Synthesis of Poly(ester−amide)s Containing Norbornadiene (NBD) Residues by the Polyaddition of NBD Dicarboxylic Acid Derivatives with Bis(epoxide)s and Their Photochemical Properties

Akinori Tsubata, Takeshi Uchiyama, 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: *N,N′*-Bis[(3-carboxynorbornadien-2-yl)carbonyl]methylenedianiline (BNMA) was synthesized in 87 % yield by the reaction of 2,5-norbornadiene-2,3-dicarboxylic acid anhydride with 4,4′-methylenedianiline. Other dicarboxylic acid derivatives containing norbornadiene (NBD) residues were also prepared by the reaction of 2,5-NBD-2,3-dicarboxylic acid anhydride with certain diamines. When the polyaddition of BNMA with bisphenol A diglycidyl ether (BPGE) was carried out using tetrabutylammonium bromide as a catalyst in NMP at 100 °C for 24 h, a polymer with a number average molecular weight of 18 000 was obtained in 91% yield. Polyadditions of other NBD dicarboxylic acid derivatives with BPGE were also performed under the same conditions. The reaction proceeded very smoothly to give the corresponding NBD poly(ester−amide)s in good yields. Furthermore, the photochemical reactions of the NBD poly(ester−amide)s were evaluated in the film state or in solution. The photochemical valence isomerization of NBD residues in the polymer films proceeded smoothly to form the corresponding quadricyclane (QC) groups upon irradiation with sunlight. The photochemical reversion of the resulting QC groups in the polymer films proceeded efficiently by irradiation of 272 nm light. The stored energy in the QC groups of the polymers was evaluated to be about 84 kJ/mol by DSC measurement of the irradiated polymer films.

Introduction

Energy conservation predicates that the creation of solar energy conversion and storage devices is an important area of research. Photochemical valence isomerization between norbornadiene (NBD) and quadricyclane (QC) has been of interest as a solar energy conversion and storage system,[1] because photoenergy can be stored as strain energy (about 96 kJ/mol) in a QC molecule for long term and then this energy can be released as thermal energy upon contact with suitable catalysts. However, the photochemical reaction of NBD does not ordinarily occur upon irradiation with sunlight, because NBD does not efficiently absorb photons in the visible region of sunlight. To resolve this problem, there are two different methods used. One is the addition of suitable photosensitizers such benzophenone derivatives to the NBD reaction system. The other is the introduction of suitable chromophores such as a carboxyl, carbamoyl, or aryl group into the NBD molecule. In actuality, Maruyama et al.[2] reported the occurrence of the photoisomerization reaction of the NBD derivatives having those chromophores to C=C bond upon irradiation by sunlight.

On the other hand, it is well-known that the carboxyl group is useful not only as the chromophore but also as the functional group in the synthesis of polymers. We have studied[3] the synthesis of polymers containing NBD moieties in the main chain or the side chain. In these research works, all of the synthesized polymers containing NBD residues in the main chain have been prepared using 2,5-NBD-2,3-dicarboxylic acid (NDC) as a starting material. For example, polyamides were synthesized[4] by polycondensations of NDC with diamines or diisocyanates. However, molecular weights of the obtained NBD polyamides are not high enough.

In the previous paper, we reported[5] the synthesis of soluble polyesters containing the NBD residue in the main chain with high molecular weight by the polyaddition reaction of NDC with bis(epoxide)s using quarternary onium salts as catalysts. However, photochemical reactivities of the obtained polymers are low, because these polymers do not have the appropriate chromophore for the photochemical reaction. This article reports on the synthesis of high photoresponsive poly(ester−amide)s containing NBD residue in the main chain by the polyaddition of NBD dicarboxylic acid derivatives, which were prepared by the addition reaction of NDC anhydride with aromatic diamines, with bis(epoxide)s and the photochemical reaction of the resulting polymers.

Experimental Section

Materials. The solvents and triethylamine (TEA) were dried using P_2O_5, CaH_2, or Na metal wire and purified by distillation. Tetrabutylammonium bromide (TBAB) was recrystallized twice from the dried ethyl acetate. Other quarternary onium salts such as tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), tetrabutylphosphonium bromide (TBPB), and tetraphenylphosphonium bromide (TPPB), 18-crown-6 ether (18-C-6), potassium bromide (KBr), potassium phenoxide (KOPh), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), dicyclohexylcarbodiimide (DCC), 4,4′-methylenedianiline (MDA), 4,4′-oxydianiline (ODA), and *o*-tolidine were used without further purification. Commercial bisphenol A diglycidyl ether (BPGE) and 3,3′,5,5′-tetramethyl-4,4′-biphenyl diglycidyl ether (MBGE) were recrystallized from the mixed solvent methanol (4)/ethyl methyl ketone (1) and from isobutyl methyl ketone, respectively. Ethylene glycol diglycidyl ether (EGGE) was purified by distillation. 2,5-NBD-2,3-dicarboxylic acid anhydride (NDCA) was prepared in 53% yield by the dehydration reaction of 2,5-NBD-2,3-dicarboxylic acid, which was synthesized by the Diels−Alder reaction of acety-

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* To whom all correspondence should be addressed.

