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Synthesis of New Photoresponsive Polyesters Containing Donor−Acceptor Norbornadiene (D−A NBD) Residues by the Polyaddition of D−A NBD Dicarboxylic Acids with Bis(epoxide)s and Their Photochemical Properties

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ABSTRACT: Polyesters containing donor−acceptor norbornadiene (D−A NBD) residues in the main chain were synthesized by the polyaddition of D−A NBD dicarboxylic acids, 5-(4-methoxyphenyl)-1,4,6,7,7-pentamethyl-2,5-norbornadiene-2,3-dicarboxylic acid and 5,6-bis(4-methoxyphenyl)-7,7-dimethyl-2,5-norbornadiene-2,3-dicarboxylic acid, with bis(epoxide)s. The photoisomerization of the NBD residues in the resulting polyesters proceeded smoothly to give the corresponding quadricyclane (QC) groups. The NBD residues in these polyesters showed resistivity to repeated cycles of the interconversion.

Introduction

The photoisomerization between norbornadiene (NBD) and quadricyclane (QC) is of interest as a solar energy conversion and storage system, because photoenergy can be stored as strain energy (about 96 kJ/mol) in a QC molecule.[1] Recently, this photochemical reaction has also been investigated as a new switching system in the optoelectronic field or as a photochromic system potentially applicable to data storage.[2]

Nishikubo et al. reported the synthesis of photoreactive polymers containing NBD residues in the side chain and also found that the NBD residues in the polymers proceeded smoothly to produce the corresponding QC groups.[3] Recently, they also reported the synthesis of polymers containing NBD residues in the main chain by the polyaddition of NBD dicarboxylic acid (NDC).[4] However, the photoreactivity of these polymers was relatively low compared to that of the polymer containing NBD residues in the side chain. To improve the photoreactivity of these polymers, they synthesized poly(ester−amide)s containing the NBD residue in the main chain by the polyaddition of NBD dicarboxylic acid derivatives, which were prepared by the addition of NDC anhydride with secondary aromatic diamines, with bis(epoxide)s and found that these poly(ester−amide)s had a high photoreactivity and could be sensitized effectively by the addition of certain photosensitizers.[5] In respect of the photoreactivity of NBD derivatives, it is known that donor−acceptor NBD derivatives (D−A NBD) absorb visible light and cyclize to the corresponding QC derivatives in high quantum yield.[6] Furthermore, it is expected that the introduction of a suitable substituent into the NBD skeleton suppresses the formation of byproducts caused by polymerization of the NBD and QC moieties, since the steric effect of the substituent inhibits the interaction of these moieties. Therefore, to produce useful photoreactive functional materials, we synthesized new photoresponsive polymers containing D−A NBD residues in the main chain by the polyaddition of D−A NBD dicarboxylic acids (D−A NDC) with various bis(epoxide)s using quaternary onium salts as catalyst and studied the photoisomerization of the resulting polymers. Furthermore, we examined the durability of the NBD residue in these polymers for repeated cycles of the interconversion.

Experimental Section

Materials. 5-(4-Methoxyphenyl)-1,4,6,7,7-pentamethyl-2,5-norbornadiene-2,3-dicarboxylic acid dimethyl ester (MAE, purchased from Sanpo Chemical Laboratory Ltd., Japan) was recrystallized from *n*-hexane. 5,6-Bis(4-methoxyphenyl)-7,7-dimethyl-2,5-norbornadiene-2,3-dicarboxylic acid dimethyl ester (MBE) was synthesized according to the reported method.[6b] Commercial bisphenol A diglycidyl ether (BPGE) was recrystallized four times from a mixed solvent of methanol (4)/ethyl methyl ketone (1). 3,3′,5,5′-Tetramethyl-4,4′-biphenyl diglycidyl ether (TMBGE) was recrystallized three times from isobutyl methyl ketone. Resorcinol diglycidyl ether (RGE) was purified by column chromatography with *n*-hexane/ethyl acetate (40/1) as eluent. 1,4-Butanediol diglycidyl ether (BDGE) was purified by distillation. Tetrabutylammonium bromide (TBAB) was recrystallized twice from dried ethyl acetate. 18-Crown-6 ether (18-C-6), potassium bromide (KBr), and citric acid were used without further purification. The solvents, triethylamine (TEA), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were dried using P_2O_5, CaH_2, or Na metal wire and purified by distillation.

Apparatus. Melting points were determined with a Yanaco MP-500D hot stage microscope. Infrared (IR) spectra were measured on a Jasco model FT/IR-420 spectrometer. Ultraviolet (UV) spectra were recorded on a Shimadzu model UV-2500PC. The ^{1}H NMR spectra were recorded on a JEOL model JNM-FX-270. 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 Multipore Hxl-M column (eluent: 10 mM LiBr DMF solution at flow rate of 1.0 mL/min, calibrated using narrow molecular weight polystyrene as

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standards). The glass transition temperature (T_g) and the amount of stored energy in the QC groups in the polymer were measured on a Seiko-Instruments differential scanning calorimeter (DSC) model SSC5200DSC120. Elemental analysis was measured on a Perkin-Elmer model PE2400 Series 2 CHNS/O analyzer.

