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# Synthesis and Solar Energy Storage Property of Polymers Containing Norbornadiene Moieties

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ABSTRACT: Polymers having a pendant 3-[(*p*-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety and their model compounds were prepared from the reaction of poly[4-(chloromethyl)styrene] and benzyl chloride with corresponding potassium salts using phase-transfer catalyst in dimethylformamide, respectively. The photochemical valence isomerization of pendant norbornadiene (NBD) to the quadricyclane (QC) moiety proceeded smoothly in the film state or polymer solution upon irradiation by sunlight or high-pressure mercury lamp. The rate of isomerization was strongly affected by the substituent of [(*p*-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety in the polymers. Especially, the polymer containing a pendant 3-[(*p*-acetylphenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety showed higher photochemical reactivity than the other NBD polymers. Furthermore, it was found that the rate of photochemical reaction in the polymer solution was much higher than that of the corresponding model compounds. On the other hand, the resulting QC groups in the polymer film scarcely reverted to the original NBD without any catalyst if it were kept in dark at room temperature for a long time and showed excellent storage stability. However, the reversion proceeded smoothly when (5,10,15,20-tetraphenyl-21*H*,23*H*-porphine)cobalt(II) (Co-TPP) was added to the polymer solution as a catalyst. The reaction was proportional to the product of both concentrations of QC group and Co-TPP, and did not appreciably depended on the para substituent of 3-[(*p*-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety in the polymers. Furthermore, it was found that the storage energy for the QC moiety derived from the para substituent of 3-(phenylcarbamoyl)-2,5-norbornadiene-2-carboxylate moiety was about 60 kJ/mol by DSC measurement of the irradiated polymers.

## Introduction

Valence isomerization between norbornadiene (NBD) and quadricyclane (QC) has been noted for solar energy storage and the conversion of solar energy into thermal energy,[1] because this reaction can convert solar energy into 97 kJ/mol of thermal energy through the strained molecules of QC. However, this system has a problem for practical use. NBD can not directly use solar light, because it has no absorption over 300 nm. There are two methods to solve this problem: (1) use of a photosensitizer such as benzophenone or acetophenone derivatives, or (2) the introduction of a chromophore into the NBD skeleton. Although low molecular photosensitizers were usually used in this system, Hautala et al.[1,2] have proposed conventional photosensitized valence isomerization from NBD to QC using insoluble polymer supported and silica gel supported 4-(*N*,*N*-dimethylamino)benzophenone. Furthermore, Neckers et al. tried to synthesize highly photostable polymeric photosensitizers containing a perfluorinated main chain[3] or a 4,4′-divinylbenzophenone unit as photosensitizer monomer and cross-linking reagent.[4] Gleria et al.[5] has found that poly[bis(4-benzoylphenoxy)phosphazene] showed high photostability when it was dispersed in dichloromethane. However, these polymeric photosensitizers as well as low molecular photosensitizers have not shown enough photostability for long time use so far. On the other hand, many NBD derivatives with some chromophores, such as carbonyl derivatives and aryl groups,[6–8] or with donor–acceptor chromophores[9–12] have been reported. The photoisomerization of these NBD derivatives shows a high quantum yield of photoisomerization and can use sunlight with a longer wavelength than that of NBD.

Recently, we have investigated the synthesis of polymers with NBD derivatives and their new conventional photochemical valence isomerization system which was carried out in the film state.[13,14] It was found that NBD polymers were easily prepared from the reaction of poly[4-(chloromethyl)styrene] (PCMS) with potassium salt of carboxylic acid derivatives of NBD using phase-transfer catalyst (PTC), and the valence isomerization of the polymer (P-3) with a pendant 3-phenyl-2,5-norbornadiene-2-carboxylate moiety containing phenyl and carbonyl groups as chromophores proceeded smoothly in the film state by UV irradiation. However, we consider that this polymer does not show satisfactory high photochemical reactivity, since this polymer has no absorption over 370 nm. Maruyama et al.[8] have reported that 3-[(*p*-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylic acids have absorption at longer wavelengths than 3-phenyl-2,5-norbornadiene-2-carboxylic acids and can convert solar energy into thermal energy effectively.

This article reports on the synthesis and the solar energy storage property of polymers (P-1a-f) having a pendant 3-[(*p*-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety. Furthermore, the photochemical valence isomerization and catalytic reversion of the polymers were investigated kinetically in the solution in order to compare it with those of the corresponding low molecular model compounds.

## Experimental Section

**Materials.** The solvents were purified in the usual way prior to use. PCMS (reduced viscosity 0.13, measured at 0.5 g/dL in DMF at 30 °C) was prepared in 66% yield by radical polymerization of 4-(chloromethyl)styrene using azobisisobutyronitrile

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in benzene. Commercial benzyl chloride, acetylenedicarboxylic acid, para-substituted anilines, dicyclohexylcarbodiimide (DCC), and (5,10,15,20-tetraphenyl-21*H*,23*H*-porphine)cobalt (II) (Co-TPP) were used without further purification. Tetrabutylammonium bromide (TBAB) was recrystallized twice from THF. The NBD derivatives 3-phenyl-2,5-norbornadiene-2-carboxylic acid and 2,5-norbornadiene-2,3-dicarboxylic acid were prepared by Diels–Alder reaction of the corresponding acetylene derivatives with freshly distilled cyclopentadiene according to reported methods.[13,14]

**Apparatus.** The $^1H$ NMR spectra were recorded on JEOL models JNM FX-200 (200 MHz) and JNM SP-100 (100 MHz) spectrometer. Infrared (IR) spectra were obtained on a JASCO model A-202 spectrophotometer. UV spectra were measured on a Shimadzu model UV-240 spectrophotometer.