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Table 1. Results of the Synthesis of NBD Dicarboxylic Acid Derivatives

monomer	diamine	yield, %	mp, °C	$\lambda_{\max}$, nm	elem. anal.	% C	% H	% N
BNMA	MDA	87	141−142	239, 333	calcd	71.24	5.02	5.36
					found	70.93	5.08	5.46
BNOA	ODA	87	142−143	244, 340	calcd	68.69	4.62	5.34
					found	68.42	4.94	5.60
BNOT	*o*-tolidine	64	>300	268, 360	calcd	71.62	5.27	5.22
					found	71.70	5.70	5.48

lenedicarboxylic acid wtih freshly distilled cyclopentadiene, using DCC according to the reported method.[6]

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 a Jeol Model JNMFX-200 (200 MHz) instrument in DMSO-d_6 with tetramethylsilane (TMS) 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 using narrow molecular weight polystyrenes as standards). The glass transition temperature (T_g) and the amount of stored energy in the QC groups in the polymer were measured on a Perkin-Elmer differential scanning calorimeter (DSC) Model DSC Station 4 at heating rates of 10 and 20 °C/min, respectively.

Typical Procedure for the Synthesis of NBD Dicarboxylic Acid Derivatives. A typical example of the reaction is as follows.

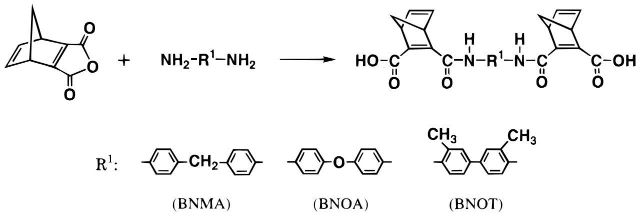
Synthesis of *N*,*N*′-Bis[(3-carboxynorbornadien-2-yl)carbonyl]methylenedianiline (BNMA). A dried acetone (45 mL) solution of NDCA (1.83 g, 11.3 mmol) was added dropwise to a dried acetone (23 mL) solution of MDA (1.12 g, 5.6 mmol) at room temperature for 1 h, and then the solution was stirred for 3 h at room temperature. The solvent was evaporated to obtain a yellow solid product. The crude product was recrystallized from ethyl acetate. The yield of BNMA was 2.54 g (87%). IR (KBr, cm^{-1}): 3600−2200 ($\nu_{\mathrm{O-H}}$), 3304 ($\nu_{\mathrm{N-H}}$), 1694 ($\nu_{\mathrm{C=O}}$). ^{1}H NMR (DMSO-d_6, TMS): δ 1.9−2.4 (m, 4.0H, CH$_2$ in NBD), 3.9 (s, 2.0H, CH$_2$), 4.0−4.3 (m, 4.0H, CH in NBD), 6.9−7.1 (m, 4.0H, CH=CH in NBD), 7.2 (d, 4.0H, aromatic protons), 7.6 (d, 4H, aromatic protons), 10.9 (broad s, 2.0H, NH), 13.7 (broad s, 2.0H, OH). Anal. Calcd for $C_{31}H_{26}O_6N_2$: C, 71.24; H, 5.02; N, 5.36. Found: C, 70.93; H, 5.08; N, 5.46.

Typical Procedure for the Polyaddition of NBD Dicarboxylic Acid Derivatives with Bis(epoxide)s. A typical example of the polyaddition of NBD derivative with bis(epoxide) is as follows.

Synthesis of Poly(ester−amide) (P-1) Containing NBD Residue from BNMA with BPGE. BNMA (0.31 g, 0.60 mmol), BPGE (0.20 g, 0.60 mmol), and TBAB (0.01 g, 0.03 mmol) were dissolved in 0.30 mL of *N*-methyl-2-pyrrolidone (NMP) in an ample tube, and it was sealed after the air inside was displaced with nitrogen. The reaction was carried out at 100 °C for 24 h. The reaction mixture was poured into methanol (200 mL), reprecipitated twice from tetrahydrofuran (THF) into methanol, and dried *in vacuo* at 60 °C. The yield of **P-1** was 0.47 g (91%). The number average molecular weight (M_n) of the polymer determined from GPC was 18 000. IR (film, cm^{-1}): 3402 ($\nu_{\mathrm{O-H}}$), 1710 ($\nu_{\mathrm{C=O}}$ of ester), 1684 ($\nu_{\mathrm{C=O}}$ of amide), 1237 ($\nu_{\mathrm{C-O-C}}$ of ester). ^{1}H NMR (DMSO-d_6, TMS): δ 1.5 (s, 6.0H, CH$_3$), 1.9−2.3 (m, 4.0H, CH$_2$ in NBD), 3.5−4.4 (m, 15.8H, CH of β-cleavage of epoxy ring and NBD, CH$_2$), 4.9−5.5 (m, 2.2H, OH, CH of α-cleavage of epoxy ring), 6.6−7.3 (m, 16H, CH=CH in NBD), 7.4−7.8 (m, 4.0H, aromatic protons), 10.4 (broad s, 2.0H, NH).

