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Synthesis of Self-Photosensitizing Polyesters Carrying Pendant Norbornadiene (NBD) Moieties and Benzophenone Groups and Their Photochemical Reactions

Isao Nishimura, Atsushi Kameyama, and Tadatomi Nishikubo*

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
Rokkakubashi, Kanagawa-ku, Yokohama 221, Japan

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ABSTRACT: Various epoxy monomers containing benzophenone (BP) groups were synthesized by reactions of potassium or lithium salts of BP derivatives with excess epichlorohydrin or epibromohydrin using tetrabutylammonium bromide (TBAB) as a phase transfer catalyst (PTC). The copolymerization of glycidyl 3-(piperidylcarbonyl)-2,5-norbornadiene-2-carboxylate (GPNC), which was prepared by the reaction of epichlorohydrin with potassium carboxylate of a norbornadiene (NBD) derivative using a PTC, and (glycidyloxy)benzophenone with phthalic anhydride (PAn) proceeded in 93% yield using TBAB as a catalyst in sulfolane at 100 °C for 24 h to give self-photosensitizing polyester **P-1** containing a pendant NBD moiety and a pendant 4-oxybenzophenone group. Copolymerizations of various epoxy monomers containing certain NBD moieties and BP groups with PAn produced corresponding polyesters with pendant NBD moieties and BP groups in good yields. The photochemical valence isomerizations of the NBD moieties and the photosensitizing isomerizations of the NBD moieties due to the energy transfer from excited BP groups to the NBD moieties in the polymers were performed in the film state or in dichloromethane solution. From this result, it was found that rates of the photochemical isomerization of the NBD moieties in the polymers were strongly enhanced by the introduction of the pendant BP, *N*-alkyl-*N*,*N*′,*N*′-trimethyl-4,4′-diaminobenzophenone (TBP), group. Furthermore, the photochemical isomerization of the NBD moieties in the polymers having a pendant TBP group proceeded effectively in a diluted dichloromethane solution compared with the mixtures of NBD polymers and low molecular weight photosensitizers such as 4,4′-bis(*N*,*N*-diethylamino)benzophenone. Glass transition temperatures (T_g's) of the prepared polyesters having NBD moieties and stored thermal energy in the corresponding quadricyclane (QC) residues in the polymers were measured by DSC analysis. Then, it was found that T_g's of NBD polyesters were 30−85 °C, and photoirradiated polyesters having QC residues released their stored thermal energies (about 90 kJ/mol) at temperatures above the T_g's of the corresponding NBD polymers.

Introduction

Photosensitizers contribute to efficient photochemical reactions, such as isomerization, dimerization, cycloaddition, and oxidation reactions of various organic compounds in the film state or in solution, which would not proceed or be less likely to proceed without the photosensitizer. Use of a photosensitizer is quite popular in the photoresist technology, in which the photosensitivity of the resist is strongly enhanced by the addition of appropriate photosensitizers. Polymeric photosensitizers have also been investigated in the field of organic photochemistry and photoresist technology. Moser and Cassidy[1] have reported *cis*−*trans* photoisomerization of *cis*-1,3-pentadiene by using poly(vinyl phenyl ketone) (PVPK) as a photosensitizer. Leermakers and James[2] have also used small pieces of PVPK film as a heterogeneous photosensitizer for photochemical *cis*−*trans* isomerization of *cis*-piperylene and the valence isomerization of norbornadiene (NBD) in isopentane. Neckers et al.[3−5] reported photodimerization of cumarin or indene, cycloaddition of benzo[*b*]thiophene to dichloroethylene, and valence isomerization of NBD to quadricyclane (QC) using a polymeric photosensitizer containing a benzophenone (BP) moiety. However, the efficiency of all these polymeric photosensitizers is generally comparable to or slightly lower than the corresponding low molecular weight photosensitizers used so far. Recently, Nishikubo et al. proposed[6−9] a novel concept such as a multifunctional polymeric photosensitizer composed of soluble or insoluble polymers having both pendant substrate-attracting groups and photosensitizing groups. These polymers have much higher photosensitization efficiency than the corresponding low molecular weight photosensitizers.

Hautala et al.[10] have reported a solar energy storage process using an NBD−QC system with heterogeneous photosensitizers such as the cross-linked polystyrene and silica gel having a pendant 4-(*N*,*N*-dimethylamino)benzophenone moiety. This process is a method for one of the effective uses of the solar energy exchange processes due to the NBD−QC isomerization reaction.[11−13] That is, this concept is quite unique in that it is clean and provides limitless energy in place of fossil fuels that cause serious environmental problems. Furthermore, polymers containing NBD moieties seem to be useful also as photoswitching materials, which utilize a change of a refractive index resulting from the isomerization reaction.[14] Taking the unique NBD characteristics into account, we have investigated[15,16] the synthesis and photochemical reaction of polymers containing NBD moieties in the side chain or in the main chain. Recently, we reported[17] the synthesis of polyesters containing NBD moieties in the side chain by the ring-opening copolymerization of epoxy monomers having several NBD moieties with carboxylic anhydrides.

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* To whom all correspondence should be addressed.

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This ring-opening alternating copolymerization proceeds smoothly and quantitatively using quaternary onium salts as the catalyst. However, the photochemical reactivity of some NBD moieties in the resulting polyesters is not high enough. To solve this problem, we consider introducing appropriate photosensitizing groups in the side chain of the polymer.

This article reports on the synthesis of epoxy monomers containing BP groups and the synthesis of self-photosensitizing polyesters carrying pendant NBD moieties and BP groups by the ring-opening copolymerization of the prepared epoxy monomers carrying BP groups and glycidyl esters having NBD moieties with dicarboxylic acid anhydride.