Synthesis of D−A NBD Dicarboxylic Acids (D−A NDC). Synthesis of 5-(4-Methoxyphenyl)-1,4,6,7,7-pentamethyl-2,5-norbornadiene-2,3-dicarboxylic Acid (MA). A 1,4-dioxane/H_2O (100/7) solution (53.5 mL) of MAE (7.68 g, 20 mmol) and KOH (11.88 g, 60 mmol) was stirred for 5 h at room temperature. The reaction mixture was diluted in H_2O and washed with diethyl ether. Then, the aqueous layer was acidified with citric acid and extracted with ethyl acetate. The organic extracts were washed with water, dried with anhydrous $MgSO_4$, and filtered. After evaporation of the solvent, the crude product was purified by recrystallization using the mixed solvent chloroform/*n*-hexane. The yield of MA was 4.78 g (67%). Mp: 186.2−187.2 °C. IR (KBr, cm^{-1}): 3600−2200 (ν_{O-H}), 1711 ($\nu_{C=O}$). ^1H NMR (DMSO-d_6, TMS): δ 0.91 (s, 3.0H, CH_3), 0.94 (s, 3.0H, CH_3), 1.04 (s, 3.0H, CH_3), 1.21 (s, 3.0H, CH_3), 1.67 (s, 3.0H, CH_3), 3.75 (s, 3.0H, CH_3O), 6.94 (d, J = 8.2 Hz, 2.0H, aromatic protons), 7.08 (d, J = 8.2 Hz, 2.0H, aromatic protons), 12.59 (br, 2.0H, OH). Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.64; H, 6.68.

Synthesis of 5,6-Bis(4-methoxyphenyl)-7,7-dimethyl-2,5-norbornadiene-2,3-dicarboxylic Acid (MB). The general hydrolyzation procedure was followed, using MBE (8.97 g, 20 mmol). The crude product was purified by recrystallization using toluene. The yield of MB was 7.14 g (85%). Mp: 186.2−187.2 °C. IR (KBr, cm^{-1}): 3700−2200 (ν_{O-H}), 1680 ($\nu_{C=O}$). ^1H NMR (DMSO-d_6, TMS): δ 1.17 (s, 3.0H, CH_3), 1.28 (s, 3.0H, CH_3), 3.73−3.75 (m, 8.0H, CH_3O, CH), 6.86 (d, J = 8.58 Hz, 4.0H, aromatic protons), 7.21 (d, J = 8.58 Hz, 4.0H, aromatic protons), 9.06 (br, 2.0H, OH). Anal. Calcd for $C_{25}H_{24}O_6$: C, 71.41; H, 5.75. Found: C, 71.15; H, 5.71.

Typical Procedure for the Synthesis of Polyesters Containing D−A NBD Residues by the Polyaddition of D−A NDC with Bis(epoxide)s. A typical example of the polyaddition of D−A NDC with bis(epoxide) is as follows.

Synthesis of PA-1 by the Polyaddition of MA with BPGE. TBAB (8.1 mg, 0.025 mmol) was dried in an ampule tube in vacuo at 60 °C for 5 h prior to use. MA (178 mg, 0.5 mmol), BPGE (170 mg, 0.5 mmol), and NMP (0.5 mL) as solvents were added into the ampule tube, and then the reaction mixture was degassed twice by consecutive freeze−pump−thaw cycles. After the ampule tube was sealed, the reaction mixture was heated at 100 °C for 24 h. The reaction mixture was poured into methanol to give a precipitate. The obtained polymer (**PA-1**) was reprecipitated twice from $CHCl_3$ into methanol and dried in vacuo. The yield of **PA-1** was 297 mg (84%). The number-average molecular weight (M_n) of the polymer estimated by GPC was 26500 and M_w/M_n was 1.90. IR (film, cm^{-1}): 3448 (ν_{O-H}), 1707 ($\nu_{C=O}$), 1245 (ν_{C-O-C}). ^1H NMR ($CDCl_3$, TMS): δ 0.87−1.07 (m, 6.0H, CH_3 at bridge in NBD), 1.07−1.18 (m, 3.0H, CH_3 in NBD), 1.28 (s, 3.0H, CH_3 in NBD), 1.43−1.78 (m, 9.0H, CH_3 in NBD, CH_3), 2.66−3.23 (br, 2.0H, OH), 3.69−4.55 (m, 12.78H, CH of β-cleavage of the epoxy ring, CH_2, OCH_3), 5.23−5.43 (m, 0.22H, CH of α-cleavage of the epoxy ring), 6.68−7.20 (m, 12H, aromatic protons). Anal. Calcd for $C_{42}H_{48}O_9$: C, 72.39; H, 6.94. Found: C, 71.98; H, 6.79.

Typical Procedure for the Photoisomerization of NBD Monomers and Polyesters. The Photoisomerization of NBD Monomers in Solution. A quartz cell was charged with a solution of a D−A NDC dimethyl ester in THF (1.0×10^{-4} mol/L), and then the solution was irradiated by a 500-W xenon lamp (Ushio Electric Co., UXL-500D-O) with a thermal-ray cut filter (Hoya; HA50), in which the energy of the incident light (2.00−2.10 mW/cm^2 (310 nm)) was monitored by an electric photon counter (ORC model UV-M30). The conversion and the photoisomerization rates from NBD residues to QC groups were calculated by the disappearance of the maximum absorption of the NBD residue, as measured by UV spectrophotometer. The photoisomerization of the NBD polymer in THF solution was carried out under similar conditions as in the case of the NBD monomers.