Typical Procedure for the Photochemical Valence Isomerization of NBD Residue in Polymer Film. A solution of a NBD polymer in THF was applied on the inside wall of a quartz cell and dried *in vacuo* at room temperature for 2 h. The polymer film 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 (2.0−2.1 mW/cm^2 (310 nm)) 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. The monochromatic light was isolated through a monochromater (Jasco Model, CT-10) with a 500-W high-pressure mercury lamp (Ushio Electric Co., USH-500D).

Scheme 1



Typical Procedure for the Photochemical Reaction of NBD Polymer in Solution. A solution (3 mL) of a NBD polymer in THF (1.0×10^{-4} mol/L as NBD residues) was charged into a quartz cell, and then the solution was irradiated by the same xenon lamp as the above with a thermal-ray cut filter, 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 Containing NBD Residue. The monochromatic light of 366 nm was isolated from a 500-W high-pressure mercury lamp using 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,[7] which used a potassium tris(oxalato)ferrate(III) aqueous solution as photon counter. Dichloromethane solution of **P-1** (1.0×10^{-4} mol/L as NBD residues) was photoirradiated for 5 min. The chemical yields of the polymer containing NBD residues was calculated from the decrease in the NBD absorptions at a specified wavelength (335 nm) using the difference in molar absorption coefficients ($\Delta\epsilon$) between NBD derivatives and QC derivatives at the wavelength.

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.* The film on the plate was irradiated for enough time to change from the NBD residue to the QC group by irradiation with a 500-W xenon lamp through a heat ray cut filter in air. The irradiated polymer film (3 mg) was packed in an aluminum sample tube for DSC analysis. The sample was heated at 20 °C/min under nitrogen.

Results and Discussion

Synthesis of Poly(ester−amide)s Containing Norbornadiene Residues by the Polyaddition of NBD Dicarboxylic Acid Derivatives with Bis(epoxide)s. NBD dicarboxylic acid derivatives were synthesized by the addition reaction of NDCA with certain diamines. As summarized in Table 1, the reaction of NDCA with MDA, ODA, and *o*-tolidine gave the corresponding BNMA, *N*,*N*′-bis[(3-carboxynorbornadien-2-yl)carbonyl]oxydianiline (BNOA), and *N*,*N*′-bis[(3-carboxynorbornadien-2-yl)carbonyl]-*o*-tolidine (BNOT) in 87, 87, and 64% yields, respectively (Scheme 1). The structure of resulting NBD monomers was confirmed by elemental

Table 2. Effect of Catalyst on the Polymerization of BNMA with BPGE[a]

catalyst	temp, °C	yield,[b] %	$M_n{}^c \times 10^{-4}$	$M_w/M_n{}^c$
none	100	84	1.87	1.64
TBAC	80	84	1.95	1.47
TBAC	100	gel	−	−
TBAB	100	91	1.82	1.48
TBAI	100	85	1.77	1.41
TBPB	100	92	1.55	1.29
TPPB	100	94	1.66	1.34
18-C-6/KBr	80	81	1.91	1.69
18-C-6/KBr	100	gel	−	−
18-C-6/KOPh	80	81	1.99	1.53
DBU	100	32	1.20	1.60
TEA	100	68	0.94	1.19

[a] The reaction was carried out with BNMA (0.6 mmol) and BPGE (0.6 mmol) using catalyst (5 mol %) in NMP (0.3 mL) for 24 h. [b] Insoluble parts in methanol. [c] Estimated by GPC based on polystyrene standards.

analysis (see Table 1), IR and ^{1}H NMR spectra (see Table 3).

The polyaddition reaction of thus obtained BNMA with bis(epoxide) BPGE was performed using various catalysts or without any catalysts (Table 2). When the reaction was carried out without a catalyst, the yield and the M_n of the resulting polymers were 84% and 19 000, respectively. The structure of the polymer (**P-1**) was confirmed by IR and ^{1}H NMR spectra (Table 3). The IR spectrum of the polymer film showed absorption peaks at 3402 (O−H stretching), 1710 (C═O stretching, ester), and 1684 cm^{-1} (C═O stretching, amide). The ^{1}H NMR spectrum of this polymer showed signals of the CH_3 protons at 1.5 ppm, CH_2 protons of the NBD residue at 1.9−2.3 ppm, CH protons of the β-cleavage of epoxy ring and NBD residue, and CH_2 protons in the main chain at 3.5−4.4 ppm, OH protons and CH protons of the α-cleavage of the epoxy ring at 4.9−5.5 ppm, CH═CH protons of the NBD residue and aromatic protons at 6.6−7.3 ppm, aromatic protons at 7.4−7.8 ppm, and NH protons at 10.4 ppm. The ratio of cleavage of the epoxy ring in the polyaddition was estimated by ^{1}H NMR, and it was found that the selectivity of β-cleavage was about 90%.

