Synthesis of New Photoresponsive Polymers Bearing Norbornadiene Moieties by Selective Cationic Polymerization of 2-[[(3-Phenyl-2,5-norbornadienyl)-2-carbonyl]oxy]ethyl Vinyl Ether and Photochemical Reaction of the Resulting Polymers

Tadatomi Nishikubo,* Atsushi Kameyama, Katsuhiko Kishi, Tatsuo Kawashima, Takahiro Fujiwara, and Chikara Hijikata

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

Received February 12, 1992; Revised Manuscript Received April 27, 1992

ABSTRACT: New photoresponsive polymers bearing norbornadiene (NBD) moieties were synthesized in high yields without any insoluble gel products by the selective cationic polymerization of 2-[[(3-phenyl-2,5-norbornadienyl)-2-carbonyl]oxy]ethyl vinyl ether (PNVE) and also by the copolymerizations with 2-phenoxyethyl vinyl ether, 2-chloroethyl vinyl ether, or isobutyl vinyl ether using $BF_3{\cdot}O(C_2H_5)_2$ as a catalyst in dichloromethane solution. The photochemical properties of the polymers thus obtained were evaluated in the film state or in dichloromethane solution. The rate of photochemical reaction of the pendant NBD moiety to the quadricyclane (QC) group in poly[2-[[(3-phenyl-2,5-norbornadienyl)-2-carbonyl]oxy]ethyl vinyl ether] [P(PNVE)] was higher than those of pendant NBD moieties in the copolymers in the film state, although the rate of the reaction of the NBD moiety of P(PNVE) was nearly the same as those of the NBD moieties in the copolymers in dichloromethane solution. Furthermore, it was found that the rate of the photoisomerization of the pendant NBD moiety and the photochemical reversion of the resulting QC groups were strongly affected by the wavelength of the irradiating light. The rate of thermal reversion of the produced QC groups in polymer films with low T_g was higher than that of the QC groups in the polymer film with high T_g, and the rate of catalytic reversion of the QC group in the polymer increased with increasing catalyst concentration in the solution.

Introduction

Photochemical valence isomerization of polymer films carrying pendant norbornadiene (NBD) moieties has been of interest from the viewpoint of solar energy conversion and storage because pendant NBD moieties in the polymers were converted very smoothly to the corresponding quadricyclane (QC) groups by photoirradiation. The QC groups in the polymers released about 92 kJ/mol of thermal energy upon reversion to the NBD moieties by contact with a catalyst such as (5, 10, 15, 20-tetraphenyl-21*H*,23*H*-porphine)cobalt(II) (Co–TPP).[1-3]

On the other hand, polymers with pendant NBD moieties appear to be useful as new photoresponsive polymers in imaging technology and also as new functional polymers for switch or device material in the optoelectronics field. This is because the QC groups produced in the polymer also reverted to the corresponding NBD moieties under photoirradiation of about 250-nm light[4] or by heating.[1]

In the previous papers, we reported[1,2] synthesis of polymers containing pendant NBD moieties by the substitution reaction on poly[(chloromethyl)styrene] with the potassium carboxylate of NBD derivatives using phase-transfer catalysts. We also studied photochemical valence isomerization of pendant NBD moieties in the polymers and catalytic reversion of the resulting QC groups using Co–TPP as a catalyst in the solution or the film state.

This paper reports on the successful synthesis of poly(vinyl ether)s bearing NBD moieties by the selective cationic polymerization of 2-[[(3-phenyl-2,5-norbornadienyl)-2-carbonyl]oxy]ethyl vinyl ether (PNVE) and the copolymerizations with some vinyl ethers such as 2-phenoxyethyl vinyl ether (PEVE), 2-isobutyl vinyl ether (IBVE), and 2-chloroethyl vinyl ether (CEVE). We also report photochemical valence isomerization of pendant NBD moieties in the polymers and reversion of the produced QC groups in the polymers by three different methods, that is, photochemical, thermal, and catalytic reversions.

Experimental Section

Materials. The solvents were dried using P_2O_5, CaH_2,or Na metal wire and purified in the usual way before use. Commercial CEVE and IBVE were dried with CaH_2 and purified by distillation. PEVE[5] was prepared by the reaction of potassium phenoxide (4.0 g, 30 mmol) with CEVE (15.2 mL, 150 mmol) using tetrabutylammonium bromide (TBAB; 1.0 g, 3 mmol) as a phase-transfer catalyst (PTC) at 80 °C for 7 h. The potassium chloride produced was filtered off, and the filtrate was dissolved in toluene, washed several times with water, and dried with anhydrous $MgSO_4$. Excess CEVE and toluene were evaporated, and then the crude product was purified on a silica gel column using ethyl acetate/hexane (1/9) as eluents. The isolated yield was 3.0 g (61%). IR (neat): 1600, 1500 (C=C of aromatics), 1245, 1205 cm^{-1} (COC), UV (CH_2Cl_2): λ_{max} 271 (ϵ_{max} = 17 000), 278 nm (ϵ_{max} = 14 000). ^1H NMR ($CDCl_3$, TMS): δ 3.7–4.3 (m, 6 H, CH_2CH_2, CH_2=C), 6.4 (dd, H, C=H), 6.7–7.4 (m, 5 H, aromatic protons). Trifluoroboron ether complex [$BF_3{\cdot}O(C_2H_5)_2$] was purified by distillation under reduced pressure. Ethyl aluminum dichloride ($EtAlCl_2$) and Co–TPP were used without further purification. TBAB was recrystallized from ethyl acetate.

Apparatus. Infrared (IR) spectra were measured on a Jasco Model IR-700 spectrometer. UV spectra were recorded on Shimadzu Models UV-240 and UV-2100S UV–vis spectrophotometers. The ^1H NMR spectra were recorded on JEOL Models JNM EX-90 (90-MHz) and JNM FX-200 (200-MHz) instruments in $CDCl_3$ or DMSO-d_6 with Me_4Si as an internal standard. Glass transition temperature (T_g) and the amount of energy storage in the pendant QC groups of the polymer were measured on a Perkin-Elmer differential scanning calorimeter Model DSC Station 4 at a heating rate at 20 or 3 °C/min.