Table 1. Effect of the Catalyst on the Polyaddition of MA with PBGE[a]

catalyst	yield,[b]%	M_n[c] × 10^{-4}	M_w/M_n[c]	ratio of cleavage[d] α:β
none	46	1.49	1.33	11:89
DBU	51	2.10	1.48	26:74
TBAB	84	2.65	1.90	14:86
18-C-6/KBr	77	2.02	1.68	12:88

[a] The reaction was carried out with MA (0.5 mmol) and BPGE (0.5 mmol) using catalyst (0.025 mmol) at 100 °C in NMP (0.5 mL). [b] insoluble parts in methanol. [c] Estimated by GPC based on polystyrene standards. [d] Determined by ^1H NMR.

Photoisomerization of NBD Residue in Polymer Film. The inside wall of a quartz cell was coated with a solution of a polymer (50 mg) in THF (2 mL) and dried in vacuo at room temperature for 2 h. The polymer film was irradiated by a 500-W xenon lamp as above with a thermal-ray cut filter. The conversion and the photoisomerization rates from NBD residues to QC groups were calculated from the disappearance of the maximum absorption of the NBD residue, as measured by UV spectrophotometer.

Thermal Reversion Isomerization of QC Groups in the Polyesters Obtained from MB with Bis(epoxide)s. The film cast on the glass plate was irradiated for 3 min to be changed from the NBD residues to the QC groups by a 500-W xenon lamp. The thermal reversion of QC groups in the irradiated polymer was carried out at room temperature in the dark. The degree of reversion from QC groups to NBD residues was calculated by the increasing maximum absorption of the NBD residue, as measured by a UV spectrophotometer.

Measurement of Stored Energy in the QC Group in the Polymer. A polymer solution in THF was cast onto a glass plate and dried in vacuo for 2 h. The film on the plate was irradiated for 20 min to be changed from the NBD residue to the QC group by a 500-W xenon lamp. The irradiated polymer (5 mg) was packed in an aluminum sample tube for DSC analysis and the sample was heated at 10 °C /min under nitrogen.

Examination of the Durability of the NBD Residue in the Polyester. The experiment was performed under argon atmosphere. Initially, the polymer film was irradiated by a 500-W xenon lamp until the absorbance of the maximum absorption of the NBD residue disappeared. Then, the irradiated film was heated on a hot plate until the absorbance of the NBD residue was reversed (**PA-1**, irradiated for 20 min and then heated at 120 °C for 25 min; **PB-1**, irradiated for 6 min and then heated at 70 °C for 40 min). The durability was evaluated from the differences in the absorbance values between the NBD residue and the QC group at maximum absorption of the NBD residue on the first and *n*th cycles of reactions.

Results and Discussion

Synthesis of Polyesters Containing D−A NBD Residues in the Main Chain by the Polyaddition Reaction of D−A NDC with Bis(epoxide)s. 5-(4-Methoxyphenyl)-1,4,6,7,7-pentamethyl-2,5-norbornadiene-2,3-dicarboxylic acid (MA) and 5,6-bis(4-methoxyphenyl)-7,7-dimethyl-2,5-norbornadiene-2,3-dicarboxylic acid (MB) were obtained from the corresponding dimethyl esters by KOH-catalyzed hydrolysis in 67% and 85% yields, respectively.

The polyaddition of the thus-obtained MA with BPGE was performed using various catalysts or without any catalyst in NMP at 100 °C for 24 h, and the results are summarized in Table 1. When the reaction was carried out without a catalyst, the yield and the M_n of the resulting polyesters were 46% and 14 900, respectively. In the reaction using DBU and 18-C-6/KBr, the yields

