# Synthesis of Polyesters Carrying Norbornadiene (NBD) Moieties by the Ring-Opening Copolymerization of Glycidyl Esters Containing NBD Moieties with Carboxylic Anhydrides and Their Photochemical Reactions

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ABSTRACT: Various epoxy monomers containing norbornadiene (NBD) moieties were prepared by reactions of potassium salts of NBD derivatives with excess epichlorohydrin using tetrabutylammonium bromide (TBAB) as a phase transfer catalyst. The copolymerization of glycidyl (3-phenyl-2,5-norbornadien-2-yl)carboxylate (GPNC) with phthalic anhydride (PAn) proceeded smoothly using TBAB as a catalyst in sulfolane at 100 °C for 24 h to give polyester **P-1** containing pendant NBD moieties. Copolymerizations of various epoxy monomers containing certain NBD moieties with carboxylic anhydrides gave the corresponding NBD polyesters in good yields. The photochemical valence isomerizations of the NBD moieties in the polymers were carried out in the film state or in the solution. Rates of the isomerizations of some NBD moieties in the polymers were strongly enhanced by the addition of photosensitizers such as 4-(*N*,*N*-dimethylamino)benzophenone (DABP). The $T_g$s of the polyesters having NBD residues and stored thermal energy in the corresponding quadricyclane (QC) groups in the polymers were measured by DSC analysis. The $T_g$s of the NBD polymers were 45−93 °C. Polyesters having QC groups after photoirradiation released their stored thermal energies (about 90 kJ/mol) at temperatures above the $T_g$s of the corresponding NBD polymers.

## Introduction

It is well-known that the ring-opening copolymerization of epoxy derivatives with carboxylic anhydrides proceeds effectively using tertiary amines, quaternary onium salts, or Lewis acids as catalysts to give the corresponding polyesters.[1−3] It is readily possible to prepare polyesters carrying functional groups in the side chain by the reaction of epoxy derivatives containing functional groups with carboxylic anhydrides. Nishikubo et al.[4,5] reported the synthesis of photoreactive polyesters carrying cinnamic ester or vinyl ether moieties in the side chain by the ring-opening alternating copolymerization of glycidyl cinnamate or glycidyl vinyl ether with carboxylic anhydrides, respectively. Recently, Yamamoto et al.[6] reported the synthesis of some biodegradable polyesters by the ring-opening copolymerization of some epoxy compounds with certain carboxylic anhydrides.

It has been pointed out that fossil fuels such as petroleum, natural gas, or coal are limited and that their combustion causes serious environmental problems such as warming of the earth resulting from produced $CO_2$ and acid rain due to incomplete combustion substances. Thus, it is very important to use sunlight having clean and limitless energy.

As one method for efficiently using sunlight energy, photochemical valence isomerization between norbornadiene (NBD) and quadricyclane (QC) derivatives[7,8] has been noted for a solar energy conversion and storage system.[9] Recently, this photochemical reaction has also been investigated as a new switching system in the optoelectronic field.[10] Since NBD does not have any absorption in the visible light region, the photochemical reaction of NBD does not proceed by the irradiation of visible sunlight. To solve this problem, an effective photosensitizer[11] or a chromophore having absorption over 300 nm[12,13] was used.

Recently, we investigated the synthesis of polymers containing NBD moieties in the main chain or the side chain, their photochemical properties, and the reversion to release the stored thermal energy in QC polymers. This result suggested that the high energy can be stored (about 92 kJ/mol) in the organic polymer and that the QC groups in the polymer film have excellent storage stability at room temperature for a long time, which are interesting results in polymer chemistry. In previous papers, Nishikubo et al.[14] and Kamogawa et al.[15] independently reported the synthesis of polyamides having NBD residues in the main chain by the polycondensation reaction of 2,5-norbornadiene-2,3-dicarboxylic acid derivatives with diamines. We also synthesized polymers carrying pendant NBD residues by the substitution reaction of poly[(chloromethyl)styrene] with NBD compounds carrying carboxylic acid using phase transfer catalysts[16] and by the addition reaction of poly(glycidyl methacrylate)s with the same NBD compounds.[17] Furthermore, poly(vinyl ether)s carrying pendant NBD residues were synthesized by the selective cationic polymerization of vinyl ether monomers having NBD moieties.[18] However, there is no report of the synthesis of polyesters containing pendant NBD moieties. This article reports on the synthesis of glycidyl esters and ether-containing NBD residues, and the synthesis of polyesters carrying pendant NBD residues by the ring-opening copolymerization of glycidyl compounds thus obtained with carboxylic anhydrides.

## 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. Commercial epichlorohydrin (ECH) and triethylamine (TEA) were purified by distillation. Tetrabutylammonium bromide

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(TBAB) was recrystallized twice from ethyl acetate. Reagent grade dicyclohexylcarbodiimide (DCC), 18-crown-6 (18-C-6), potassium bromide (KBr), 4-(*N*,*N*-dimethylamino)benzophenone (DABP), and 4,4′-bis(*N*,*N*-diethylamino)benzophenone (BEBP) were used without further purification. NBD derivatives such as 3-phenyl-2,5-norbornadiene-2-carboxylic acid (PNC), 4-[(3-phenyl-2,5-norbornadien-2-yl)carbonyl]phenoxide (PNCP), and 2,5-norborandiene-2,3-dicarboxylic acid (NDC) were prepared by Diels−Alder reaction of the corresponding acetylene derivatives with freshly distilled cyclopentadiene according to reported methods.[16c,d] 3-(Piperidylcarbonyl)-2,5-norbornadiene-2-carboxylic acid (PCNC, mp 147−148 °C), 3-(*N*,*N*-dipropylcarbamoyl)-2,5-norbornadiene-2-carboxylic acid (DCNC, mp 130−131 °C), and 3-(methoxycarbonyl)-2,5-norbornadiene-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 as reported methods.[16] Potassium salts of NBD derivatives were obtained by the reaction of PNC, PNCP, PCNC, DCNC, and MCNC with potassium hydroxide in methanol.

**Apparatus.** Infrared (IR) spectra were measured on a Jasco Model IR-700 spectrometer. Ultraviolet (UV) spectra were recorded on a Shimadzu Model UV-240. The $^1$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 groups in the polymers were measured on a Perkin-Elmer differential scanning calorimeter Model DSC Station 4 at a heating rate at 10 or 20 °C/min.

**Typical Procedure for the Synthesis of Epoxy Derivatives Containing the Norbornadiene Residue.** A typical example of the reaction is as follows.