**Typical Procedure for Synthesis of 3-[(*p*-Substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylic Acid.** Typical syntheses are as follows: To the solution of 2,5-norbornadiene-2,3-dicarboxylic acid (36.03 g, 0.2 mol) and *p*-acetylaniline (27.03 g, 0.2 mmol) in 700 mL of acetone was added dropwise a solution of DCC (41.27 g, 0.2 mol) in 200 mL at 0–5 °C. The reaction mixture was stirred for overnight at room temperature. White precipitates of dicyclohexylurea were filtered, and then the filtration was concentrated in vacuo. Crude products 36.30 g (61.0%) were recrystallized from dichloromethane/*n*-hexane. Mp.: 168–9 °C. IR (KBr): 3450 (N—H), 1700 (C═O of carboxylic acid), 1680 (C═O of ketone), 1610 (amide I), 1590 (C═C) cm$^{-1}$. $^1H$ NMR (DMSO-$d_6$): $\delta$ 2.2 (q, 2 H, —CH$_2$—), 2.4 (s, 3 H, CH$_3$), 4.0 (d, 2 H, —CH—), 6.8 (s, 2 H, CH═CH), 7.4–7.8 (m, 4 H, aromatic protons), 10.9 (s, 2 H, O—H and N—H). Anal. Calcd for $C_{22}H_{19}NO_3$: C, 68.66; H, 5.08; N, 4.73. Found: C, 68.81; H, 5.04; N, 4.88.

**Typical Procedure for Substitution Reaction of PCMS with Potassium Salt of NBD Derivatives Using PTC.** Typical examples of the reaction are as follows: A mixture of PCMS (1.22 g, 8 mmol) and potassium salt of 3-(phenylcarbamoyl)-2,5-norbornadiene-2-carboxylic acid (3.52 g, 12 mmol) was stirred at 50 °C for 96 h with TBAB (0.16 g, 0.5 mmol) used as a phase-transfer catalyst in 18 mL of DMF, and then the reaction mixture was poured into water. The polymer was filtered, washed thrice each with water and acetone, and dried under vacuum at 50 °C. The yield of polymer was 2.02 g. The degree of substitution of the polymer was 97.0 mol %, calculated from elemental analysis of chlorine (2.93 mg/g). The reduced viscosity was 0.16 dL/g (measured at 0.5 g/dL in DMF at 30 °C). IR (film): 1690 and 1670 (C═O), 1620 (C═C), 1260 (C—O—C) cm$^{-1}$. $^1H$ NMR (CDCl$_3$): $\delta$ 0.8–2.3 (—CH$_2$— and main chain protons), 4.1 and 4.4 (—CH—), 5.2 (CH$_2$OCO), 6.1–7.8 (CH═CH and aromatic protons), 11.0 (N—H).

**Typical Procedure for Synthesis of Benzyl 3-[(*p*-Substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate.** Typical syntheses are as follows: A mixture of potassium 3-[(*p*-acetylphenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate (3.01 g, 9 mmol), benzyl chloride (1.69 g, 13.4 mmol), and TBAB (0.29 g, 0.9 mmol) was stirred in 18 mL of DMF at 50 °C for 24 h. The mixture was poured into 300 mL of water. The precipitation was filtered and dried in vacuo. 2.82 g (82.0%) of crude products was obtained. The products were recrystallized twice from dichloromethane/*n*-hexane. Mp: 120–121 °C. IR (KBr): 1680 (C═O), 1600 (C═C), 1250 (C—O—C) cm$^{-1}$. $^1H$ NMR (CDCl$_3$): $\delta$ 2.2 (m, 2 H, —CH$_2$—), 2.5 (s, 3 H, CH$_3$), 4.2 and 4.4 (broad s, 2 H, —CH—), 5.3 (s, 2 H, —CH$_2$OCO), 6.9 (m, 2 H, CH═CH), 7.4 (s, aromatic protons of benzyl group), 7.6–8.1 (m, 4 H, aromatic protons of anilide), 11.0 (s, 1 H, N–H). Anal. Calcd for $C_{22}H_{19}NO_3$: C, 74.39; H, 5.46; N, 3.63. Found: C, 73.90; H, 5.44; N, 3.61.

**Typical Procedure for the Photochemical Valence Isomerization of the Pendant NBD Moiety in the Polymer.** A solution of the polymer (0.01 g) in THF (3 mL) was cast on the inside wall of a quartz cell and dried. The polymer film on the cell was irradiated by a 250-W high-pressure mercury lamp (Ushio Electric Co., USH-250D) without a filter at a distance of 30 cm in air. The rate of disappearance of the maximum absorption was measured by a UV spectrophotometer. The sunlight irradiation of the polymer was also carried out by the same procedure.