Experimental Section

Materials. The solvents were dried using P_2O_5, CaH_2, or Na metal wire and purified in the usual way before use. Phthalic anhydride (PAn) was recrystallized twice from chloroform. Epichlorohydrin was purified by distillation. Tetrabutylammonium bromide (TBAB) was recrystallized twice from ethyl acetate. Reagent grade dicyclohexylcarbodiimide (DCC), epibromohydrin, *n*-butyllithium (BL) suspended in *n*-hexane, 4-(*N*,*N*-dimethylamino)benzophenone (DABP), 4,4′-bis(*N*,*N*-diethylamino)benzophenone (BEBP), 4-aminobenzophenone (ABP), and 4,4′-diaminobenzophenone (DBP) were used without further purification. 2,5-NBD-2,3-dicarboxylic acid (NDC) was prepared by Diels−Alder reaction of the acetylenedicarboxylic acid with freshly distilled cyclopentadiene according to reported methods.[16] 3-(Piperidylcarbonyl)-2,5-NBD-2-carboxylic acid (PCNC) (mp: 147−148 °C), 3-(*N*,*N*-dipropylcarbamoyl)-2,5-NBD-2-carboxylic acid (DCNC) (mp: 130−131 °C), and 3-(methoxycarbonyl)-2,5-NBD-2-carboxylic acid (MCNC) (mp: 106−107 °C) were synthesized by the condensation reaction of piperidine, dipropylamine, or methanol with NDC, respectively, using DCC in acetone according to the reported methods.[16] Potassium salts of NBD derivatives were prepared by the reaction of PCNC, DCNC, and MCNC with potassium hydroxide in methanol. Glycidyl 3-(piperidylcarbonyl)-2,5-NBD-2-carboxylate (GPNC), glycidyl 3-(*N*,*N*-dipropylcarbamoyl)-2,5-NBD-2-carboxylate (GNDC), and glycidyl 3-(methoxycarbonyl)-2,5-NBD-2-carboxylate (GMNC) were synthesized by the reaction of potassium salts of PCNC, DCNC, or MCNC with excess epichlorohydrin according to the literature.[17]

Measurements. Infrared (IR) spectra were measured on a JASCO Model IR-700 spectrometer. Ultraviolet (UV) spectra were recorded on a Shimadzu Model UV-240. ^{1}H NMR spectra were recorded on JEOL Models JNMEX-90 (90 MHz) and JNMFX-200 (200 MHz) instruments in $CDCl_3$ with Me_4Si as an internal standard. The molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with the use of a Toso Model HLC-8020 GPC equipped with a refractive index detector using TSK gel columns (eluent: DMF, calibrated with narrow molecular weight polystyrene standards). The glass transition temperature (T_g) and the amount of stored energy in the pendant QC residue in the polymers were measured on a Perkin-Elmer differential scanning calorimeter Model DSC Station 4 at a heating rate of 10 °C/min.

Synthesis of 4-(Glycidyloxy)benzophenone (GOBP). The substitution reaction of potassium 4-benzoylphenolate (9.0 g, 36.6 mmol) and epichlorohydrin (20.7 mL, 220 mmol) was carried out using TBAB (1.1 g, 1.8 mmol) as a phase transfer catalyst (PTC) at 80 °C for 2 h. The reaction mixture was diluted in dichloromethane, and the produced potassium chloride was filtered off. The filtrate was washed several times with water and dried with anhydrous $MgSO_4$. Excess epichlorohydrin and dichloromethane were evaporated, and then the crude GOBP thus obtained was recrystallized from methanol. The yield of GOBP was 6.5 g (93%). Mp: 80.0−80.8 °C. IR (neat): 1645 (C═O), 1600, 1575 (C═C), 1249 (C−O−C, ether), and 911 cm^{-1} (C−O−C, cyclic ether). ^{1}H NMR ($CDCl_3$, TMS): δ 2.78 (dd, $J = 4.88$ Hz, $J = 2.69$ Hz, 1H, CH_2 in epoxy ring), 2.93 (dd, $J = 4.88$ Hz, $J = 4.39$ Hz, 1H, CH_2 in epoxy ring), 3.38 (m, 1H, CH in epoxy ring), 4.00 (dd, $J = 11.23$ Hz, $J = 5.86$ Hz, 1H, O−CH_2), 4.33 (dd, $J = 11.23$ Hz, $J = 2.93$ Hz, 1H, O−CH_2), 6.95−7.02 (m, 2H, aromatic protons), 7.42−7.60 (m, 3H, aromatic protons), and 7.72−7.85 ppm (m, 4H, aromatic protons).

Synthesis of 4-(*N*-Glycidyl-*N*-methylamino)benzophenone (GMBP). A solution of ABP (4.0 g, 20.0 mmol) in tetrahydrofuran (40 mL) (THF) was added to an *n*-hexane solution of BL (12.5 mL, 1.6 mol/L) at −78 °C with stirring. The reaction of this solution with iodomethane (1.2 mL, 20.0 mmol) was carried out using TBAB (0.32 g, 1.0 mmol) as a PTC at 50 °C for 3 h. The reaction mixture was diluted with ethyl acetate, and the produced lithium chloride was filtered off. The filtrate was washed several times with water and dried with anhydrous $MgSO_4$. Excess ethyl acetate was evaporated, and then the crude 4-(*N*-methylamino)benzophenone (MABP) thus obtained was purified by silica gel column chromatography using a mixture of ethyl acetate/*n*-hexane (1/3) as the eluent. The yield of MABP was 2.0 g (48%). A solution of MABP (2.0 g, 9.6 mmol) in THF (18 mL) was added to an *n*-hexane solution of BL (6.0 mL, 1.6 mol/L) at −78 °C with stirring. The reaction of this solution with epibromohydrin (8.1 mL, 96 mmol) was performed using TBAB (0.16 g, 0.48 mmol) as a PTC at 70 °C for 12 h. The reaction mixture was diluted with ethyl acetate, and the produced lithium bromide was filtered off. The filtrate was washed several times with water and dried with anhydrous $MgSO_4$. Excess ethyl acetate was evaporated, and then the crude 4-(*N*-glycidyl-*N*-methylamino)benzophenone (GMBP) thus obtained was purified by silica gel column chromatography using a mixture of ethyl acetate/*n*-hexane (1/3) as the eluent. The yield of GMBP, which was a colorless syrup, was 1.1 g (41%). IR (neat): 1641 (C═O), 1593 (C═C, aromatic), 1445 (C−N, aliphatic), 1320 (C−N, aromatic), and 925 cm^{-1} (C−O−C, cyclic ether). ^{1}H NMR ($CDCl_3$, TMS): δ 2.53 (dd, $J = 4.39$ Hz, $J = 2.44$ Hz, 1H, CH_2 in epoxy ring), 2.78 (dd, $J = 4.37$ Hz, $J = 3.90$ Hz, 1H, CH_2 in epoxy ring), 3.08 (s, 3H, N−CH_3), 3.16 (m, 1H, CH in epoxy ring), 3.46 (dd, $J = 15.63$ Hz, $J = 4.88$ Hz, 1H, O−CH_2), 3.77 (dd, $J = 15.63$ Hz, $J = 2.93$ Hz, 1H, O−CH_2), 6.68−6.76 (m, 2H, aromatic protons), 7.39−7.70 (m, 3H, aromatic protons), and 7.72−7.82 ppm (m, 4H, aromatic protons).