Scheme 1

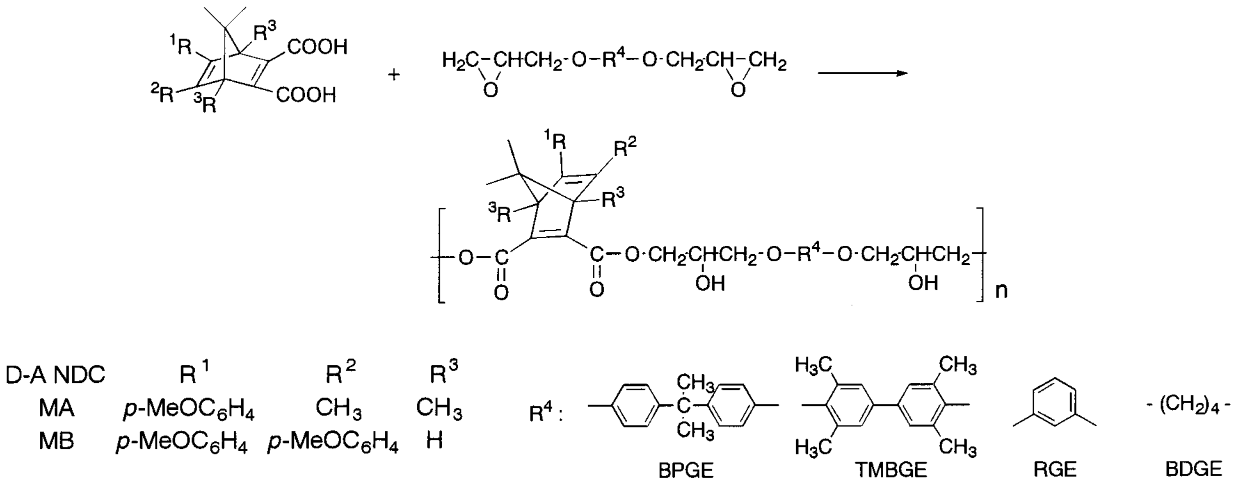


Table 2. Polyaddition of Various D−A NBD Dicarboxylic Acids with Bis(epoxide)s[a]

polym no.	NDC	epoxide	yield, %	M_n[c] × 10^{-4}	M_w/M_n[c]	λ_{max}, nm	λ_{edge}, nm
PA-1	MA	BPGE	84[b]	2.65	1.90	252, 320	455
PA-2	MA	TMBGE	83[b]	2.77	1.90	256, 328	449
PA-3	MA	RGE	60[c]	1.63	1.57	253, 327	448
PA-4	MA	BDGE	34[d]	3.98	1.44	253, 325	448
PB-1	MB	BPGE	84[b]	2.01	1.89	279, 360	548
PB-2	MB	TMBGE	84[b]	1.38	1.62	−, 360	520
PB-3	MB	RGE	90[c]	1.1	1.91	281, 360	521
PB-4	MB	BDGE	89[d]	1.5	3.52	288, 360	523

[a] The reaction was carried out with D−A NBD dicarboxylic acid (0.5 mmol) and bis(epoxide) (0.5 mol) using TBAB (0.025 mmol) at 100 °C in NMP (0.5 mL). [b] Insoluble parts in methanol. [c] Insoluble parts in *i*-PrOH. [d] Insoluble parts in mixed solvent of *i*-PrOH and *n*-hexane (1:1). [e] Estimated by GPC (DMF) based on polystyrene standards.

of the resulting polyesters were 51 and 77%, respectively, and M_ns were 21 000 and 20 200, respectively. Further investigation of the reaction using TBAB as catalyst was carried out. The yield and M_n of the resulting polyester were 84% and 26 500, respectively. These results suggest that TBAB is a suitable catalyst for the polyaddition reaction of MA with BPGE. The ratio of cleavage of the epoxy ring in the polyaddition was estimated by ^{1}H NMR. Intensity ratio of the aromatic proton (6.6−7.2 ppm) to the methine proton (5.2−5.3 ppm) of the α-cleavage of the epoxy ring indicated that β-cleavage of the epoxy ring proceeded selectively under each reaction condition, and the ratio of α to β was 11:89 to 26:74.

Furthermore, the polyaddition reaction of MA and MB with certain bis(epoxy) compounds was carried out using TBAB as catalyst in NMP at 100 °C for 24 h (Scheme 1), and the results are summarized in Table 2. The structure of the polymer was confirmed by IR and ^{1}H NMR spectra (Table 3). The M_ns of the polyesters obtained from the polyadditions of MA with BPGE, TMBGE, RGE, and BDGE were 27000, 28000, 16000, and 40000, respectively, and the yields of these polyesters were 84, 83, 60, and 34%, respectively. Although the M_n of the polyester obtained from BDGE as bis(epoxide) was the highest, its yield was the lowest. In the case of the reaction with BDGE bearing a straight alkyl chain, it seemed that the reaction of the propagating terminal of the polymer chain with dicarboxyic acid did not proceed smoothly in the later stage of the polyaddition because the reaction media was not mixed well due to the intertwined polymer chain. Then, the polyaddition did proceed within a part of the reaction media and the polyester with high molecular weight was obtained in low yield. That is, low molecular weight polymers could not be recovered due to their good solubility into a poor solvent.

The polyaddition reaction of MB with bis(epoxide)s was also carried out under similar conditions. The M_ns of the polyesters obtained from the polyadditions of MB with BPGE, TMBGE, RGE, and BDGE were 20 000, 14 000, 11 000, and 15 000, respectively, and the yields of these polyesters were 84, 84, 90, and 89%, respectively.

It was found that the M_n of the polyester obtained from the polyaddition of MA was relatively higher than that obtained from the reaction of MB. It seems that the dissociation of carboxylic acid of MB to the carboxylate anion was suppressed by two electron-donating methoxyphenyl groups, so polyaddition of MB did not proceed well as in the case of MA.

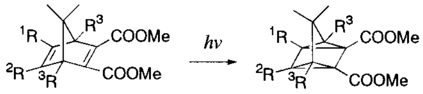
Photoisomerization of the NBD Polymers. As shown in Scheme 2, D−A NBD derivatives had an absorption in the visible region and especially the absorption edge of MBE reached nearly 500 nm, because they had a charge-transfer absorption band ascribed to charge-transfer interaction between the donor olefin and acceptor olefin parts of the molecule.[6a] The photoisomerization of the THF solutions (1 × 10^{-4}mol/L) of MAE and MBE was carried out by irradiation with a 500-W xenon lamp. As shown in Figure 1, D−A NBD derivatives had very high photochemical reactivity; the observed rate of the photoisomerization of these NBD derivatives obeyed first-order kinetics, and MBE had a relatively higher reactivity than MAE.