Synthesis of 2-[[(3-Phenyl-2,5-norbornadienyl)-2-carbonyl]oxy]ethyl Vinyl Ether (PNVE). The reaction of 4.3 g (17.2 mmol) of potassium (3-phenyl-2,5-norbornadienyl)-2-carboxylate[6] and 8.7 mL (85.9 mmol) of CEVE was carried out using 0.57 g (1.72 mmol) of TBAB as a PTC at 80 °C for 6 h. The reaction mixture was diluted in toluene, and the potassium chloride produced was filtered. The filtrate was washed several times with water and dried with anhydrous $MgSO_4$. Excess CEVE and toluene were evaporated, and then the crude PNVE thus obtained

0024-9297/92/2225-4469$03.00/0

was purified by a silica gel column chromatograph using ethyl acetate/hexane (2/8) as eluents. The isolated yield of PNVE [bp 149–152 °C (0.43 mmHg)] was 4.3 g (89%). IR (neat): 1700 (C=O, ester), 1640, 1620 (C=C), 1235 (COC, ester), 1100 cm^{-1} (COC, ether), UV (CH_2Cl_2): λ_{max} 295 nm (ϵ_{max} = 6270). ^{1}H NMR ($CDCl_3$, TMS): δ 2.2 (dd, 2 H, bridged CH_2 in NBD), 3.8–4.4 (m, 8 H, OCH_2CH_2O, CH_2=CO, CH in NBD moiety), 6.4 (dd, 1 H, C=CHO), 6.9 (m, 2 H, CH=CH), 7.2–7.7 (m, 5 H, aromatic protons). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.25; H, 6.26.

Typical Procedure for Cationic Polymerization of PNVE. A typical example of the cationic polymerization was as follows. PNVE (0.63 g, 2.2 mmol) was dissolved in dichloromethane, and the solution was cooled with dry ice/methanol. To the monomer solution was added with stirring 8.4 μL (0.067 mmol) of $BF_3{\cdot}O(C_2H_5)_2$, and then the polymerization was carried out at −40 °C for 3 h under dry nitrogen. The polymerization was terminated by the addition of a small amount of triethylamine, and then the solution was poured into methanol to give a precipitate. The obtained polymer was reprecipitated twice from THF into methanol and dried in vacuo at room temperature. The yield of soluble poly[2-[[(3-phenyl-2,5-norbornadienyl)-2-carbonyl]oxy]ethyl vinyl ether] [P(PNVE)] was 0.51 g (80%). To evaluate the solubility, the resulting polymer was dissolved in THF, and the insoluble part was filtered off by a 3G type glass filter and dried. The reduced viscosity of the polymer in DMF was 0.10 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film): 1700 (C=O), 1610 (C=C), 1237 (COC, ether), 1100 cm^{-1} (COC, ether). UV (film): λ_{max} 295 nm. ^{1}H NMR ($CDCl_3$, TMS): δ 0.9–2.5 (m, 4 H, CH_2 in NBD and main chain in the polymer), 3.2–4.4 (m, 7 H, OCH_2CH_2O, CH in NBD and main chain in the polymer), 6.9 (m, 2 H, CH=CH), 7.0–7.6 (m, 5 H, aromatic protons).

Typical Procedure for Cationic Copolymerization of PNVE with Another Vinyl Ether. Cationic copolymerization of 0.35 g (1.24 mmol) of PNVE and 0.20 g (1.22 mmol) of PEVE was performed in 2 mL of a dichloromethane solution using 9.3 μL (0.074 mmol) of $BF_3{\cdot}O(C_2H_5)_2$ as a catalyst at −40 °C for 3 h with stirring under dry nitrogen, and then the polymer solution was treated in the same way as the above polymerization of PNVE. The yield of copolymer was 0.54 g (99%). The contents of PNVE and PEVE units in the copolymer were 52.9 and 47.1%, respectively, which were determined by UV spectrophotometry. The reduced viscosity of the polymer in DMF was 0.22 dL/g, measured at a concentration of 0.5 g/dL at 30 °C.

Typical Procedure for Photochemical Valence Isomerization between the Pendant Norbornadiene (NBD) Moiety and the Quadricyclane (QC) Group in a Polymer Film. A solution of P(PNVE) (0.01 g) in THF (3 mL) was coated on the inside wall of a quartz cell and dried. The polymer film on the quartz was irradiated by a 500-W xenon lamp (Ushio Electric Co., UXL-500D-O) through a monochromator (Jasco Model CT-10), in which the energy of the incident light was monitored by an electric photoncounter (ORC Model UV-M30). Rates of disappearance or appearance of the absorption peak at 295 nm due to the NBD moiety were measured by a UV spectrophotometer.

Typical Procedure for Thermal Reversion of the Pendant QC Group in a Polymer Film. The photoirradiated polymer film bearing QC groups was heated in a test chamber at an appropriate temperature, and then the degree of conversion of the QC groups was recorded on a UV spectrophotometer.

Typical Procedure for Photochemical Reaction of the Pendant NBD Moiety in P(PNVE) and for Catalytic Reversion of the Resulting QC Groups in Solution. A solution of P(PNVE) (1.0 × 10^{-4} mol/L) with Co–TPP (1.0–3.0 × 10^{-5} mol/L) or without Co–TPP in dichloromethane was charged into a quartz cell, and then the solution in the quartz was irradiated by a 500-W high-pressure mercury lamp (Ushio Electric Co., USH-500D) through a filter (Toshiba UV-31) at a distance of 30 cm, in which the intensity of the incident light was kept always at 2.19–2.22 mW/cm^2 (at 365 nm). Rates of disappearance or appearance of absorption peaks at 295 nm due to the NBD moiety were monitored by a UV spectrophotometer.