Synthesis of *N*-Glycidyl-*N*,*N*′,*N*′-trimethyl-4,4′-diaminobenzophenone (GTBP). A solution of DBP (4.3 g, 20.0 mmol) in THF (100 mL) was added to an *n*-hexane solution of BL (37.6 mL, 1.6 mol/L) at −78 °C with stirring. After 3 h, the reaction of this solution with iodomethane (3.7 mL, 60.0 mmol) was performed using TBAB (0.32 g, 1.0 mmol) as a PTC at 50 °C for 3 h. The reaction mixture was treated in the same way as in the synthesis of MABP. The yield of *N*,*N*,*N*′-trimethyl-4,4′-diaminobenzophenone (TMBP), which was a colorless syrup, was 0.87 g (17%). A solution of TMBP (0.87 g, 3.5 mmol) in THF (5 mL) was added to an *n*-hexane solution of BL (2.2 mL, 1.6 mol/l) at −78 °C. After 1 h, the product was reacted with epibromohydrin (3.0 mL, 35 mmol) using TBAB (0.055 g, 0.17 mmol) as a PTC at 70 °C for 12 h. The reaction mixture was treated by the same method as for the synthesis of GMBP. The yield of *N*-glycidyl-*N*,*N*′,*N*′-trimethyl-4,4′-diaminobenzophenone (GTBP), which was a colorless syrup, was 0.07 g (7%). IR (neat): 1620 (C═O), 1598 (C═C, aromatic), 1447 (C−N, aliphatic), 1320 (C−N, aromatic), and 925 cm^{-1} (C−O−C, cyclic ether). ^{1}H NMR ($CDCl_3$, TMS): δ 2.57 (dd, $J = 4.89$ Hz, $J = 2.69$ Hz, 1H, CH_2 in epoxy ring), 2.78 (dd, $J = 4.89$ Hz, $J = 4.15$ Hz, 1H, CH_2 in epoxy ring), 3.06 (s, 6H, N−CH_3), 3.09 (s, 3H, N−CH_3), 3.19 (m, 1H, CH in epoxy ring), 3.49 (dd, $J = 15.74$ Hz, $J = 4.76$ Hz, 1H, O−CH_2), 3.78 (dd, $J = 15.74$ Hz, $J = 2.93$ Hz, 1H, O−CH_2), 6.62−6.72 (m, 4H, aromatic protons), and 7.68−7.76 ppm (m, 4H, aromatic protons).

Typical Procedure of Ring-Opening Copolymerization. A typical example of the copolymerization of glycidyl ester carrying an NBD moiety and an epoxy compound containing a BP group with PAn is as follows.

Synthesis of Polyester Having a Pendant NBD Moiety and BP Group (P-1) from GPNC and GOBP with PAn. GPNC (0.50 g, 1.8 mmol), GOBP (0.051 g, 0.2 mmol), PAn (0.30 g, 2.0 mmol), and TBAB (0.0032 g, 0.1 mmol) were dissolved in sulfolane (0.67 mL), and then the solution was heated at 100 °C for 24 h. The reaction mixture was poured into diethyl ether (200 mL), reprecipitated twice from acetone into diethyl ether, and dried in vacuo at room temperature. The yield of polymer **P-1** was 0.79 g (93%). The number average molecular weight (M_n) of the polymer determined from GPC was 8.4×10^3. IR (film): 1716 (C=O, ester), 1620 (C=O, amide), 1590 (C=C), and 1269 cm^{-1} (C−O−C, ester). ^1H NMR ($CDCl_3$, TMS): δ 1.08−1.72 (m, 5.4H, CH_2 in piperidyl ring), 1.88−2.40 (m, 1.8H, bridged CH_2 in NBD), 2.84−4.80 (m, 9.4H, CH_2, CH in NBD, N−CH_2), 5.32−5.68 (m, 1H, CH), 6.75−7.02 (m, 2.2H, CH=CH, aromatic protons), and 7.40−7.90 ppm (m, 4.7H, aromatic protons).

Typical Procedure for Photochemical Valence Isomerization of the NBD Moiety in a Polymer Film. A solution of a polymer (0.001 g) in chloroform (0.05 mL) was applied on the inner wall of a quartz cell, and the polymer film thus formed was dried in vacuo at room temperature for 24 h. The polymer film on the quartz was irradiated by a 500 W xenon lamp (Ushio Electric Co., UXL-500D-O) with a thermal-ray cut filter (HOYA: HA50) in air, in which the energy of the incident light (2.0 mW/cm^2) was monitored by an electric photon counter (ORC Model UV-M30). The rate of the disappearance of the absorption due to the NBD moiety was measured by a UV spectrophotometer.

Typical Procedure for Photochemical Reaction of an NBD Polymer in Solution. A solution (3 mL) of an NBD polymer (1.0×10^{-4} mol/L as NBD moieties) in dichloromethane was charged into a quartz cell, and then the solution in the cell was irradiated by the same xenon lamp as the above with a thermal-ray cut filter in nitrogen, in which the energy of the incident light (2.0 mW/cm^2) was measured by the same equipment as for the polymer film. The rate of disappearance of the absorption due to the NBD moiety was monitored using a UV spectrophotometer.

Determination of Quantum Yield for Photochemical Isomerization in the Self-Photosensitizing Reaction System. The monochromatic light of $\lambda = 313$ nm was isolated from a 500 W high-pressure mercury lamp (Ushio Electric Co., USH-500D) using a color filter (Corning Co.: CS7-54) and potassium chromate (10^{-2} mol/L) in a 1 wt % aqueous solution of potassium carbonate. The quantum yield was measured according to the method of Hatchard and Parker,[18] who used potassium tris(oxalato)ferrate(III) aqueous solution as the photon counter. Dichloromethane solutions (1×10^{-4} mol/L) of polymers **P-2, P-3, P-5, P-6, P-8,** and **P-9** were photoirradiated for 5 min. The chemical yields of polymers carrying the NBD moieties were calculated from a decrease in the NBD absorptions at 265 nm using the difference in molar absorption coefficients (ϵ) between the NBD derivatives and QC derivatives at this wavelength.

Measurement of Stored Thermal Energy in the QC Residue in the Polymer. A polymer film was cast from a dichloromethane solution on a poly(tetrafluoroethylene) plate and dried in vacuo. The film on the plate was irradiated long enough to change the NBD moiety to the QC residue via radiation from a 500 W xenon lamp through a heat ray cut filter in air. The irradiated polymer film (5−10 mg) was packed in an aluminum sample tube and heated at 10 °C/min under nitrogen for DSC analysis.