**Synthesis of Glycidyl 3-Phenyl-2,5-norbornadiene-2-carboxylate (GPNC).** The reaction of 1.2 g (4.8 mmol) of potassium 3-phenyl-2,5-norbornadiene-2-carboxylate and 2.3 mL (28.8 mmol) of ECH was carried out using 0.14 g (0.24 mmol) of TBAB as a phase transfer catalyst at 80 °C for 3 h. The reaction mixture was diluted in dichloromethane (DCM), and the produced potassium chloride was filtered off. The filtrate was washed several times with water and dried with anhydrous $MgSO_4$. Excess ECH and DCM were evaporated, and then the crude GPNC thus obtained was purified by silica gel column chromatography using ethyl acetate/hexane (1/3) as eluent. The isolated yield of GPNC was 1.0 g (85%). IR (neat): 1700 (C=O, ester), 1592, 1572 (C=C), 1234 (C−O−C, ester), 906 cm$^{-1}$ (C−O−C, cyclic ether). $^1$H NMR ($CDCl_3$, TMS): $\delta$ 2.10 (dt, 1H, bridged $CH_2$ in NBD moiety), 2.29 (dt, 1H, bridged $CH_2$ in NBD), 2.56 (ddd, 1H, $CH_2$ in epoxy ring), 2.78 (dd, 1H, $CH_2$ in epoxy ring), 3.17 (dddd, 1H, CH in epoxy ring), 3.88 (dt, 1H, CH in NBD moiety), 3.97 (dd, 1H, $OCH_2$), 4.12 (dt, 1H, CH in NBD moiety), 4.40 (ddd, 1H, $OCH_2$), 6.95 (dd, 1H, CH=CH), 7.02 (dd, 1H, CH=CH), 7.30−7.53 (m, 5H, aromatic protons). Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.00. Found: C, 75.58; H, 5.99.

**Typical Procedure for the Ring-Opening Alternating Copolymerization of Epoxy Derivatives Containing the Norbornadiene Residue with Carboxylic Anhydride.** A typical example of the copolymerization of an epoxy derivative carrying the NBD residue with carboxylic anhydride is as follows.

**Synthesis of Polyester Having the NBD Moiety (P-1) from GPNC with Phthalic Anhydride (PAn).** GPNC (0.54 g, 2 mmol), phthalic anhydride (0.30 g, 2 mmol), and TBAB (0.0032 g, 0.1 mmol) were dissolved in 0.67 mL of sulfolane, and the reaction was carried out at 100 °C for 24 h. The reaction mixture was poured into methanol (200 mL), reprecipitated twice from acetone into methanol, and dried *in vacuo* at room temperature. The yield of polymer **P-1** was 0.8 g (90%). The number-average molecular weight ($M_n$) of the polymer determined from GPC was $3.3 \times 10^4$. IR (film): 3450 (O−H), 1730 (C=O), 1595 (C=C), 1255 cm$^{-1}$ (C−O−C, ester). $^1$H NMR ($CDCl_3$, TMS): $\delta$ 1.89−2.28 (m, 2H, bridged $CH_2$ in NBD), 3.67−4.15 (m, 2H, CH in NBD), 4.20−4.68 (m, 4H, $CH_2$), 5.32−5.68 (m, 1H, CH), 6.75−6.99 (m, 2H, CH=CH), 7.10−7.78 (m, 9H, aromatic protons).

**Typical Procedure for the Photochemical Valence Isomerization of the NBD Moiety in Polymer Film.** A solution of a polymer (0.001 g) in chloroform (0.05 mL) was applied on the inside wall of a quartz cell and 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 residue was measured using a UV spectrophotometer.

**Typical Procedure for the Photochemical Reaction of NBD Polymer in Solution.** A solution (3 mL) of a NBD polymer ($1.0 \times 10^{-4}$ mol/L as NBD moieties) in DCM or THF was charged into a quartz cell, and then the solution in the cell was irradiated by the same xenon lamp as above with a thermal-ray cut filter in nitrogen, in which the intensity of the incident light was monitored by a UV spectrophotometer.

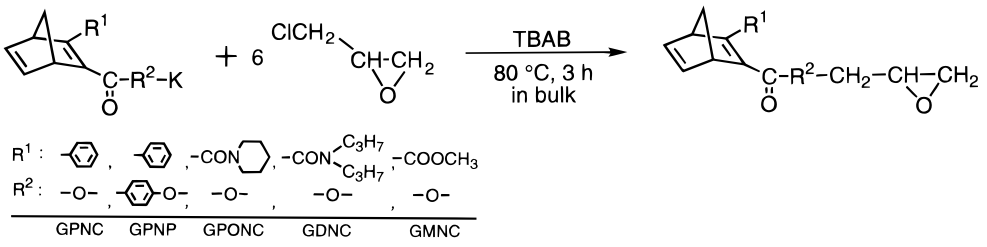
**Determination of the Quantum Yield for the Photochemical Reaction of the Polymer Carrying the Pendant NBD Moiety.** Monochromatic light of $\lambda$ = 313 nm was isolated from a 500-W high-pressure mercury lamp (Ushio Electric Co., USH-500D) using a color filter (Corning Co.: CS7-54) and potassium 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,[19] which used potassium tris(oxalato)ferrate(III) aqueous solution as a photon counter. DCM solutions ($1 \times 10^{-4}$ mol/L) of polymers **P-1** to **P-5** were photoirradiated for 5 min. The chemical yields for each polymer carrying NBD residues were calculated from decreases in the NBD absorptions at a specified wavelength (300 or 330 nm) using the difference in molar absorption coefficients ($\Delta\epsilon$) between the NBD derivatives and the QC derivatives as the specified wavelength.

**Measurement of Stored Thermal Energy in the QC Group in the Polymer.** A polymer solution in dichloromethane was cast onto a poly(tetrafluoroethylene) plate and dried *in vacuo*. The film on the plate was irradiated for enough time to change from the NBD moiety to the QC group by irradiation with 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 for DSC analysis. The sample was heated at 10 °C/min under nitrogen.

