

Synthesis of Poly(phenylene sulfide) Containing Pendant Norbornadiene Moieties and Their Valence Isomerization

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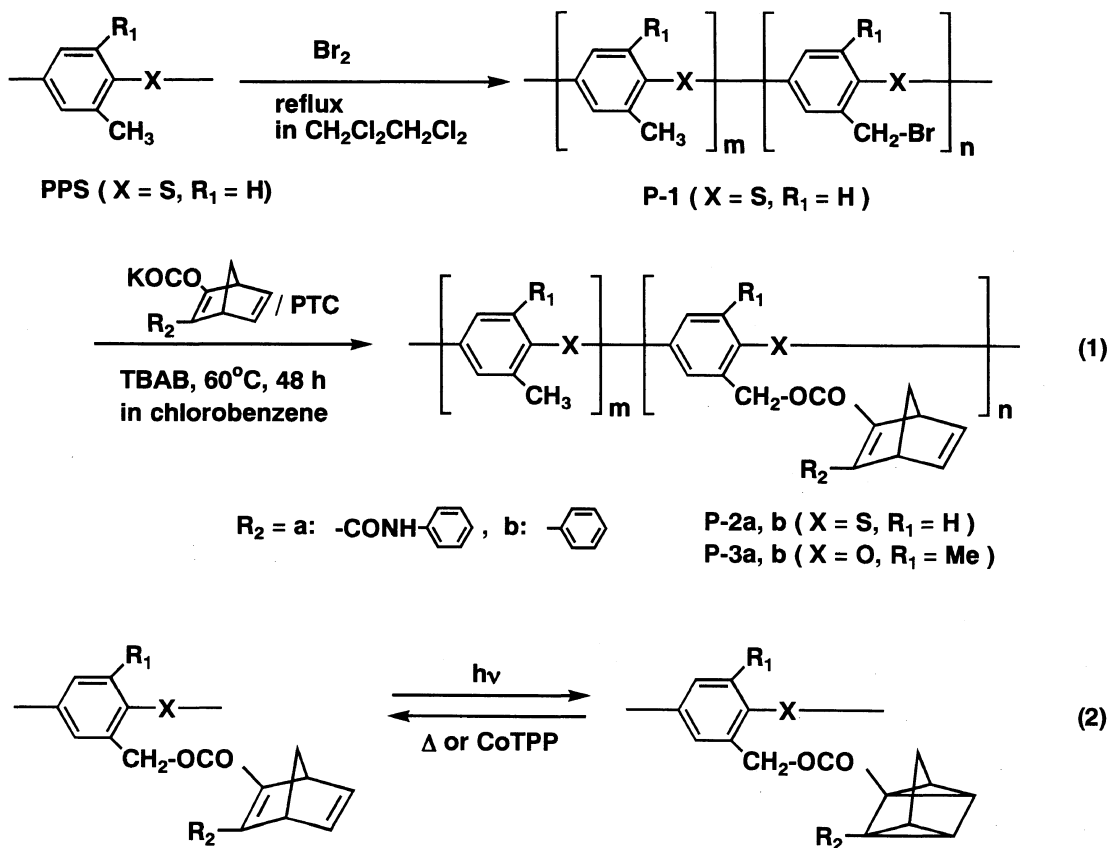
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We studied the synthesis of polymers containing norbornadiene (NBD) moieties and the photochemical valence isomerization of pendant NBD moieties in the polymer film.¹⁻³ Previous papers^{4,5} report that introduction of NBD moiety into rigid polymer matrices such as poly(2,6-dimethyl-*p*-phenylene oxide) (PPO) and polyimide causes the storage and thermal stability of the obtained polymer of NBD or quadricyclane (QC) moieties to increase markedly. NBD polymers derived from poly(*p*-phenylene sulfide) (PPS) with similar structure to PPO should show good stability. Some chemical modifications of PPS have been investigated.⁶

This article reports on novel synthesis of thermal stable NBD polymers (P-2a, b) containing rigid PPS main chain prepared from the reaction of bromomethylated PPS (P-1) with potassium salt of carboxylic acid of NBD using phase transfer catalyst (PTC) (Scheme 1). We discuss effects of the rigid main chain on the photochemical valence isomerization and thermal reversion isomerization of the reactive pendants on the polymer chain, and ability of the polymers to undergo many cycles between both reactions, compared to those of the corresponding NBD polymers (P-3a, b) prepared from brominated PPO.



Scheme 1. Synthesis and reaction of NBD polymer.