Results and Discussion

Synthesis of Polyesters Carrying Pendant Norbornadiene (NBD) Moieties and Photosensitizing Groups by Ring-Opening Copolymerizations. Epoxy compounds having benzophenone (BP) groups were synthesized by the substitution reaction of potassium or lithium salts of some BP derivatives with excess epichlorohydrin or epibromohydrin using TBAB as the PTC. The reaction of potassium 4-benzoylphenolate with epichlorohydrin gave the corresponding epoxy compound containing the 4-oxybenzophenone (OBP) group, GOBP, in 93% yield. GMBP and GTBP were also prepared in 41 and 7% yields, respectively, by reactions of lithium salts of 4-(*N*-methylamino)benzophenone and *N*,*N*,*N*′-trimethyl-4,4′-diaminobenzophenone with excess epibromohydrin at 50 °C for 12 h.

Table 1. Synthesis of Polyesters Carrying Pendant NBD Moieties and BP Groups by Ring-Opening Copolymerizations of Epoxy Monomers with PAn[a]

polym no.	epoxy monomer		yield,[b] %	composition[c]			$M_n \times 10^{-3}$ [d]	M_w/M_n [d]
	NBD	BP		NBD unit	BP unit	PAn		
P-a	GPNC		86	100	0	100	17.0	1.5
P-1	GPNC	GOBP	93	90	10	100	8.4	2.0
P-2	GPNC	GMBP	86	90	10	100	2.4	1.2
P-3	GPNC	GTBP	87	90	10	100	5.3	1.7
P-b	GDNC		87	100	0	100	19.0	1.3
P-4	GDNC	GOBP	93	90	10	100	5.2	1.7
P-5	GDNC	GMBP	79	90	10	100	2.0	1.2
P-6	GDNC	GTBP	88	90	10	100	8.0	1.5
P-c	GMNC		86	100	0	100	13.0	1.1
P-7	GMNC	GOBP	89	90	10	100	6.4	1.5
P-8	GMNC	GMBP	86	90	10	100	3.7	1.9
P-9	GMNC	GTBP	83	90	10	100	5.2	1.5

[a] The reaction was carried out with NBD derivatives (1.8 mmol), benzophenone derivatives (0.2 mmol), and PAn (2 mmol) using TBAB (0.5 mol %) in sulfolane (0.67 mL) at 100 °C for 24 h. [b] Insoluble parts in ether. [c] Determined by ^1H NMR. [d] Estimated by GPC based on polystyrene standards.

The ring-opening copolymerization of the obtained GOBP (10 mol %) and GPNC (90 mol %) with PAn was carried out using 0.5 mol % of TBAB as the catalyst in sulfolane at 100 °C for 24 h, and polyester **P-1** containing 10 mol % of the pendant OBP group and 90 mol % of the NBD moiety was obtained in 93% yields without any gel products (Table 1).

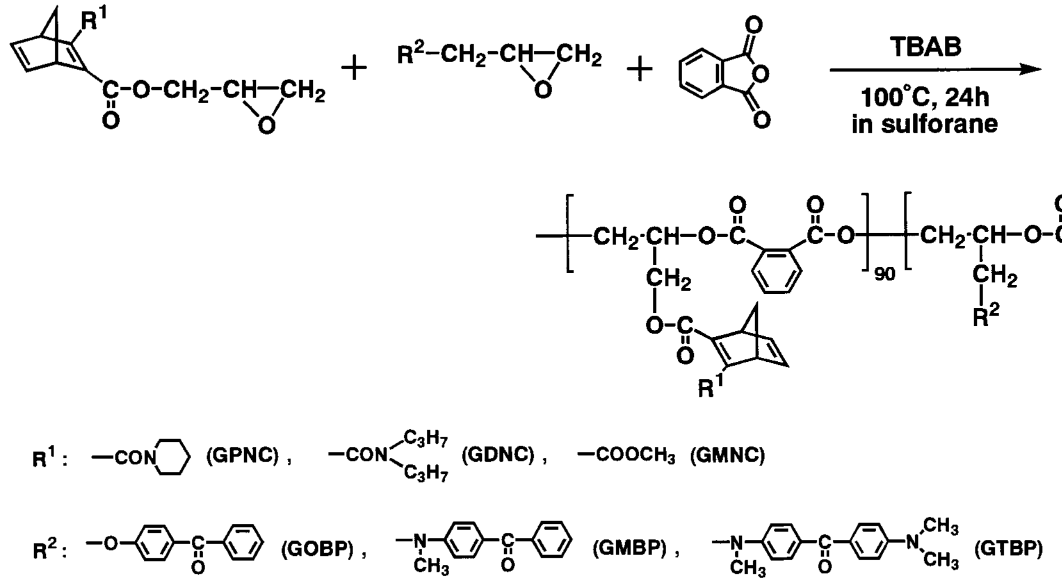
The structure of this polymer was confirmed by IR and ^1H NMR spectra (Table 2). The IR spectrum of the **P-1** film showed a strong absorption at 1730 cm^{-1} due to the C=O stretching of ester and weak absorptions at 1645 cm^{-1} due to the C=O stretching of ketone and at 1595 cm^{-1} due to the C=C stretching of the NBD moiety. The ^1H NMR spectrum of this polymer showed signals of C−CH_2 protons in the NBD moiety at δ = 1.9−2.3, methine protons in the NBD moiety at 3.7−4.2, methylene protons in the main chain and side chain of the polymer at 4.2−4.7, a methine proton in the main chain of the polymer at 5.3−5.7, CH=CH protons in the NBD moiety at 6.8−7.0, and aromatic protons in the OBP groups and in the main chain at 7.1−7.8 ppm. The compositions of the resulting copolymers, which were calculated by the intensity ratio of the CH_2 protons in the main chain and side chain to the CH=CH protons of the NBD moiety, and to aromatic protons in the main chain and BP group were consistent with the feed ratios of the monomers. That is, as shown in Scheme 2, polyester **P-1** with a theoretical amount of the pendant OBP group and NBD moiety was obtained by the ring-opening copolymerization of GPNC and GOBP with PAn.