## Results and Discussion

**Synthesis of Polyesters Carrying Pendant Norbornadiene Moieties by the Ring-Opening Alternating Copolymerizations of Epoxy Derivatives Having NBD Residues with Anhydrides.** Epoxy monomers having NBD moieties were synthesized in good yields by the substitution reactions of potassium salts of the NBD derivatives with excess epichlorohydrin using tetrabutylammonium bromide (TBAB) as a phase transfer catalyst (Scheme 1). The reaction of potassium (3-phenyl-2,5-norbornadiene-2-carboxylate gave the corresponding glycidyl (3-phenyl-2,5-norbornadiene-2-carboxylate (GPNC) in 85% yield. 4-(Glycidyloxy)phenyl 2-(3-phenyl-2,5-norbornadienyl) ketone (GPNP), glydidyl 3-(piperidylcarbonyl)-2,5-norbornadiene-2-carboxylate (GPONC), glycidyl 3-(*N*,*N*-dipropylcarbamoyl)-2,5-norbornadiene-2-carboxylate (GNDC), and glycidyl 3-(methoxycarbonyl)-2,5-norbornadiene-2-carboxylate (GMNC) were also prepared in 61, 81, 88, and 58% yields, respectively, by reactions of the potassium salts of PNCP, PCNC, DCNC, and MCNC with excess epichlorohydrin under the conditions similar to those applied for the synthesis of GPNC. Thus obtained epoxy

**Scheme 1**



**Scheme 2**

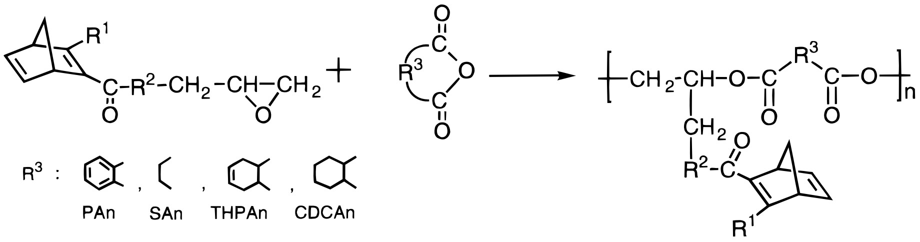


**Table 1. IR, $^1$H NMR, and Elemental Analysis of Epoxy Derivatives Having NBD Residues**

| monomer | yield, % | IR spectra, cm$^{-1}$ | $^1$H NMR spectra, ppm | elem anal. |
|---|---|---|---|---|
| GPNC | 85 | 1700 (C=O, ester),<br>1592, 1572 (C=C),<br>1234 (COC, ester),<br>906 (COC, cyclic ether) | 2.10 (dt, 1H, bridged $CH_2$ in NBD), 2.29 (dt, 1H, bridged $CH_2$ in NBD), 2.56 (ddd, 1H, $CH_2$ in epoxy ring), 2.78 (dd, 1H, $CH_2$ in epoxy ring), 3.17 (dddd, 1H, CH in epoxy ring), 3.88 (dt, 1H, CH in NBD), 3.97 (dd, 1H, $OCH_2$), 4.12 (dt, 1H, CH in NBD), 4.40 (ddd, 1H, $OCH_2$), 6.95 (dd, 1H, CH=CH), 7.02 (dd, 1H, CH=CH), 7.30−7.53 (m, 5H, aromatic protons) | $C_{17}H_{16}O_3$: Anal. calcd C, 76.10; H, 6.00; found C, 75.58; H, 5.99 |
| GPNP | 61 | 1710 (C=O, ester),<br>1630, 1595 (C=C),<br>1247 (COC, ester),<br>1027 (COC, ether),<br>913 (COC, epoxy ring) | 2.14 (d, 1H, bridged $CH_2$ in NBD), 2.44 (d, 1H, bridged $CH_2$ in NBD), 2.70 (dd, 1H, $CH_2$ in epoxy ring), 2.86 (dd, 1H, $CH_2$ in epoxy ring), 3.29 (dddd, 1H, CH in epoxy ring), 3.87 (dd, 1H, $OCH_2$), 4.02 (dd, 2H, CH in NBD), 4.18 (dd, 1H, $OCH_2$), 6.71 (d, 2H, aromatic protons), 6.99 (dd, 1H, CH=CH), 7.05 (dd, 1H, CH=CH), 7.08−7.14 (m, 5H, aromatic protons), 7.57 (d, 2H, aromatic protons) | $C_{23}H_{20}O_3$: Anal. calcd C, 80.21; H, 5.85; found C, 79.80; H, 6.04 |
| GPONC | 81 | 1700 (C=O, ester),<br>1620 (C=O, amide),<br>1558 (C=C),<br>1233 (COC, ester),<br>905 (COC, cyclic ether) | 1.15−1.85 (m, 6H, $CH_2$ in piperidyl ring), 1.93−2.48 (m, 2H, bridged $CH_2$ in NBD), 2.58−2.80 (m, 2H, $CH_2$ in epoxy ring), 3.30−4.58 (m, 9H, CH in epoxy ring and NBD moiety, $NCH_2$, $OCH_2$), 6.82−7.08 (m, 2H, CH=CH) | $C_{17}H_{21}O_4N$: Anal. calcd C, 67.31; H, 6.98; N, 4.62; found C, 66.80; H, 6.93; N, 4.28 |
| GDNC | 88 | 1709 (C=O, ester),<br>1619 (C=O, amide),<br>1558 (C=C),<br>1232 (COC, ester),<br>903 (COC, ether) | 0.70−1.10 (m, 6H, $CH_3$), 1.40−1.78 (m, 4H, $CH_2$), 1.93−2.48 (m, 2H, bridged $CH_2$ in NBD), 2.60−2.88 (m, 2H, $CH_2$ in epoxy ring), 2.90−3.56 (m, 5H, CH in epoxy ring, $NCH_2$), 3.64−4.50 (m, 4H, CH in NBD, $OCH_2$), 6.84−7.04 (m, 2H, CH=CH) | $C_{18}H_{25}O_4N$: Anal. calcd C, 67.69; H, 7.89; N, 4.39; found C, 67.18; H, 7.87; N, 4.29 |
| GMNC | 58 | 1713 (C=O, ester),<br>1624 (C=C),<br>1233 (COC, ester),<br>905 (COC, ether) | 2.04−2.40 (m, 2H, bridged $CH_2$ in NBD), 2.60−2.92 (m, 2H, $CH_2$ in epoxy ring), 3.12−3.36 (m, 1H, CH in epoxy ring), 3.80 (s, 3H, $CH_3$), 3.92−4.60 (m, 4H, CH in NBD, $OCH_2$), 6.84−7.04 (m, 2H, CH=CH) | $C_{20}H_{18}O_3$: Anal. calcd C, 62.39; H, 5.64; found C, 61.90; H, 5.77 |

monomers containing certain NBD moieties were confirmed by elemental analyses and IR and $^1$H NMR spectra (see Table 1).