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EXPERIMENTAL

Materials

The solvents were purified by distillation prior to use. 2-Methylated PPS ($M_n = 2600$) was donated by Idemitsu Petrochemical Co., Ltd. NBD polymers (P-3a, b, content of NBD moiety: 44.0 mol%) derived from PPO, and NBD derivatives, 3-(phenylcarbamoyl)-2,5-norbornadiene-2-carboxylic acid (NBD-a), and 3-phenyl-2,5-norbornadiene-2-carboxylic acid (NBD-b) prepared previously were used.²⁻⁴ Commercial grades of bromine, dioctyl adipate (DOA), and tetrabutylammonium bromide (TBAB) were used without further purification.

Typical Procedure for Synthesis of P-1

To a solution of PPS containing methyl groups (12.3 g, 100 mmol) in 500 mL 1,1,2,2-tetrachloroethane was added dropwise a solution of bromine (2.6 mL, 50 mmol) in 100 mL 1,1,2,2-tetrachloroethane. The reaction mixture was refluxed for 1.5 h. The mixture was poured into 1 L methanol. The polymer was purified by reprecipitating from tetrahydrofuran (THF) solution with methanol, and dried at 60°C *in vacuo*. The yield of P-1b was 5.4 g. The degree of bromination (n) was 39.3 mol% (Br content: 0.324 g/g). Reduced viscosity was 0.18 dL g⁻¹ (0.5 g dL⁻¹ in chloroform at 30°C). IR (film): 1190 cm⁻¹ (C–O–C). ¹H NMR (CDCl₃): $\delta = 2.28$ (–CH₃), 4.56 (–CH₂–Br), and 6.8–7.5 ppm (aromatic protons).

Typical Procedure for Substitution Reaction of P-1 with Potassium Salt of NBD Derivatives Using PTC

A mixture of P-1 (degree of bromination: 39.3 mol%, 0.587 g, 1.50 mmol) and potassium salt of NBD-a (0.483 g, 1.65 mmol) was stirred using TBAB (48 mg, 0.15 mmol) as PTC in 20 mL chlorobenzene at 80°C for 24 h. The mixture was poured into 300 mL methanol and reprecipitated from THF with methanol. The polymer was dried *in vacuo* at 60°C for 2 days to give 0.515 g of polymer. The degree of substitution of the polymer was 99.8 mol%, calculated from elemental analysis of bromine. The reduced viscosity was 0.44 dL g⁻¹ (measured at 0.5 g dL⁻¹ in chloroform at 30°C). IR (film): 1690 and 1660 (C=O), 1600 (C=C), 1190 cm⁻¹ (C–O–C). ¹H NMR (CDCl₃): $\delta = 2.00$ and 2.08 (–CH₂– of NBD), 2.28 (–CH₃), 3.92 and 4.36 (–CH–), 5.37 (–CH₂–OCO), 6.6–7.8 ppm (CH=CH and aromatic protons).

Typical Measurement of Photochemical Valence Isomerization of Pendant NBD Moiety in the Polymer

A solution of the polymer (0.1 g), DOA (0.01 g), and CoTPP 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 500 W xenon lamp (Ushio Electric Co., UXL-500D) with a Pyrex filter at a distance of 30 cm in air. The rate of disappearance of maximum absorption was measured by a UV spectrophotometer.

Measurement of Reversion from Pendant QC Group in the Polymer to the NBD Moiety

The polymer film on the cell was sufficiently irradiated as described above. The rate of appearance of the maximum absorption of the resulting NBD moiety was measured at room temperature by UV spectrophotometry.

Table I. Synthesis of NBD polymer from bromomethylated PPS^a

NBD polymer	m	n^b	Conv.	Yield	η_{sp}/C^c
			%	g	dL g ⁻¹
P-2a	0.607	0.393	99.8	0.515	0.44
P-2b	0.607	0.393	92.9	0.610	0.58

^a Reactions of bromomethylated PPS (1.5 mmol of bromomethyl groups) with potassium salt of NBD derivatives (1.65 mmol) were carried out using TBAB (0.15 mmol) in 20 mL chlorobenzene at 60°C for 2 days. ^b n : Degree of bromination, $m = 1 - n$. ^c Measured at 0.5 g dL⁻¹ in chloroform at 30°C.

metry.

RESULTS AND DISCUSSION

NBD polymers were prepared by bromination of the methyl groups of PPS and substitution reaction of the resulting bromomethyl groups with potassium carboxylate derivatives of NBD using PTC according to the synthesis of P-3a,b reported previously.⁴ The polymers containing pendant NBD moieties were obtained by reaction of P-1 with 1.1 equivalents of potassium carboxylate derivatives of NBD using TBAB in chlorobenzene at 60°C for 48 h. Reactions of P-1 with potassium salts of NBD-a and NBD-b proceeded quantitatively to give P-2a,b, respectively, under these conditions (Table I). The IR spectrum of original P-2a film showed strong absorption at 1690 and 1660 (C=O stretching), 1600 (C=C stretching), and 1190 cm⁻¹ (C–O–C stretching). The ¹H NMR spectra of this polymer showed signals of main chain and methylene protons of the NBD moiety at $\delta = 2.00$ and 2.08, methine protons at 3.92 and 4.36, –CH₂–OCO protons at 5.37, and CH=CH and aromatic protons at 6.6–7.8 ppm. Esterification was calculated from elementary analysis of bromine, and also from the intensity of proton signals of –CH₂–OCO protons at 5.37 and unreacted –CH₂–Br protons at 4.56 ppm.

