical distance ($33 \mu\text{m}$), and at different concentrations of (1), the reaction rate increased with the elevation of the concentration, but markedly decreased over 0.88 mol/dm^3 (Table I, runs 1 to 6). In 10-min irradiation at a fixed concentration of the monomer (0.88 mol/dm^3) and optical distance ($33 \mu\text{m}$), and at different light intensities, no reaction occurred at the lowest light intensity of 1.5 mW/cm^2 , but the reaction rate increased with the elevation of the light intensity higher than 5 mW/cm^2 and reached a constant level at irradiation intensities over 10 mW/cm^2 (Table I, runs 7 to 11). In 10-min irradiation at a fixed concentration of the monomer (0.88 mol/dm^3) and light intensity (10 mW/cm^2), the reaction rate remained unchanged to be high within a range between $8.3 \mu\text{m}$ and $33 \mu\text{m}$ of the optical distance (Table I, runs 9, 12 and 13).

Photopolymerization of Bis-BDC-derivatized PEG (2)

A DMF solution containing bis-BDC-derivatized PEG (2) was placed between two quartz glass slides held a short distance apart and UV irradiated in a similar manner as above. Figure 5 shows the changes in the GPC spectrum with irradiation time at a fixed concentration of (2) (0.44 mol/dm^3), light intensity (10 mW/cm^2) and optical distance ($33 \mu\text{m}$). The intensity of the peak of the original material (2) (elution time, about 38 min) decreased with irradiation time, and the intensities of both peaks on the high molecular weight side and of *N,N,N',N'*-tetraethylthiuram disulfide on the low molecular weight side (about 40 min) increased. The intensity of the peaks equivalent to the molecular weight of dimers

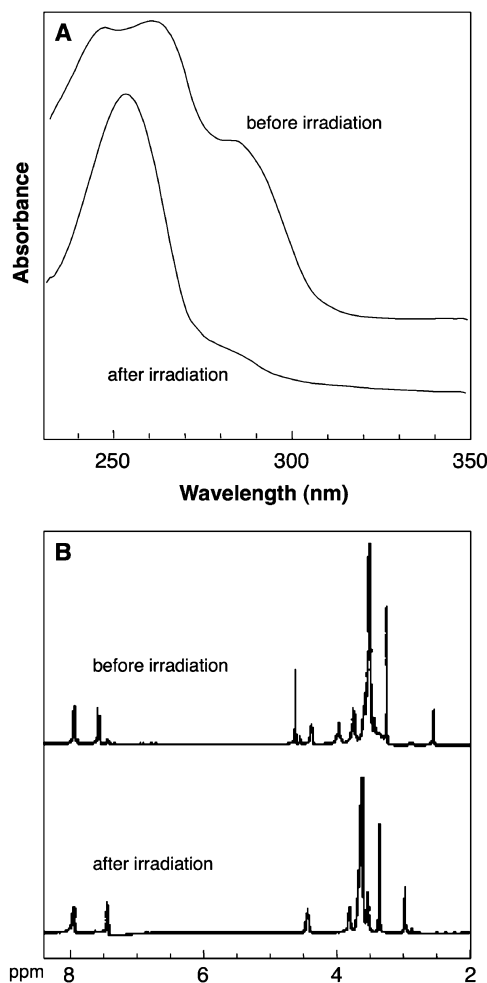


Figure 4. UV absorption spectra (A) and ^1H NMR spectra (B) of mono-BDC-derivatized PEG (1) before and after UV irradiation. Conditions: initial concentration of (1); 0.88 mol/dm^3 , UV intensity; 10 mW/cm^2 , irradiation time; 20 min, optical distance; $33 \mu\text{m}$.

Table I. Results for the dimerization of mono-BDC-derivatized PEG (1) in DMF

run	Concentration of (1) (mol/dm^3)	Irradiation time (min)	Light intensity (mW/cm^2)	Optical distance (μm)	Reaction rate ^a (%)
1	0.11	20	10	33	45
2	0.22	20	10	33	46
3	0.44	20	10	33	53
4	0.88	20	10	33	82
5	1.76	20	10	33	35
6	3.52	20	10	33	25
7	0.88	10	1.5	33	0
8	0.88	10	5	33	55
9	0.88	10	10	33	85
10	0.88	10	20	33	89
11	0.88	10	30	33	85
12	0.88	10	10	16.5	82
13	0.88	10	10	8.3	87

^acalculated from the amount of the decrease in the peak area of (1) in the GPC measurements.