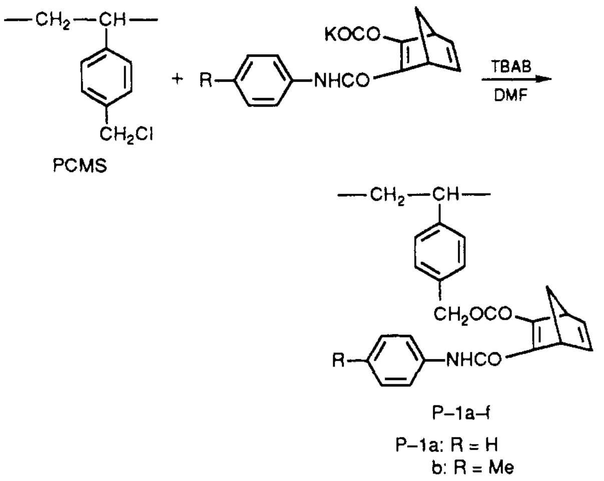
**Measurement of the Photochemical Valence Isomerization of the Pendant NBD Moiety of the Polymer and Model Compound in the Solution.** The NBD solution (7.5 × 10$^{-5}$ mol/L) in 400 mL of dichloromethane was charged in a 400-mL Pyrex glass cylindrical reactor with a water jacket immersion and thermometer. Nitrogen gas was bubbled through the solution for 60 min before UV light irradiation. Photochemical valence isomerization of NBD in the solution was carried out at 30 °C using a 500-W high-pressure mercury lamp (Ushio Electric Co., USH-500D) without filter at a distance of 30 cm under nitrogen atmosphere. The rate of valence isomerization from NBD to QC was calculated from the disappearance of the maximum absorption of the NBD moiety which was measured by UV spectrophotometer.

**Measurement of the Reversion from the Pendant QC Group in the Polymer to the NBD Moiety.** The solution of the QC moiety (3.5 mL, 7.5 × 10$^{-5}$ mol/L) prepared by the irradiation of the corresponding NBD solution in dichloromethane was charged in a standard quartz cell. To the solution was added a small amount of Co-TPP solution (10$^{-2}$ mol/L) in dichloromethane at 25 °C. The rate of appearance of the maximum absorption of the resulting NBD moiety was measured by a UV spectrophotometer.

**Measurement of Energy Storage in QC Group of the Polymer.** A polymer solution in THF was cast on a poly(tetrafluoroethylene) plate and dried. The film on the plate was irradiated for 30 min by a 250-W high-pressure mercury lamp without a filter at a distance of 30 cm. The irradiated polymer was packed in an aluminum sample tube for DSC analysis. The sample was heated at 3 °C/min.

## Results and Discussion

Polymers P-1a–f and P-3 having pendant NBD derivatives were synthesized from the phase transfer catalyzed reaction of PCMS with 1.5 equiv of potassium salt of 3-[(*p*-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylic acid or 3-phenyl-2,5-norbornadiene-2-carboxylic acid according to our previous papers (eq 1).[13,14] The results and conditions are summarized in Table I. The reaction proceeded very smoothly with high conversions to give the corresponding polymers using TBAB as PTC in DMF at 50 °C for 4 days. The model compounds, benzyl esters (M-1a–f and M-3) of 3-[(*p*-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylic acids, were also prepared in high yields from the reaction of the corresponding potassium salts with an excess amount of benzyl chloride under similar conditions as summarized in Table II (eq 2). The $^1H$ NMR spectra and λ max of the UV spectrum of the resulting polymers and their model



(1)

P-1a–f

P-1a: R = H
b: R = Me
c: R = OMe
d: R = Cl
e: R = Ac
f: R = NO$_2$

Table I
The Synthesis of Polymers

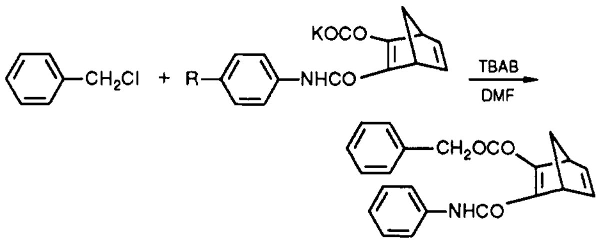
| polym | R | conv, % | $\eta_{sp}/C^a$ | $Q$,[b] kJ/mol |
|---|---|---|---|---|
| P-1a | H | 97.0 | 0.16 | 64.5 |
| P-1b | Me | 72.7 | 0.20 | 45.3 |
| P-1c | OMe | 80.8 | 0.18 | 67.0 |
| P-1d | Cl | 90.8 | 0.23 | 57.8 |
| P-1e | Ac | 81.8 | 0.21 | 64.5 |
| P-1f | $NO_2$ | 97.2 | 0.12 | |
| P-3 | | 94.0 | 0.13 | 94.7 |

[a] Measured at a concentration of 0.5 g/dL at 30 °C. [b] Heat of reversion isomerization from QC to NBD moiety in the irradiated polymer film was measured by DSC analysis.