Table I
Conditions and Results of Cationic Polymerization of PNVE[a]

run no.	PNVE, mmol	solvent	temp, °C	yield, % sol	yield, % insol	η_{red},[b] dL/g
1	8.0	toluene	−10	92.9	3.1	0.16
2	8.0	toluene	−40	85.2	9.7	0.13
3	8.0	toluene	−75	76.3	4.5	0.12
4[c]	1.8	toluene	−40	trace		
5	1.8	dichloromethane	10	67.2	12.4	0.14
6	1.8	dichloromethane	−10	94.8	0	0.13
7	2.2	dichloromethane	−40	80.2	0	0.10

[a] Polymerization was carried out with the concentration at 100 mmol/L using 3 mol % of $BF_3{\cdot}O(C_2H_5)_2$ as a catalyst for 3 h. [b] Measured at a concentration of 0.5 g/dL in DMF at 30 °C. [c] Polymerization was carried out using $EtAlCl_2$ as a catalyst.

Results and Discussion

Cationic Polymerization and Copolymerization of PNVE. The cationic polymerization of PNVE was performed in toluene or dichloromethane solution using $BF_3{\cdot}O(C_2H_5)_2$ or $EtAlCl_2$ as catalysts at various temperatures, and the reaction conditions and results are summarized in Table I. When the cationic polymerization was carried out with $BF_3{\cdot}O(C_2H_5)_2$ in dried toluene at −10, −40, or −75 °C, P(PNVE)s were obtained in high yields. Polymers thus obtained contained 3–10 wt % of insoluble gel products. However, polymers without any insoluble gel products were obtained in high yields when the cationic polymerization of PNVE took place in dichloromethane at −10 or −40 °C under the same catalytic conditions. In addition, it was found that the resulting P(PNVE) contained 12 wt % of insoluble gel products when the cationic polymerization was carried out at 10 °C and that no polymer resulted from the cationic polymerization of PNVE using $EtAlCl_2$ as a catalyst in toluene.

The IR spectrum of the soluble P(PNVE) showed absorption peaks at 1710 and 1620 cm^{-1} due to C=O and C=C bonds, respectively, and showed the disappearance of the absorption peak due to the C=C bond of the vinyl ether group at 1640 cm^{-1}. The ^{1}H NMR spectrum of the polymer showed a dramatic change from the spectrum of the PNVE monomer and showed the disappearance of the signal at 6.4 ppm based on C=CHO, although a signal at 6.8 ppm due to CH=CH remained, and new signals appeared at 1.6 and 3.5 ppm derived from methylene and methine protons of the polymer backbone.

This result suggests that selective cationic polymerization of vinyl ether groups in the PNVE molecule proceeded successfully to give the corresponding P(PNVE) containing a pendant NBD moiety in which dichloromethane and $BF_3{\cdot}O(C_2H_5)_2$ were a suitable solvent and catalyst for the cationic polymerization of PNVE, respectively.

The cationic copolymerizations of PNVE with other vinyl ethers such as PEVE, IBVE, and CEVE were also performed using 3 mol % of $BF_3{\cdot}O(C_2H_5)_2$ as the catalyst at −40 °C (Table II). Although the prepared P(PNVE–PEVE) contained some insoluble gel products when the copolymerization of PNVE with PEVE was carried out in toluene, the obtained copolymers P(PNVE–PEVE), P(PNVE–IBVE), and P(PNVE–CEVE) did not contain any such gel products when the copolymerizations of PNVE with PEVE, IBVE, or CEVE were performed in dichloromethane solution under the same conditions. In these cationic copolymerizations, it was also found that the yields of copolymers were high and that the compositions of the resulting copolymers, which were determined

Table II
Conditions and Results of Cationic Copolymerizations of PNVE (I) with Other Monomers (II)[a]

run no.	comonomer	feed ratio, I:II	solvent	yield, % sol	yield, % insol	composition,[b] I:II	η_{red},[b] dL/g	T_g, °C
6	none	100:0	dichloromethane	80.2	0	100:0	0.10	37
8	PEVE	70:30	dichloromethane	91.3	0	74.4:25.6	0.12	29
9	PEVE	50:50	toluene	73.6	2.5	41.6:58.4	0.28	
10	PEVE	50:50	dichloromethane	93.8	0	52.9:47.1	0.22	18
11	PEVE	30:70	dichloromethane	95.4	0	25.0:75.0	0.26	14
12	IBVE	50:50	dichloromethane	85.0	0	56.7:43.3	0.16	26
13	CEVE	50:50	dichloromethane	73.9	0	48.9:51.1	0.12	28

[a] Polymerization was carried out with the concentration at 100 mmol/L using 3 mol % of $BF_3 \cdot O(C_2H_5)_2$ as a catalyst at −40 °C for 3 h. [b] The composition of the copolymer was estimated by UV spectrophotometry. [c] Measured at a concentration of 0.5 g/dL in DMF at 30 °C.

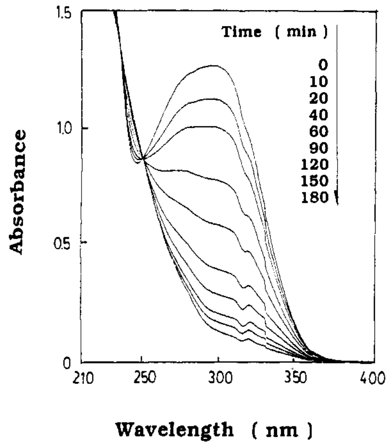
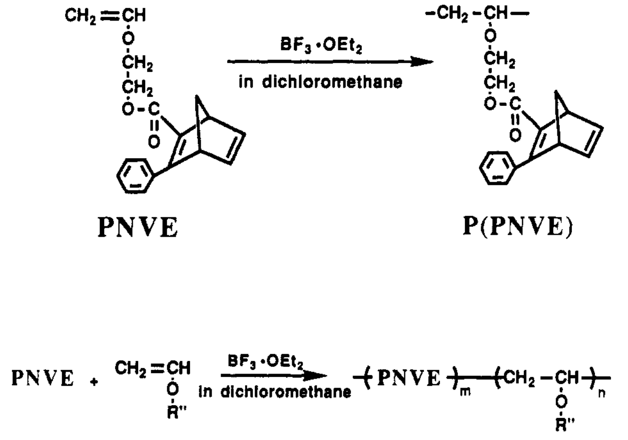


Figure 1. Change of the UV spectrum of P(PNVE) under irradiation of 311-nm light in the film state.