As summarized in Table 2, the polyaddition reaction of BNMA with BPGE was enhanced by adding quaternary onium salts or crown ether complexes as catalysts, and the polymers with relatively high molecular weight were obtained at 80−100 °C. In this reaction system, it seems that TBAC, 18-C-6/KBr, and 18-C-6/KOPh have high catalytic activity, although gel products were produced when the reaction was carried out at 100 °C. On the other hand, when the polyaddition reaction was carried out using DBU or TEA as basic catalysts, the polymers with relatively low molecular weight were obtained in 32 and 68% yields, respectively. It seems that the imidation of BNMA occurred as a side reaction during the polyaddition of BNMA with BPGE when organic bases were used as catalysts.

The polyaddition reaction of NBD dicarboxylic acid derivatives with certain bis(epoxy) compounds was carried out using TBAB as a catalyst in NMP at 100 °C for 24 h to give the corresponding poly(ester−amide)s (Scheme 2), and the results are summmarized in Table 4. The yields of the polymers (**P-1**, **P-2**, and **P-3**) prepared by the polyaddition reaction of various NBD derivatives such as BNMA, BNOA, and BNOT with BPGE were 91, 95, and 85%, respectively. The M_ns of these polymers were 18 000, 18 000, and 16 000, respectively. The ^{1}H NMR and IR spectra of these polymers also showed signals and absorption peaks of the corresponding structure (Table 3). The polyaddition reaction of BNMA with other bis(epoxy) compounds such as MBGE and EGGE was performed under the same conditions, and the corresponding poly(ester−amide)s **P-4** and **P-5** with M_ns of 4000 and 28 000 were obtained, respectively.

These results suggest that high molecular weight poly(ester−amide)s containing NBD residues in the main chain excepting **P-4** were successfully synthesized

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

compd.	IR data, cm^{-1}	^{1}H NMR data, ppm
BNMA	3600−2200 (OH), 3304 (NH), 1694 (C═O)	1.92−2.4 (m, 4.0H, CH_2 in NBD), 3.9 (s, 2.0H, CH_2), 4.0−4.3 (m, 4.0H, CH in NBD), 6.9−7.1 (m, 4.0H, CH═CH in NBD), 7.2 (d, 4H, aromatic protons), 7.6 (d, 4.0H, aromatic protons), 10.9 (broad s, 2.0H, NH), 13.7 (broad s, 2.0H, OH)
BNOA	3600−2000 (OH), 3290 (NH), 1694 (C═O)	2.0−2.3 (m, 4.0H, CH_2 in NBD), 3.9−4.2 (m, 4.0H, CH in NBD), 6.9−7.2 (m, 8H, CH═CH in NBD, aromatic protons), 7.5−7.8 (m, 4.0H, aromatic protons), 11.0 (broad s, 2.0H, NH), 13.9 (broad s, 2.0H, OH)
BNOT	3300−2200 (OH), 3200 (NH), 1694 (C═O)	1.9−2.3 (m, 4.0H, CH_2 in NBD), 4.1−4.4 (m, 4.0H, CH in NBD), 6.9−7.1 (m, 4.0H, CH═CH in NBD), 7.6−8.0 (m, 6H, aromatic protons), 11.5 (broad s, 2.0H, NH), 14.5 (broad s, 2.0H, OH)
P-1	3402 (OH), 3306 (NH), 1710 (C═O, ester), 1684 (C═O, amide)	1.5 (s, 6.0H, CH_3), 1.9−2.3 (m, 4.0H, CH_2 in NBD), 3.5−4.4 (m, 15.8H, CH of β-cleavage of epoxy ring and NBD, CH_2), 4.9−5.5 (broad, 2.2H, OH, CH of α-cleavage of epoxy ring), 6.6−7.3 (m, 16H, CH═CH in NBD, aromatic protons), 7.4−7.8 m, 4.0H, aromatic protons), 10.4 (broad s, 2.0H, NH)
P-2	3410 (OH), 3306 (NH), 1710 (C═O, ester), 1683 (C═O, amide)	1.5 (s, 6.0H, CH_3), 1.8−2.4 (m, 4.0H, CH_2 in NBD), 3.7−4.4 (m, 13.8H, CH of β-cleavage of epoxy ring and NBD, CH_2), 4.8−5.5 (broad, 2.2H, OH, CH of α-cleavage of epoxy ring), 6.6−7.3 (m, 16H, CH═CH in NBD, aromatic protons), 7.5−7.9 (m, 4.0H, aromatic protons), 10.5 (broad s, 2.0H, NH)
P-3	3416 (OH), 3264 (NH), 1710 (C═O, ester), 1688 (C═O, amide)	1.5 (s, 6.0H, CH_3), 1.9−2.8 (m, 10.0H, CH_2 in NBD, CH_3), 3.8−4.5 (m, 13.7H, CH of β-cleavage of epoxy ring and NBD, CH_2), 4.9−5.6 (broad, 2.3H, OH, CH of α-cleavage of epoxy ring), 6.6−8.1 (m, 16H, CH═CH in NBD, aromatic protons), 10.3 (broad s, 2.0H, NH)
P-4	3408 (OH), 3250 (NH), 1713 (C═O, ester), 1685 (C═O, amide)	1.7−2.5 (m, 16.0H, CH_2 in NBD, CH_3), 3.4−4.7 (m, 15.7H, CH of β-cleavage of epoxy ring and NBD, CH_2), 4.9−5.5 (broad, 2.3H, OH, CH of α-cleavage of epoxy ring), 6.8−7.8 (m, 16H, CH═CH in NBD, aromatic protons), 10.4 (broad s, 2.0H, NH)
P-5	3422 (OH), 3280 (NH), 1713 (C═O, ester), 1684 (C═O, amide)	1.8−2.4 (m, 4.0H, CH_2 in NBD), 3.0−4.4 (m, 19.8H, CH of β-cleavage of epoxy ring and NBD, CH_2), 4.7−5.4 (broad, 2.2H, OH, CH of α-cleavage of epoxy ring), 6.8−7.8 (m, 12H, CH═CH in NBD, aromatic protons), 10.4 (broad s, 2.0H, NH)