Table II
The Synthesis of the Model Compounds

| compd | R | yield, % | mp, °C | | elementary analysis, % C | H | N |
|---|---|---|---|---|---|---|---|
| M-1a | H | 91.1 | 117–118 | calcd | 76.50 | 5.56 | 4.06 |
| | | | | found | 76.52 | 5.57 | 4.04 |
| M-1b | Me | 85.0 | 86–87 | calcd | 76.86 | 5.89 | 3.90 |
| | | | | found | 76.86 | 5.96 | 3.91 |
| M-1c | OMe | 80.8 | 113–114 | calcd | 73.58 | 5.64 | 3.73 |
| | | | | found | 73.27 | 5.70 | 3.75 |
| M-1d | Cl | 93.0 | 95–96 | calcd | 69.55 | 4.78 | 3.71 |
| | | | | found | 69.16 | 4.71 | 3.97 |
| M-1e | Ac | 82.0 | 120–121 | calcd | 74.39 | 5.46 | 3.63 |
| | | | | found | 73.90 | 5.44 | 3.85 |
| M-1f | $NO_2$ | 99.5 | 123–125 | calcd | 67.66 | 4.65 | 7.21 |
| | | | | found | 67.22 | 4.47 | 7.61 |
| M-3 | | 87.7 | 68–69[a] | | | | |

[a] See ref 14.



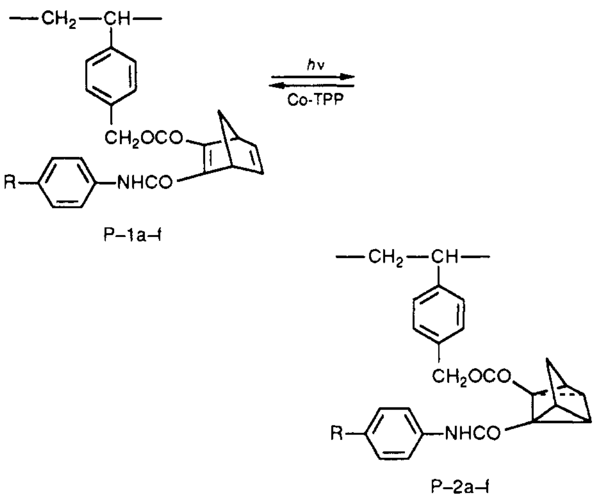
(2)

M–1a–f

M–1a: R = H
b: R = Me
c: R = OMe
d: R = Cl
e: R = Ac
f: R = $NO_2$

compounds are summarized in Table III. The IR spectra of P-1a film showed strong absorptions at 3400 (N—H stretching), 1680 (C=O stretching), 1620 cm$^{-1}$ (C=C stretching), and 1260 cm$^{-1}$ (C—O—C stretching). The $^1$H NMR spectra of this polymer showed signals of main-chain protons and methylene protons of NBD moiety at $\delta$ = 1.0–2.3, methine protons at 4.1 and 4.3, $CCH_2O$ protons at 5.2, and CH=CH and aromatic protons at 6.0–8.0. The IR spectra of model compound M-1a showed absorptions at 1700 and 1680 (C=O stretching), 1630 (C=C stretching), and 1270 cm$^{-1}$ (C—O—C stretching). The $^1$H NMR spectrum of this compound showed signals of methylene protons at 2.2, methine proton at 4.1 and 4.4, $—CH_2OCO$ protons at 5.3, and CH=CH and aromatic protons at 7.0–7.9. The IR and $^1$H NMR spectra of the polymers resemble those of the corresponding model compounds. Although the degree of conversion was calculated from elementary analysis of chlorine, it was also obtained from the intensity ratio of proton signals of $—CH_2$ OCO protons at 5.3 and unreacted $—CH_2Cl$ protons at 4.3.

The photochemical reaction of the polymer film was carried out by irradiation with a 250-W high-pressure mercury lamp or sunlight in air. The film thickness was adjusted to show the same absorption at 350 nm. The typical UV spectrum changes of P-1a in the film state by irradiation with sunlight and the corresponding model compound in the solution of dichloromethane by the UV irradiation were shown in Figures 1 and 2, respectively. When the polymer and model compound were irradiated, the absorption maximum near 324 nm due to the NBD moiety decreased and the absorption at about 252 nm due to the QC moiety increased, although UV spectra in the film state were slightly different from those of the corresponding model compound solutions in dichloromethane. The IR spectrum also changed by the irradiation. The irradiation of P-1a film caused the absorptions of C=O bond at 1680 cm$^{-1}$ and C=C bond at 1620 cm$^{-1}$ to decrease and a new strong broad absorption of C=O bond at 1675 cm$^{-1}$ to appear. Two isosbestic points were observed in the UV spectral changes of the polymers and model compounds except for P-1f and M-1f containing nitro group by the photoirradiation. This indicates that the photochemical valence isomerization of NBD moiety to the corresponding QC moiety in the polymer occurred selectively in the film state as well as in the solution (eq 3).



P–1a–f

P–2a–f

(3)

The conversion ($X_{NBD}$) from NBD moiety to QC moiety was calculated by the absorbance of $\lambda_{max}$ of the UV spectrum. The rates of photochemical reaction of NBD moieties in the polymer films were shown in Figure 3. The rate was strongly affected by the para substituents on the benzene rings, in which the rate increased in the order, P-1e > P-3 > P-1d ≥ P-1a > P-1b > P-1c. Therefore, the photochemical valence isomerization was dependent on the substituent of [(*p*-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety in the polymers. Interestingly enough P-1e showed higher photochemical reactivity than P-3, although P-3, containing the 3-phenyl-2,5-norbornadiene-2-carboxylate moiety, had high photochemical reactivity (eq 4).[13] The high reactivity of P-1e may be attributed to the acetophenone structure which was a good photosensitizer for NBD.[15] In addition, P-1e can use light under 440 nm, while P-3 does not have absorption over 370 nm.