Ring-opening copolymerizations of various glycidyl esters having NBD moieties and epoxy monomers containing BP groups with PAn were also performed using TBAB as the catalyst in sulfolane at 100 °C for 24 h to give corresponding polyesters containing pendant BP groups and NBD moieties (Scheme 1), and the

Table 2. IR and ^{1}H NMR Data of NBD Polymers

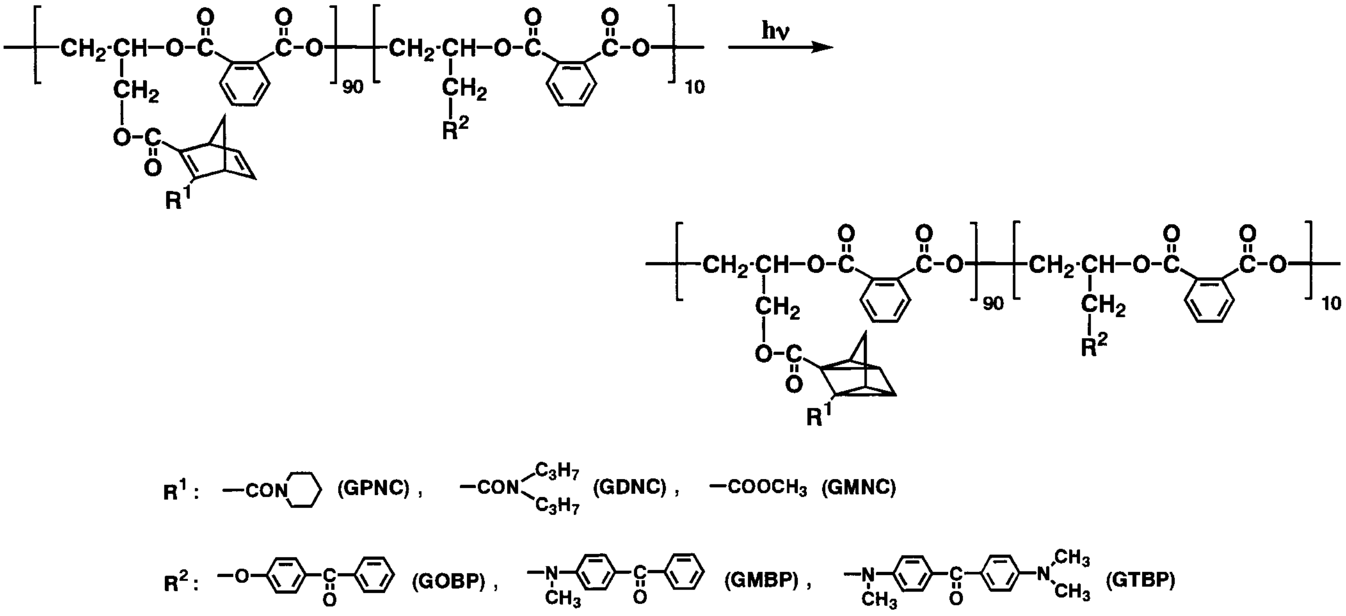
polym no.	IR spectra (cm^{-1})	^{1}H NMR spectra (ppm)
P-1	1716 (C=O, ester), 1620 (C=O, amide), 1590 (C=C), 1269 (C—O—C, ester)	1.08−1.72 (m, 5.4H, CH_2 in piperidyl ring), 1.88−2.40 (m, 1.8H, bridged CH_2 in NBD), 2.84−4.80 (m, 9.4H, CH_2, CH in NBD, N−CH_2), 5.32−5.68 (m, 1H, CH), 6.75−7.02 (m, 2.2H, CH=CH, aromatic protons), 7.40−7.90 (m, 4.7H, aromatic protons)
P-2	3400 (O—H), 1725 (C=O, ester), 1614 (C=O, amide), 1580 (C=C), 1268 (C—O—C, ester)	1.20−1.80 (m, 5.4H, CH_2 in piperidyl ring), 1.95−2.45 (m, 1.8H, bridged CH_2 in NBD), 2.90−4.90 (m, 9.7H, N−CH_3, CH_2, CH in NBD, N−CH_2), 5.20−5.90 (m, 1H, CH), 6.70−7.10 (m, 1.8H, CH=CH), 7.35−8.10 (m, 4.9H, aromatic protons)
P-3	3400 (O—H), 1725 (C=O, ester), 1614 (C=O, amide), 1580 (C=C), 1268 (C—O—C, ester)	1.00−1.90 (m, 5.4H, CH_2 in piperidyl ring), 1.90−2.50 (m, 1.8H, bridged CH_2 in NBD), 2.84−4.90 (m, 10.3H, N−CH_3, CH_2, CH in NBD, N−CH_2), 5.30−5.80 (m, 1H, CH), 6.60−7.20 (m, 1.8H, CH=CH), 7.20−8.20 (m, 4.8H, aromatic protons)
P-4	3400 (O—H), 1725 (C=O, ester), 1619 (C=O, amide), 1599 (C=C), 1252 (C—O—C, ester)	0.50−1.10 (m, 5.4H, CH_3), 1.20−1.90 (m, 3.6H, CH_2), 1.90−2.50 (m, 1.8H, bridged CH_2 in NBD), 2.70−3.50 (m, 3.6H, N−CH_2), 3.55−4.10 (m, 1.8H, CH in NBD moiety), 4.15−4.90 (m, 4H, CH_2), 5.30−5.80 (m, 1H, CH), 6.75−7.02 (m, 2.2H, CH=CH, aromatic protons), 7.40−7.90 (m, 4.7H, aromatic protons)
P-5	3400 (O—H), 1726 (C=O, ester), 1619 (C=O, amide), 1570 (C=C), 1251 (C—O—C, ester)	0.50−1.90 (m, 9H, CH_3, CH_2), 1.90−2.50 (m, 1.8H, bridged CH_2 in NBD), 2.80−5.00 (m, 9.7H, N−CH_3, N−CH_2, CH in NBD moiety, CH_2), 5.40−5.80 (m, 1H, CH), 6.70−7.20 (m, 1.8H, CH=CH), 7.24−8.20 (m, 4.9H, aromatic protons)
P-6	3400 (O—H), 1726 (C=O, ester), 1619 (C=O, amide), 1570 (C=C), 1251 (C—O—C, ester)	0.40−1.85 (m, 9H, CH_3, CH_2), 1.85−2.40 (m, 1.8H, bridged CH_2 in NBD), 2.70−4.90 (m, 10.3H, N−CH_3, N−CH_2, CH in NBD moiety, CH_2), 5.30−5.80 (m, 1H, CH), 6.60−7.10 (m, 1.8H, CH=CH), 7.20−8.00 (m, 4.9H, aromatic protons)
P-7	3480 (O—H), 1730 (C=O, ester), 1620 (C=C), 1250 (C—O—C, ester)	1.96−2.36 (m, 1.8H, bridged CH_2 in NBD), 3.40−4.05 (m, 4.5H, O−CH_3, CH in NBD moiety), 4.10−5.00 (m, 4H, CH_2), 5.40−5.80 (m, 1H, CH), 6.80−7.12 (m, 1.8H, CH=CH), 7.35−8.00 (m, 4.9H, aromatic protons)
P-8	3480 (O—H), 1730 (C=O, ester), 1620 (C=C), 1250 (C—O—C, ester)	1.95−2.35 (m, 1.8H, bridged CH_2 in NBD), 2.96−3.20 (m, 0.3H, N−CH_2), 3.50−4.05 (m, 4.5H, CH_3, CH in NBD moiety), 4.15−4.80 (m, 4H, CH_2), 5.20−5.80 (m, 1H, CH), 6.80−7.00 (m, 1.8H, CH=CH), 7.40−8.00 (m, 4.9H, aromatic protons)
P-9	3480 (O—H), 1730 (C=O, ester), 1620 (C=C), 1250 (C—O—C, ester)	1.96−2.40 (m, 1.8H, bridged CH_2 in NBD), 2.90−3.20 (m, 0.9H, N−CH_2), 3.44−5.00 (m, 8.5H, O−CH_3, CH in NBD moiety, CH_2), 5.40−5.84 (m, 1H, CH), 6.70−7.10 (m, 1.8H, CH=CH), 7.40−8.00 (m, 4.8H, aromatic protons)