The ring-opening copolymerization of thus obtained GPNC with phthalic anhydride (PAn) was carried out to prepare polyester **P-1** containing the pendant NBD moiety, and results are summarized in Table 2. Polyesters **P-1** were prepared in 73 and 72% yields without any gel products using 0.5 mol % of TEA and 18-C-6/KBr complex as catalysts in sulfolane at 100 °C for 24 h, respectively. However, molecular weights of the thus obtained **P-1** were not high enough. On the other hand, polyester **P-1** with high molecular weight was synthesized in 90% yield without any gel products under the same reaction conditions when 0.5 mol % of TBAB was used as the catalyst. This result indicates that although the copolymerization of GPNC with PAn proceeds using TEA, 18-C-6/KBr complex, or TBAB as catalysts, TBAB

**Table 2. Results of the Ring-Opening Copolymerization of GPNC with PAn[a]**

| run no. | cat. | solvent | temp, °C | time, h | yield, % | $M_n^b \times 10^{-4}$ | $M_n/M_w^b$ |
|---|---|---|---|---|---|---|---|
| 1 | TEA | sulfolane | 100 | 24 | 57 | 2.2 | 1.3 |
| 2 | 18-C-6/KBr | sulfolane | 100 | 24 | 74 | 1.8 | 2.3 |
| 3 | TBAB | sulfolane | 100 | 24 | 90 | 3.3 | 1.8 |
| 4 | TBAB | DMF | 100 | 24 | 86 | 1.5 | 1.8 |
| 5 | TBAB | NMP | 100 | 24 | 96 | 1.6 | 1.8 |
| 6 | TBAB | sulfolane | 60 | 24 | 77 | 1.4 | 1.5 |
| 7 | TBAB | sulfolane | 80 | 24 | 97 | 2.9 | 2.2 |
| 8 | TBAB | sulfolane | 100 | 3 | 73 | 2.1 | 1.5 |
| 9 | TBAB | sulfolane | 100 | 12 | 72 | 2.4 | 1.5 |

[a] The reaction was carried out with GPNC (2 mmol) and PAn (2 mmol) using catalyst (0.5 mol %) in solvent (0.67 mL). [b] Estimated by GPC based on polystyrene standards.

has a higher catalytic activity than TEA and 18-C-6/KBr complex.

The structure of this polymer was confirmed by IR and $^1$H NMR spectra (Table 3). The IR spectrum of **P-1** film showed strong absorption peaks at 1730 cm$^{-1}$ due to C=O stretching and 1595 cm$^{-1}$ due to C=C stretching. The $^1$H NMR spectrum of this polymer showed signals of C−CH$_2$ protons of the NBD residue at $\delta$ = 1.9−2.3, methine protons in the NBD residue at $\delta$ 3.7−4.2, methylene protons in the main chain and side chain at $\delta$ 4.2−4.7, methine protons in the main chain at $\delta$ 5.3−5.7, CH=CH protons of the NBD residue at $\delta$ 6.8−7.0, and aromatic protons in the NBD residues and in the main chain at $\delta$ 7.1−7.8 ppm. The compositions of the resulting copolymers, which were determined by the intensity ratio of the CH$_2$ protons in the main chain vs aromatic protons in the main chain by $^1$H NMR, were close to the feed ratio of the monomers. That is, as shown in Scheme 2, polyester **P-1** with the pendant NBD moiety was obtained by the ring-opening alternating copolymerization of GPNC with PAn.

The copolymerization of GPNC with PAn also took place using 0.5 mol % of TBAB as the catalyst at 100 °C for 24 h in certain organic solvents (Table 2). The molecular weight of the polymer prepared in sulfolane was higher than those of the polymers obtained in DMF and NMP. It seems that sulfolane has a higher polarity in those solvents and gives high molecular weight polymer.

Furthermore, the effects of the reaction temperature and the reaction time were examined on the copolymerization of GPNC with PAn in the presence of 0.5 mol % of TBAB as the catalyst in sulfolane (Table 2). When the reaction was performed at 100 °C for 24 h, copolymers were obtained with high molecular weights in good yields.

Ring-opening copolymerizations of various epoxy derivatives carrying NBD moieties with certain carboxylic anhydrides were performed using TBAB as a catalyst in sulfolane at 100 °C for 24 h to give corresponding polyesters containing pendant NBD moieties (Scheme 2), and the results are summarized in Table 4. The copolymerizations of GPNC with various anhydrides such as SAn, CDAn, and THAn were carried out under similar conditions, and the corresponding polyesters **P-2**, **P-3**, and **P-4**, which have different polymer skeletons but the same NBD moiety, were obtained in 70, 76 and 51% yields, respectively. The $M_n$s of the resulting **P-2**, **P-3**, and **P-4** were 13 000, 11 000, and 10 000. The polymers obtained by the above reactions did not contain any gel products, and the compositions of the resulting copolymers, which were determined by $^1$H NMR, showed the corresponding structure. These results indicate that the copolymerizations of GPNC with carboxylic anhydrides proceed very smoothly, although PAn with aromatic groups had a slightly higher reactivity than SAn, CDAn, and THAn with aliphatic groups.

Ring-opening alternating copolymerizations of other epoxy monomers containing certain NBD moieties such as GPNP, GPNC, GDNC, and GMNC with PAn proceeded smoothly under the same conditions, and polyesters **P-5**, **P-6**, **P-7**, and **P-8** carrying the corresponding NBD moieties were obtained in high yields and without any gel products, respectively (Table 4).

These results indicate that the ring-opening alternating copolymerizations of various epoxy derivatives containing NBD residues with carboxylic anhydrides occurred very smoothly when TBAB was used as the catalyst in sulfolane at 100 °C for 24 h, and new photoresponsive polyesters carrying NBD moieties were obtained in good yields.