The photochemical valence isomerization of NBD moiety in the polymer solution of dichloromethane was carried out at 30 °C under nitrogen current. This reaction of the polymers as well as model compounds obeyed first-order kinetics as shown in Figure 4. The observed reaction rate was also affected by the substituent of 3-[(*p*-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety in the polymers (Table IV). That is, the

Table III
UV and $^1$H NMR Spectra of Polymers and Model Compounds

| compd | $\lambda_{max}$, nm ($CH_2Cl_2$) | $^1$H NMR, ppm ($CDCl_3$) |
|---|---|---|
| P-1a | 324<br>317[a] | 0.8–2.3 (—$CH_2$— and main-chain protons), 4.1 and 4.4 (—CH—), 5.2 (—$CH_2$—OCO), 6.1–7.8 (CH=CH and aromatic protons) |
| P-1b | 324<br>(310)[a,b] | 1.0–2.4 (—$CH_2$— and main-chain protons), 4.1 and 4.3 (—CH—), 5.1 ($CH_2OCO$), 6.0–8.0 (CH=CH and aromatic protons) |
| P-1c | 338<br>338[a] | 1.0–2.3 (—$CH_2$— and main-chain protons), 2.2 ($CH_3$), 4.1 and 4.3 (—CH—), 5.2 ($CH_2OCO$), 6.0–7.7 (CH=CH and aromatic protons) |
| P-1d | 351<br>354[a] | 1.0–2.3 (—$CH_2$— and main-chain protons), 3.7 ($CH_3$), 4.1 and 4.3 (—CH—), 5.2 ($CH_2OCO$), 6.0–7.7 (CH=CH and aromatic protons) |
| P-1e | 323<br>273 (350)[a,b] | 1.0–2.3 (—$CH_2$— and main-chain protons), 3.5 ($CH_3$), 4.1 and 4.3 (—CH—), 5.2 ($CH_2OCO$), 6.0–8.0 (CH=CH and aromatic protons) |
| P-1f | c<br>342[a] | 1.0–2.3 (—$CH_2$— and main-chain protons), 2.8 (—$CH_2$—), 3.9 (—CH—), 5.0 ($CH_2OCO$), 6.0–8.2 (CH=CH and aromatic protons) |
| P-3 | 292<br>297[a] | 0.7–1.7 (—$CH_2$— and main-chain protons), 1.9 ($CH_3$), 3.9 (—CH—), 4.9 ($CH_2OCO$), 6.0–7.5 (CH=CH and aromatic protons) |
| M-1a | 324 | 2.2 (q, 2 H, —$CH_2$—), 4.1 and 4.4 (broad s, 2 H, —CH—), 5.3 (s, 2 H, $CH_2OCO$), 7.0–7.9 (m, 12 H, CH=CH and aromatic protons) |
| M-1b | 324 | 2.1 (m, 2 H, —$CH_2$—), 4.2 and 4.4 (broad s, 2 H, —CH—), 5.3 (s, 2 H, $CH_2OCO$), 5.9 (m, 2 H, CH=CH), 7.1–7.9 (m, 9 H, aromatic protons) |
| M-1c | 335 | 2.1 (m, 2 H, —$CH_2$—), 2.3 (s, 3 H, $CH_3$), 4.2 and 4.4 (broad s, 2 H, —CH—), 5.3 (s, 2 H, $CH_2OCO$), 6.9 (m, 2 H, CH=CH), 7.0–7.8 (m, 9 H, aromatic protons) |
| M-1d | 349 | 2.1 (m, 2 H, —$CH_2$—), 3.8 (s, 3 H, $CH_3$), 4.2 and 4.4 (broad s, 2 H, —CH—), 5.3 (s, 2 H, $CH_2OCO$), 6.8–7.8 (m, 11 H, CH=CH and aromatic protons) |
| M-1e | 323 | 2.2 (m, 2 H, —$CH_2$—), 2.5 (s, 3 H, $CH_3$), 4.2 and 4.4 (broad, 2 H, —CH—), 5.3 (s, 2 H, $CH_2OCO$), 6.9 (m, 2 H, CH=CH), 7.4 (s, 5 H, aromatic protons of benzyl group), 7.6–8.1 (m, 4 H, aromatic protons of anilide) |
| M-1f | 345 | 2.1 (m, 2 H, —$CH_2$—), 4.2 and 4.4 (broad s, 2 H, —CH—), 5.3 (s, 2 H, $CH_2OCO$), 6.9 (m, 2 H, CH=CH), 7.2–8.6 (m, 9 H, aromatic protons) |
| M-3 | 295 | 2.2 (m, 2 H, —$CH_2$—), 3.7 and 4.0 (broad s, 2 H, —CH—), 5.2 (s, 2 H, $CH_2OCO$), 7.0 (m, 2 H, CH=CH), 7.4 (m, 10 H, aromatic protons) |

[a] $\lambda_{max}$ of polymer film. [b] Shoulder absorption. [c] Insoluble in dichloromethane.