Scheme 1



results are summarized in Table 1. The copolymerizations of GPNC with various epoxy monomers such as GMBP having a 4-(*N*-alkyl-*N*-methylamino)benzophenone (MBP) group and GTBP having an *N*-alkyl-*N*,*N*′,*N*′-trimethyl-4,4′-diaminobenzophenone (TBP) group were carried out under similar conditions and the corresponding polyesters **P-2** and **P-3**, which have the same NBD moiety and different pendant BP groups such as MBP and TBP groups, were obtained in 86 and 87% yields, respectively. M_n's of the resulting **P-2** and **P-3** were 2400 and 5300, respectively. The polymers obtained from the above reactions did not contain any gel products, and the compositions of the resulting copolymers, which were determined by ^{1}H NMR (Table

Scheme 2



2), showed the corresponding structure listed in Table 1. These results indicate that the copolymerizations of GPNC and epoxy monomers having various BP groups with PAn proceeded very smoothly.

Ring-opening copolymerizations of other NBD monomers such as GDNC and GMNC and photosensitizing monomers such as GOBP, GMBP, and GTBP with PAn proceeded smoothly under the same conditions, and polyesters **P-4**–**P-9** carrying corresponding NBD moieties and BP groups were obtained in high yields without any gel products, respectively (Table 1). For the reference of the photochemical reaction, ring-opening copolymerizations of epoxy monomers containing NBD moieties with PAn were carried out under the same conditions, and polyesters **P-a**, **P-b**, and **P-c** containing corresponding NBD moieties were obtained.[17] M_n's of these polymers were 13 000–19 000. M_n's of polyesters **P-1**–**P-9** containing pendant BP groups were lower than those of polyesters **P-a**–**P-c** having no pendant BP group.

These results indicate that the ring-opening copolymerizations of various epoxy compounds containing BP groups and NBD moieties with PAn proceeded smoothly when TBAB was used as the catalyst in sulfolane at 100 °C for 24 h and that new self-photosensitizing polyesters carrying various BP groups and NBD moieties were obtained in good yields, although the molecular weight decreased in copolymerizations of epoxy monomers containing pendant BP groups.

Isomerizations of the Pendant NBD Moieties Photosensitized by BP Groups in the Polymers. Photochemical valence isomerization of the polyester **P-a** film, which has only a pendant NBD moiety and no BP group, was carried out on a quartz cell by photoirradiation using a xenon lamp. As shown in Figure 1a, an absorption at 265 nm due to the NBD moiety in **P-a** decreased, and the NBD moiety isomerized quantitatively to the QC residue by 12 h of irradiation. In this photochemical reaction, there is an isosbestic point at 230 nm. This result indicates that the photochemical isomerization of the pendant NBD moiety to the corresponding QC residue in the polymer film proceeded selectively without any side reactions upon UV light irradiation.

Photosensitizing isomerizations of the pendant NBD moieties in polyesters **P-1**, **P-2**, and **P-3** films were also performed in the same manner, and changes of these UV spectra were shown in Figure 1b–d. The photochemical isomerizations of all these polymers proceeded with isosbestic points as seen in **P-a.** Absorptions at 265 nm due to the NBD moieties in **P-1**, **P-2**, and **P-3** decreased, and the NBD moieties in the polymers isomerized quantitatively to the QC residues after 240, 10, and 1 min of irradiation, respectively, although **P-2** and **P-3** exhibited a slight decrease in the absorption at 350 nm due to decompositions of some BP groups. This means that the pendant NBD moieties in the polymers were effectively sensitized by the pendant BP groups, and the photochemical isomerization of NBD moieties in **P-1**, **P-2**, and **P-3** proceeded without any side reactions.

Correlations between conversions of the photochemical isomerization of **P-1**, **P-2, P-3**, and **P-a** films, which have the same NBD moiety and different BP groups, and photoirradiation time are shown in Figure 2. This result suggests that the progress of the isomerization of the pendant NBD moieties was strongly influenced by the kind of BP groups in the polymers.

As shown in Figure 3, the observed rates of the photochemical reaction of the NBD moieties in **P-1**, **P-2**, **P-3**, and **P-a** films obeyed first-order kinetics. This means that the photochemical reactivity of polyesters containing pendant NBD moieties can be evaluated from the rate constants.

First-order rate constants of the photochemical isomerization of all the polymers in the film state or in dichloromethane solution are summarized in Table 3. These results indicate that the self-photosensitizing polyesters **P-1**–**P-9** were readily isomerized from NBD to QC by effective energy transfer from pendant BP groups, not only in the film state but also in the solution. The rates of the photosensitizing isomerization of the NBD moieties in dichloromethane solution were slightly lower than those of the polymer films containing the same self-photosensitizing groups. The rates of the photosensitizing isomerization of polyesters **P-a**, **P-b**, or **P-c** with low molecular weight DABP in the film were almost the same as the corresponding self-photosensi-