Furthermore, the photoisomerization of the polyesters obtained from the polyaddition of the D−A NDC was carried out in film state. Changes in the UV spectra of **PA-1** in the film state are shown in Figure 2. The maximum absorption of the NBD residues decreased and the NBD residues isomerized quantitatively to the corresponding QC groups after 180 s by irradiation. In addition, two isosbectic points at 223 and 240 nm were observed. This result means that the photoisomerization of the NBD residues in **PA-1** to the QC groups occurred selectively without any side reactions. As shown in Figures 3 and 4, the NBD residues in these polymers in the film state isomerized very fast, and the observed rate of the photoisomerization of the NBD residues

Table 3. IR and ^{1}H NMR Data for NBD Polymers

polym no.	IR data, cm^{-1}	^{1}H NMR data, ppm
PA-1	3448 (ν_{O-H}), 1707 ($\nu_{C=O}$), 1245 (ν_{C-O-C})	0.87−1.07 (m, 6.0H, CH_3 at bridge in NBD), 1.07−1.18 (m, 3.0H, CH_3 in NBD), 1.28 (s, 3.0H, CH_3 in NBD), 1.43−1.78 (m, 9.0H, CH_3 in NBD, CH_3), 2.66−3.23 (br, 2.0H, OH), 3.69−4.55 (m, 12.78H, CH of β-cleavage of the epoxy ring, CH_2, OCH$)_3$ 5.23−5.43 (m, 0.22H, CH of α-cleavage of the epoxy ring), 6.68−7.20 (m, 12H, aromatic protons)
PA-2	3449 (ν_{O-H}), 1707 ($\nu_{C=O}$), 1245 (ν_{C-O-C})	0.87−1.07 (m, 6.0H, CH_3 at bridge in NBD), 1.07−1.18 (m, 3.0H, CH_3 in NBD), 1.28 (s, 3.0H, CH_3 in NBD), 1.65−1.83 (m, 3.0H, CH_3 in NBD, CH_3 CH_3),2.11−2.40 (m, 12.0H, CH_3), 2.80−3.40 (br, 2.0H, OH), 3.69−4.65 (m, 12.7H, CH of β-cleavage of the epoxy ring, CH_2, OCH_3), 5.23−5.43 (m, 0.3H, CH of α-cleavage of the epoxy ring), 6.78−7.20 (m, 8.0H, aromatic protons)
PA-3	3487 (ν_{O-H}), 1707 ($\nu_{C=O}$), 1245 (ν_{C-O-C})	0.94 (s, 3.0H, CH_3 at bridge in NBD), 0.99 (s, 3.0H, CH_3 at bridge in NBD), 1.10 (s, 3.0H, CH_3 in NBD), 1.25 (s, 3.0H, CH_3 in NBD), 1.70 (s, 3.0H, CH_3 in NBD), 3.33−4.63 (m, 14.8H, CH of β-cleavage of the epoxy ring, CH_2, OCH_3, OH), 5.20−5.43 (m, 0.2H, CH of α-cleavage of the epoxy ring), 6.35−7.13 (m, 8H, aromatic protons)
PA-4	3468 (ν_{O-H}), 1707 ($\nu_{C=O}$), 1245 (ν_{C-O-C})	0.97 (s, 3.0H, CH_3 at bridge in NBD), 1.02 (s, 3.0H, CH_3 at bridge in NBD), 1.12 (s, 3.0H, CH_3 in NBD), 1.28 (s, 3.0H, CH_3 in NBD), 1.61 (s, 4.0H, CH_2CH_2), 1.73 (s, 3.0H, CH_3 in NBD), 2.96−4.41 (m, 18.8H, CH of β-cleavage of the epoxy ring, CH_2, OCH_3, OH), 5.03−5.23 (m, 0.2H, CH of α-cleavage of the epoxy ring), 6.88 (d, J = 8.25 Hz, 2.0H, aromatic protons), 7.09 (d, J = 8.25 Hz, 2.0H, aromatic protons)
PB-1	3479 (ν_{O-H}), 1707 ($\nu_{C=O}$), 1248 (ν_{C-O-C})	1.24 (s, 3.0H, CH_3 at bridge in NBD), 1.34 (s, 3.0H, CH_3 at bridge in NBD) 1.59 (s, 6.0H, CH_3), 2.99 (br, 2.0H, OH), 3.60−4.50 (m, 17.6H, CH in NBD, CH of β-cleavage of the epoxy ring, CH_2, OCH_3), 5.20−5.45 (m, 0.4H, CH of α-cleavage of the epoxy ring), 6.63−6.83 (m, 8.0H, aromatic protons), 7.00−7.32 (m, 8.0H, aromatic protons)
PB-2	3505 (ν_{O-H}), 1707 ($\nu_{C=O}$), 1248 (ν_{C-O-C})	1.28 (s, 3.0H, CH_3 at bridge in NBD), 1.38 (s, 3.0H, CH_3 at bridge in NBD) 2.12-2.40 (m, 12.0H, CH_3), 2.80−3.30 (br, 2.0H, OH), 3.56−4.62 (m, 17.7H, CH in NBD, CH of β-cleavage of the epoxy ring, CH_2, OCH_3), 5.22−5.30 (m, 0.3H, CH of α-cleavage of the epoxy ring), 6.63−7.37 (m, 12.0H, aromatic protons)
PB-3	3484 (ν_{O-H}), 1707 ($\nu_{C=O}$), 1248 (ν_{C-O-C})	1.00−1.55 (m, 6.0H, CH_3 at bridge in NBD), 2.90−3.63 (br, 2.0H, OH), 3.63−4.62 (m, 17.8H, CH in NBD, CH of β-cleavage of the epoxy ring, CH_2, OCH_3), 5.23-5.43 (m, 0.2H, CH of α-cleavage of the epoxy ring), 6.22−7.40 (m, 12.0 H, aromatic protons)
PB-4	3453 (ν_{O-H}), 1707 ($\nu_{C=O}$), 1248 (ν_{C-O-C})	1.16−1.42 (m, 6.0H, CH_3 at bridge in NBD), 1.42−1.74 (m, 4.0H, CH_2CH_2), 3.00-4.62 (m, 23.7H, CH in NBD, CH of β-cleavage of the epoxy ring, CH_2, OCH_3, OH), 5.04−5.30 (m, 0.3H, CH of α-cleavage of the epoxy ring), 6.77−6.80 (m, 4.0H, aromatic protons), 7.20−7.31 (m, 4.0H, aromatic protons)