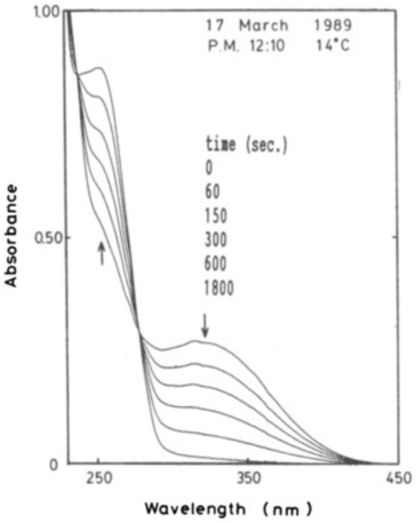


**Figure 1.** Change of UV spectra of P-1a film upon irradiation by winter sunlight.

polymers showed photochemical reactivity in following order, P-1e > P-1a > P-1d > P-1b > P-1c, which was almost the same as that of the corresponding model compounds in the solution and the polymer in the film state. When the reactivity was compared with that of the model compounds, the former was higher than the latter, while P-3 showed the same photoreactivity as its model compound M-3.[13] Especially, the observed rate constant $k_{obsd}$ of P-1a and P-1d was almost twice times higher than those of M-1a and M-1d, respectively. Therefore, the polymer containing the 3-[(*p*-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety was favorable for the photochemical valence isomerization from NBD to QC.

The reversion of QC derivatives to NBD compounds proceeds gradually without any catalyst when it is stored for a long time.[14] The storage stability of resulting QC moieties in the irradiated polymers (P-2a–f and P-4) can be evaluated by the extent of reversion to the original NBD moiety when the polymer films were kept in dark at room temperature (Table V). It has previously been reported that the pendant QC moiety in the P-4 film showed much higher storage stability than those of the pendant QC moiety in the polymer solution and the corresponding low molecular QC compounds in the solution.[14] Only 7.4 and 6.1 mol % of the pendant QC moiety in the resulting polymers (P-2a and P-2e) from P-1a and P-1e

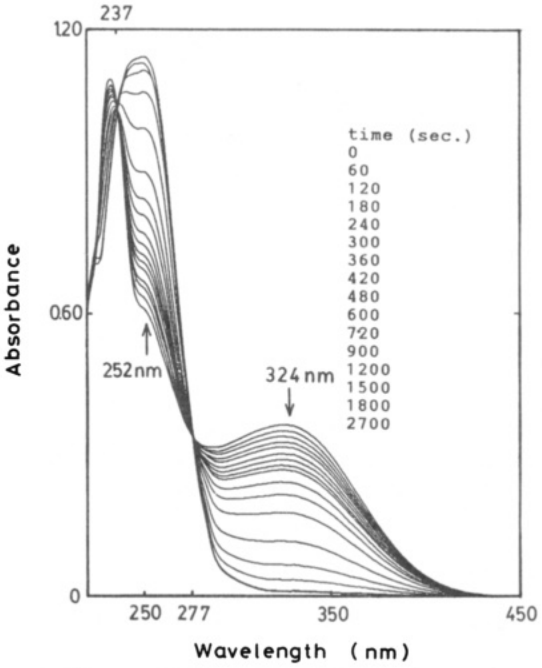


**Figure 2.** Change of UV spectra of M-1a under irradiation by a 500-W high-pressure mercury lamp in dichloromethane solution ($7.5 \times 10^{-5}$ mol/L) at 30 °C.

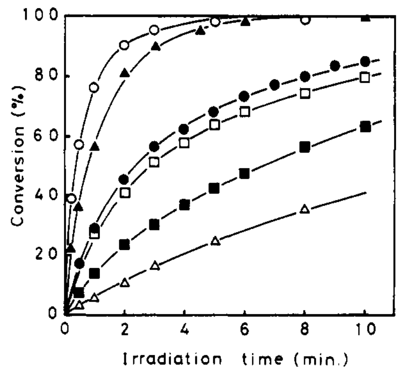


**Figure 3.** Photochemical valence isomerization of the pendant NBD moiety in the polymer film upon irradiation by a 250-W high-pressure mercury lamp: (●) P-1a, (■) P-1b, (△) P-1c, (□) P-1d, (○) P-1e, and (▲) P-3.

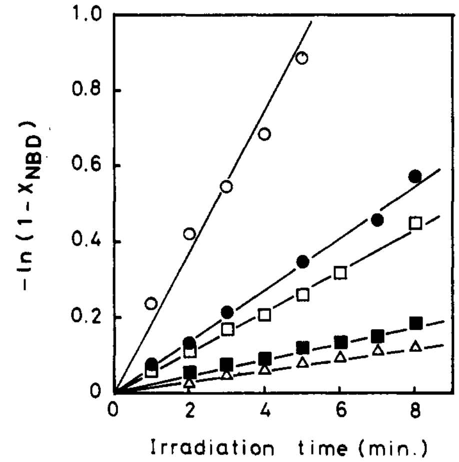


**Figure 4.** First-order kinetics of photoisomerization of polymer under irradiation by a 500-W high-pressure mercury lamp in dichloromethane solution ($7.5 \times 10^{-5}$ mol/L) at 30 °C: (●) P-1a, (■) P-1b, (△) P-1c, (□) P-1d, and (○) P-1e.