The photochemical reaction of polymer films was carried out by irradiation with a 500 W xenon lamp through a Pyrex glass filter. The typical UV spectrum change of P-2a and P-3a in the film state by irradiation is shown in Figure 1. When the P-2a film was irradiated, maximum absorption near 324 nm decreased and the absorption at about 252 nm due to the QC moiety increased. An isosbestic point was observed in the UV spectral changes of the polymers (P-2a–c) by the irradiation over 310 nm. The spectral changes agreed with those of P-3a.³ The photochemical valence isomerization of NBD in P-2a to QC moieties would thus appear to proceed selectively (eq 2). P-2a show lower photochemical reactivity than P-3a, since the UV spectrum of P-2a had a strong maximum absorption near 280 nm due to the main chain.

QC compound is unstable, and the reversion from QC to NBD occurs gradually when stored for long time at room temperature. Previous papers²⁻⁴ report that QC moieties in polymer film became more stable than the corresponding low molecular weight QC, and the addition of 5,10,15,20-tetraphenyl-21H,23H-porphine) cobalt(II) (CoTPP) causes the reaction to accelerate in

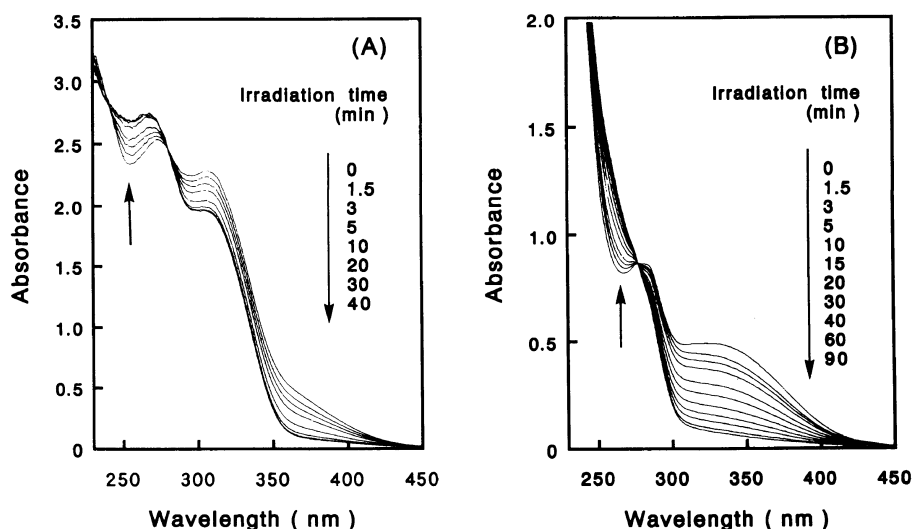


Figure 1. Change of UV spectrum: (A) Photochemical valence isomerization of P-2a film and (B) P-3a of irradiated with a 500 W xenon lamp through a Pyrex glass filter.

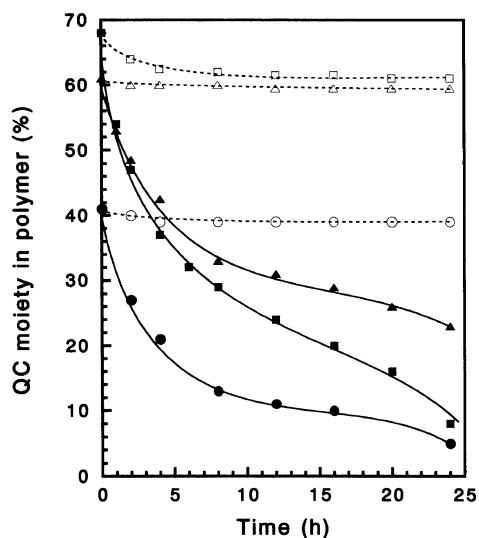


Figure 2. Catalytic reversion isomerization of irradiated polymer film with 10 mol% of CoTPP. (○), P-2a; (●), P-2a + 5 wt% of DOA; (△), P-3a; (▲), P-3a + 5 wt% of DOA; (□), P-3b; (■), P-3b + 5 wt% of DOA.