Scheme 2

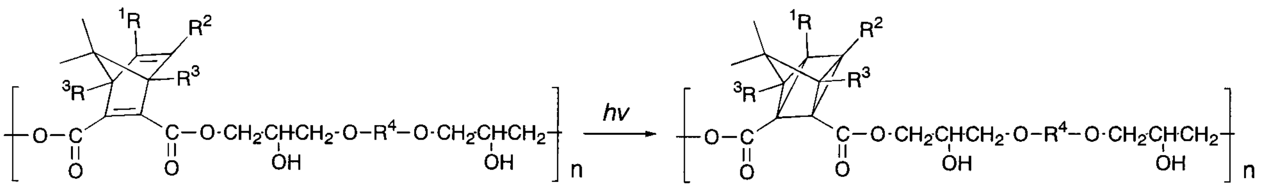


D-A NBD	R^1	R^2	R^3	λ_{max}	λ_{edge}
MAE	p-MeOC_6H_4	CH_3	CH_3	251, 317	416
MBE	p-MeOC_6H_4	p-MeOC_6H_4	H	280, 354	499

obeyed first-order kinetics. The photoisomerization of **PA-1−4** and **PB-1−4** was also carried out in the film state and in THF solution under similar irradiation conditions and the results are summarized in Table 4. The rate of the photoisomerization was affected by the structure of the NBD residue but not by that of bis(epoxide)s. Then, the polyesters obtained from MB had higher photochemical reactivity than the polyesters obtained from MA. It seems that the lower photochemical reactivity of **PAs** compared to **PBs** may be due to little absorption at the maximum absorption and the shorter absorption wavelength of the maximum absorption. However, the photoisomerization rate of **PB-4** was slightly higher than that of the others. It was reported that the photoisomerization rate of NBD derivatives was affected by the polarity of the solvent [7] and that the photoisomerization rate of NBD residues in polymers was affected by the structure of the polymer chain.[3d] BDGE contained in the polyester did not have an absorption band in the same region as that of the NBD residue. So, it seems that the structure of bis(epoxide)s to some extent reflected the photoisomerization rate of the NBD residue. Furthermore, the photoisomerization rate of the NBD residues in **PAs** was slightly higher than that of the corresponding NBD monomers, namely MAE, but that of NBD residues in **PBs** was lower than that of MBE. This result may be due to the fact that two C═C bonds of the NBD molecules did not take suitable conformations for photoisomerization, since two 4-methoxyphenyl groups at C-5 and C-6 on the NBD residue and main chain of polymer were sterically hindered in **PBs**.

Reversion of the QC Groups to the NBD Residues in the Polyester Bearing MB Groups in the Main Chain in the Film State at Room Temperature in the Dark. It was found that the QC groups in the polyester obtained from the polyaddition of MB with bis(epoxide) were not thermally stable, and they reverted to the starting NBD residues at room temperature. Thus, the reversion of the QC groups in these photoirradiated polymers was examined at room temperature in the dark. The conversion of QC groups to NBD residues in the polymer film was calculated from the increase of an absorption at 360 nm due to the NBD residue using UV spectrometer. As shown in Figure 5, about 70% of the QC groups in the photoirradiated **PB-4** reverted to the NBD residues in 1 h at room temperature, and two isosbectic points at 221 and 234 nm were observed in the UV spectrum. This result means that the thermal reversion of the QC groups to the NBD residues in the polymer film occurred selectively without side reactions. Examinations of other polyesters bearing MB groups were carried out and results are summarized

Scheme 3



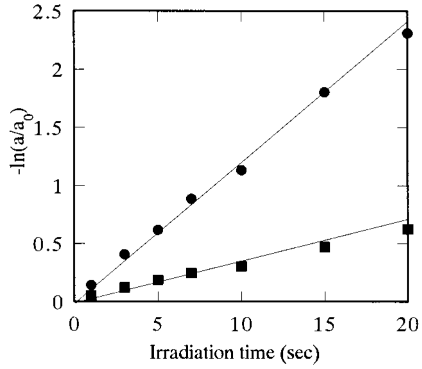


Figure 1. First-order rates of photoisomerization of D–A NBD derivatives in THF solution: (■) MAE; (●) MBE.