**Table IV**
**First-Order Rate Constant of Photochemical Valence Isomerization of NBD Moiety under Irradiation**

| | $k_{obsd} \times 10^4$, $s^{-1}$ | | | $k_{obsd} \times 10^4$, $s^{-1}$ | |
|---|---|---|---|---|---|
| R | polymer | model compd | R | polymer | model compd |
| H | 12.18 | 6.50 | Cl | 11.17 | 5.48 |
| Me | 4.03 | 3.58 | Ac | 24.32 | 22.50 |
| OMe | 3.08 | 2.32 | | | |

**Table V**
**Stability of the Pendant QC Moiety in the Polymer**[a]

| | degree of reversion of the QC moiety, mol% | | | | | |
|---|---|---|---|---|---|---|
| polym | 2 | 31 | 40 | 180 | 210 | 365, day |
| P-2a | 0 | 0.6 | 1.2 | 3.9 | 4.9 | 7.4 |
| P-2e | 2.2 | 2.9 | 3.5 | 3.1 | 3.5 | 6.1 |
| P-4[b] | 0.4 | 3.0 | 4.4 | 15.0 | 18.3 | 31.0 |

[a] The irradiated polymer film containing the pendant QC moiety was kept in dark at room temperature. [b] See ref 14.

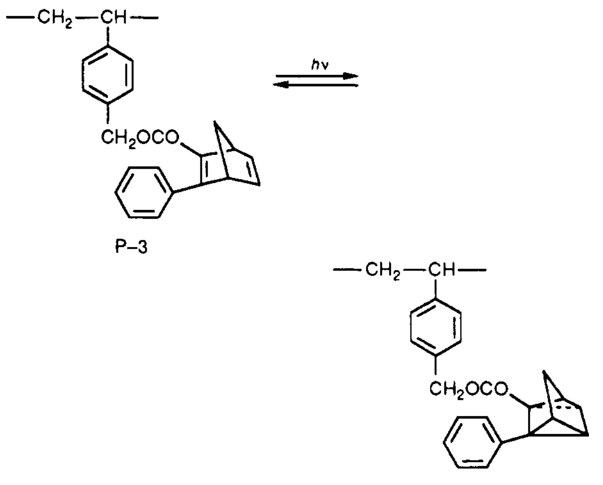
containing the 3-(phenylcarbamoyl)-2,5-norbornadiene-2-carboxylate structure reverted to the NBD after 1 year, while 31 mol % of the QC moiety in P-4 was changed. This indicated that the pendant QC group resulting from the pendant 3-(phenylcarbamoyl)-2,5-norbornadiene-2-carboxylate structure in the polymer film showed high storage stability.

Catalytic reversion from QC to NBD in the irradiated polymers and model compounds was investigated in a dichloromethane solution at 25 °C. It has been reported that Co-TPP and the related catalysts were useful catalysts for the reversion reaction.[2,13,14,16] The typical reversion ($X_{QC}$) from the resulting QC moiety to the original NBD was shown in Figure 5. The reaction proceeded very smoothly in the presence of Co-TPP and obeyed first-order kinetics (Figure 6). The observed rate constant $k_{obsd}$ plotted against the catalyst concentration showed a straight line passing through the origin (Figure 7). Therefore, the reversion was proportional to the product of both concentrations of QC group and Co-TPP. As summarized in Table VI, the reversion was not appreciably dependent on the para substituent of 3-[(p-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety in the polymers. In addition, the reaction in the polymer was lower than that of the model compound. The same tendency was observed in the reaction of 3-phenyl-2,5-norbornadiene-2-carboxylate type. This suggested that the bulky polymer matrix prevented the reversion from QC to NBD. The rate of the reversion of the 3-(phenylcarbamoyl)-2,5-norbornadiene-2-carboxylate type was much lower than that of 3-phenyl-2,5-norbornadiene-2-carboxylate type. It seems that the QC moiety of the former, which showed high storage stability, is also more stable for Co-TPP than that of the latter.

**Table VI**
**First-Order Rate Constant of Catalytic Reversion of the QC Moiety**

| | $k_{obsd} \times 10^3$, $s^{-1}$ | | | $k_{obsd} \times 10^3$, $s^{-1}$ | |
|---|---|---|---|---|---|
| R | polymer | model compd | R | polymer | model compd |
| H | 0.533 | 1.32 | Cl | 0.496 | 1.30 |
| Me | 0.476 | 1.21 | Ac | 0.708 | 1.13 |
| OMe | 0.479 | 1.26 | a | 4.16 | 15.60 |

[a] 3-Phenyl-2,5-norbornadiene-2-carboxylate type.



(4)

Thermal reversion of the pendant QC moiety was observed in the DSC curve of the irradiated polymers as shown in Figure 8. The storage energy of QC moieties resulting from P-1a–e and P-3 determined from DSC analysis was about 60 and 94.7 kJ/mol, respectively. It seems that the thermal energy storage capacity of NBD–QC system for the pendant 3-(phenylcarbamoyl)-2,5-norbornadiene-2-carboxylate structure was smaller than that for the pendant 3-phenyl-2,5-norbornadiene-2-carboxylate structure in the polymer film.