Scheme 2

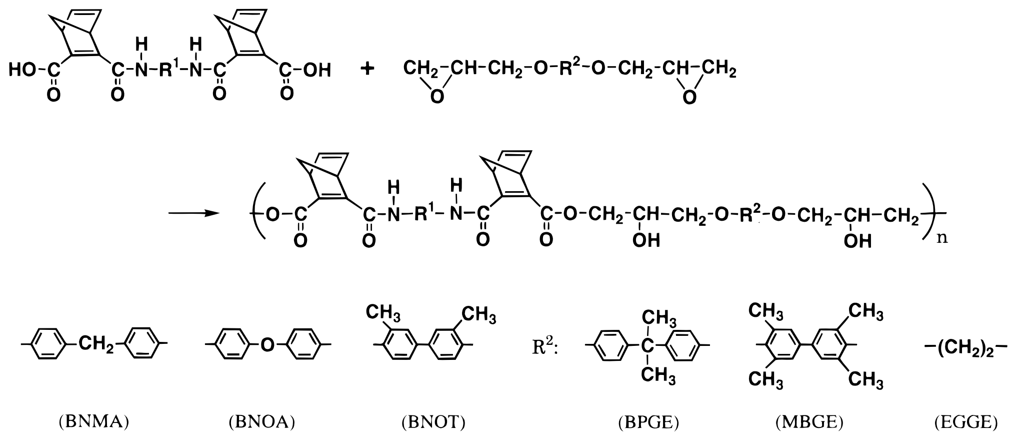


Table 4. Polyadditions of NBD Dicarboxylic Acid Derivatives with Bis(epoxide)s[a]

polym no.	NBD deriv	epoxide	yield,[b] %	M_n[c] × 10^{-4}	M_w/M_n[c]	T_g, °C	λ_{max}, nm	λ_{edge}, nm
P-1	BNMA	BPGE	91	1.82	1.48	132	233, 335	460
P-2	BNOA	BPGE	95	1.82	1.41	132	242, 344	475
P-3	BNOT	BPGE	85	1.63	1.55	127	273, 366	500
P-4	BNMA	MBGE	73	4.02	5.82	159	245, 335	460
P-5	BNMA	EGGE	65	2.81	2.09	105	240, 330	460

[a] The reaction was carried out with the NBD derivative (0.6 mmol) and BPGE (0.6 mmol) using TBAB (5 mol %) in NMP (0.3 mL) at 100 °C for 24 h. [b] Insoluble parts in methanol. [c] Estimated by GPC based on polystyrene standards.