**Table 3. IR and $^1$H NMR Data of NBD Polymers**

| polym no. | IR spectra, cm$^{-1}$ | $^1$H NMR spectra, ppm |
|---|---|---|
| **P-1** | 3450 (OH), 1730 (C=O), 1595 (C=C), 1255 (COC, ester) | 1.89−2.28 (m, 2H, bridged CH$_2$ in NBD), 3.67−4.15 (m, 2H, CH in NBD), 4.20−4.68 (m, 4H, CH$_2$), 5.32−5.68 (m, 1H, CH), 6.75−6.99 (m, 2H, CH=CH), 7.10−7.78 (m, 9H, aromatic protons) |
| **P-2** | 3455 (OH), 1740 (C=O), 1593 (C=C), 1233 (COC, ester) | 1.80−2.84 (m, 6H, bridged CH$_2$ in NBD, COCH$_2$), 3.36−4.60 (m, 6H, CH in NBD, OCH$_2$), 4.90−5.50 (m, 1H, CH), 6.60−8.20 (m, 7H, CH=CH, aromatic protons) |
| **P-3** | 3482 (OH), 1736 (C=O), 1593 (C=C), 1233 (COC, ester) | 1.80−3.30 (m, 8H, bridged CH$_2$ in NBD, CH$_2$ in cyclohexene ring, COCH), 3.70−4.60 (m, 6H, CH in NBD, CH$_2$), 4.80−5.40 (m, 1H, CH), 5.4−6.0 (m, 2H, CH=CH in cyclohexene ring), 6.80−7.80 (m, 7H, CH=CH in NBD, aromatic protons) |
| **P-4** | 3495 (OH), 1736 (C=O), 1593 (C=C), 1233 (COC, ester) | 0.80−3.10 (m, 12H, CH$_2$ in cyclohexane ring, bridged CH$_2$ in NBD, CH in cyclohexane ring, COCH), 3.70−4.50 (m, 6H, CH in NBD, CH$_2$), 5.00−5.40 (m, 1H, CH), 6.80−7.80 (m, 7H, CH=CH, aromatic protons) |
| **P-5** | 3428 (OH), 1728 (C=O), 1596 (C=C), 1247 (COC, ester) | 2.00−2.60 (m, 2H, bridged CH$_2$ in NBD), 3.90−4.80 (m, 6H, CH in NBD, CH$_2$), 5.30−5.80 (m, 1H, CH), 6.50−7.90 (m, 15H, CH=CH, aromatic protons) |
| **P-6** | 3400 (OH), 1725 (C=O, ester), 1614 (C=O, amide), 1580 (C=C), 1268 (COC, ester) | 1.08−1.72 (m, 6H, CH$_2$ in piperidyl ring), 1.88−2.40 (m, 2H, bridged CH$_2$ in NBD), 2.84−4.80 (m, 10H, CH$_2$, CH in NBD, NCH$_2$), 5.40−5.78 (m, 1H, CH), 6.64−6.98 (m, 2H, CH=CH), 7.40−7.96 (m, 4H, aromatic protons) |
| **P-7** | 3400 (OH), 1726 (C=O, ester), 1619 (C=O, amide), 1570 (C=C), 1251 (COC, ester) | 0.50−1.10 (m, 6H, CH$_3$), 1.20−1.90 (m, 4H, CH$_2$), 1.90−2.50 (m, 2H, bridged CH$_2$ in NBD), 2.70−3.50 (m, 4H, NCH$_2$), 3.55−4.10 (m, 2H, CH in NBD moiety), 4.15−4.90 (m, 4H, CH$_2$), 5.30−5.80 (m, 1H, CH), 6.70−7.00 (m, 2H, CH=CH), 7.40−7.90 (m, 4H, aromatic protons) |
| **P-8** | 3480 (OH), 1730 (C=O, ester), 1620 (C=C), 1250 (COC, ester) | 1.90−2.40 (m, 2H, bridged CH$_2$ in NBD), 3.70 (s, 3H, CH$_3$), 3.80−4.10 (m, 2H, CH in NBD), 4.15−4.90 (m, 4H, CH$_2$), 5.40−5.80 (m, 1H, CH), 6.80−7.00 (m, 2H, CH=CH), 7.40−8.00 (m, 4H, aromatic protons) |

**Table 4. Synthesis of Polyesters Carrying Pendant NBD Moieties by the Ring-Opening Copolymerization of Epoxides with Anhydrides**[a]

| polym no. | epoxide | anhyd | yield,[b] % | composition[c] epoxide | composition[c] anhyd | $M_n{}^d \times 10^{-4}$ | $M_w/M_n{}^d$ |
|---|---|---|---|---|---|---|---|
| **P-1** | GPNC | PAn | 90 | 100 | 100 | 3.3 | 1.8 |
| **P-2** | GPNC | SAn | 70 | 100 | 100 | 1.3 | 1.7 |
| **P-3** | GPNC | THPAn | 76 | 100 | 100 | 1.3 | 1.6 |
| **P-4** | GPNC | CDCAn | 50 | 100 | 100 | 1.1 | 1.4 |
| **P-5** | GPNP | PAn | 61 | 100 | 100 | 2.5 | 2.1 |
| **P-6** | GPONC | PAn | 86[e] | 100 | 100 | 1.7 | 1.5 |
| **P-7** | GDNC | PAn | 87[e] | 100 | 100 | 1.9 | 1.3 |
| **P-8** | GMNC | PAn | 86[e] | 100 | 100 | 1.3 | 1.1 |

[a] The reaction was carried out with epoxides (2 mmol) and dicarboxylic anhydrides (2 mmol) using TBAB (0.5 mol %) in sulfolane (0.67 mL) at 100 °C for 24 h. [b] Insoluble part in methanol. [c] Determined by $^1$H NMR. [d] Estimated by GPC based on polystyrene standards. [e] Insoluble part in ether.

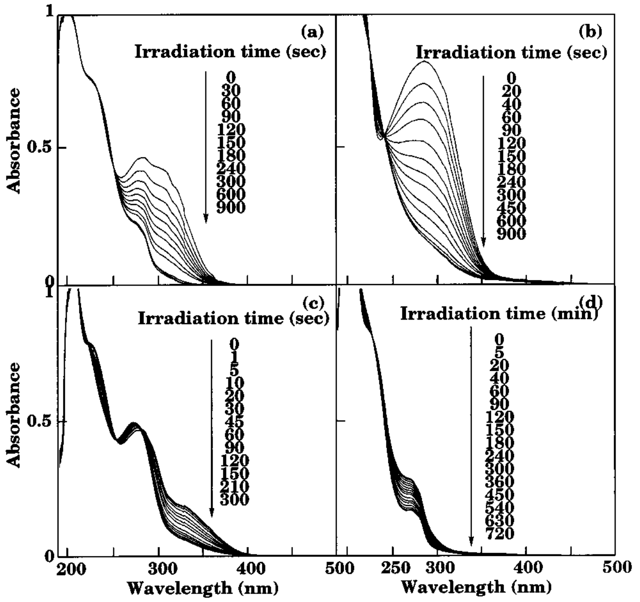


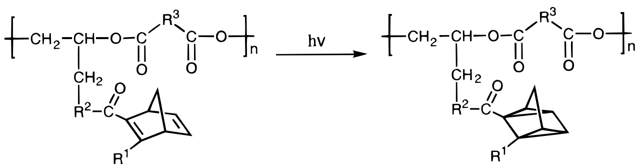
**Figure 1.** Change of UV spectra of NBD polymers in the film state with irradiation by a Xe lamp (2.0 mW/cm$^2$): (a) **P-1**; (b) **P-2**; (c) **P-5**; (d) **P-6**.