## Conclusions

From all those results, the following were concluded: (1) Polymers having the pendant 3-[(p-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety and their model compounds were prepared from the reaction

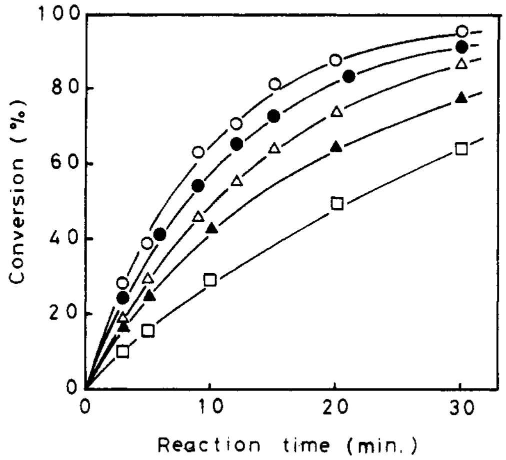


**Figure 5.** Catalytic reversion of M-1a in dichloromethane solution ($7.5 \times 10^{-5}$ mol/L) at 25 °C; Co-TPP concentration: (○) 1.61, (●) 1.34, (△) 1.07, (▲) 0.87, and (□) $0.54 \times 10^{-4}$ mol/L.

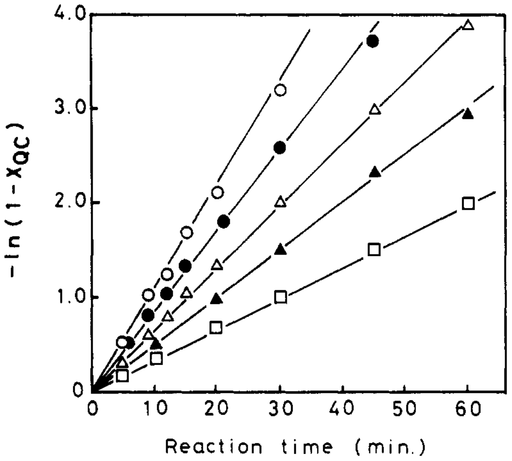


**Figure 6.** First-order kinetics of catalytic reversion of M-1a in dichloromethane solution ($7.5 \times 10^{-5}$ mol/L) at 25 °C: Co-TPP concentration: (○) 1.61, (●) 1.34, (△) 1.07, (▲) 0.87, and (□) 0.54 $\times 10^{-4}$ mol/L.

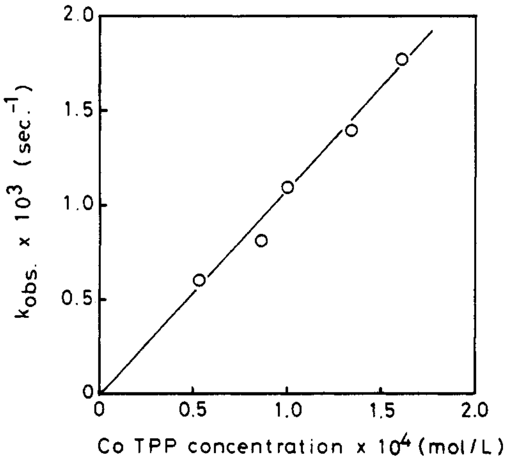


**Figure 7.** Relationship between the observed rate constant of catalytic reversion of M-1a and the Co-TPP concentration.

of poly[4-(chloromethyl)styrene] and benzyl chloride with corresponding potassium salts using PTC in DMF, respectively.

(2) The photochemical valence isomerization of the pendant NBD–QC moiety proceeded very smoothly in the film state as well as the polymer solution upon the irradiation by sunlight or the high-pressure mercury lamp.

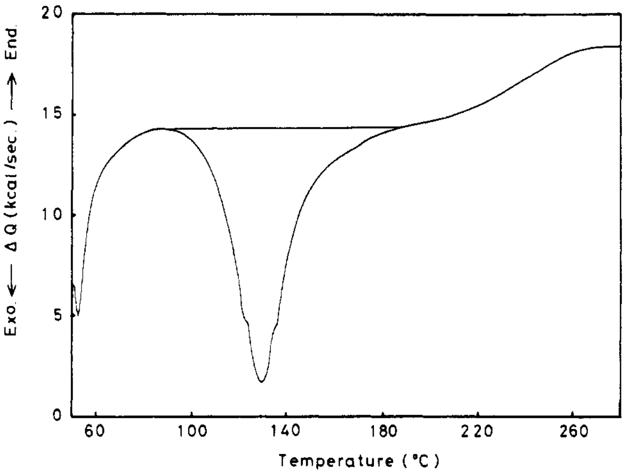


**Figure 8.** DSC curve of photoirradiated P-1a film.

(3) The rate of isomerization was strongly affected by the substituent of [(*p*-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety in the polymers. Especially, P-1e, containing the pendant 3-[(*p*-acetylphenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety, showed high photochemical reactivity.

(4) The rate of photochemical reaction of polymer was much higher than that of the corresponding model compounds in solution.

(5) The QC moiety derived from the 3-(phenylcarbamoyl)-2,5-norbornadiene-2-carboxylate moiety in the polymers scarcely reverted to the original NBD and showed excellent stability.

(6) The catalytic reversion of the resulting QC moiety to the original NBD proceeded smoothly in the solution with Co-TPP as the catalyst at room temperature. The reversion was proportional to the product of both concentrations of the QC group and Co-TPP, and did not appreciably depended on the para substituent of 3-[(*p*-substituted phenyl)carbamoyl]-2,5-norbornadiene-2-carboxylate moiety in the polymers.

(7) The storage energy for the QC moiety was about 60 kJ/mol by DSC measurement of the irradiated polymers.

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