the film state as well as solution. However, the catalytic reversion reaction hardly took place in rigid polymer matrices such as PPO and PPS at room temperature (Figure 2). When 5 wt% of DOA was added to the polymer as a plasticizer, the reversion proceeded smoothly although the photochemical valence isomerization was not altered. This suggests that the plasticizer promotes the isomerization from QC to NBD in the polymer film. However, the addition of excessive DOA made the film opaque and interfered with the photochemical valence isomerization. When the plasticizer and CoTPP were added to the polymer films, photochemical valence isomerization of the NBD moiety to QC moiety by irradiation and catalytic reversion of the resulting QC moiety to the original NBD moiety at room temperature for 24 h were repeated (Figure 3), causing reversion of QC group to decrease gradually and photochemical reaction to increase. Significant decay of the amplitude of QC groups and decomposition of NBD and QC groups

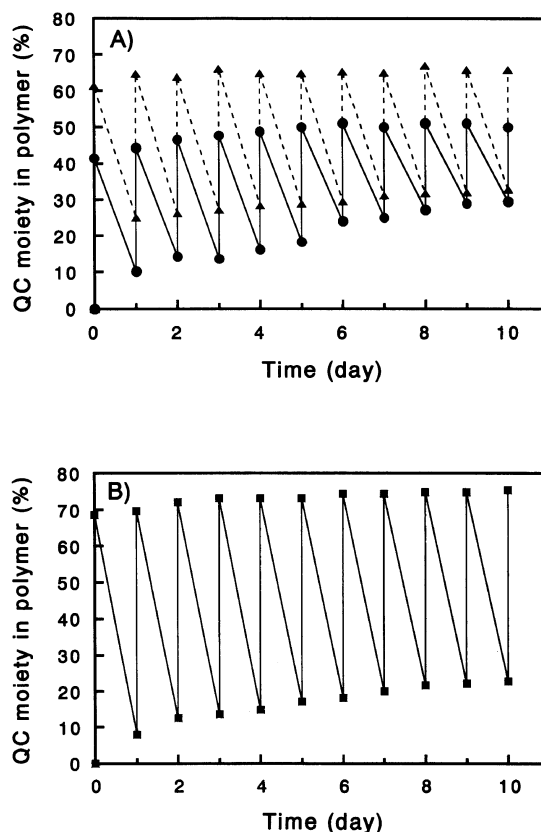


Figure 3. Time of photochemical valence isomerization of a polymer with 10 mol% of CoTPP and 5 wt% of DOA upon irradiation and catalytic reversion isomerization at room temperature for 24 h. A) (●), P-2a;^a (▲), P-3a;^a B) (■), P-3b.^b

^aIrradiation carried out for 30 min. ^bIrradiation carried out for 5 min.

were not observed by the repetition. The stability of P-2a is almost the same as that of P-3a and P-3b.

The reversion from QC to NBD was accelerated and proceeded without any catalyst when the QC compound was heated. The QC polymer prepared from poly(*p*-chloromethylstyrene) decomposed under these conditions, and thermal reversion was not observed. The

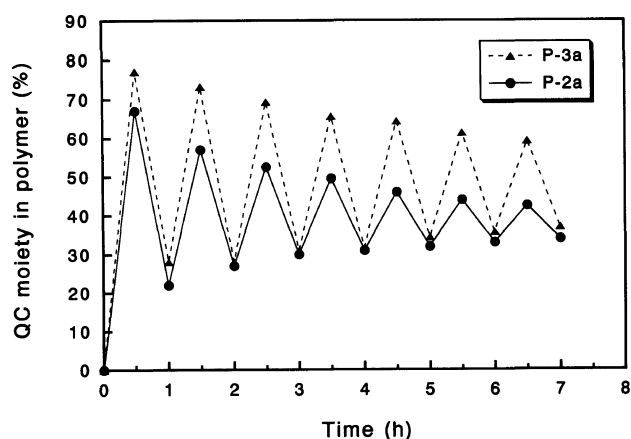


Figure 4. Time of photochemical valence isomerization of a polymer on irradiation for 30 min and thermal reversion isomerization at 160°C for 30 min. (●), P-2a; (▲), P-3a.

IR and UV spectra of the heated polymer were similar to those of the original NBD polymer, P-2a. The thermal reversion of QC moieties in the PPS matrix occurred. The photochemical valence isomerization of NBD moiety of P-2a to QC moiety by irradiation for 30 min and

thermal reversion of the resulting QC moiety to the original NBD moiety at 160°C for 30 min repeated more than 7 times (Figure 4). Although P-2a and P-3a gradually degraded, P-2a showed less thermal stability than P-3a.

NBD or QC moieties in PPS thus have high thermal stability. However, the photochemical valence isomerization and the thermal stability are slightly lower than those of the corresponding PPO polymer.

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