Scheme I



R'': $-(CH_2)_2-OPh$; PEVE and P(PNVE-PEVE),
$-CH_2CH(CH_3)_2$; IBVE and P(PNVE-IBVE),
$-(CH_2)_2-Cl$; CEVE and P(PNVE-CEVE).

by UV spectrophotometry were close to the feed ratio of the monomers.

This result means that selective cationic copolymerization of the vinyl ether group in PNVE with other vinyl ether monomers gave soluble photoresponsive copolymers in high yields without any insoluble gel production using $BF_3 \cdot O(C_2H_5)_2$ in dichloromethane solution (Scheme I).

Photochemical Isomerization of the Pendant NBD Moiety in Polymer Films. Photochemical valence isomerization of the pendant NBD moiety in a P(PNVE) film was performed on a quartz cell by photoirradiation using a xenon lamp. As shown in Figure 1, an absorption peak at 295 nm due to the NBD moiety in P(PNVE) decreased rapidly, indicating that the NBD moiety isomerized to the QC group after only 3 min of irradiation with 311-nm light. As can be seen, there are two isosbestic points at 237 and 251 nm. This result indicates that the photochemical reaction of the pendant NBD moiety to the corresponding QC group in the polymer occurred very smoothly and selectively without any side reaction upon irradiation with 311-nm light (Scheme II).

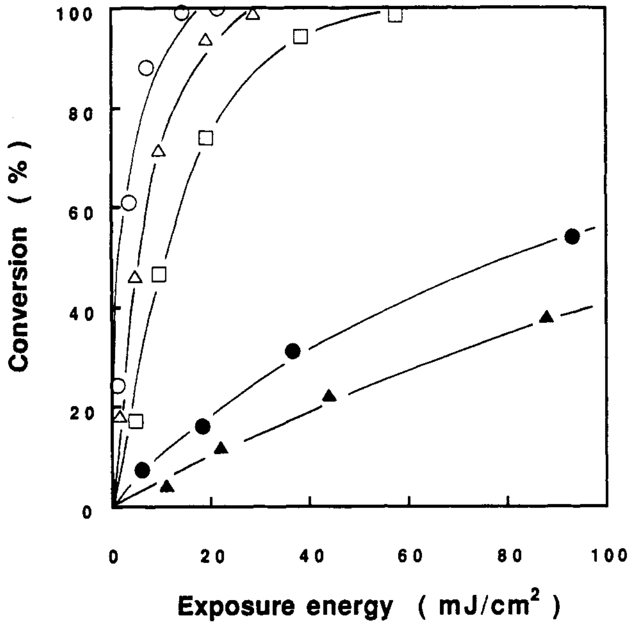
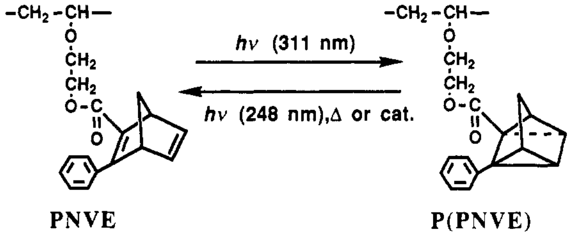


Figure 2. Plots of the degree of photoisomerization of the NBD moiety in a P(PNVE) film vs exposure energy by a xenon lamp: (△) 293 nm; (○) 311 nm; (□) 338 nm; (●) 345 nm; (▲) 365 nm.

Scheme II



The photochemical reaction of the pendant NBD moieties to the QC groups in the polymer film also proceeded by irradiation with 293-, 338-, 345-, and 365-nm light, respectively. As summarized in Figure 2, the pendant NBD moiety in the polymer was isomerized to the corresponding QC group by only 20 mJ/cm² irradiation with 311-nm light. However, the degree of conversion of the NBD moiety in the polymer film was about 40 mol % upon 100 mJ/cm² irradiation with 365-nm light. That is, the rate of photochemical reaction of the pendant NBD moiety corresponded to the optical density of the polymer film (see Figure 1) with the exception of irradiation with 293-nm light. It seems that some photochemical reversion of the produced QC groups also occurred upon irradiation with 293-nm light.

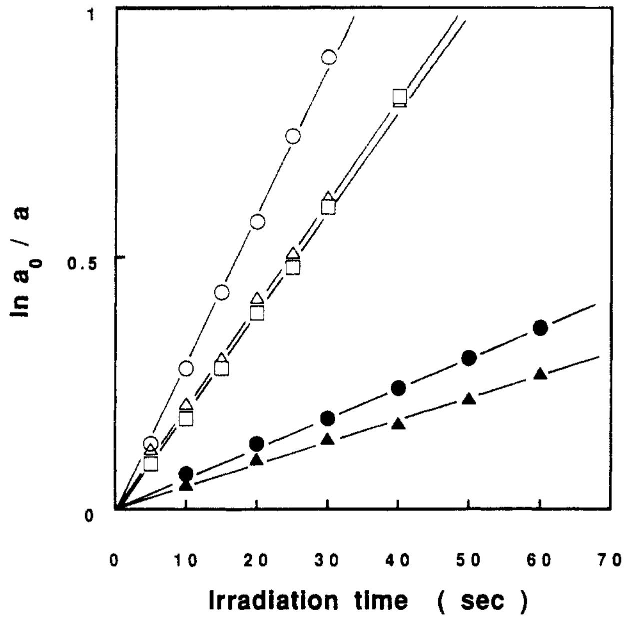


Figure 3. Rate of the photochemical reaction of the NBD moiety in a P(PNVE) film under irradiation with a xenon lamp: (△) 293 nm; (○) 311 nm; (□) 338 nm; (●) 345 nm; (▲) 365 nm.