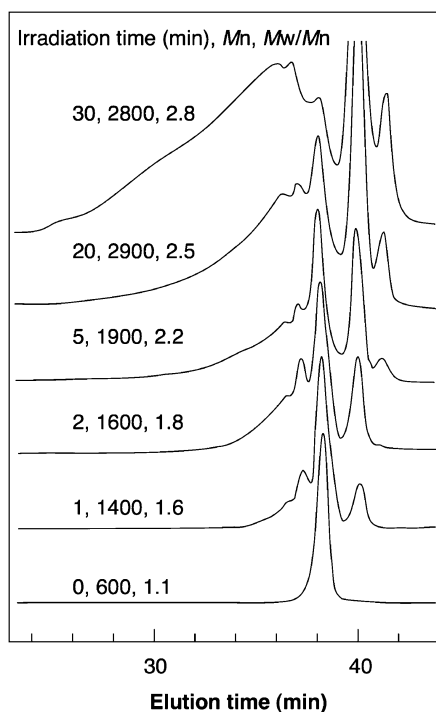


Figure 5. GPC spectral change of bis-BDC-derivatized PEG (**2**) by UV irradiation. Conditions: initial concentration of (**2**); 0.44 mol/dm^3 , UV intensity; 10 mW/cm^2 , optical distance; $33 \mu\text{m}$.

(about 37 min) and trimers (about 36.5 min) increased by irradiation for a short period, and the peak gradually moved toward the high molecular weight side. The peak obtained by 30-min irradiation on the high molecular weight side was very broad, and distributed up to about 10^6 as PEG although a small amount of the original material was remained. This indicated that almost all bis-BDC-derivatized PEGs (**2**) were polymerized by UV irradiation.

Table II summarizes the results of polymerization. At a fixed intensity of light of 10 mW/cm^2 , the reaction rate determined by the decrease in the peak area of the starting material (**2**) on the GPC spectra was 40% by 1-min irradiation, and gradually increased with the prolongation of irradiation to reach about 90% by 30-min irradiation (runs 2 to 7). The $(X_n - 1)/X_n$, where X_n is the reaction rate which was calculated by the increase in the mean molecular weight of the polymer products determined by GPC spectrometry, agreed well with the above reaction rate (p) up to 20 min of irradiation. During this period, about 5 molecules were coupled, then p increased but $(X_n - 1)/X_n$ remained unchanged, giving rise to differences between p and $(X_n - 1)/X_n$. It was considered that radical coupling occurred successively up to about 80% of the reaction rate.

At an light intensity of 30 mW/cm^2 , the reaction rate increased to about 60% by 1-min irradiation, and further increased with irradiation time, then reached a constant level of about 80% by irradiation for longer than 5 min (runs 8 to 13). The polymerization more rapidly increased by higher light intensities. p agreed well with $(X_n - 1)/X_n$.

Table II. Kinetic results for the photopolymerization of bis-BDC-derivatized PEG (**2**) in DMF^a

run	Light intensity (mW/cm^2)	Irradiation time (min)	Reaction rate p^b	Molecular weight (M_n) ($\times 10^3 \text{ g/mol}^c$)	Degree of coupling ^d x_n	$(x_n - 1)/x_n$
1	0	0	0	0.6	1.0	0.00
2	10	1	0.4	1.4	2.3	0.57
3	10	2	0.56	1.6	2.7	0.63
4	10	5	0.67	1.9	3.2	0.68
5	10	10	0.69	2.4	4.0	0.75
6	10	20	0.82	2.9	4.8	0.79
7	10	30	0.91	2.8	4.7	0.79
8	30	1	0.59	1.7	2.8	0.65
9	30	2	0.73	1.9	3.2	0.68
10	30	5	0.83	2.5	4.2	0.76
11	30	10	0.82	3.2	5.3	0.81
12	30	20	0.83	2.8	4.7	0.79
13	30	30	0.84	3.1	5.2	0.81
14	15	10	0.84	3.2	5.3	0.81
15	15	20	0.94	3.9	6.5	0.85
16	15	30	0.94	3.7	6.2	0.84

^aCondition; concentration of (**2**) = 0.45 mol/dm^3 , optical distance = $33 \mu\text{m}$, optical distance = $16.5 \mu\text{m}$. ^bcalculated from the amount of the decrease in the peak area of (**2**) in the GPC measurements. ^cdetermined from GPC measurements. ^dobtained from molecular weight determination.

When the optical distance was halved from above ($33 \mu\text{m}$), the reaction rate was about 80% by 10-min irradiation, and almost all materials disappeared by 20-min irradiation (reaction rate, about 95%) (runs 14 to 16). However, the value of $(X_n - 1)/X_n$ remained about 80% after 10-min irradiation. At thinner optical distance of the solution, p was higher (higher than 90%), but there was no difference in the molecular weight between the polymers produced at the reaction rate of 90% and 80%.