**Table 5. First-order Rate Constants of Photochemical Valence Isomerizations of the NBD Moieties in the Polymers**[a]

| polym no. | $k_{obsd} \times 10^3$ (s$^{-1}$) in the film state ($\lambda_{max}$ (nm)) | $k_{obsd} \times 10^3$ (s$^{-1}$) in solution[b] THF ($\lambda_{max}$ (nm)) | $k_{obsd} \times 10^3$ (s$^{-1}$) in solution[b] DCM ($\lambda_{max}$ (nm)) |
|---|---|---|---|
| **P-1** | 5.6 (295) | 5.8 (300) | 6.7 (300) |
| **P-2** | 6.2 (280) | 6.5 (300) | 6.4 (300) |
| **P-3** | 6.9 (295) | 6.8 (300) | 7.7 (300) |
| **P-4** | 6.0 (300) | 6.1 (300) | 7.4 (300) |
| **P-5** | 15.3 (330) | 25.5 (330) | 18.2 (330) |
| **P-6** | 0.07 (265) | 0.08 (270) | 0.08 (270) |
| **P-7** | 0.08 (265) | 0.08 (270) | 0.08 (270) |
| **P-8** | 0.29 (250) | 0.35 (260) | 0.88 (260) |

[a] Irradiated by a 500-W xenon lamp. [b] Concentration = 1 × $10^{-4}$ mol/L.

**Scheme 3**



**Photochemical Isomerization of the Pendant NBD Moiety in the Polymer.** Photochemical valence isomerization of the pendant NBD moiety in polymer **P-1** film was carried out on a quartz cell by photoirradiation using a xenon lamp. As shown in Figure 1, an absorption at 275 nm due to the NBD moiety in **P-1** decreased, and the NBD moiety isomerized quantitatively to the QC group after only 15 min of irradiation. As shown in Figure 1, there are also two isosbestic points at 215 and 230 nm. This result indicates that the photochemical isomerization of the pendant NBD moiety to the corresponding QC group in the polymer film occurred very smoothly and selectively without any side reactions upon the irradiation.

Photochemical valence isomerizations of the pendant NBD moieties in **P-2**, **P-5**, and **P-6** films were also performed by the same method, and changes of these UV spectra are shown in Figure 1. The photochemical isomerizations of all these polymers proceeded with isosbestic points as did that of **P-1**. This means that the photochemical reactions of **P-2**, **P-5**, and **P-6** have no side reactions. Furthermore, the photochemical isomerizations of **P-3** and **P-4** carrying the same NBD moiety as **P-1** were investigated under the same conditions. The absorption of these polymers was different (Table 5), but the isomerization from NBD to QC in each polymer was finished in about 15 min. This result indicates that the main chain does not influence the photochemical isomerization of the polymers carrying the same NBD residue.

On the other hand, the rates of the photochemical isomerizations of **P-1**, **P-5**, and **P-6** with the same main chain and different NBD residues were quite different. This result indicates that the photochemical isomerization of the NBD polymers was influenced by the absorption maxima and absorption region of the respective polymers, and **P-5** containing a chalcone group as the aromatic chromophore on the NBD moiety hardly had a higher photochemical reactivity than **P-6** containing a disubstituted amide group as the aliphatic chromophore on the NBD moiety.

Figure 2 shows the change of the UV spectra due to the photochemical isomerization of **P-1** in tetrahydrofuran (THF) or dichloromethane (DCM) solutions (1 × $10^{-4}$ mol/L). This result indicates that the photochemical isomerization of the pendant NBD moiety to the corresponding QC moiety in the solutions proceeded without any side reaction upon the photoirradiation, because there are isosbestic points. It was also found that $\lambda_{max}$ of the absorptions in the solutions were red shifted compared to the film state (see Figures 1 and 2 and Table 5). The red shift of $\lambda_{max}$ of the absorption may occur due to the change of the polymer matrix resulting from the change of the polarity of the reaction media.

The relationship between conversions of the photochemical isomerization of **P-1**, **P-5**, **P-6**, **P-7**, and **P-8**

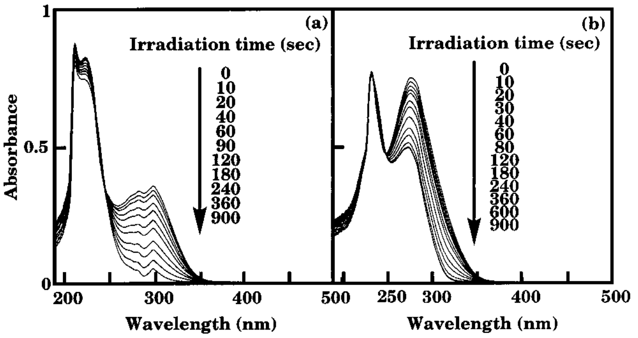


**Figure 2.** Change of UV spectra of **P-1** in solution ($1 \times 10^{-4}$ mol/L) with irradiation by a Xe lamp (2.0 mW/cm$^2$): (a) THF; (b) DCM.

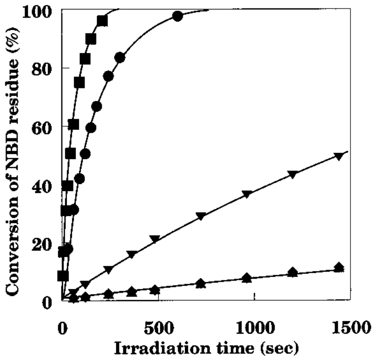


**Figure 3.** Conversions of the photoisomerization of polyesters in the film state: (●) **P-1**; (■) **P-5**; (◆) **P-6**; (▲) **P-7**; (▼) **P-8**.