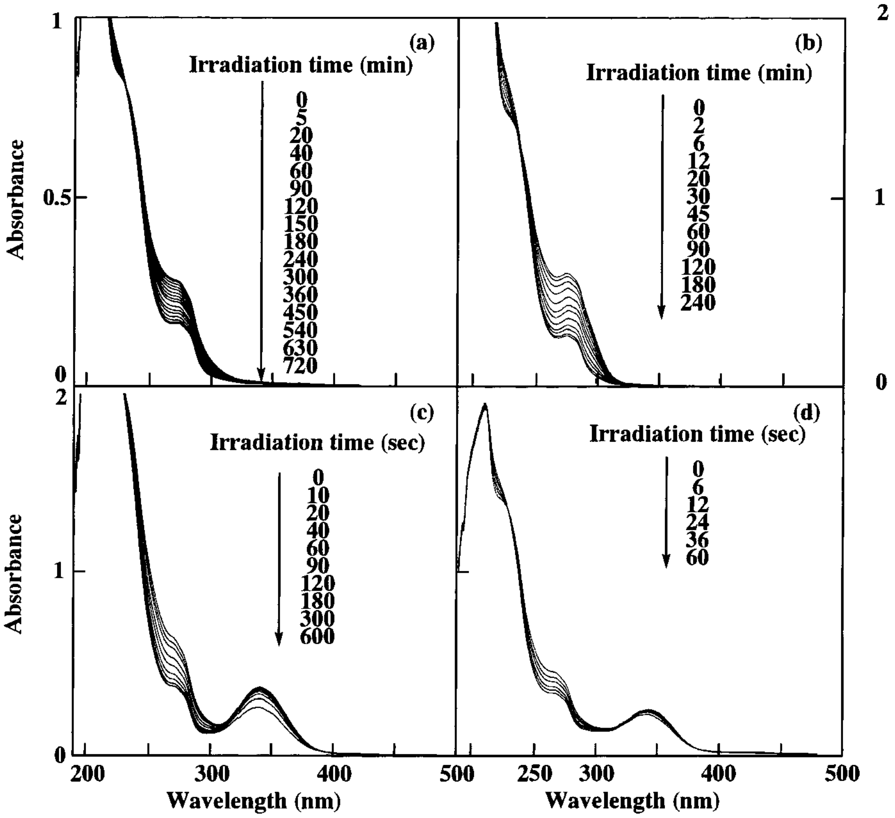


Figure 1. Change of UV spectra of NBD polymers having pendant BP groups in the film state induced by irradiation with a Xe lamp (2.0 mW/cm^2): (a) **P-a**; (b) **P-1**; (c) **P-2**; (d) **P-3**.

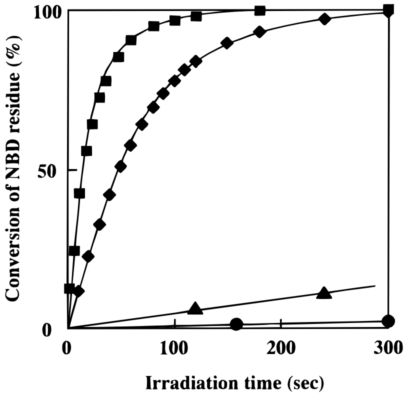


Figure 2. Conversions of the photochemical isomerizations of polyesters in the film state: (●) **P-a**; (▲) **P-1**; (◆) **P-2**; (■) **P-3**.

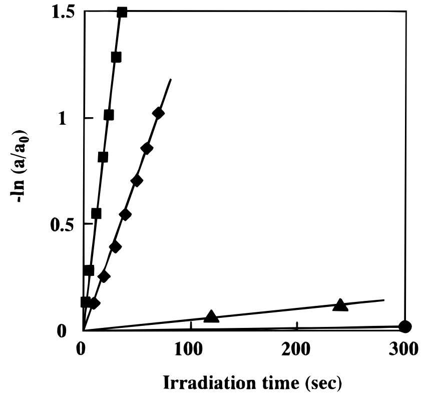


Figure 3. Rates of photochemical valence isomerization of NBD residues in polyesters in the film state: (●) **P-a**; (▲) **P-1**; (◆) **P-2**; (■) **P-3**.

tizing polymers **P-2**, **P-5**, or **P-8** containing pendant MBP groups. On the other hand, photosensitizing isomerizations of **P-a**, **P-b**, or **P-c** with low molecular weight DABP hardly occurred in diluted dichloromethane solution because of a low probability of the NBD moiety colliding with DABP. From these results, it is reasonable that the rates of the photosensitizing reactions of self-photosensitizing polyesters **P-1**–**P-9** are the same as those of the polyesters **P-a**, **P-b**, or **P-c** with corresponding low molecular weight photosensitizers in the film states. However, the photosensitizing reactions of polyesters **P-a**, **P-b**, or **P-c** with low molecular weight photosensitizers scarcely proceeded in the solution.

The relationships between the contents of the pendant MBP groups in **P-2** or the contents of DABP in **P-a** and first-order rate constants are shown in Figure 4. This result suggests that increasing MBP concentration tends to increase the rate of photochemical reaction up to 10 mol %. However, the introduction of 15 mol % of the MBP group in the polymer decreased the rate of photochemical reaction of the NBD moiety. This saturation may be due to the filter effects[17] of the photosensitizers on the photochemical reactions. Furthermore, in dichloromethane solution, the photochemical reactivities of self-photosensitizing polymers **P-2** were about the same as in the film states, although effective energy transfer from low molecular weight photosensitizer DABP to the NBD moiety in **P-a** did not occur in a dilute solution.

Quantum yields for **P-2**, **P-3**, **P-5**, **P-6**, **P-8**, and **P-9** in dichloromethane solutions (1×10^{-4} mol/L) are summarized in Table 4. Since there are no absorptions due to the polymer main chains and NBD moieties at 313 nm, quantum yields for the photosensitizing reactions from the pendant BP groups to the NBD moieties are considered to be hardly influenced by the polymer

Table 3. First-Order Rate Constant of Photochemical Valence Isomerization of the NBD Moiety Using Photosensitizers under Photoirradiation[a]

polym no.	NBD monomer unit	photo-sensitizing monomer unit	low molecular weight photosensitizing additive	$k_{obsd} \times 10^3$, s^{-1} in the film state	$k_{obsd} \times 10^3$, s^{-1} in solution[b]
P-a	GPNC (100)		none	0.07	0.08
			MOBP (7 mol %)[c]	0.77	
			DABP (7 mol %)[c]	31.3	0.13
			BEBP (7 mol %)[c]	32.3	
P-1	GPNC (90)	GOBP (10)		0.47	
P-2	GPNC (90)	GMBP (10)		15.6	4.3
P-3	GPNC (90)	GTBP (10)		41.1	25.1
P-b	GDNC (100)		none	0.08	0.08
			MOBP (7 mol %)[c]	0.58	
			DABP (7 mol %)[c]	16.3	0.09
			BEBP (7 mol %)[c]	27.0	
P-4	GDNC (90)	GOBP (10)		0.59	
P-5	GDNC (90)	GMBP (10)		8.3	3.1
P-6	GDNC (90)	GTBP (10)		72.1	23.4
P-c	GMNC (100)		none	0.29	0.35
			MOBP (7 mol %)[c]	0.40	
			DABP (7 mol %)[c]	3.7	0.61
			BEBP (7 mol %)[c]	4.1	
P-7	GMNC (90)	GOBP (10)		0.40	
P-8	GMNC (90)	GMBP (10)		9.0	3.5
P-9	GMNC (90)	GTBP (10)		17.9	15.9

[a] Irradiated by 500-W xenon lamp. [b] Concentration=1×10^{-4} mol/L in dichloromethane. [c] Concentration (mol %) in parentheses.