DISCUSSION

We synthesized 2 kinds of PEG derivatives in which BDC groups were derivatized into one terminal (**1**) or both terminals (**2**) (Figure 2), and UV irradiated DMF solutions containing each PEG derivative. As we expected, a dimer was produced from the PEG derivative with BDC groups at one terminal (**1**), and a polymer was produced from the PEG derivative with BDC groups at both terminals (**2**). This was probably due to bibenzyl bond formation by the coupling between benzyl radicals that had been generated in the PEG terminals by UV irradiation of BDC groups as shown in Figure 1.

The reactivity of bibenzyl bond formation depended on the light intensity, irradiation time, concentration of BDC groups, and optical distance of the solution. Since the pair of radicals, generated by photodissociation of BDC, is rapidly recombined to generate BDC, the amount of BDC is much larger than that of the pair of radicals (Figure 1, reactions I and II). Therefore, there is little existence of radicals even under UV irradiation. This is confirmed by the fact that polymerization of vinyl monomer using BDC is much slower than that using conventional thermal radical polymerization initiators such as AIBN. To induce the coupling between benzyl radicals generated from BDC efficiently, it is necessary to increase

the probability of encountering radicals by an elevation of the concentration of dithiocarbamate in the reaction system. In the irradiation of dithiocarbamate-derivatized PEG at one terminal performed at different concentrations of the dithiocarbamate solution, the reaction rate increased with the elevation of the concentration, but started to decrease at 0.88 mol/dm^3 (Table I runs 1 to 6). Because dithiocarbamate itself absorbs the UV light, a large amount of dithiocarbamate on the side close to the light source absorbed a large amount of light beams if the concentration of dithiocarbamate was high, and homogeneous photoactivation of dithiocarbamate could not be obtained in the optical direction, resulting in the heterogeneous distribution of radicals in the reaction system. Therefore, the coupling reaction progressed preferentially on the side close to the light source, and that is probably the reason for the reduced reaction rate in the entire system. If radicals can homogeneously exist in the reaction system at a high concentration, the reaction rate in the entire system would be high. This can be obtained by a short optical distance and a high light intensity. In fact, little dimerization occurred if the light intensity was low (Table I run 7), and the reaction rate markedly increased with elevation of the light intensity (runs 7 to 9) and tended to reach the maximum at light intensities higher than 10 mW/cm^2 (runs 9 to 11). The reaction rate remained unchanged at optical distances shorter than $33 \mu\text{m}$ (runs 9, 12 and 13), but the optical distance would considerably affect the reaction rate if the concentration of BDC compounds is high.

In polymerization using PEG with BDC at both terminals (2), the reaction rate increased with irradiation time (Table II, runs 2 to 7), and rapidly increased at higher light intensities (runs 8 to 13). The reaction rate further increased at shorter optical distances in this experimental condition (runs 14 to 16). Under the above conditions, coupling of molecules successively occurred at reaction rate up to about 80% to produce polymers. This indicated that there were little chain transfers to the solvent and surrounding molecules. The coupling number in the polymer products was about 5 on average. Unfortunately, polydispersity of the obtained polymers were very wide. There were deviations from the theoretical reaction rate at that higher than 80%. The reaction rate (p) obtained from the consumption of monomers increased, while the coupling number (X_n) determined using the molecular weight of the products remained unchanged, suggesting that intra-molecular coupling occurred. Because the molecular weight of polymerization products in a condensation polymerization system extremely increases if the reaction rate exceeds 99%, it is essential to elevate the degree of reaction rate between molecules. Therefore, in the present reaction system, it was considered necessary to improve the reaction rate and to optimize the polymerization condition with narrow molecular weight distributions, which may be induced by homogeneous photo-reaction in the presence of high concentration of monomers.

On the other hand, we attempted to investigate the usefulness of star-shaped cationic polymers as a base chemical structure for a novel high-performance gene carrier.^{23–26} These polymers, known as star vector, were prepared by iniferter-

based living radical polymerization of *N,N*-dimethylaminopropylacrylamide (DMAPAAM), using the respective multidithiocarbamate-derivatized benzenes (multifunctional iniferters). The gene expression efficiency was enhanced with the increase in the branching number of the polymers in COS-1 cells. This study indicated that the terminal ends of the DC-derivatized polymers could be crosslinked by only photoirradiation without use of any chemical crosslinking agents such as glutaraldehyde or diisocyanate. The crosslinking may be applied for molecular architecture to prepare more complex-shaped polymers, such as mesh or hyper-branch, which may have advantage for enhancement of gene transfection activity as a gene delivery vectors. The evaluation of gene expression efficiency in the crosslinked polymers was on going. The result will be reported in the near future.

CONCLUSION

In this study, polymerization was shown to be possible by the UV irradiation of a dilute solution of PEG with BDC groups derivatized into both terminals as a model compound. If BDC residues can be introduced into both terminals, this method could be applicable to other compounds. In addition, secondary polymerization by coupling after vinyl polymerization is considered possible by combination with living radical polymerization of dithiocarbamate, and we are currently testing this possibility.

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