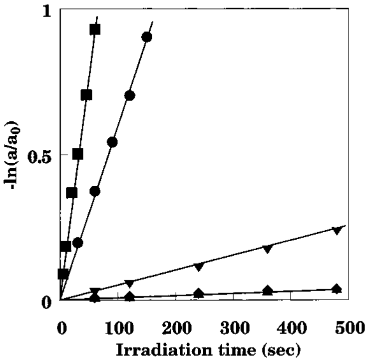


**Figure 4.** First-order rates of polyesters in the film state: (●) **P-1**; (■) **P-5**; (◆) **P-6**; (▲) **P-7**; (▼) **P-8**.

films, which have the same polyester skeleton, and photoirradiation time is shown in Figure 3. This result indicates that the progress of isomerization of the pendant NBD residues was strongly dependent on the kind of the NBD groups in the polymers. The photochemical reaction of **P-8**, having a methyl ester group as the chromophore on the NBD moiety, proceeded more smoothly than that of **P-6** or **P-7**, having disubstituted amide groups on the NBD moieties, although the rate of the photochemical reaction of **P-8** was much lower than those of **P-1** and **P-5** with aromatic groups as chromophores on the NBD moieties.

As shown in Figure 4, it was also found that the observed rates of photochemical reactions of the NBD residues in **P-1**, **P-5**, **P-6**, **P-7**, and **P-8** films obeyed first-order kinetics. First-order rate constants of the photochemical isomerizations of all polymers on the film state or in the solution are summarized in Table 5. These results indicate that rates of the photochemical reactions in the solutions were slightly higher than those of the films of the same polymers. From this

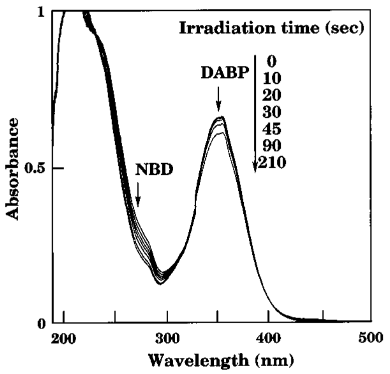


**Figure 5.** Change of UV spectrum of **P-6** film with DABP (7 mol %) with irradiation by a Xe lamp (2.0 mW/cm$^2$).

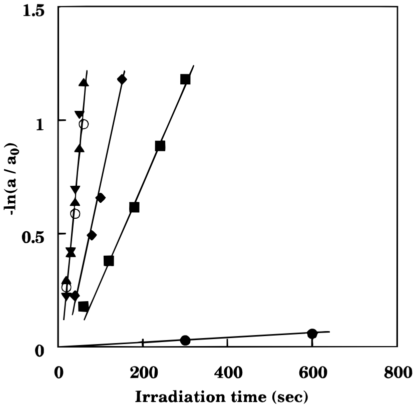


**Figure 6.** First-order rates of photoisomerizations of **P-6** with DABP in the film state: (●) without DABP; (■) with 1 mol % of DABP; (◆) with 3 mol % of DABP; (▲) with 5 mol % of DABP; (▼) with 9 mol % of DABP; (○) with 15 mol % of DABP.

result and the results of the red shift of the absorption maxima (Figure 2), the rate of the photochemical isomerization of **P-1** was faster in solution than in the film state.

Since the photochemical reactivities of **P-6** and **P-7** with N,N-disubstituted amide groups and of **P-8** with a methyl ester group on the NBD moieties were very low, the photochemical isomerizations of these polyesters were examined in the film state or in THF solution using DABP and BEBP, which are well-known as typical photosensitizers for some photoresists.[16] As shown in Figure 5, the photochemical reaction of **P-6** in the film state with DABP (7 mol %) was performed under the same conditions. The photoisomerization of **P-6** with DABP proceeded very smoothly, requiring only about 3 min of irradiation, although the photoisomerization of **P-6** without DABP needed about 12 h (Figure 1). There was also an isosbestic point in spite of a slight decrease in the absorption at 350 nm resulting from some decomposition of DABP.

Figure 6 shows that the observed rates of photochemical reaction of **P-6** film under various DABP concentrations obeyed first-order kinetics but displayed induction times. The relationship between DABP concentrations and the resulting first-order rate constants is shown in Figure 7. Increasing DABP concentration tends to increase the rate of photochemical reaction until 9 mol %, but further addition of DABP has no additional effect. This saturation may be due to the filter effect of the sensitizer on the photochemical reaction. Furthermore, the photochemical reaction of **P-6** in THF solution ($1 \times 10^{-4}$ mol/L) with DABP (7 mol %) was performed under the same conditions. This result was different from the

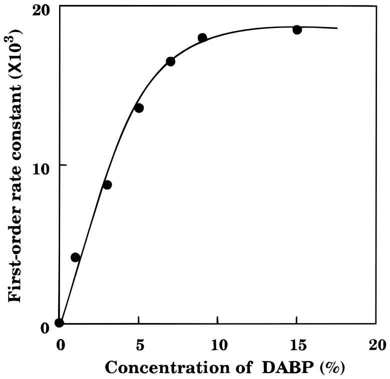


**Figure 7.** Effect of DABP concentration on the photochemical reaction of **P-6** with DABP in the film state.

**Table 6. First-Order Rate Constants of Photochemical Valence Isomerizations of the NBD Moieties in the Polymers Using Photosensitizers**[a]

| polym no. | photosensitizer | $k_{\mathrm{obsd}} \times 10^3$ ($s^{-1}$) in the film state | $k_{\mathrm{obsd}} \times 10^3$ ($s^{-1}$) in THF solution[b] |
|---|---|---|---|
| **P-6** | none | 0.07 | 0.08 |
| | DABP (7 mol %) | 31.3 | 0.13 |
| | BEBP (7 mol %) | 32.3 | |
| **P-7** | none | 0.08 | 0.08 |
| | DABP (7 mol %) | 16.3 | 0.09 |
| | BEBP (7 mol %) | 27.0 | |
| **P-8** | none | 0.29 | 0.35 |
| | DABP (7 mol %) | 3.7 | 0.61 |
| | BEBP (7 mol %) | 4.1 | |

[a] Irradiated by a 500-W xenon lamp. [b] Concentration = 1 × $10^{-4}$ mol/L.