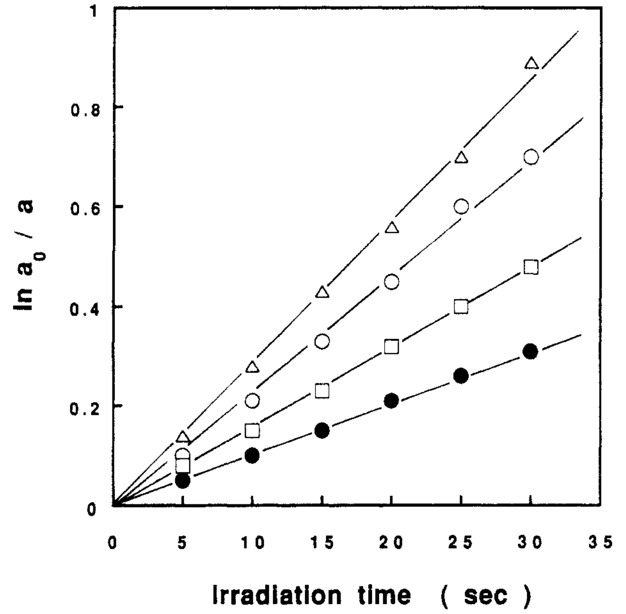


Figure 4. Rate of photochemical reaction of the NBD moiety in some polymer films under irradiation with 311-nm light: (△) P(PNVE); (●) P(PNVE$_{53}$–PEVE$_{47}$); (○) P(PNVE$_{49}$–CEVE$_{51}$); (□) P(PNVE$_{57}$–IBVE$_{43}$).

As shown in Figure 3, it was also found that the observed rates of photochemical reaction of the NBD moiety in the polymer film obeyed first-order kinetics with each photoirradiation.

As summarized in Figure 4, the observed rates of the photochemical reaction of the copolymers also obeyed first-order kinetics upon irradiation with 311-nm light. Furthermore, it was found that the rate of photochemical reaction of the pendant NBD moiety in a homopolymer was faster than those in the copolymers, and the rates of photochemical reaction of pendant NBD moieties in the copolymers decreased as follows: P(PNVE$_{49}$–CEVE$_{51}$) > P(PNVE$_{57}$–IBVE$_{43}$) > P(PNVE$_{53}$–PEVE$_{47}$). This result indicates that there is no correlation between the rate of photochemical reaction of the polymer and the T_g of the polymer film. Accordingly, it seems that either energy migration from one excited NBD moiety to another NBD moiety might have occurred along the polymer chain in the film state, or steric hindrance of the neighboring bulky NBD moiety in the homopolymer might have enhanced the photochemical valence isomerization of the excited NBD moiety in the homopolymer in the film state.

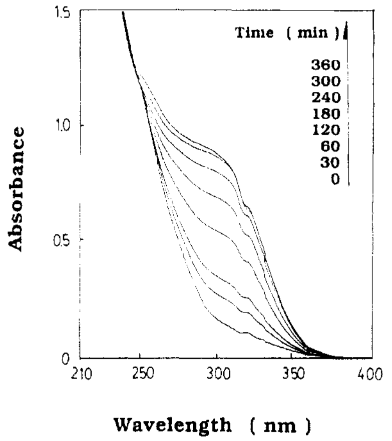


Figure 5. Change of the UV spectrum of the produced QC group in P(PNVE) under irradiation with 248-nm light in the film state.

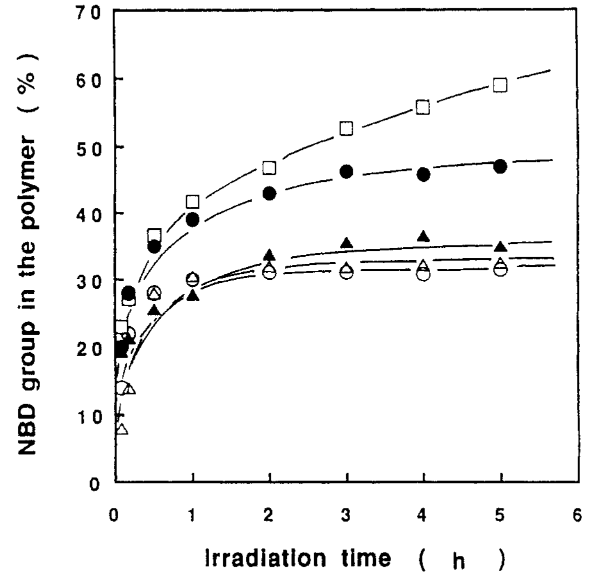


Figure 6. Plots of the degree of reversion of the QC group in a P(PNVE) film vs exposure time by a xenon lamp: (△) 240 nm; (○) 244 nm; (□) 248 nm; (●) 250 nm; (▲) 254 nm.

Photochemical Reversion of the Resulting QC Group in Polymer Films. When the pendant QC group produced in a P(PNVE) film on the quartz cell was irradiated with 248-nm light, its UV spectrum reverted to that of the corresponding NBD moiety, with two isosbestic points at 237 and 251 nm. The degree of reversion of the QC groups was mostly saturated at 60 mol % conversion (Figure 5). It seems that photochemical reversion of pendant QC groups in the polymer film attained a photostationary state under this irradiation condition.

As summarized in Figure 6, the rate of reversion of the QC group to the NBD moiety in the polymer film was strongly affected by the wavelength of the irradiating light, and the observed rate of the reversion upon irradiation with 248-nm light was faster than rates upon irradiation with 240-, 244-, 250-, or 254-nm light, although detailed correlation between the degree of conversion of QC groups to the NBD moiety in the polymer film and the exposure dose could not be confirmed, because the equipment to measure the exposure energy at each wavelength was not available.

Furthermore, as shown in Figure 7, the rate of the photochemical reversion of the pendant QC group in

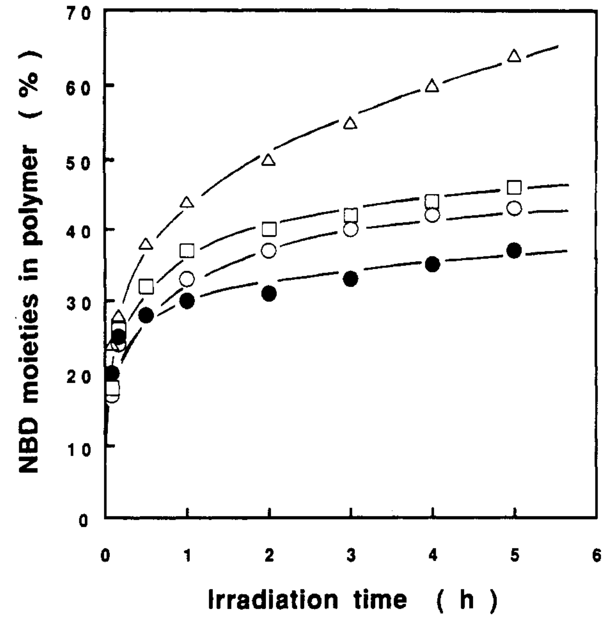


Figure 7. Plots of the degree of reversion of the QC group in polymer films vs exposure time under irradiation with 248-nm light: (△) P(PNVE); (○) P(PNVE$_{49}$-CEVE$_{51}$); (□) P(PNVE$_{57}$-IBVE$_{43}$); (●) P(PNVE$_{53}$-PEVE$_{47}$).