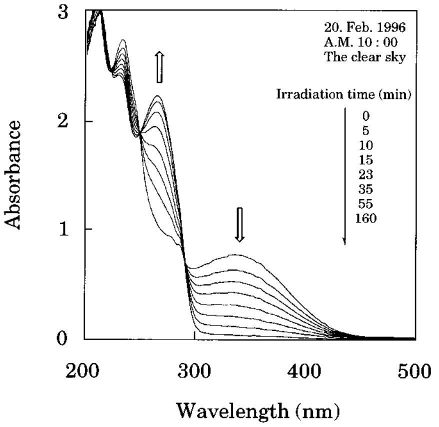


Figure 1. Change of UV spectra of **P-1** in the film state upon irradiation by winter sunlight.

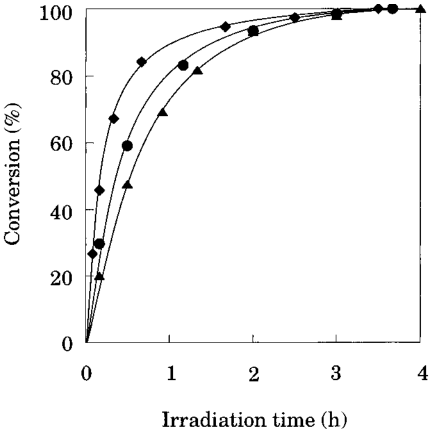


Figure 2. Conversions of the photoisomerization of polymers in the film state: (●) **P-1**; (▲) **P-2**; (◆) **P-3**.

by the addition reaction of NBD dicarboxylic acid derivatives with certain bis(epoxy) compounds.

Photochemical Valence Isomerization of NBD Polymers in the Film State. The photochemical valence isomerization of the NBD residues in polymer films was carried out on a quartz cell by the irradiation of sunlight. As shown in Figure 1, an absorption at 335 nm due to the NBD residue in **P-1** decreased. It was also found that the NBD residue in **P-1** isomerized quantitatively to the QC group after 90 min by irradiation of winter sunlight on February 20, 1996. In addition, three isosbestic points at 233, 249, and 290 nm were observed in the UV spectrum. This result means that the photochemical valence isomerization of NBD residue to the corresponding QC group in the polymer film occurred selectively without side reactions upon solar irradiation.

The change of UV spectra of polymers **P-1**−**P-3** were examined in the film state under air upon photoirradiation with a xenon lamp, and the conversions from the NBD residues to the QC groups in the polymers were calculated from the decreases of optical densities of the polymers at 335, 344, and 366 nm, respectively. As shown in Figure 2, the photoisomerization reaction of these polymers containing NBD residues proceeded completely for about 4 h. It was also proved that the observed rates of photochemical reaction of the NBD residues in the polymers obeyed first-order kinetics (Figure 3). This result showed that **P-3** had a higher photochemical reactivity than **P-1** and **P-2** in the film state.

The UV spectrum of the photoirradiated **P-1** containing the QC group in the main chain reverted to that of the corresponding NBD residue with three isosbestic points at 233, 249, and 290 nm, when the QC group in the polmer film was irradiated with 272 nm light through a monochromater using a 500-W high-pressure mercury lamp (Figure 4). This result means that the photochemical reversion of QC group to the corresponding NBD residue in the polymer film occurred selectively.

As shown in Figure 5, the rate of reversion of the QC group to the NBD residue in the polymer film was affected by the wavelength of the irradiating light, and the observed rate of the reversion upon irradiation with 272 nm light was faster than rates upon irradiation with

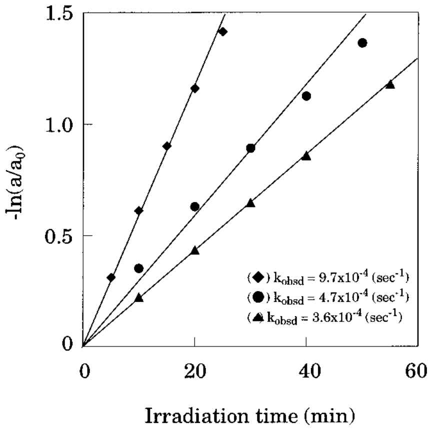


Figure 3. Rates of photochemical valence isomerization of NBD residues in polymers in the film state: (●) **P-1**; (▲) **P-2**; (◆) **P-3**.

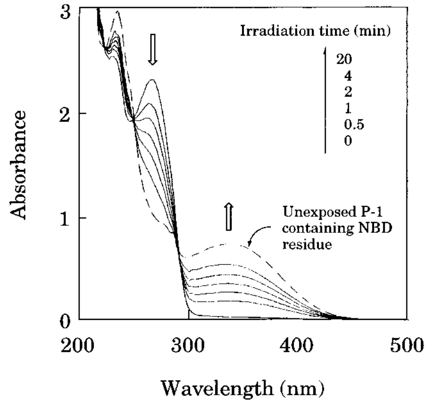


Figure 4. Change of UV spectra of QC group in **P-1** under irradiation with 272 nm light in the film state.