**Table 7. Quantum Yields of Photochemical Valence Isomerization of NBD Polymers**[a]

| | P-1 | P-2 | P-3 | P-4 | P-5 |
|---|---|---|---|---|---|
| chemical yield, % | 2.2 | 3.1 | 2.7 | 2.7 | 10.2 |
| quantum yield, $\phi$ | 0.39 | 0.41 | 0.37 | 0.33 | 0.41 |

[a] Quantum yields of polymers were measured with 313 nm light in dichloromethane (1 × $10^{-4}$ mol/L) at room temperature.

result on the film state and indicated that energy transfer hardly occurred in the dilute solution because of low contact of the NBD residue with DABP.

First-order rate constants of the photochemical isomerizations of **P-6** to **P-8** using DABP and BEBP in the film state or in solution are summarized in Table 6. Energy transfer from DABP or BEBP to NBD residues in **P-7** or **P-8** in the film state occurred as effectively as it did in **P-6**. It was also found that **P-6** and **P-7** having N,N-disubstituted amide groups as chromophores on the NBD moieties were sensitized more strongly by the addition of DABP and BEBP than **P-8** having a methyl ester group as a chromophore on the NBD moiety. Furthermore, the photosensitizing reactions of **P-7** and **P-8** were performed upon the same DABP concentration to the NBD residues in the THF solutions. However, the photosensitizing reaction in the solution scarcely occurred.

Quantum yields for **P-1** to **P-5** in DCM solutions (1 × $10^{-4}$ mol/L) are summarized in Table 7. Since there are no absorptions of the polymer main chains at 313 nm, quantum yields for the photochemical isomerization of the NBD moieties are considered to be hardly influenced by the polymer skeleton. The quantum yield of **P-5** was found 0.41, which is relatively large. However, polymers **P-6** to **P-8** were subject to negligible photochemical isomerization under the same reaction conditions, because there is little absorption at 313 nm.

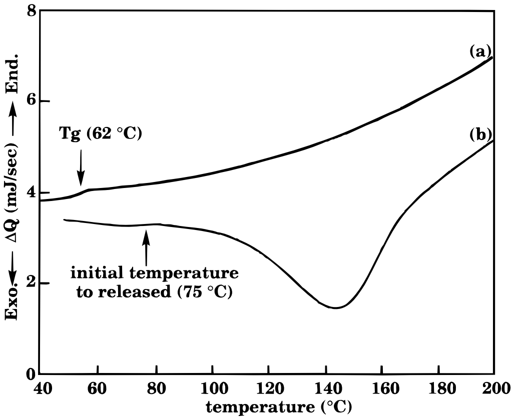


**Figure 8.** DSC curves of **P-1** film before and after photoirradiation: (a) second run of polyester **P-1**; (b) first heating of polyester **P-1s** after photoirradiation.

**Table 8. Thermal Properties of the NBD Polymers**[a]

| polym no. | $M_n$[b] × $10^{-4}$ | $M_w/M_n$[b] | $T_g$,[a] °C | initial temp to release,[a] °C | stored thermal energy,[a] kJ/mol |
|---|---|---|---|---|---|
| **P-1** | 3.3 | 1.8 | 62 | 75 | 91 |
| **P-2** | 1.3 | 1.7 | 45 | 53 | 82 |
| **P-3** | 1.3 | 1.6 | 64 | 75 | 85 |
| **P-4** | 1.1 | 1.4 | 62 | 80 | 90 |
| **P-5** | 2.5 | 2.1 | 93 | 116 | 89 |
| **P-6** | 1.7 | 1.5 | 65 | 57 | 89 |
| **P-7** | 1.9 | 1.3 | 50 | 59 | 90 |
| **P-8** | 1.3 | 1.1 | 57 | 72 | 85 |

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

These results mean that polymers containing NBD moieties with aromatic substituents as chromophores have very high quantum yields and good photochemical reactivity and have good potential for use as solar energy storage−exchange polymers.

**Measurement of $T_g$s of NBD Polymers and of Stored Thermal Energy in the QC Polymers.** NBD polymer films and enough photoirradiated polymer films were packed in an aluminum sample tube for DSC analysis. The sample was heated at 10 °C/min under nitrogen. Figure 8 shows DSC curves of **P-1** film and photoirradiated **P-1** film. The $T_g$ of **P-1** before photoirradiation was 62 °C, and no further release of thermal energy was found on further heating. On the other hand, photoirradiated **P-1** film released thermal energy at 75 °C, and at 142 °C it released the highest thermal energy. Furthermore, the released thermal energy of the photoirradiated **P-1** film was about 91 kJ in the 1 mol of NBD residue in the polymer.

The $T_g$s of all NBD polymers and stored thermal energies of the QC polymers are summarized in Table 8. The $T_g$s of **P-1**, **P-2**, **P-3**, and **P-4** with the same NBD residue and different polymer skeletons were 62, 45, 64, and 62 °C, respectively. It seems that the $T_g$s of the polymers are little influenced by the main chain structure. Furthermore, the $T_g$s of **P-1**, **P-5**, **P-6**, **P-7**, and **P-8** with different NBD residues and the same polymer main chain were 62, 93, 65, 50, and 57 °C, respectively. This result indicates that the $T_g$ of the polymer depends strongly on the pendant NBD residues. That is, the $T_g$ of **P-8** containing the NBD residue having a methyl ester group was lower than that of **P-5** with a bulky and aromatic group on the NBD residue.

Polyesters having QC groups, which were photoirradiated of the NBD polymers, smoothly released their stored thermal energy (about 90 kJ/mol). Furthermore, it was found that the initiating temperatures to release their stored thermal energy in the polymers were higher than the $T_g$s of the corresponding NBD polymers. This means that the reversion from the QC group to the NBD moiety in the polymer was related to the configurational change due to the QC structure.

From all these results, the following conclusions can be obtained. (1) Various epoxy monomers containing different NBD moieties were prepared by the reaction of the potassium salts of NBD derivatives with excess epichlorohydrin using TBAB as a phase transfer catalyst. (2) Ring-opening alternating copolymerization of various epoxy monomers containing NBD groups with various carboxylic anhydrides gave the corresponding polyesters (**P-1** to **P-8**). (3) The photochemical valence isomerization of the obtained NBD polymers proceeded smoothly in the film state or in the solution. Furthermore, in the case of low photoreactive polymer (**P-6** to **P-8**), the rates of isomerizations were strongly enhanced by the addition of photosensitizers such as DABP. (4) All of the polyesters having QC groups after photoirradiation smoothly released their stored thermal energy at temperatures above the $T_g$s of the corresponding NBD polymers. It was also proved that the polyesters released about 90 kJ/mol of the stored thermal energy.

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