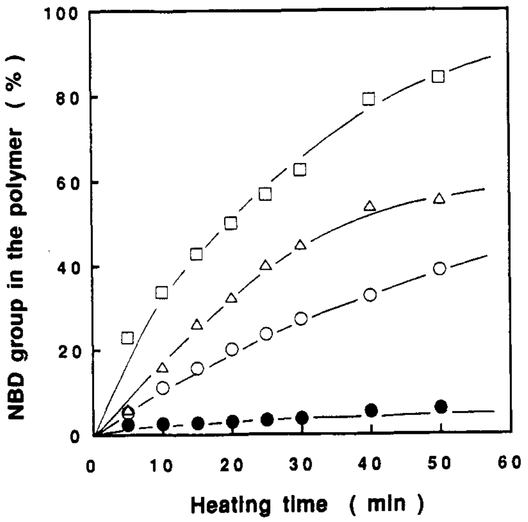


Figure 8. Plots of the degree of reversion of the QC group in a P(PNVE) film vs heating time at various temperatures (°C): (□) 100; (△) 90; (○) 80; (●) 70.

P(PNVE) was faster than those of the pendant QC groups in the copolymers, and the rate of the reversion of the QC groups in the P(PNVE$_{53}$-PEVE$_{47}$) was lower than those of the QC groups in P(PNVE$_{57}$-IBVE$_{43}$) and P(PNVE$_{49}$-CEVE$_{51}$) when the photoirradiation was carried out with 248-nm light.

These results show that the photochemical valence isomerization between pendant NBD moieties and the QC groups in polymer films is strongly affected by both the wavelength of the photoirradiation and by the composition of the polymer backbone.

Thermal Reversion of the Pendant QC Group in Polymer Films. Thermal reversion of the QC group, which was produced by irradiation with 311-nm light, in a homopolymer film was carried out at various temperatures. As shown in Figure 8, the rate of thermal reversion increased with the reaction temperature. The rate of thermal reversion of the QC groups in the copolymer films was also measured under the same conditions. As shown in Figure 9, the rates of reversion of the QC groups in P(PNVE$_{53}$-PEVE$_{47}$) and P(PNVE$_{57}$-IBVE$_{43}$) were much higher than that of the QC group in P(PNVE) at 100 °C, and most of the QC groups in the copolymers reverted to the NBD moiety with 30-min heating. This result indicates that the rate of thermal reversion of the QC group in the polymer film with low T_g was higher than that of the QC group in the polymer film with high T_g.

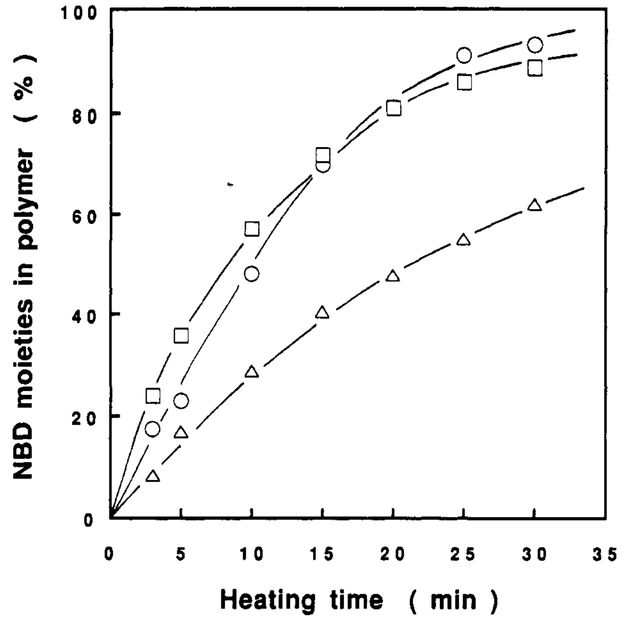


Figure 9. Plots of the degree of reversion of the QC group in polymer film vs heating time at 100 °C: (□) P(PNVE$_{53}$-PEVE$_{47}$); (○) P(PNVE$_{57}$-IBVE$_{43}$); (△) P(PNVE).

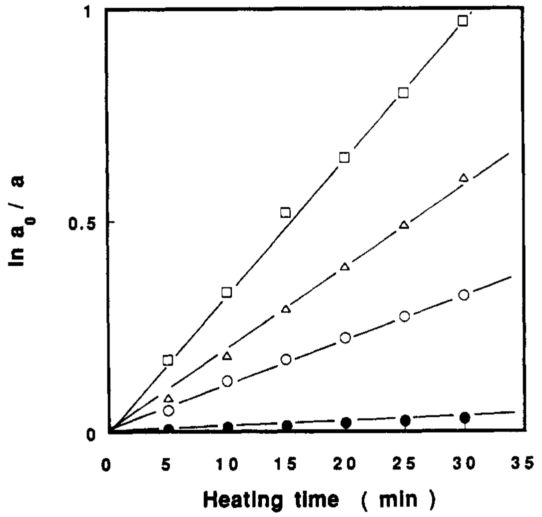


Figure 10. Rate of thermal reversion of the QC group in polymer films at various temperatures (°C): (□) 100; (△) 90; (○) 80; (●) 70.

Furthermore, it was found that the observed rate of thermal reversion of P(PNVE) obeyed first-order kinetics at 70–100 °C (Figure 10). The Arrhenius plots based on the above-observed pseudo-first-order rate constant (k_1) of the reaction are shown in Figure 11, and the apparent activation energy of the reaction was estimated as 66.3 kJ/mol.