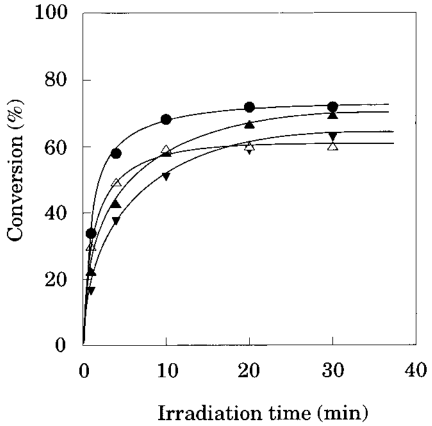


Figure 5. Reversion of the QC group in **P-1** film: (▼) 264 nm; (▲) 268 nm; (●) 272 nm; (△) 276 nm.

264, 268, or 276 nm light. However, a detailed correlation between the conversion of the QC group to the NBD residue in the polymer film and the exposure energy could not be confirmed, because the equipment to measure the exposure energy at each wavelength was not available. Futhermore, it was found that degrees of the conversion of the QC groups were saturated at 60−70 mol % upon irradiation with 264, 268, 272, and 276 nm light. It seems that photochemical reversion of QC group in the polymer film attained a photostationary state under each irradiation condition.

The repetition between the NBD residue and QC group in the **P-1** film was tested by the irradiation of 366 nm for 30 min followed by the irradiation of 272 nm light for 30 min (Figure 6). This result showed that the polymer decomposed gradually with photoirradiation, because the conversions of NBD and QC groups were decreased step by step in the cycle.

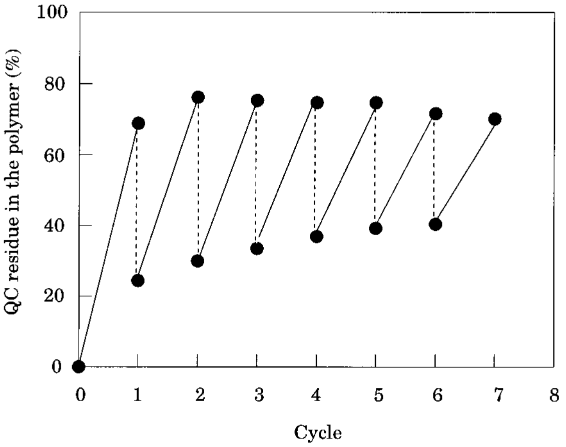
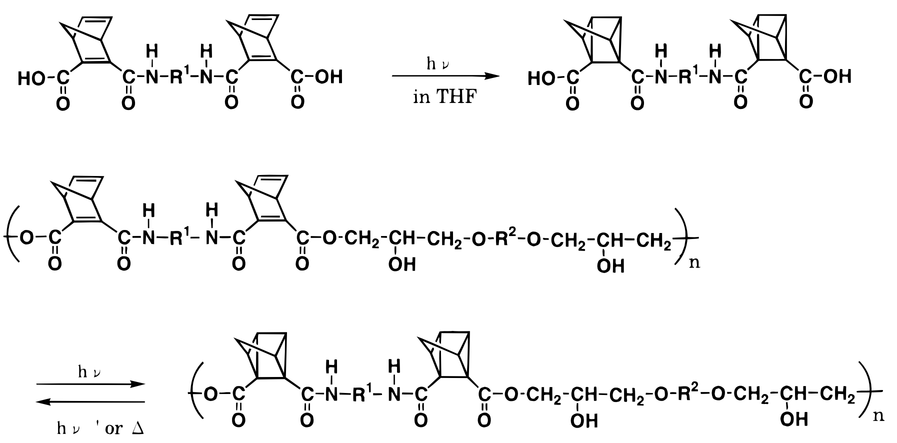


Figure 6. Cycle reaction between NBD residue and QC group in **P-1** film: (—) irradiated with 366 nm light for 30 min; (---) irradiated with 272 nm light for 30 min.

Photochemical Valence Isomerization of the NBD Monomers and Polymers in the Solutions. The photochemical valence isomerization of the NBD dicarboxylic acid derivatives (BNMA, BNOA, and BNOT) and polymers (**P-1**−**P-3**) in THF solutions was carried out under the similar conditions as did in the film state (Scheme 3), and the change of UV spectra of BNMA and **P-1** was showed in Figure 7. The NBD residues of BNMA and **P-1** isomerized smoothly to the corresponding QC groups with isosbestic points at 247 and 286 nm in BNMA or 249 and 287 nm in **P-1** by photoirradiation. Furthermore, the rate of the photochemical reaction obeyed first-order kinetics similar to the photochemical reaction of the polymer in the film state. As shown in Table 5, rate constants of **P-1**, **P-2**, and **P-3** were 1.8×10^{-4}, 1.5×10^{-4}, and 2.5×10^{-4}, respectively. Rate constants of the corresponding low molecular weight NBD compounds (monomers) such as BNMA, BNOA, and BNOT were 2.7×10^{-4}, 2.0×10^{-4}, and 3.0×10^{-4}, respectively. These results mean that the photochemical reactivities of polymers were slightly lower than those of the corresponding low molecular weight NBD compounds due to the lower rates of conformation change of the polymer backbone in the solution, although the differences in structures, such as NBD carboxylic acid in monomers or polymers, should be considered. However, we could not compare directly between the rates of photochemical reaction of the polymers in the film state and in THF solution from these data, because irradiation conditions of the polymers in the film state and in solution are different.