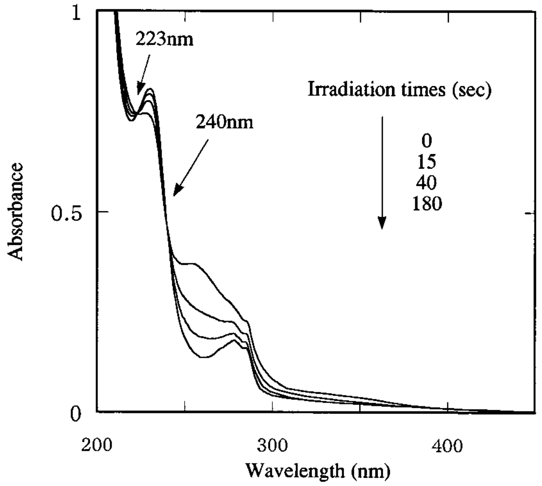


Figure 2. Change of UV spectra of **PA-1** in the film state upon irradiation with a xenon lamp.

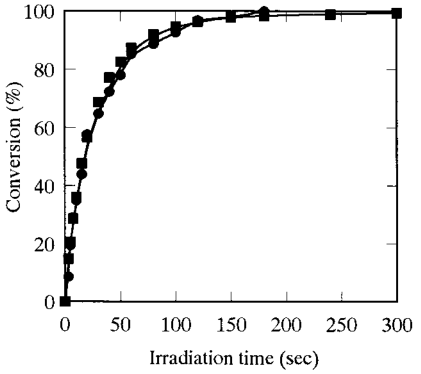


Figure 3. Rates of photoisomerization of polymers in the film state: (■) **PA-1**; (●) **PB-1**.

in Figure 6. As shown in Figure 6, the conversions of **PB-1**, **PB-2**, and **PB-3** in 1 h were 40, 32, and 36%, respectively, and first-order rate constants of the reversion were 8.68, 6.74, 7.23, and 20.2 ($k \times 10^3$/min^{-1}), respectively. These results suggest that the reversion rate of the QC groups to the NBD residues in the polymer was intimately affected by the structure of the starting bis(epoxide); namely, the reactivity of the reversion of the QC groups to the NBD residues was higher at flexible polymer chains than that at rigid polymer chains, although the reactivity of the photoisomerization of the NBD residues in these polymers was almost the same. It was reported that QCs obtained from D–A NBDs were thermally unstable as to extend the absorption band of NBDs to longer wavelength and QCs that have an alkyl group at C-1 and C-4 were more

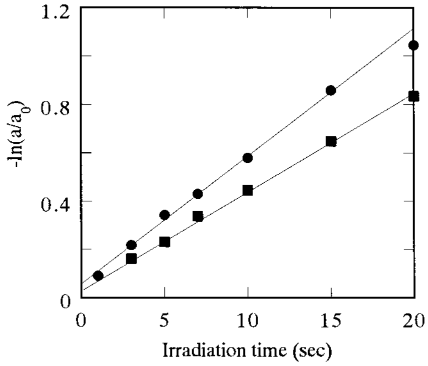


Figure 4. First-order rates of photoisomerization of polymers in the film state: (■) **PA-1**; (●) **PB-1**.

Table 4. First-Order Rate Constants of Photoisomerization of NBD Monomers and NBD Polymers[a]

compound	$k_{obsd} \times 10^{-2}$, s^{-1} in the film state	$k_{obsd} \times 10^{-2}$, s^{-1} in the THF solution[b]
MAE		3.05
MBE		11
PA-1	4.33	3.2
PA-2	4.5	3.11
PA-3	4.42	3.01
PA-4	4.4	4.06
PB-1	5.21	6.07
PB-2	5.18	6.33
PB-3	5.37	5.94
PB-4	6.09	8.15

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

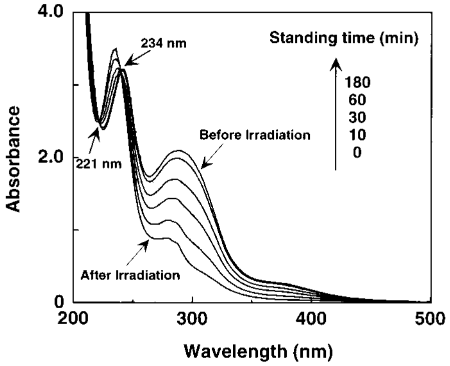


Figure 5. Change of UV spectra of irradiated **PB-4** in the film state standing in the dark room.