DSC measurements on the photoirradiated polymer showed that the QC group in a P(PNVE) film released about 86.5 kJ/mol of thermal energy.

Photochemical Reaction of the Pendant NBD Moiety in a Polymer and Catalytic Reversion of the Resulting QC Groups in Solution. Although the rate of photochemical reaction of the pendant NBD moiety in a P(PNVE) film was faster than those of the NBD moiety in the films of copolymers under irradiation with 311-nm

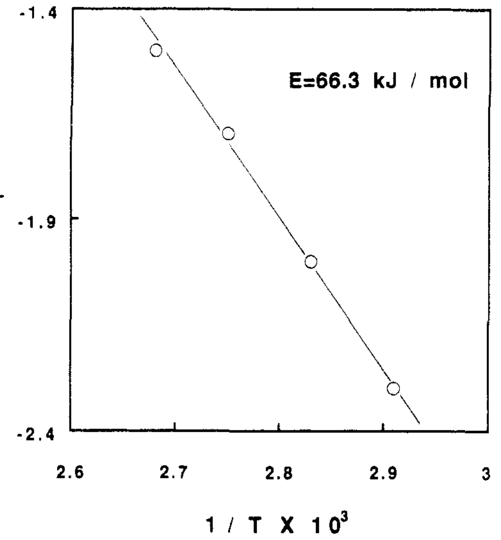


Figure 11. Arrhenius plots of the observed pseudo-first-order rate constant on the thermal reversion of the QC group in the irradiated P(PNVE) film.

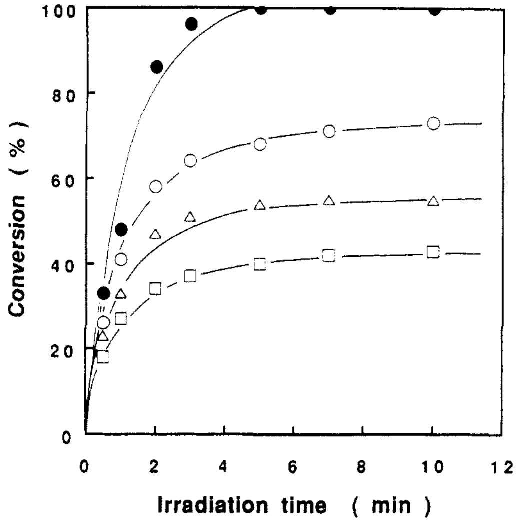


Figure 12. Plots of the degree of photoisomerization of the NBD moiety in P(PNVE) vs irradiation time by a high-pressure mercury lamp with >310-nm light in dichloromethane: (●) without Co–TPP; (○) with 10 mol % of Co–TPP; (△) with 20 mol % of Co–TPP; (□) with 30 mol % of Co–TPP.

light, the rate of photochemical reaction of the pendant NBD moiety in P(PNVE) was almost the same as the rates of pendant NBD moieties in the copolymers in solution when the photoirradiation was carried out with >310-nm light in dichloromethane solution without any catalyst. That is, the rate of the photochemical valence isomerization of the pendant NBD moiety in the polymer was not affected by the composition of the copolymer in solution, and the pendant NBD moiety in every polymer such as P(PNVE), P($PNVE_{53}$–$PEVE_{47}$), P($PNVE_{49}$–$CEVE_{51}$), and P($PNVE_{57}$–$IVBE_{43}$) changed completely to the QC group with only 5-min irradiation.

As shown in Figure 12, the rate of photochemical reaction of the pendant NBD moiety in P(PNVE) decreased with an increase in the Co–TPP concentration in the solution. It seems that there are two reasons: the filter effect due to Co–TPP catalyst, which has strong absorptions at 265, 410, and 527 nm; and the catalytic reversion of the produced QC groups by the added Co–TPP catalyst in solution. A similar tendency has also been found[2] in the photochemical reaction of the pendant NBD moiety in the polymer film with Co–TPP catalyst. Interestingly, the rate of photochemical reaction of the pendant NBD moiety in P(PNVE–PEVE)s decreased gradually with increasing PNVE units in the copolymer, when the photochemical reaction was performed in the presence of 10 mol % of Co–TPP catalyst in dichloromethane solution (Figure 13).

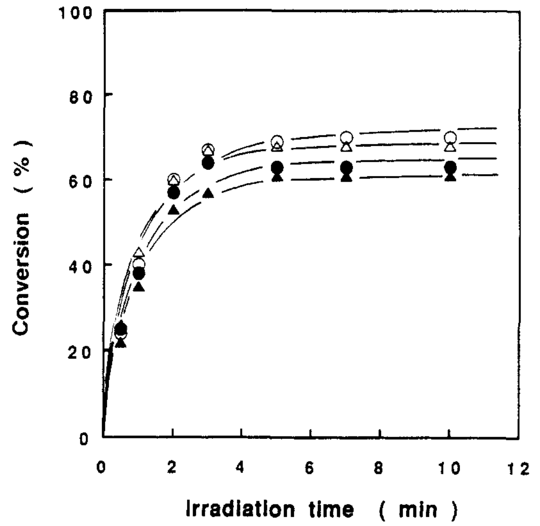


Figure 13. Plots of the degree of photoisomerization of the NBD moiety in P(PNVE–PEVE)s with 10 mol % of Co–TPP vs irradiation time by a high-pressure mercury lamp with >310-nm light in dichloromethane: (○) P(PNVE); (△) P($PNVE_{47}$–$PEVE_{26}$); (●) P($PNVE_{53}$–$PEVE_{47}$); (▲) P($PNVE_{25}$–$PEVE_{75}$).