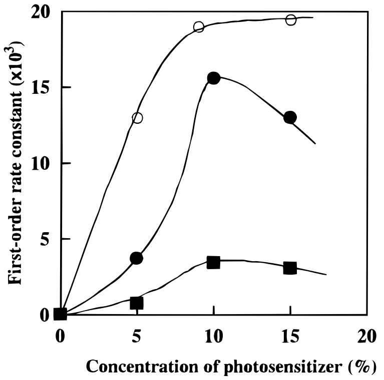


Figure 4. Effect of the concentration of the photosensitizing group in the polymer in the film state and in dichloromethane solution: (●) **P-2** containing 5, 10, or 15 mol % of pendant MBP groups in the film state; (■) **P-2** containing 5, 10, or 15 mol % of pendant MBP in dichloromethane solution (1×10^{-4} mol/L); (○) **P-a** with 5, 10, or 15 mol % of DABP in the film state.

Table 4. Quantum Yields of Photochemical Valence Isomerization of NBD Polymers[a]

polym no.	P-2	P-3	P-5	P-6	P-8	P-9
chemical yield, %	9.1	12.8	8.9	11.8	2.3	7.1
quantum yield, ϕ	0.71	0.84	0.64	0.81	0.25	0.62

[a] Quantum yields of polymers were measured with 366 nm light in dichloromethane (1×10^{-4} mol/L) at room temperature.

skeleton and NBD moieties. The quantum yield of **P-2** was found to be 0.71, which is relatively large. The quantum yields of all these polymers were about 0.7. This means that since NBD polymers containing pendant MBP or TBP groups have very high quantum yields and good photochemical reactivities, these polymers have great possibility for use as solar energy storage–exchange materials.

Measurement of T_g's of NBD Polymers and of Stored Thermal Energy in the QC Residue in Polymers. Unirradiated polymer films and the photoirradiated polymer films were packed in aluminum sample tubes for DSC analysis. These samples were heated at 10 °C/min under nitrogen. Figure 5 shows DSC curves of the unirradiated **P-2** film and the photoirradiated **P-2** film. T_g of **P-2** before photoirradiation was 46 °C, and no release of thermal energy was found on further heating. On the other hand, the photoirradiated **P-2** film released thermal energy at 107 °C, and at 157 °C it released the highest thermal energy. Furthermore, the released thermal energy of the photoirradiated **P-2** film was calculated to be 90 kJ/mol of the NBD moiety in the polymer.

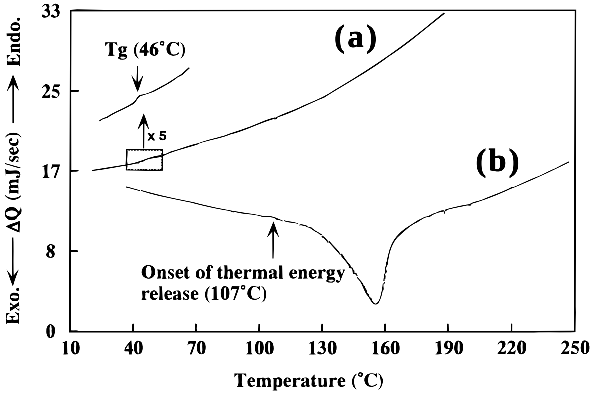


Figure 5. DSC curve of **P-2** film before and after photoirradiation: (a) second run of unirradiated polyester **P-2** film; (b) first heating of the photoirradaited polyester **P-2** film containing QC residue.

Table 5. Thermal Properties of the NBD Polymer

polym no.	$M_n \times 10^{-3}$ [a]	M_w/M_n[a]	T_g,[b] °C	initial temp of release,[b] °C	stored thermal energy,[b] kJ/mol
P-1	8.4	2.0	70	105	89
P-2	2.4	1.2	46	108	90
P-3	5.3	1.7	85	96	80
P-4	5.2	1.7	56	97	84
P-5	2.0	1.2	40	113	92
P-6	8.0	1.5	55	60	85
P-7	6.4	1.5	36	127	77
P-8	3.7	1.9	49	108	84
P-9	5.2	1.5	30	55	92

[a] Estimated by GPC based on polystyrene standards. [b] Calculated by DSC.

T_g's of all NBD polymers and stored thermal energies of the QC residue in the polymers are summarized in Table 5. Furthermore, T_g's of **P-1**, **P-2**, **P-3**, and **P-a** with different BP groups and the same NBD moiety were 70, 46, 85, and 65 °C, respectively. This means that the T_g of the polymer depended strongly on both the pendant BP groups and the M_n of the polymers.

Polymers containing QC residues, which were photoirradiated NBD polymers, had good thermal energy storage properties (about 90 kJ/mol). Furthermore, it was found that the initiating temperatures for the release of their stored thermal energy in the polymers were usually higher than T_g's of the NBD polymers. This means that the reversion from the QC residue to the NBD moiety in the polymer is related to the change of the configuration of the QC polymers.

Summary

(1) Various epoxy monomers containing BP groups were synthesized by the reaction of potassium or lithium salts of BP derivatives with excess epichlorohydrin or epibromohydrin using TBAB as a phase transfer cata-

lyst. (2) Ring-opening copolymerizations of various epoxy monomers containing NBD moieties and BP groups with PAn gave the corresponding self-photosensitizing polyesters (**P-1**−**P-9**). (3) Photosensitizing reactions of the obtained polymers proceeded smoothly, not only in the film state but also in dichloromethane solution. Furthermore, these polymers isomerized in high quantum yields from NBD moieties to QC residues through the energy transfer steps from BP groups. (4) All polyesters containing QC residues after photoirradiation had good thermal energy storage properties and can release their stored thermal energy smoothly at higher temperatures above T_g's of the NBD polymers. It was also found that the stored thermal energies in QC polyesters were about 90 kJ/mol.

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