The quantum yield of **P-1** of the isomerization from NBD residue to QC group in dichloromethane solution (1×10^{-4} mol/L) was evaluated with a chemical actinometer. The quantum yield of the isomerization at 366 nm was 0.01. This quantum yield is similar to the reported[8] ones for NBD derivatives, which have a *N*-phenylcarbamoyl group, although there is a difference in the conditions such as solvent, monomer, or polymer. However, it is relatively low compared to the reported[9] of quantum yields of NBD polymers containing a pendant 3-phenyl-2,5-NBD-2-carboxylate residue. It seems that the relatively low quantum yield may be due to little absorption at 366 nm or to some influence of the chromophore.

Scheme 3



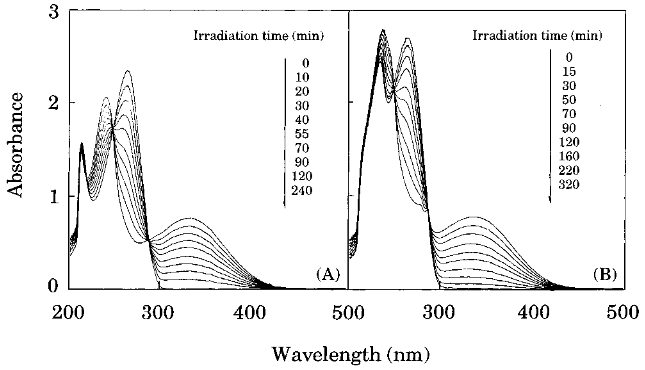


Figure 7. Change of UV spectra of BNMA (A) and **P-1** (B) in THF solution (1×10^{-4} mol/L as NBD residue) upon irradiation with a xenon lamp.

Table 5. First-Order Rate Constant of Photochemical Valence Isomerization of Monomers and Polymers in THF Solution[a]

compound	$k_{obsd} \times 10^4$, s^{-1}	compound	$k_{obsd} \times 10^4$, s^{-1}
BNMA	2.7	polymer 2	1.5
polymer 1	1.8	BNOT	3.0
BNOA	2.0	polymer 3	2.5

[a] The reaction was carried out in THF solution (1×10^{-4} mol/L as NBD residue) upon irradiation with a 500 W Xe lamp.

Measurement of Stored Thermal Energy in the QC Polymers. P-1 film was irradiated for sufficient time with a xenon lamp, and then it was packed in an aluminum sample tube for DSC analysis. The sample was heated at 20 °C/min under nitrogen. The stored thermal energy of this polymer was about 84 kJ/mol. This value is higher than the reported[10] one (45−67 kJ/mol) for polymers containing pendant 3-(*N*-phenylcarbamoyl)-2,5-NBD-2-carboxylate moieties, which may have imidization as a side reaction in the reversion process, but lower than that (91−93 kJ/mol) of polymers[3] containing pendant 3-phenyl-2,5-NBD-2-carboxylate moieties. If the similar side reaction proceeded as did the polymer with pendant 3-(*N*-phenylcarbamoyl)-2,5-NBD-2-carboxylate moieties reverting from QC groups to NBD residues of **P-1**, the degree of side reaction of this polymers would be lower compared to that for the polymer bearing 3-(*N*-phenylcarbamoyl)-2,5-NBD-2-carboxylate moieties in the side chain. It may be due to the requirement to change the conformation of polymer main chain.

Conclusion

From all these results, the following conclusions can be obtained. (1) The polyaddition reaction of NBD dicarboxylic acid derivatives with bis(epoxide)s was carried out, and the corresponding soluble and high molecular weight poly(ester−amide)s containing NBD residues in the main chain were obtained in good yields. (2) The photochemical valence isomerization of the obtained polymers proceeded very smoothly in the film state or in THF solution. Furthermore, the photochemical reversion of the QC group to the NBD residue of the photoirradiated polymer **P-1** also proceeded in the film state upon irradiation of monochromatic light. (3) Rates of the photoisomerization of the NBD residues in the polymers in THF solution are almost the same as those of the NBD residue in the monomers. (4) The value of the stored thermal energy of the QC groups in **P-1** was about 84 kJ/mol by DSC measurement of the photoirradiated polymer film.

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