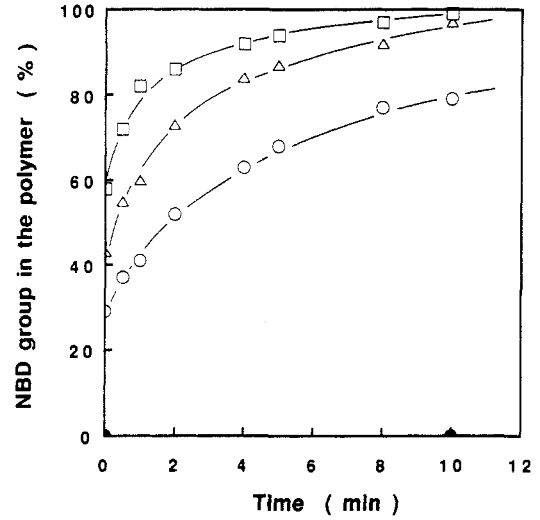


Figure 14. Rate of the catalytic reversion of the produced QC groups in P(PNVE) in dichloromethane solution in the presence of Co–TPP as the catalyst: (●) without Co–TPP; (○) with 10 mol % of Co–TPP; (△) with 20 mol % of Co–TPP; (□) with 30 mol % of Co–TPP.

Photoirradiation of P(PNVE) was carried out for 10 min in dichloromethane solution in the presence of Co–TPP with >310-nm light, and then the rate of catalytic reversion of the produced QC groups was examined in the same solution. As shown in Figure 14, the rate of the reversion increased with an increase in the Co–TPP concentration in dichloromethane solution, which is a meaningful result.

The rate of catalytic reversion of the produced QC group in the polymers was also affected by the composition of the polymer, and the rates of reversion of the copolymers were higher than that of P(PNVE) in dichloromethane solution in the presence of 10 mol % of Co–TPP catalyst. P($PNVE_{53}$–$PEVE_{47}$) showed the highest rate of reversion (Figure 15).

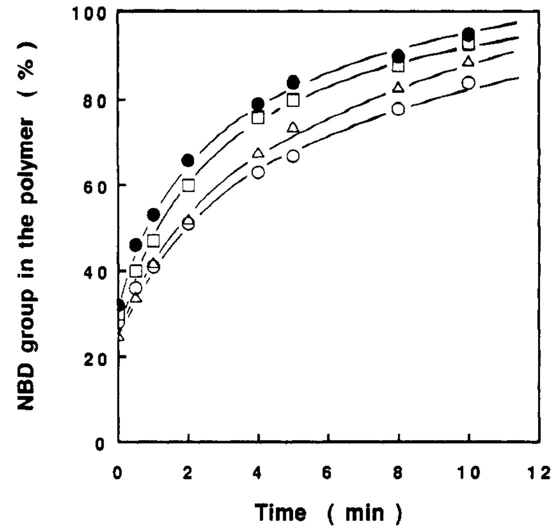


Figure 15. Rate of the catalytic reversion of the produced QC groups in copolymers in dichloromethane solution in the presence of 10 mol % of Co–TPP as the catalyst: (○) P(PNVE); (△) P(PNVE$_{57}$–IBVE$_{43}$); (□) P(PNVE$_{49}$–CEVE$_{51}$); (●) P(PNVE$_{53}$–PEVE$_{47}$).

The catalytic reversion of the produced QC groups in P(PNVE–PEVE) copolymers was also examined in dichloromethane solution containing 10 mol % of Co–TPP. As summarized in Figure 16, the rate of catalytic reversion of the QC group in the polymer increased with a decrease in the fraction of PNVE units in the copolymers.

From these results, it may be hypothesized that aggregation of the pendant QC groups in the copolymers was hindered by the comonomer units and that the Co–TPP catalyst was able to come into contact very easily with the QC groups in the copolymers in solution. Accordingly, the rates of catalytic reversion of the pendant QC groups in the copolymers were higher than rates of the QC groups in the P(PNVE) homopolymer.

Acknowledgment. This work was supported by a grant from the Ministry of Education, Science and Culture of Japan (No. 03650752), which is gratefully acknowledged.

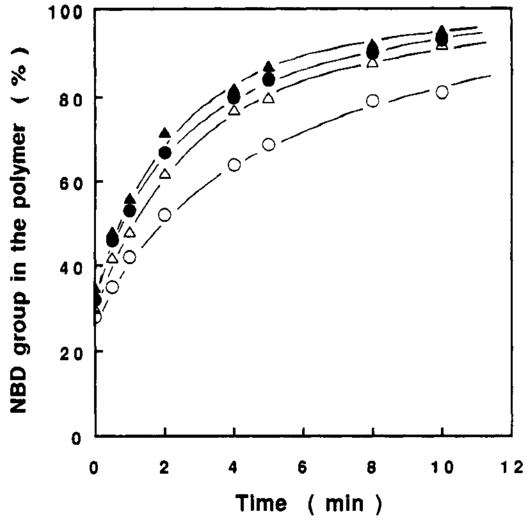


Figure 16. Rate of the catalytic reversion of the produced QC groups in P(PNVE–PEVE)s in dichloromethane solution in the presence of 10 mol % of Co–TPP as the catalyst: (○) P(PNVE); (△) P(PNVE$_{74}$–PEVE$_{26}$); (●) P(PNVE$_{53}$–PEVE$_{47}$); (▲) P(PNVE$_{25}$–PEVE$_{75}$).

References and Notes

(1) (a) Nishikubo, T.; Sahara, A.; Shimokawa, T. *Polym. J.* **1987**, *19*, 991. (b) Nishikubo, T.; Shimokawa, T.; Sahara, A. *Macromolecules* **1989**, *22*, 8.
(2) Nishikubo, T.; Hijikata, C.; Iizawa, T. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 671.
(3) Iizawa, T.; Hijikata, C.; Nishikubo, T. *Macromolecules* **1992**, *25*, 21.
(4) Kamogawa, H.; Yamada, M. *Macromolecules* **1988**, *21*, 918.
(5) (a) Crivello, J. V.; Conlon, D. A. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1785. (b) Choi, W. K.; Sawamoto, M.; Higashimura, T. *Polym. J.* **1987**, *19*, 889.
(6) Nishikubo, T.; Kawashima, T.; Inomata, K.; Kameyama, A. *Macromolecules*, in press.

Registry No. PNVE, 128835-65-4; CEVE, 110-75-8; P(PNVE) (homopolymer), 128835-66-5; (PNVE)(PEVE) (copolymer), 142320-42-1; (PNVE)(IBVE) (copolymer), 142320-43-2; (PNVE)(CEVE) (copolymer), 142320-44-3; potassium (3-phenyl-2,5-norbornadienyl)-2-carboxylate, 950-91-4.