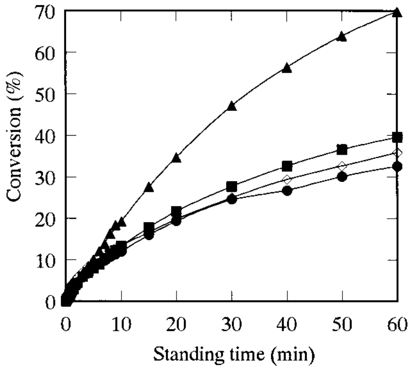


Figure 6. Rates of reversion of the produced QC groups in polymers: (■) **PB-1**; (●) **PB-2**; (◇) **PB-3**; (▲) **PB-4**.

Table 5. Thermal Properties of the D−A NBD Polyesters[a]

polym no.	T_g, °C	stored thermal energy, kJ/mol
PA-1	102	71.0
PA-2	124	68.3
PA-3	81	63.6
PA-4		57.1
PB-1	108	77.1
PB-2	124	59.5
PB-3	77	15.0
PB-4		18.4

[a] Calculated by DSC.

stable than those unsubstituted at C-1 and C-4.[6b,d] It may be due to a similar reason to these results that the QC groups contained in the **PAs** were thermally more stable than that in the **PBs**. Then, it was found that the QC groups with certain substitutents reverted to the NBD residues in the polymer without a catalyst, and the reversion rate could be controlled by the structure of the polymer chain as well as the structure of the NBDs.

Thermal Properties of the Polyesters. T_g of the polyester containing D−A NBD residues was measured on DSC at a heating rate of 10 °C/min. As summarized in Table 5, T_gs of **PA-1**, **PA-2**, **PA-3**, **PB-1**, **PB-2**, and **PB-3** were 102, 124, 81, 108, 124, and 77 °C, respectively, and T_gs of **PA-4** and **PB-4** were not determined by DSC analysis. It was found that the structure of the bis(epoxide) using the polyaddition reaction was intimately reflected in the T_g of the polyester. Furthermore, the released thermal energy from the corresponding QC groups in the irradiated polymer films was measured on DSC. As summarized in Table 5, the irradiated **PA-1**−**PA-4** bearing the corresponding QC groups released 57−71 kJ/mol of thermal energy and the irradiated **PB-1**−**PB-4** bearing the corresponding QC groups released 15−77 kJ/mol of thermal energy. In the case of the irradiated **PB-1**−**PB-4**, interestingly, two exothermic peaks were detected at about 53 and 125 °C by DSC analysis. From this result, it seems that the QC groups reverted to NBD residues through a certain intermediate; then, two changes in state, namely, QC to intermediate and that to NBD, are detected. The released thermal energy from the QC groups in the irradiated **PBs** was lower than that from **PAs**. In particular, the values obtained from **PB-3** and **PB-4** were very low, because the thermally unstable QC groups might revert to the corresponding NBD residues during the experimental process.

Examination of the Durability of the NBD Residue in the Polyester. We also examined the durability of the NBD residue in the polyester for repeated cycles of the interconversion. The repetition between the NBD residue and the QC group in the **PA-1** and **PB-1** was examined by irradiation of the polymer film with a 500-W xenon lamp, followed by heating the irradiated film on a hot plate. The durability was evaluated from the differences in the absorbance values between the NBD residue and the QC group at maximum absorption of the NBD residue in the first and *n*th cycles of reactions. As shown in Figure 7, the degradation of the NBD residues in **PA-1** and **PB-1** was 30% after 200 and 300 cycles, respectively, and that of the NBD residues in **PB-1** was ca. 50% after 500 cycles. It is apparent that **PAs** and **PBs** containing D−A NBD residues are more durable than the other NBD polymers as the introduction of a suitable substituent into the NBD skeleton suppresses the formation of byproducts caused by the polymerization of the NBD and QC moieties, since the steric effect of the substituent inhibits the interaction of these moieties. Thermal reversion of the QC groups to the NBD residues in **PA-1** and **PB-1** was carried out at 120 and 70 °C, respectively. Since the side reaction occurs readily at high temperature, **PB-1** might show better durability than **PA-1**.

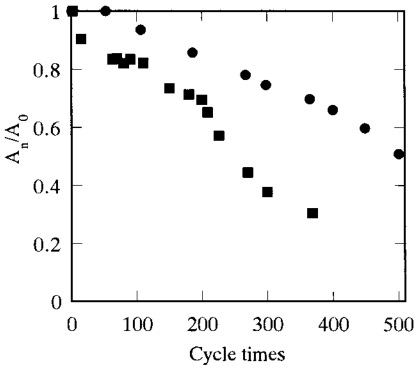


Figure 7. Durability of D−A NBD polymers; (■) **PA-1**; (●) **PB-1**.

Conclusion

From all these results, the following conclusions can be drawn. (1) Polyesters containing D−A NBD residues in the main chain were obtained by the polyaddition reaction of D−A dicarboxylic acid with bis(epoxide)s. (2) The obtained polyesters had excellent photochemical reactivity, and the photoisomerization rate of these polyesters was to same extent affected by the structure of the polymer chain. (3) QC groups with certain substitutents reverted to NBD residues in the polymer without a catalyst, and the reversion rate could be controlled by the structure of the polymer chain. (4) The NBD residues in these polyesters showed resistivity to repeated cycles of the interconversion.

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